

**SOME LUMINESCENT MATERIALS
FOR DOSIMETRIC APPLICATIONS AND
PHYSICAL RESEARCH**

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LIST OF ORIGINAL PUBLICATIONS

This thesis is based on ten papers listed below, and a discussion of the results. These papers are referred to by Roman numerals from **I** to **X** in the text. The discussion of the results summarises and supplements the original papers.

- I. Molecular excitons and electron-hole processes in K_2SO_4 and $CaSO_4$, Tokbergenov, I.; Feldbach, E.; Kerikmäe, M.; Lushchik, A.; Nagirnyi, V.; Nurakhmetov, T.; Savikhin, F.; Vasilchenko, E. *Radiation Effects and Defects in Solids*, **1999**, 150, 103–107.
- II. Electronic excitations and luminescence in some alkaline earth metal sulphates, Tokbergenov, I.; Savikhin, F.; Rakhimov, D.; Myrzakhmet, M.; Nurakhmetov, T.; Kerikmäe, M. 12th International conference on radiation physics and chemistry of inorganic materials, September 23–27, **2003**, Tomsk, Russia. Proceedings, p.p. 466–469. Tomsk Polytechnic University, 2003 (*in Russian*).
- III. Determination of manganese in thermoluminescent materials by inductively coupled plasma atomic emission spectrometry and spectrophotometry, Lust, A.; Paama, L.; Kerikmäe, M.; Must, M.; Perämäki, P. *Proc. Estonian Acad. Sci. Chem.*, **2002**, 51(2), 126–133.
- IV. Photoluminescence of Concentration Series of $CaF_2:Mn$ Phosphors Excited by VUV Radiation, Denks, V.P.; Kerikmäe, M.P.; Lust, A.L.; Savikhina, T.I. *Solid State Physics*, **2000**, 42(2), 261–269.
- V. The formation of Compton-electron traces in thermoluminescent detectors, Allsalu, M.-L.; Kerikmäe, M.; Pung, L.; Savikhin, F.; Seeman, V. Luminescent receivers and transformers of ionizing radiation, All-Union Symposium, 1987, Proceedings, p.p. 29–36, Tartu University, **1987** (*in Russian*).
- VI. Optically Stimulated Luminescence of Some Thermoluminescent Detectors as an Indicator of Absorbed Dose, Jaek, I.; Kerikmäe, M.; Lust, A. *Radiation Protection Dosimetry*, **2002**, 100(1–4), 459–462.
- VII. Investigation of a New Emission Band of $SrS-Ce$ Phosphor, Rammo, I.; Kerikmäe, M.; Lepist, M.; Matisen I. *Journal of Applied Spectroscopy* (Minsk), **1995**, 62(3), 165–168.

- VIII. Impurity Absorption of SrS-Ce Phosphors, Rammo, I.; Kerikmäe, M., Lepist, M. Matisen I., Pung, L; Ritslaid, K. *Journal of Applied Spectroscopy* (Minsk), **1997**, 64(4), 542–544.
- IX. Studies of the Structure of Ce^{3+} Centres in SrS Phosphors, Rammo, I.; Kerikmäe, M., Lepist, M. Matisen I., Pung, L; Ritslaid, K.; Haav, A. *Journal of Applied Spectroscopy* (Minsk), **1997**, 64(2), 173–178.
- X. Energy Transfer and Storage Mechanism in Infrared Sensitive Storage Phosphor SrS:Eu,Sm , Danilkin, M.I.; Kerikmäe, M.P.; Klimonsky, S.O.; Kuznetsov, V.D.; Makarov, E.F.; Permyakov, J.V.; Primenko, A.E.; Seeman, V.O. *Nuclear Instruments and Methods A*, **2004**, accepted for publication.

INTRODUCTION

All the branches of science, industry and medicine, where ionising radiation is used, require exact dosimetric equipment for radiation dose monitoring. There are two different tasks, personnel and environmental dosimetry. Both tasks are best implemented using thermoluminescence dosimeters (TLD). The TLD have the following advantages:

- ❑ high sensitivity to ionising radiation;
- ❑ low non-radiation effects on dose storage and readout;
- ❑ low dependence of thermoluminescence yield on the radiation dose rate;
- ❑ wide measuring range (from 10^{-6} Sv to 10^5 Sv);
- ❑ storage of information for long time (years) without losses;
- ❑ good measurement reproducibility;
- ❑ high radiation stability;
- ❑ thermal and chemical stability;
- ❑ reusability;
- ❑ possibility of proper TLD choice for a certain task, including a good tissue equivalence for personnel dosimetry and predictable output dependence on exciting photon (X-ray) energy;
- ❑ small size;
- ❑ low production cost, good synthesis repeatability;
- ❑ possibility of selective radiation dosimetry.

Thermoluminescence may be broadly defined as the emission of light when solid is heated to a temperature below that of incandescence, and in general the properties noted are a result of crystal imperfections. All crystals have defects, which may be due to a vacancy at one of the lattice points, an impurity atom at a lattice point, or an interstitial atom or ion in the lattice structure. Regardless of type, the presence of imperfections will introduce new energy levels into the normal lattice energy bands. It is possible, that some of the energy levels will constitute metastable states and be able to trap whether electrons or holes for extended periods of time. The excitation can be stored also in some metastable excited charge-transfer states which will appear when impurity ion demonstrate a well-pronounced covalent bond with ligands. Many different natural minerals and synthetic inorganic compounds demonstrate the thermoluminescence phenomenon, however, only a small part of them satisfy the requirements mentioned above for TLD.

The mechanism of excitation energy transformation into the output light is one of the most crucial points in the luminescent materials designing. Both the threshold of radiation dose detection and accuracy of measurements depend on the efficiency of energy transformation in TLD, or TLD sensitivity. Only a small fraction of absorbed energy of ionising radiation is released later at TLD annealing in the form of thermoluminescence light output. There are inevitable losses at energy transformation in TLD. Mihaltshenko [1], Shvarts [2],

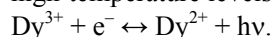
Lushchik [3] have proved that the maximal possible theoretical energy yield of recombining electron-hole pairs cannot exceed 60% of absorbed energy of ionising radiation. This represents Stokes losses, because the average luminescence quanta energy $E_{\text{lum}} = h\nu$ is always less than energy band gap E_g , so the maximal output cannot exceed the ratio $h\nu/E_g$. In fact, the energy of created by ionising radiation electron-hole pairs is always larger than E_g . The excess energy is always lost during migration of electron-hole pairs (or separate electrons and holes). This process is often referred to as thermalisation. As the result, the excess energy is transformed into lattice vibrations, or phonons. Both Stokes losses and thermalisation losses depend on the electronic energy band structure of the particular luminescent material. According to Savikhin estimations [4], only about 50% of the absorbed excitation energy can be transformed into luminescence in alkali halides (if there are no losses due to quenching impurities or side processes). However, these estimations of the luminescence output are too optimistic: in the reality, the thermoluminescence output of LiF-based TLD does not exceed 0.03–0.06% of the absorbed excitation energy. The difference is so large because an essential part of the excitation energy is transformed and irradiated instantaneously after the moment of excitation at different luminescence centres as the scintillation. Only a small portion of energy is stored in the form of trapped electrons and holes. Then, there are tunnel recombination processes in some complex centres, and also inevitable radiationless transitions and side recombinations when the charge carriers are released from traps. As the result, only a small fraction of the total absorbed ionising radiation energy can be detected at the thermoluminescence readout. Side recombination processes bring about non-linearity in the thermoluminescence output against the dose and dose rate. So, the classical recombination processes are very sensitive to casual impurities (luminescence quenchers), and hence, this is the case when materials of very high purity are to be used. What concerns various complex centres, in which energy could be both stored and released later in one complex centre, these complex centres often demonstrate inevitable losses due to either internal quenching, or tunnel processes, or quenching through charge-transfer excited states. The role of different mechanisms of energy transfer and energy losses is very different depending on the nature of luminescent material and its' composition, including intrinsic and impurity defects and their specific complexes. The structure of defects is controlled to a high extent by the technology of synthesis. That is why the most essential task is to find the interrelations between the technology, structural defects and properties of the thermoluminescent materials.

The basic purpose of the present work is to correlate the required properties of TLD and other luminescent materials with the technology of synthesis and with their lattice imperfections.

1. CHEMISTRY AND PHYSICS OF LUMINOPHORS: LITERATURE OVERVIEW

1.1. Luminophors based on sulphates of alkaline earth metals

Sulphates of alkaline earth metals are investigated as hosts materials for TLD ($\text{CaSO}_4\text{-Dy}$, $\text{SrSO}_4\text{-Eu}$), and also the electronic structure and luminescence mechanisms are studied in them. $\text{CaSO}_4\text{-Dy}$ is recommended as environmental detector by many authors [5–8]. The luminescence spectrum of $\text{CaSO}_4\text{-Dy}$ consists of three narrow bands, a weak one in infrared (1.82 eV), and two more intensive in the region of visible light (2.2 eV and 2.7 eV). Thus, the readout of TLD based on this luminophor is quite convenient. Tae-Jin Choi et al [9] investigated energetic parameters of traps responsible for the peaks on glow curve. According to their data, the peak at 483 K (210°C) is connected with monomolecular kinetics, and corresponding trap depth is 1.45 eV, with a frequency factor being $w_0=1\cdot 10^{14} \text{ sek}^{-1}$. However, high-temperature region of glow curve is non-elementary (several traps are responsible for the maximum at $T_{\text{max}}=508 \text{ K}$ (235°C), with $w_0=3\cdot 10^{11} \text{ sek}^{-1}$). Matthews et al [10] also supposed the monomolecular kinetics for $\text{CaSO}_4\text{-Dy}$. According to Spurny et al [11], the high-temperature levels interact with optically excited states of Dy^{3+} :



This phenomenon is typical for systems with strong electron coupling. The EPR data are presented in paper [12].

The attempts to improve characteristics and to study thermoluminescence mechanisms of $\text{CaSO}_4\text{-Dy}$ are continued up to present day. A very extensive comparative study is reported by Lakshmanan et al [13], concerning the features of newly designed $\text{CaSO}_4\text{-Dy}$: crystal morphology, glow curve shape, emission spectra, dependence of sensitivity, detection threshold, storage stability, sensitivity to UV, and other features on activator concentration, grain size, etc. R.S. Kher et al [14] have studied mechanically induced luminescence (ML) and thermoluminescence (TL) of γ -irradiated $\text{CaSO}_4\text{-Dy}$ phosphor. Despite of the different ways of excitation, the same states are supposed to be responsible for both ML and TL. A.K. Banski et al have studied annealing and reusability of TLD-s based on $\text{CaSO}_4\text{-Dy}$ [15]. According to J.S. Yang [16], the sensitivity of $\text{CaSO}_4\text{-Dy}$ may be increased twice, compared with commercial Teledyne tablets, by embedding the teflon into pellets. The spectral and dose characteristics of $\text{CaSO}_4\text{-Dy}$ were studied using both ultraviolet excitation and excitation with ionising radiation [17]. Radiation response of the TLD tablets was studied also with phototransferred thermoluminescence method (PTTL) [18].

E. Cruz-Zaragoza et al [19] have tested the $\text{CaSO}_4\text{-Dy}$ detectors to evaluate their response to gamma-radiation at liquid nitrogen temperature. The TL

response to dose at liquid nitrogen temperature is found to be linear but lower about 20% than at room temperature.

Electron spin resonance (ESR) spectra of both pure CaSO_4 and doped one with Dy and P have been measured by E.F.O. de Jesus et al [20]. The ESR spectra demonstrated the presence of ESR lines usually known in CaSO_4 , with the g-factor around 2.036, and an intense line with $g=2.001$ observed only in pure material. This line, connected probably with an axial SO_4^- , grows linearly with absorbed dose until 1,0 kGy and shows long-term stability in time.

Among the tried for optically stimulated afterglow (OSA) materials [**paper VI**], CaSO_4 -Dy is the most promising one for readout of absorbed dose by an OSA method.

The excitation spectrum of Dy^{3+} in CaSO_4 was studied yet by Zapasskiy and Feofilov [21]. The excitation band at 5.17 eV corresponds to the direct excitation of Dy^{3+} (f-f transition, $^6\text{H}_{15/2} \rightarrow ^4\text{I}_{15/2}$). Intensive excitation band at 6.4–8 eV is connected with $4f^9 \rightarrow 6d$ transition, while at higher energies (8–9 eV) the band is overlapped with charge-transfer transition creating an exciton near the Dy^{3+} activator impurity.

Despite of the extensive studies connected with TLD, the intrinsic luminescence of alkaline earth metal sulphates was not investigated in details. There are only few papers connected with intrinsic electronic structure and electronic excitations in CaSO_4 . For example, the reflection spectrum of CaSO_4 single crystal was measured with a synchrotron radiation source in a wide range of incident photon energies (8–36 eV) at room temperature [22]. Both exciton peak and the threshold of creation of electron-hole pairs have been observed.

1.2. Luminophors based on lithium tetraborate

Thermoluminophors based on lithium tetraborate are nice materials for personal dosimetry due to their effective atomic number $Z_{\text{eff}}=7.4$ being very close to that value ($Z_{\text{eff}}=7.42$) of human tissue [23]. It is even possible to adjust Z_{eff} of thermoluminophor according to different tissues of human organism by varying the concentration of SiO_2 in $\text{Li}_2\text{B}_4\text{O}_7$ -Mn,Si.

The sensitivity of $\text{Li}_2\text{B}_4\text{O}_7$ -Mn,Si to gamma radiation and thermal neutrons is lower than that of many other TLD materials. The maximum of emission spectrum of this luminophor is situated in red region about 605 nm, and this is one of the factors decreasing the efficiency of readout [24,25]. Minimum detectable dose is 10–20 μGy . There are two TL maximums on the glow curve: $T_1=328\text{ K}$ (55°C) and $T_2=493\text{ K}$ (220°C). A new maximum at 523 K (250°C) appears at irradiation doses higher than $D=300\text{ Gy}$. The shape of glow curve is the same when excited either by α - or γ -radiation [26]. Soares et al [27] have measured the TL response to α -excitation compared to γ -excitation. According to an opinion of some authors [28,29], the main disadvantage of this

luminophor is connected with noticeable losses of stored dose information (fading) caused by light, humidity, etc. The presence of low-temperature TL peak is responsible for fading too. One possible way to get partly round the problem is to preheat the exposed TLD at 373 K (100°C) for 2 hours before the readout. This trick removes and discards a low-temperature TL peak disposed to fading.

Panasonic uses thermoluminophor $\text{Li}_2\text{B}_4\text{O}_7\text{-Mn,Si}$ in commercial beta/gamma dosimeter UD-802, and also in the universal beta/gamma/neutron dosimeter UD-813 [30]. K.G. Veinot and N.E. Hertel have measured and calculated angular responses of Panasonic UD-809 thermoluminescent dosimeters to neutrons [31]. High-resolution luminescence spectra of $\text{Li}_2\text{B}_4\text{O}_7\text{-Mn}$ (TLD-800) were measured by T. Vilaithong et al [32].

Takenaga et al [33] have invented and patented a new thermoluminophor on the base of lithium tetraborate doped with copper and silver. The sensitivity to gamma-irradiation dose was improved compared to the luminophor doped with manganese.

C. Furetta et al [34] have investigated the thermoluminescence of $\text{Li}_2\text{B}_4\text{O}_7$ polycrystalline powder, both undoped and doped with either Cu or Eu, in order to estimate the applicability of these materials in dosimetry. Glow curves of β -irradiated samples were recorded. The dependence of TL glow curve shapes and the TL peak intensities on the dopant concentrations were studied.

Thermoluminescence mechanism in $\text{Li}_2\text{B}_4\text{O}_7\text{-Cu}$ was investigated by Watanabe et al [35]. The absorption spectra of non-irradiated and irradiated samples were measured. The irradiation is supposed to change the Cu^{2+} into Cu^+ . The ESR-spectra of Cu-doped $\text{Li}_2\text{B}_4\text{O}_7$ reveal the typical BOHC centres, “five-line-plus-a-shoulder” between the $\pm 1/2M_n$ -lines. The idea of the BOHC playing an important role in the TL emission process appears from the observed changes of ESR spectra of the Cu-doped $\text{Li}_2\text{B}_4\text{O}_7$ at heating.

M. Martini et al [36] have studied spectrally resolved thermoluminescence of $\text{Li}_2\text{B}_4\text{O}_7\text{-Cu}$ single crystals. Two peaks have been detected at the glow curve, about 418 K (145°C) and 479 K (206°C). The latter was proved to be thermally stable. The TL output in this peak is linear in a wide range against the absorbed dose. The high sensitivity and suitable temperature position of main TL peak make the crystals very promising for dosimetric application.

S. Miljanic et al [37] have studied the dose dependence on the X-ray energy in terms of values of personal dose equivalent $H_p(10)$ for $\text{Li}_2\text{B}_4\text{O}_7$ doped either with Cu, In or with Cu, In, Ag. Measured energy responses were compared with calculated data for $H_p(10)$ values. The results confirmed the satisfactory tissue equivalence for investigated $\text{Li}_2\text{B}_4\text{O}_7$ -based TLD materials.

M. Prokic [38] has reported main dosimetric characteristics of new thermoluminescent detectors in form of sintered pellets based on $\text{Li}_2\text{B}_4\text{O}_7\text{-Cu,Ag,P}$. A significant improvement in the sensitivity was gained. A very wide linear response range up to 10^3 Gy is evident from the experimental results. Advanced dosimetric characteristics make sintered solid TLD based on

$\text{Li}_2\text{B}_4\text{O}_7\text{-Cu,Ag,P}$ very promising for different dosimetrical applications, particularly in medical dosimetry, and also for personnel monitoring.

1.3. Luminophors based on manganese-doped calcium fluoride

The thermoluminophor $\text{CaF}_2\text{-Mn}$ is used in environmental dosimetry [39–43]. This thermoluminescent material has extremely wide range of linearity of response to dose, from 0.5 mGy to about 10^3 Gy, which means about seven orders of magnitude [44,46]. This fact makes this material very attractive for different applications — it may be used either in routine or in accident dosimetry. The thermoluminophor $\text{CaF}_2\text{-Mn}$ has a low fading due to relatively deep electron traps, and it is insensitive to daylight [47,48]. The luminophor $\text{CaF}_2\text{-Mn}$ has a single TL peak at 513–553 K (240–280°C). However, some researchers consider it to consist of several unresolved peaks connected with different types of trapping centres [45,49,50].

The conventional way to measure a thermoluminescence response to dose assumes heating a TLD below incandescence temperature after it has been exposed to ionising radiation. However, $\text{CaF}_2\text{-Mn}$ appears to be unstable at high annealing temperatures due to partial oxidation of activator (Mn^{2+}) in luminophor. There are some attempts to get around the problem using other means to measure the energy stored in TLD by radiation dose, for example, optically stimulated luminescence (OSL) [51], cryogenic optically stimulated luminescence (COSL) [48,52,53], or laser beam stimulation [54–56]. The OSL and COSL methods give the possibility to use organic binders and plastic materials in construction of TLD [57].

Besides of being a suitable TLD material, CaF_2 doped with both manganese and a rare earth ion is a model object for studying mechanisms of resonance energy transfer in solids, so important for development of different luminophors, laser materials, etc. [58–60]. Isotropic fluorite crystals are almost the only promising material for short-wavelength ($h\nu \geq 6$ eV) laser optics [61,62]. The study of luminescent processes in $\text{CaF}_2\text{-Mn}$ excited in the UV spectral region has been the subject of many experimental as well as theoretical works [58,60,63–65]. Low energy excited states (the $3d^5$ electron shell) of Mn^{2+} luminescence centres situated in regular cation sites of the CaF_2 lattice have been studied, and also their shift and splitting in crystal lattice field.

Physical processes in $\text{CaF}_2\text{-Mn}$ excited by photons with energies $h\nu \geq 6$ eV are reported in papers [66,5].

Based on CaF_2 thermoluminophors are widespread, and their thermoluminescent characteristics and luminescence mechanisms have been studied for about 40 years. Nevertheless, the problem of purity and stability against air

oxygen still puts a challenging task for chemists to work out the better technology of manganese-doped calcium fluoride.

1.4. Luminophors based on calcium and strontium sulphides

The longest history of investigations, the widest possible applications, a variety of models, perpetual studies — these are the traits of luminophors based on alkaline earth sulphides (AES). Strontium sulphide doped with rare earth impurities was prepared yet by Lenard [67] more than hundred years ago. Lenard and collaborators have studied infrared-sensitive storage luminophors SrS-Eu,Sm and SrS-Ce,Sm. A stored at irradiation excitation can be stimulated to glow out by incident infrared radiation. This feature has predestined the employment of these materials for visualisation of infrared images in first night viewing devices. The energy storage and release was explained by model of $\text{Eu}^{2+} \leftrightarrow \text{Eu}^{3+}$ and $\text{Sm}^{3+} \leftrightarrow \text{Sm}^{2+}$ transformations due to exchange of electrons and holes between two impurities. This model was suggested for Eu, Sm activator pair by Title [68] on the basis of EPR and optical studies of SrS-Eu,Sm. However, our latest studies disagree with this model [paper X].

The next era of AES-based luminescent materials has started since W. Lehmann [69] reported his studies of cathodoluminescence of CaS-Eu,Cl and CaS-Ce,Cl. The works of Mai Pham-Thi [70–72] belong to next generation of attempts to develop efficient cathodoluminophors on the basis of AES.

However, these attempts were not realised in wide practical applications till now because of specific incompatibility of sulphide-ions with a common technology of suspensions for colour screens. Polyvinyl alcohol used as a photosensitive fixating agent is very sensitive to sulphide anions causing a momentary polymerisation. The photosensitiser, either potassium bichromate or ammonium bichromate, reacts with the AES-based luminophor, and the number of sulphide anions increases more and more due to destruction of luminophor microcrystals. This causes the suspension to get collapsed into a jelly-like mass. New photosensitive compositions of nova days are already stable against sulphide anions, and so, a new challenge arises to develop efficient luminophors for colour screens. Also, there are still other promising modern applications, like screens of plasma TV sets, projection tubes, thin film electroluminescent devices (TFEL). This latter application gets more and more researchers to work at. Many papers deal with thin luminescent layers based on SrS with different activators, e.g. Ce [73–75], Eu and Sm [76], Pr [77], and Cu [78]. The models of luminescence centres and mechanisms often refer to Sr vacancies involved in the centres [73,76,79]. It is worth mentioning that the cation vacancies in SrS were studied only recently [80].

A very old acquaintance of researchers — storage luminophor SrS-Eu,Sm — acquires presently more and more attention [76,82,83] with regard to high-tech applications like optical-magnetic storage media [83].

The AES-based luminophors are not widely used as materials for TLD because of high sensitivity to daylight and superlinearity of output against the dose and dose rate. However, the selective neutron dosimeters were created by our research group on the basis of CaS-Bi,Na,Zn,Ni [**paper V**]. Despite of the successful practical application, the structure of luminescence centres, mechanisms of luminescence and energy transfer in CaS-Bi luminophor are not yet completely clear and attract the attention of researchers [81].

Many of interesting problems are not still clear in AES: formation of complex centres, properties of charge-transfer states, and impurity-bound excitons. The lack of fundamental knowledge was caused by the absence of pure materials at that time when the studies of AES have been only started. We hope that the further improvement of the quality of AES-based luminescent materials helps to advance both fundamental and applied researches.

2. THE GOALS OF THE INVESTIGATION

The problems concerning the synthesis and properties of luminescence materials, included in the present work, are the following:

- ❑ to find the optimal conditions of CaSO_4 and SrSO_4 synthesis, including conditions of co-precipitation with doping impurities;
- ❑ to produce the undoped sulphates of very high purity for study of intrinsic luminescence processes at high-energy (vacuum ultraviolet) excitation;
- ❑ to develop a technology of synthesis of $\text{Li}_2\text{B}_2\text{O}_7\text{-Mn,Si}$ thermoluminophor with suitable for TLD characteristics, including synthering of TLD in a form of tablets;
- ❑ to study the luminescence and also thermoluminescent properties of pure CaF_2 and $\text{CaF}_2\text{-Mn}$ in connection with technological improvements;
- ❑ to examine the possibility to get round a problem of oxidation of Mn^{2+} in CaF_2 either by oxygen traces or atmospheric oxygen, especially in connection with the studies of intrinsic luminescence and energy transfer mechanisms in CaF_2 ;
- ❑ to study non-linear dose response in based on CaS-Bi thermoluminophors in order to obtain thermoluminescent material suitable for dosimetry of fast neutrons (recoil protons);
- ❑ to study the possibility of known TLD like $\text{CaSO}_4\text{-Dy}$, $\text{CaF}_2\text{-Mn}$, and others, to be readout using optically stimulated afterglow (OSA) method;
- ❑ to formulate basic requirements for luminophors meant for readout by OSA method;
- ❑ to study conditions of formation of complex luminescent centres in SrS-Ce and SrS-Eu,Sm luminophors, including the role of intrinsic defects (cation vacancies) and technological aspects of creating proper lattice defects and their complexes.

3. RESULTS AND DISCUSSION

3.1. Chemistry and dosimetric properties of luminescent materials

There are three partially overlapping branches of thermoluminescent dosimetry. Most common TLD show linear output against the dose and dose rate, this feature is required for a convenience of practical use of TLD. However, sometimes superlinear dependence on the dose and the dose rate is a desired feature — this is the case when one needs to overcome problems of tissue equivalence in the dosimetry of fast neutrons. Next, optically stimulated luminescence (OSL) phenomenon gives a very attractive and simple readout technique for practical use. The dosimeters with OSL readout can be based either on some already known TLD, or on specially designed for OSL new materials, or even on some natural minerals (e.g., in palaeontological research).

3.1.1. Luminescence materials for TLD with linear dose dependence

We have studied and developed various materials for linear TLD in our laboratory. Some of them were introduced into everyday practice and are presently used worldwide. For example, produced in our laboratory TLD pellets based on the lithium tetraborate doped with divalent manganese are accepted and practically used at the Dosimetry Service of SUVA (Swiss National Accident Insurance Fund, or Schweizerische Unfallversicherungsanstalt). The synthesis and properties of used in dosimetry thermoluminescent materials are described in this section. The materials described in this section are discussed in our **papers [I,II,III,IV,VI]**. These materials are extensively studied for physical properties (luminescence mechanisms, electronic structure, etc.), so we shall return in the next sections to the discussion of obtained physical results.

The linearity of response to the absorbed dose depends on several factors. The simplest case is obvious: no side recombination and storage processes, and the only kind of trapped state is involved into the energy storage. Nevertheless, side recombination processes are sometimes linear, and hence, can be present without affecting the linearity of dose response. Moreover, sometimes the quenchers are able to improve the linearity by decreasing the effects of Compton-electron traces overlapping (see **paper [V]**). The sensitivity of TLD is obviously decreased by quenchers, yet the linearity could be extended to a wider range of doses. Generally, the development of convenient TLD with a good linearity requires very pure starting materials and rigidly controlled technology of synthesis.

Basic characteristics of some linear TLD developed and studied in our laboratory are presented in the Table 1.

Table 1. Basic characteristics of some detectors

Detector *Sizes, mm: Ø4–10, h = 0.3–1.0	CaSO ₄ - Dy	SrSO ₄ - Eu	Li ₂ B ₄ O ₇ - Ag,Cu	Li ₂ B ₄ O ₇ - Mn	CaF ₂ - Mn	LiF-Ti, Mg (TLD-700, commercial sample)
Linearity of measurements, up to the dose, C/kg	0,3	25,0	0,1	0,1	30,0	≤ 0,1
Sensitivity, quanta/C	3·10 ¹⁷	1·10 ¹⁸	4·10 ¹⁶	2·10 ¹⁵	3·10 ¹⁶	3·10 ¹⁵
Part of the stored light released at heating below 420 K, %	10	–	15	–	3	≈10
Positions of the luminescence spectrum maxima, nm	470, 510	375	368, 530	605	516	400
Effective atomic number	14.4	24.9	7.4	7.4	16.3	8.1
Losses of the stored energy of ionising radiation during one month fading), %	2	2	5	3***	1	3
TL curve main peak position, K (at heating rate 2 K/s)	483	493	478	493	533	483

*** measured after a pre-heating at 350 K, 30 min.

Luminophor CaSO₄-Dy

CaSO₄-Dy is a good material for environmental dosimetry. It has a high sensitivity and linear dose dependence in a sufficient range of radiation doses for environmental monitoring. Here we discuss the details of preparation and thermoluminescent properties of CaSO₄-Dy, while luminescence data and electronic structure obtained in **papers [I, II]** are reviewed in the next sections. CaSO₄-Dy is a very good material for optically stimulated readout of stored dose information. This feature is studied in **paper [VI]** and discussed also in next sections.

Three different methods of synthesis were tried to obtain the desired thermoluminophor characteristics:

- re-crystallisation of CaSO₄ together with doping agent from hot acidic solutions containing H₂SO₄;

- b) doping agent and CaSO_4 solid state reaction;
- c) co-precipitation of doping agent together with CaSO_4 from water solutions of $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{SO}_4$.

The thermoluminescence (TL) curve main maximum was observed at different positions, depending on the synthesis method (See Fig. 1). Thus, re-crystallisation method (a) gives the maximum at about 490–500 K (220–230°C), solid state reaction method (b) — at about 340 K (65°C), and co-precipitation method (c) — at about 513 K (240°C). When compared by light output sum, the luminophors obtained by method (c) demonstrate about one-half efficiency of ones obtained by method (a). What concerns the solid-state synthesis (b), the low temperature of TL curve maximum makes this method unusable because of too fast decay of stored dose information. The re-crystallisation method (a) is quite difficult technically because it involves treatments with hot H_2SO_4 . Thus we have undertaken the detailed studies to improve the co-precipitation method (c) with the purpose to obtain both high-temperature main peak of the TL curve and higher light output efficiency.

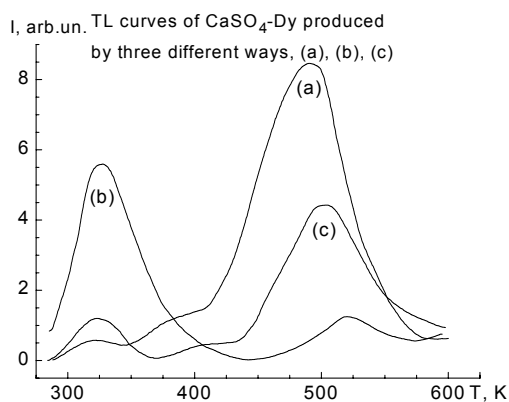
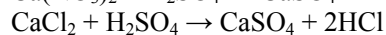
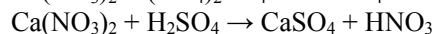
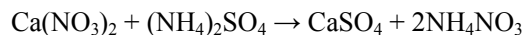


Figure 1. TL curves of $\text{CaSO}_4\text{-Dy}$ prepared by different methods.

One of the possible ways to improve the thermoluminophor characteristics is optimisation of co-precipitation conditions. It is obvious that the ratio of concentrations of Ca^{2+} and SO_4^{2-} ions during co-precipitation should affect the luminophor properties.

For co-precipitation of doping agent the following source materials and reactions were used:



The starting $\text{Ca}(\text{NO}_3)_2$, $(\text{NH}_4)_2\text{SO}_4$, and CaCl_2 purity grade was “chemically pure” or “special purity”. These starting materials were additionally refined to remove residual impurities of transition and especially heavy metals. Impurities were extracted from water solutions of starting materials using a solution of 1% complex-producing extragent 8-oxyquinoline in chloroform. The following residual impurities were discovered by spectral analysis in the materials after the additional refinement:

Cu, Pb, Mn, Fe — about $10^{-6}\%$;
 Ag — less than $1 \times 10^{-6}\%$;
 Mg, Sr — about $4 \times 10^{-2}\%$;
 Na, Cl — about $10^{-3}\%$ or less;
 Ba — up to $6 \times 10^{-1}\%$.

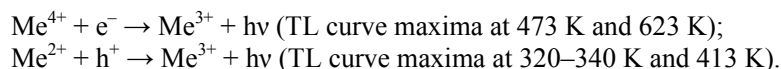
The TL output was found to depend also on the temperature in the reactor during sedimentation of CaSO_4 . The TL output increases when temperature is increased in the range of 5–90°C. The most pronounced effect of temperature increase is observed in the range of 80–90°C. The effect is connected with formation of a new CaSO_4 crystal structure. The dependence of thermoluminophor properties on the ratio of concentrations of Ca^{2+} and SO_4^{2-} ions is represented below in the Table 2.

Table 2. Sensitivity and shape of glow curve dependence on the Ca^{2+} and SO_4^{2-} ions concentrations ratio for luminophor $\text{CaSO}_4\text{-Dy}$.

Composition	$[\text{Ca}^{2+}] : [\text{SO}_4^{2-}]$	m_{γ} , quanta/C	$\Delta S_{\text{TL}} < 150^\circ\text{C}$, % (excited by ^{90}Sr)
$\text{Ca}(\text{NO}_3)_2 + (\text{NH}_4)_2\text{SO}_4$ [method(c ^I)]	2 : 1	$4.7 \cdot 10^{15}$	10.8
	4 : 1	$6.6 \cdot 10^{15}$	14.3
	6 : 1	$5.4 \cdot 10^{15}$	11.1
	9 : 1	$3.2 \cdot 10^{15}$	31.1
$\text{Ca}(\text{NO}_3)_2 + \text{H}_2\text{SO}_4$ [method(c ^{II})]	1 : 1	$4.2 \cdot 10^{16}$	10.0
	1 : 5	$7.4 \cdot 10^{16}$	6.0
	1:10	$1.4 \cdot 10^{16}$	4.0
	1:13	$1.4 \cdot 10^{16}$	5.0
	1:14	$1.6 \cdot 10^{16}$	6.0
	1:15	$2.4 \cdot 10^{16}$	4.0
	1:20	$2.2 \cdot 10^{16}$	4.0
CaSO_4 re-crystallised with Dy in a solution containing H_2SO_4 [method (a)]	—	$2.6 \cdot 10^{17}$	15.0

Optimal ratio of Ca^{2+} and SO_4^{2-} ions concentrations in case of reaction between $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{SO}_4$ is 4:1 according to Table 2. The sensitivity turns to decrease at a higher Ca^{2+} concentration. In case of reaction between $\text{Ca}(\text{NO}_3)_2$ and H_2SO_4 optimal concentration ratios range from 1:5 to 1:15. The solubility of CaSO_4 increases at higher concentrations of H_2SO_4 . Despite of obtaining larger microcrystals at higher concentrations of H_2SO_4 , one should take into account a decrease of TL output. The thermoluminophors $\text{CaSO}_4\text{-Dy}$ obtained either by method (c^I) or method (c^{II}) with a large excess of H_2SO_4 (ratio of concentrations $[\text{Ca}^{2+}]:[\text{SO}_4^{2-}] = 1:15$) demonstrate a sensitivity to gamma- or Roentgen radiation close to that of $\text{CaSO}_4\text{-Dy}$ obtained by method (a). However, the synthesis (c^{II}) is much easier to carry out, because there is no necessity to work with a high concentration of hot H_2SO_4 . Also, the product obtained by method (c^{II}) has a homogeneous and small grain size making easier to produce TLD detectors in a form of tablets.

EPR studies of paramagnetic centres in $\text{CaSO}_4\text{-Dy}$ (or CaSO_4 with some other activators, Tm or Tb) showed that an activator possesses different charge states in a luminophor. At the electron stage of thermostimulated recombination processes the released from traps electrons are captured by Me^{4+} centres (Me = Dy, Tm, Tb), and the holes released from traps are captured at the hole stage by bivalent Me^{2+} impurities. These processes can be represented schematically:



This model is in accordance with the data published in different papers. However, some other models are also suggested. For example, Matthews [10] suggests that Dy plays a role of electron trap, and the electron released from it recombine with some $(-\text{O}-\text{SO}_2-)$ or $(-\text{O}-\text{SO}_2-\text{O}-)$ radical. The energy released at recombination is transferred then to Dy^{3+} where a quantum of light is emitted.

Luminophor $\text{SrSO}_4\text{-Eu}$

The luminescence properties of $\text{SrSO}_4\text{-Eu}$ are studied in **papers [I,II]** and discussed below. Here we regard the preparation techniques and thermoluminescent properties of the $\text{SrSO}_4\text{-Eu}$. The starting materials for luminophor production were $\text{Sr}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{SO}_4$. They were additionally refined to remove residual impurities of transition and especially heavy metals. Impurities were extracted from water solutions using a 1% chloroform solution of complex-producing extragent 8-oxyquinoline, just by the same technique as for $\text{CaSO}_4\text{-Dy}$ synthesis. The spectral analysis showed that the concentrations of undesired impurities were reduced to about $10^{-5}\%$. The synthesis procedure was the following:

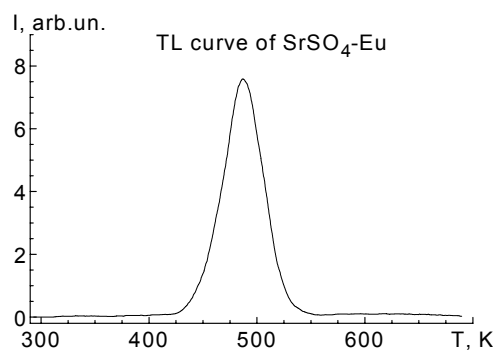


Figure 2. TL curve of SrSO₄-Eu

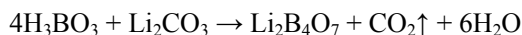
Different quantities of high-concentration “special purity” H₂SO₄ were brought into the reaction vessel taking into account the total volume after mixing with distilled water to become 200 cm³. Then Eu₂O₃ was added to the acidic solution. The solution was heated up to a temperature of 70±2°C, and then starting Sr(NO₃)₂ and (NH₄)₂SO₄ solutions were added into a beaker at a rate of 40 cm³/hour using peristaltic pumps. The precipitated sulphate was aged for 2 hours. The obtained SrSO₄ together with co-precipitated europium sulphate was filtered and dried at 105°C for 24 hours. To obtain the luminescent material, the dried co-precipitated sulphates were annealed at 1150°C for 60 minutes.

The optimal luminophor properties (including the sensitivity for gamma- and X-rays) were obtained when activator was co-precipitated with the [Sr²⁺] and [SO₄²⁻] concentrations ratio kept 1:2 during the reaction. The sensitivity of SrSO₄-Eu to gamma-rays (⁶⁰Co) amounted to 2.4·10¹⁴ quanta·kg·C⁻¹·g⁻¹. There is practically the only peak near 493 K (220°C) at a TL curve when the Eu concentration is 0.5 atom % (See Fig. 2). This peak keeps dose information for a long period of time (month fading do not exceed 2%, see the Table 1), making SrSO₄-Eu suitable for practical applications as TLD.

Luminophors Li₂B₄O₇-Cu,Ag and Li₂B₄O₇-Mn,Si

The alkaline metals can constitute several types of borates: mono-, tetra-, and pentaborates. Some results indicate also the possibility of still other alkaline metal borate compositions [84]. It is a feature of borates to change their composition in solutions according to the added reactive concentration.

The most common synthesis of the initial lithium tetraborate is proceeded by the following reaction:



Lithium tetraborate trihydrate $\text{Li}_2\text{B}_4\text{O}_7 \cdot 3\text{H}_2\text{O}$ is crystallised from the solution during the reaction. The solubility of lithium tetraborate at room temperature is very high, about 3.609 g/cm^3 , so the solution can be easily kept oversaturated. This makes difficult to extract the product of reaction from the solution. Lithium tetraborate trihydrate loses water of crystallisation at $200\text{--}240^\circ\text{C}$ ($470\text{--}510 \text{ K}$). The melting point of anhydrous $\text{Li}_2\text{B}_4\text{O}_7$ is reported in different literature sources ranging from 850°C to 917°C ($1120\text{--}1190 \text{ K}$). In practice, the melting point strongly depends on the slightest variations of structural composition, giving effects of “partial melting” as if it was amorphous glass-like material.

The mechanisms of luminescence and thermoluminescence excitation of $\text{CaSO}_4\text{-Mn}$ and $\text{Li}_2\text{B}_4\text{O}_7\text{-Mn}$ luminophors have the following common features:

1. doping activator impurities do not essentially affect the TL curve;
2. excitation spectrum is determined by the activator;
3. TL excitation spectrum is similar to the excitation spectrum of luminescence bands.

One of the most essential advantages of $\text{Li}_2\text{B}_4\text{O}_7$ -based TLD is excellent tissue equivalence: $Z_{\text{eff.}} = 7.4$ for a $\text{Li}_2\text{B}_4\text{O}_7$ -based TLD, and $Z_{\text{eff.}} = 7.42$ for human soft tissue. When the binding material SiO_2 is introduced into the TLD tablets, the exact tissue equivalence can be obtained for different tissues of human body. Thermoluminophor $\text{Li}_2\text{B}_4\text{O}_7\text{-Cu,Ag}$ possesses very high sensitivity to daylight, and this was the reason to get rid of this material in further studies. Nevertheless, the $\text{Li}_2\text{B}_4\text{O}_7\text{-Mn}$ presently produced is insensitive to daylight. It has very attractive tissue equivalence, making this material very suitable for practical use. There are two maxima at TL curve of $\text{Li}_2\text{B}_4\text{O}_7$ -based TLD: at $T_1=328 \text{ K}$ (55°C) and at $T_2=493 \text{ K}$ (220°C). The former maximum has an essential fading, so it is not used in readout (TLD is pre-heated without reading to get rid of the low-temperature part of stored light sum). This simple method is suitable due to negligible interaction between deep and shallow traps in $\text{Li}_2\text{B}_4\text{O}_7$ -based thermoluminophors. The synthered $\text{Li}_2\text{B}_4\text{O}_7\text{-Mn,Si}$ tablets are like a dense ceramics with a good solidity. The TLD in a form of synthered tablets do not loss the dose information due to external factors like humidity, etc. However, the peak at TL curve near $T_1=328 \text{ K}$ (55°C) should be disregarded at readout.

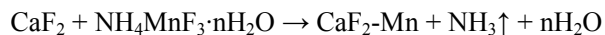
Luminophor $\text{CaF}_2\text{-Mn}$

Essential difference exists between theoretical (calculated) [1–3] and measured thermoluminescence yield in $\text{CaF}_2\text{-Mn}$. This difference is not connected with losses due to external quenching, rather some radiative recombination processes take place yet at a moment of excitation. One could suppose that it is

possible to increase the trapping and subsequent thermoluminescence probability versus momentary recombination simply by increasing the number of trapping centres. Unfortunately, this does not work in practice due to a growing probability of creating associates and aggregates of defects. The probability of tunnel recombination also increases due to the decreasing distance between trapping and recombination centres. The minimal dose detection threshold is connected with non-radiative recombinations and a background (black body) emission of a TLD reader. The threshold depends also on mechanically induced doses and chemiluminescence of the thermoluminescent material. The chemiluminescence mainly results from oxidation of either impurities (flux, dopants) or even the host material. Also the problem of low stability and reproducibility often arises due to oxidation of manganese dopant by oxygen of air. One of the known methods to avoid, or at least to reduce, the oxidation effects is to improve the construction of dosimeters and design new readout methods and procedures. This way, however, increases the size and price of dosimetric equipment. Another way is more preferable: to design the stable against oxidation $\text{CaF}_2\text{-Mn}$ luminescent material.

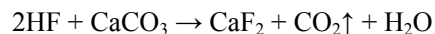
Our task was to work out the technology of $\text{CaF}_2\text{-Mn}$ eliminating this problem while preserving the suitable thermoluminescent properties. Let us first describe shortly the previous approaches to synthesis of $\text{CaF}_2\text{-Mn}$.

One of the methods previously used is based on the following reaction [85,86,88–92]:



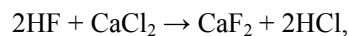
The mixture of initial CaF_2 and $\text{NH}_4\text{MnF}_3 \cdot n\text{H}_2\text{O}$ was placed into a platinum crucible and annealed at 1473 K (1200°C) for 16 hours in an inert gas atmosphere. The Pt catalyses reactions of NN_3 with atmospheric oxygen, so the products NO and NO_2 are released and partially stored in a host lattice, capable of further oxidation of Mn^{2+} . The Mn impurity in higher than 2+ oxidation states is responsible for low-energy traps involved into fading.

Another method suggested by Palmer [93,94] was based on the reaction:



The hydrofluoric acid was added to a suspension of CaCO_3 containing Mn impurity. The obtained CaF_2 precipitate contained some traces of calcium carbonate making worse the luminophor properties.

When CaF_2 was obtained by a reaction [44]:



($C_{\text{Mn}}=1.5 \text{ mol}\%$), the improper TL curve was observed.

There are some other methods of synthesis proposed, for example, either from water solutions of CaCl_2 and MnCl_2 with adding equivalent portion of NH_4F solution [95], or from CaCO_3 and MnCO_3 solid state mixture dispersed in water and reacted with HF . The final annealing was proceeded in Ar or He inert gas atmosphere.

An essential fact was derived from the previous works [86], that Mn impurity cannot be only mechanically mixed with the other reagents because of essentially non-uniform distribution of Mn ion in the final product due to low diffusion rates at the temperature of final annealing. Hence, the only way of synthesis is a co-precipitation of manganese fluoride with calcium fluoride.

The samples of oxygen-free calcium fluoride used in present work were synthesised by Aime Lust at the Institute of Chemical Physics of University of Tartu employing the technology developed by herself [87]. The initial compounds, co-precipitation conditions, concentration of activator (dopant), temperature, atmosphere, and time of syntheses were varied. Special attention was paid to the uniformity of manganese distribution in a final CaF_2 -Mn luminophor, and also the real concentration of Mn dopant in the luminophor were measured [**paper III**].

The co-precipitation of host material together with Mn dopant was proceeded in a specially designed apparatus made of fluoroplast-4. The dilute solutions of calcium and manganese salts were added simultaneously at a regulated rate into the reaction vessel using peristaltic pumps, and HF was also added here. The reaction vessel was heated by water vapour. The precipitate was aged in a beaker for 2–3 hours. The precipitate was decanted and washed carefully, then dried, and annealed in air for 2 hours at 673 K (400°C). The high-temperature annealing was proceeded for 0.5 hour at 1423 K (1150°C) in the atmosphere of inert argon specially purified from residual oxygen. All the initial compounds were of special purity. HF contained less than $10^{-5}\%$ of heavy and transition metals, less than $10^{-3}\%$ of Ba and Sr. CaCl_2 contained less than $10^{-5}\%$ of Al, Cu, Ag, Fe, Mn, Mg, and less than $10^{-4}\%$ of Pb, Bi, Cr, Si. The concentration of Mn dopant was varied in the initial solution, while the real obtained concentration was determined in a specially arranged investigation.

Table 3. The results of ICP-AES and spectrophotometric analyses of powder luminophors $\text{CaF}_2\text{:MnF}_2$ and $\text{CaF}_2\text{:Mn}$ thermoluminescent detectors and calculated with four tests relative standard deviations (RSD).

Sample	Mn, % (m/m)				
	In initial solutions	ICP-AES		Spectrophotometry	
		C _{AVER} ± SD	RSD, %	C _{AVER} ± SD	RSD, %
CaF ₂ :MnF ₂					
1	0.01	0.12 ± 0.0012	1.00	0.10 ± 0.0018	1.80
2	0.05	0.27 ± 0.0026	0.98	0.28 ± 0.0027	0.96
3	0.10	0.51 ± 0.0049	0.96	0.49 ± 0.0098	2.00
4	0.20	0.62 ± 0.0055	0.88	0.59 ± 0.012	2.03
5	0.40	1.49 ± 0.0044	0.90	1.54 ± 0.028	1.82
6	0.80	2.20 ± 0.0094	0.63	2.12 ± 0.044	2.08
7	1.00	2.53 ± 0.017	0.69	2.50 ± 0.048	1.92
8	1.20	2.39 ± 0.019	0.80	2.46 ± 0.042	1.71
9	1.60	1.63 ± 0.011	0.65	1.55 ± 0.029	1.87
10	2.00	1.78 ± 0.016	0.65	1.73 ± 0.040	2.31
CaF ₂ :Mn					
1	0.10	0.58 ± 0.0042	0.72	0.62 ± 0.014	2.26
2	0.20	0.68 ± 0.0051	0.76	0.73 ± 0.013	1.78
3	0.40	1.46 ± 0.010	0.68	1.44 ± 0.028	1.94
4	0.80	1.66 ± 0.012	0.70	1.56 ± 0.031	1.99

While the quantitative composition of the studied luminophor was very important for theoretical conclusions, the concentration of activator in the initial powder luminophor ($\text{CaF}_2\text{:MnF}_2$) and in thermoluminophor $\text{CaF}_2\text{:Mn}$ tablets were determined and compared by two methods: inductively coupled plasma atomic emission spectrometry (ICP-AES), and spectrophotometry [paper III].

A sequential PU 7000 Philips (Unicam Analytical Systems, Cambridge, UK) inductive coupled plasma atomic emission spectrometer was used for the measurements. The spectrophotometric measurements were performed with Lambda 2S Perkin-Elmer UV/VIS spectrometer. TL curves were measured with a modernized TLD reader UPF-02 (Moscow, Russia). The obtained results are presented in the Table 3.

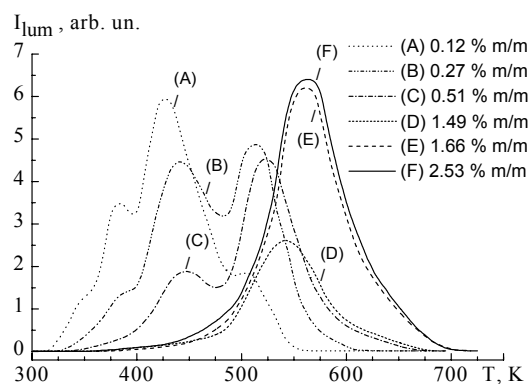


Figure 3. Effect of actual Mn concentration on the shape of TL curves. (A)–(F) are actual concentrations of Mn in molar percent, and corresponding TL curves.

Both methods, ICP-AES and spectrophotometry, give the consistent results. The ICP-AES method is more rapid and convenient in use compared with spectrophotometric method, which is more complicated and time-consuming. The manganese actual concentration changes non-monotonically with the variations of manganese concentration in the initial solution. However, the actual concentration influences the thermoluminescent properties of $\text{CaF}_2\text{-Mn}$ thermoluminophors (see Fig. 3). Thermoluminophors with actual concentration of manganese being 1.7–2.0 mol.% are shown to be most suitable for production of TLD.

Our experimental research succeeded in developing very stable against oxidation of Mn samples working in air without essential changes of their properties up to 100 exposure-readout cycles. The new stable thermoluminescent material has a single TL peak and a lower dose detection threshold compared with that of previously known TLD based on $\text{CaF}_2\text{-Mn}$. This material is foreseen for detection of high (extreme) doses in radiation accidents due to an extraordinarily wide range of linearity of dose response (up to $(2\text{--}4) \cdot 10^5$ Gy).

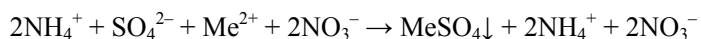
3.1.2. TLD materials with non-linear dose dependence

The problem of tissue-equivalence appears to be very essential for dosimetry of fast neutrons. Fast neutrons interact very differently with solid state and tissue. The cross-section of their interaction strongly depends on the mass of the nucleus. The most effective interaction occurs with the lightweight nuclei, namely, with hydrogen, or protons. Living organisms contain much water.

Hence, the fast neutrons absorbed in living organism produce energetic recoil protons. These protons strongly ionise the tissue and produce a large amount of free radicals. As the recoil protons are charged particles, the ionisation density is very high, and hence, the regions with multiple destroyed chemical bonds are produced. Destroyed by recoil protons tissue requires longer recovery times. This means, that biological equivalent of dose is very high for fast neutrons compared with any other kind of ionising radiation. The biological effect of fast neutrons is considered to be 10–20 times higher than that of gamma radiation. However, the fast neutrons are not so effective to produce radiation effects in solid state dosimeters. Typical TLD contain nuclei with the average mass high enough to obtain so small recoil energy at interaction with fast neutrons that direct radiation effects are negligible. Neither excitation nor radiation damage direct effects could be used in practical TLD dosimetry of fast neutrons. The problem of effective excitation of TLD by fast neutrons is usually solved by combining a thermoluminescent material with some hydrogen-containing material acting as a converter of fast neutrons into protons. This generator of recoil protons is sometimes called “irradiator”. So, the next problem appears — how to recognise the dose produced by recoil protons from the background dose of accompanying gamma-radiation? The solution is based on high ionisation density produced by protons in comparison with gamma-quanta. One needs to develop a luminescent material with the TL output strongly depending on the volume density of excitation [**paper V**]. Some preliminary studies have been indicated that the required properties were approachable with thermoluminescent materials based on CaS. However, no commercial calcium sulphide of suitable for luminescent materials purity was available. So, a task was given to develop a technology of synthesis of high purity alkaline earth sulphides (AES). Our work succeeded in the development of new technologies of high-purity AES (CaS, SrS, BaS) and AES-based luminescent materials [96]. A high-purity SrS was used as a host lattice for luminophors SrS-Ce and SrS-Eu,Sm studied in **papers [VII–X]**.

To obtain reliable and repeatable luminophor sets, the basic compound should be of high purity and of certain composition corresponding to its' formula. These requirements are fulfilled using high purity starting materials and repeatable conditions of treatment, including the temperature of annealing with doping agents, grain re-crystallisation conditions, etc. For example, the initial calcium sulphate can be obtained with different water content and in several different crystal modifications and phase states (monoclinic, rhombohedral, hexagonal, rhombic, cubic, and also several phase states of these crystal modifications). The reaction abilities of different CaSO₄ modifications are different, and the reduction of sulphate to sulphide with hydrogen proceeds well only with certain modifications. We shall mention later this point once more in connection with treatment of initial sulphates.

The starting sulphates MeSO_4 ($\text{Me} = \text{Ca}, \text{Sr}, \text{Ba}$) were precipitated from initial solutions of $\text{Me}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{SO}_4$:



The initial solutions of $\text{Me}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{SO}_4$ salts were purified (no matter how pure were initial commercial reactives) by extraction residual impurities with complex-producing extracting agent 8-oxyquinoline dissolved in chloroform. The extraction was proceeded at two different pH values (5.5 and 8.0) by continuous mixing of a water solution of either $\text{Me}(\text{NO}_3)_2$ or $(\text{NH}_4)_2\text{SO}_4$ salt with chloroform solution of 8-oxyquinoline.

The alkaline earth sulphates were precipitated from hot acidic solutions ($\text{pH}=1.0$). The bittern containing H_2SO_4 solution was prepared in the reaction vessel. Then the purified solutions of initial $\text{Me}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{SO}_4$ were permanently added into a bittern using two peristaltic pumps to keep the constant ratio and concentrations of SO_4^{2-} and Me^{2+} ions in the reaction solution. To remove the residual impurities, a fast preliminary precipitation was proceeded (about 5% of total amount), and the first fraction of precipitated alkaline earth sulphate was removed. The main part of the product was obtained at a slow precipitation rate with permanent mixing at temperature about 80°C . The precipitate was repeatedly and carefully washed with triply distilled in quartz water to remove the residual halogen and alkaline metal ions. Then the powder sulphate was dried and annealed at 900°C in air for two hours. The annealing was repeated after stirring the powder until the traces of organic compounds were burned out. This procedure has occurred to be very crucial to overheating: the partially dissociated modification of anhydrous calcium sulphate can be formed [97] at high temperature, and the further reduction of such sulphate to sulphide goes then with difficulty.

After firing out the traces of organic compounds, the reduction of sulphate by hydrogen stream into sulphide was proceeded in a vertical quartz tube at temperature of 1220 K (950°C). The percentage of MeS in the product was about 98%. The amount of oxides (or dissolved oxygen) was found to fall into the range 0.6–1.5%. Chemical analysis has revealed the sulphite and tiosulphate to be about 0.5% each. The traces of transition metals ($\text{Fe}, \text{Cu}, \text{Pb}, \text{Mn}, \text{Cr}$) were determined by spectral analysis: less than $1\cdot 10^{-5}\%$ of each metal. The residual amounts of Cl^- and Na^+ ions were estimated by luminescence analysis of less than $5\cdot 10^{-2}\%$. EPR studies also agree with this estimation.

Our studies has shown that the percentage of sulphide increases, and homogeneity of dopant distribution improves when the mixture of sulphide, sulphate, elementary sulphur, and the doping agent, is annealed at $1370\text{--}1420\text{ K}$ ($1100\text{--}1150^\circ\text{C}$). The re-crystallisation of sulphide occurs hereby improving the luminophor properties.

Luminophor CaS-Bi

There are some special features of the superlinear thermoluminophors required for the dosimetry of fast neutrons. I. Jaek has carried out the detailed study of these features [98]. The TL output produced by gamma-irradiation should be decreased in comparison with the output from the recoil protons. The most effective distinguishing of doses caused by fast neutrons dose and gamma-radiation is achieved in thermoluminophors with two different dosimetric peaks [paper V]. The interaction of different traps occurs at the irradiation. There are the traps of two different kinds, the deeper ones with a small concentration, and the shallower ones with a large concentration. The deeper traps with a smaller concentration are storing the information on gamma-dose, while the shallower traps are storing the dose of fast neutrons (recoil protons) giving a higher density of excitation in particle tracks. The second-order processes take place when the excitations from different particle tracks are overlapping, and excitations are interacting with each other near the trapping centres. This is the case when the excitation density is very high in the track. However, the interaction of excitation occurs also between the tracks of gamma-quanta at high doses. This puts a limit for distinguishing gamma-radiation and fast neutron doses. The interaction of excitations from gamma-quanta occurs if they are transferred too far and reach the same trapping centre. This causes the superlinear response to gamma-dose at relatively low gamma-radiation doses. To extend the linearity for gamma-radiation dose, some quenchers (Ni, Fe, Co) are introduced into the thermoluminophor. The quenchers effectively kill the solitary migrating excitations from gamma-quanta, while they are ineffective to work against high-density excitations in tracks of recoil protons. A typical dependence of TL output on the dose of gamma-radiation is shown in Figure 4. The dose dependence remains linear up to the dose about 1 Gy. At higher doses, or in case of crossing or overlapping tracks, the superlinear dependence occurs. Also, this is especially true for high excitation densities in tracks of recoil protons. So, at the dose about 10^2 Gy the TL output per one dose unit is 10 times higher than at the dose of 1 Gy. This feature makes possible to decrease the sensitivity to gamma-radiation by an order of magnitude in comparison with the effect of fast neutrons (recoil protons).

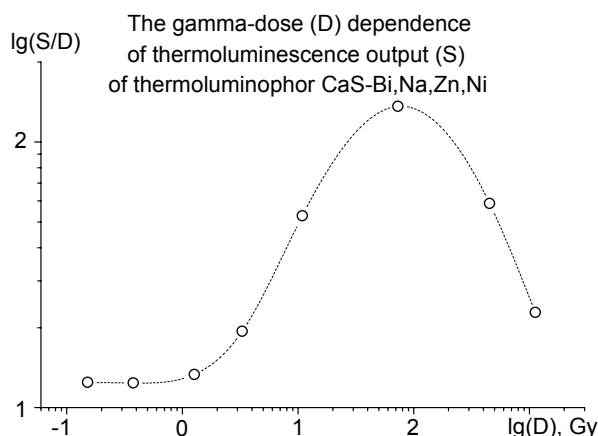


Figure 4. The typical dependence of TL output on the dose of gamma-radiation for CaS-Bi,Na,Zn,Ni thermoluminophor.

The new thermoluminophor for dosimetry of fast neutrons was developed at analytical chemistry chair of University of Tartu in a working partnership with radiation physics department of Physics Institute of Tartu headed by professor I. Jaek. The non-linear properties of thermoluminophor were found to depend both on the composition and on the order in which the doping impurities were introduced. The luminophor shows emission bands in the range of 380–520 nm. These bands are connected with $6s6p \rightarrow 6s^2$ transitions in Bi^{3+} ion. The emission bands are also influenced by a co-doping Na^+ impurity. This indicates that the complex centres containing both Bi^{3+} and Na^+ are formed. The TL curve main maximum is observed at 453 K (180°C) (heating rate 2 K/s), and additional maxima appear at 393 K (120°C) and 493 K (220°C). The typical sensitivity of thermoluminophor to gamma-rays (^{60}Co) is $4 \cdot 10^{15}$ quanta/C. The energetic output is $2 \cdot 10^{-4}$ (for α -particles, ^{239}Pu). The thermoluminophor has the linear working range at doses from $1 \cdot 10^{-4}$ to $3 \cdot 10^{-2}$ C/kg (by gamma-radiation). The luminophor is sensitive to daylight — a TL is effectively excited in blue region. This requires to store the TLD and to work with them in the dark.

One more problem studied in connection with CaS-Bi thermoluminophors is the mechanical effects on TL curves. The mechanical actions (vibrations, strokes, shaking, pressing) produce high-temperature maxima at the TL curve, about 570–670 K (300–400°C). This effect was previously studied for LiF and $\text{CaF}_2\text{-Mn}$ thermoluminophors. The mechanical effects on TL output of CaS-Bi are illustrated in Table 4. The luminophor was ground strongly in a quartz mortar for 3 minutes. The dose information below 520 K (250°C) was not

affected by grinding, while the high-temperature region of TL curve was essentially enhanced (see Table 4).

Table 4. The excited CaS-Bi (dose $1 \cdot 10^{-3}$ C/kg) TL curve partial light sums before and after luminophor grinding.

	TL curve partial light sums							
T, K	323	373	423	473	523	573	623	673
T, °C	50	100	150	200	250	300	350	400
$1 \cdot 10^{-3}$ C/kg	28	185	330	580	860	910	965	1140
$1 \cdot 10^{-3}$ C/kg ground 3 min	30	185	330	580	880	1070	1700	3575

The nature of mechanical effects was studied separately with pure CaS [99]. The EPR studies of plastically deformed samples showed the presence of cation and anion vacancies and different complexes. The induced by mechanical effect defects are being annealed at temperature about 723 K (450°C). This temperature is too low for real ionic processes. So, one can suppose that the defects are generated and transported by dislocations. The electric fields of dislocations and the induced lattice defects are responsible for mechanical effects on TL curve. To decrease the mechanical effects, one needs to prevent dislocations from moving and crossing each other. The simplest way is to soften the mechanical effects by introduction of elastic binding material into a TLD tablet. Thermo-resistant silicon varnish have been introduced into TLD tablets, and mechanically induced doses decreased by factor 1.7. However, the most effective means against the effects of dislocation movement gives the introduction of Ni into the thermoluminophor composition. It is not known exactly by what mechanisms Ni impurity acts in sulphides. Probably, it occurs involved into complexes with intrinsic defects generated by dislocations and stops their movement. Also, Ni is a quencher killing the excitations produced in the regions where dislocations are moving. Practically, as low amount of Ni as $1 \cdot 10^{-4}$ mol.% removes the mechanical effects completely, or, at least, makes mechanical effects lower than the background TL signal.

3.1.3. Luminescent materials for dosimeters with optically stimulated readout

Thermoluminescence measuring devices for dosimetric applications are quite complicated ones despite of very simple basic principle of operation. The problems are connected with a background readout from thermal (black body) radiation of heater, TLD stability in air at elevated temperatures, emission of

fired dust particles, thermal contact of heater with a detector and time of heating required for readout and complete emptying of stored dose information. Optically stimulated readout seems to be much simpler in technical implementation. However, it assumes some additional requirements for TLD materials.

Many thermoluminescent materials demonstrate the optically stimulated afterglow (OSA) phenomenon after storage of energy. The decaying luminescence is observed after irradiation the luminophor with quanta of different energies being inefficient to create the additional stored excitation but suitable to cause the exhaustion of energy already stored in the luminophor.

The first applications of OSA were not connected with dosimetry — this phenomenon was used first in night-vision devices and infrared light communications. Infrared(IR)-sensitive storage phosphors were studied yet at the end of 19-th century [67]. These phosphors were based on SrS doped with a pair of rare-earth impurities, Eu and Sm, or Ce and Sm. The solid solutions were usually prepared in a single-stage synthesis, when doped with rare earth impurities strontium carbonate was annealed with sulphur in a closed or sealed ampoule. P. Lenard has suggested these luminophors for invisible IR-light communications, and simple signalling devices were tried while the World War I. Pre-excited IR-sensitive storage phosphors SrS:Eu,Sm or SrS:Ce,Sm were used to detect infrared light signals. IR-sensitive storage phosphors were employed also in first night-vision devices during the World War II. The effect of IR-stimulation of a storage phosphor was used to make visible the infrared image projected onto a screen containing the excited storage phosphor (usually SrS:Ce,Sm). The screen needed to be continuously excited with near UV or violet light to fill up the phosphor with energy.

One of the well-known applications of storage phosphors with OSL-based readout is connected with X-ray storage screens. A screen is exposed to X-rays instead of an ordinary photoplate. Readout of X-ray storage screen is proceeded with a laser beam stimulating the luminescence, which is measured and stored digitally point by point. The amount of light produced at the screen point is proportional to the energy stored here by X-irradiation. Thus an image is reconstructed point-by-point. The image stored digitally can be printed out or watched at any time when necessary. Commonly used in X-ray storage screens phosphor BaFBr:Eu gives out a blue emission when stimulated by red laser beam.

It is a common feature of the described above storage luminophors with OSL-based readout, that the quanta of lower energy than the output luminescence are used for output stimulation. Generally, the light with quanta of different energies can be used for output stimulation, including the higher ones than of output luminescence. However, the problem of spectral separation of the luminescence output from stimulating light is limiting the possibilities of measuring techniques with simultaneous stimulation and registration of output. The complete stimulation spectrum can be measured and used in practice with a time-resolution technique instead of spectral separation. The intensity of the

optically stimulated afterglow (OSA) is measured and integrated in time after a pulse of stimulating light. To avoid measuring the directly excited inter-centre luminescence, a small delay is used between the end of stimulating pulse and the start of measurements.

The OSA spectra of both commercial (LiF(TLD-100) and $\text{Al}_2\text{O}_3\text{:C}$) and produced in our laboratory TLD materials ($\text{CaSO}_4\text{-Dy}$ and $\text{CaF}_2\text{-Mn}$ [87]) were studied in our **paper** [VI]. The samples were prepared by co-precipitation of a host compound with a doping impurity followed by high-temperature annealing (see the preparation details in previous chapters).

Most of the studied materials possess effective optical stimulation bands falling into the range of transparency of the host material but situated at lower wavelengths than their luminescence bands. This shows that the OSA method is applicable with the studied materials. The OSA spectra of $\text{CaSO}_4\text{-Dy}$ and $\text{CaF}_2\text{-Mn}$ are shown in Fig. 5. The spectra were measured using Xe arc lamp and SPM monochromator and were corrected with regard to spectral distribution of light intensity of the installation. The delay between a pulse of stimulating light and measurements was usually 50 ms, except for $\text{CaF}_2\text{-Mn}$, where a delay of 150 ms was required due to slow forbidden luminescence transitions directly excited by stimulating pulse light in Mn^{2+} ion. The samples were X-rayed before measurements of OSA spectra and thermo-optical bleaching.

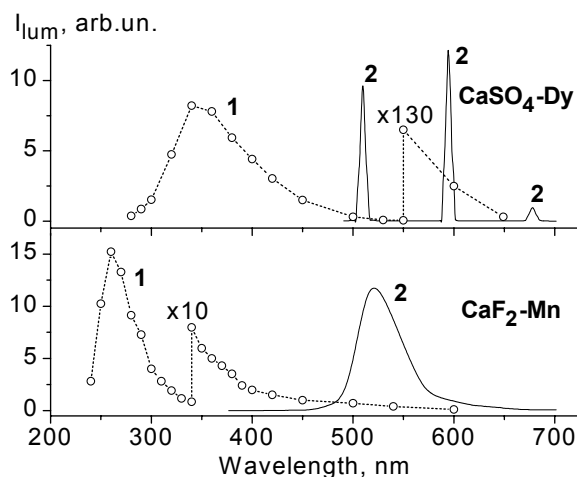


Figure 5. The OSA spectra (curves 1) and X-Ray excited luminescence spectra (curves 2) of $\text{CaSO}_4\text{-Dy}$ and $\text{CaF}_2\text{-Mn}$ thermoluminophors.

The $\text{CaSO}_4\text{-Dy}$ thermoluminophor demonstrated a linear dependence of OSA signal on the stored dose (see Fig. 6), similarly to an ordinary TL readout.

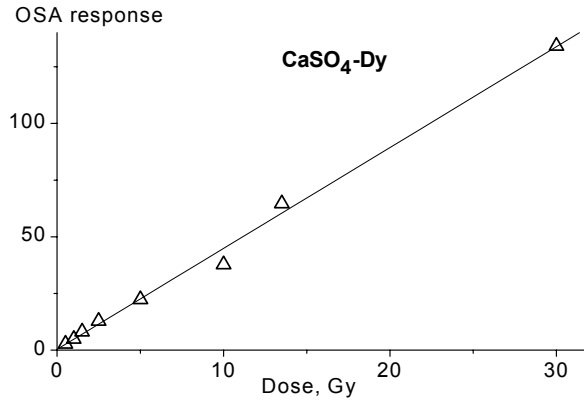


Figure 6. The OSA signal versus dose for the $\text{CaSO}_4\text{-Dy}$ thermoluminophor.

One of the most attractive advantages of $\text{CaSO}_4\text{-Dy}$ among the other studied materials is the possibility to use an unfiltered light of incandescent halogen lamp for OSA measurements. The OSA response of $\text{CaSO}_4\text{-Dy}$ is linear at least up to dose of 30 Gy.

The general requirements for implementation of OSA method in dosimetry are formulated in **paper [VI]**:

1. The optical stimulation bands should be connected with emptying of the proper “dosimetric” traps revealed and used in TL readout. The decrease of intensity of dosimetric TL peaks after stimulating in corresponding optical bands (thermo-optical bleaching) indicates that both TL and OSA methods are dealing with the same traps.
2. The stimulating light should not excite recombination luminescence including the thermoluminescence, or should not increase the population of traps with charge carriers. The problem could be complicated because of possibility of different charge-transfer transitions induced by quanta with energies lower than band gap of the material. So, one should check all the possible thermoluminescence excitation bands before using the OSA method, and restrict the stimulating light to prevent it from overlapping with TL excitation bands.
3. To achieve the maximum sensitivity, one needs to use short dead-times between the stimulation light pulse and luminescence measurement, so-called delay time. However, the excitation of forbidden transitions with stimulating light causes a long-time fluorescence after a stimulating pulse. This problem is actual for $\text{CaF}_2\text{-Mn}$ thermoluminophor where slow forbidden transitions in Mn^{2+} ion are excited. The intercentre processes with

involved charge-transfer states are also often giving a long-time afterglow. So, it is sometimes difficult to distinguish the OSA signal and the directly excited by pulse fluorescence in case of slow transitions and short delay times. This puts a limit of sensitivity for some materials with slow fluorescence, and requires special studies of such materials before the OSA method implementation.

The thermoluminophor $\text{CaSO}_4\text{-Dy}$ synthesised in our laboratory is very suitable for optically stimulated readout, and meets all the requirements for implementation of OSA method.

3.2. Luminescent materials for physical research of luminophors and their luminescence mechanisms

The more physicists know about chemical preparations and technological details of the material under investigation, the better models can they suggest to explain the obtained results. Both solid-state chemistry and solid-state physics are going side by side in studying the varieties of either intrinsic or impurity defects, and also their complexes. The technological details essentially affect the structure of lattice defects and thus the properties of luminophor.

3.2.1. Alkaline Earth Sulphides: classical materials with various models of luminescence mechanisms

The role of complex luminescence and trapping centres appears to be very essential in well-known “classical” luminescent materials — Alkaline Earth Sulphides (AES) doped with rare-earth impurities. We are to mention that the efficiency of energy transfer is rather high in complex centres in these particular luminophors, and quenching processes are not dominating in complex centres where rare earth dopants (Ce^{3+} , Eu^{3+} , Eu^{2+}) are involved.

SrS-Ce phosphor is attracting attention of researchers as the possible material for electroluminescent panels [100,101]. However, the structure of luminescence centres where Ce^{3+} being involved in is still unknown. To study the nature of luminescence centres, several sets of samples were prepared [papers VII–IX]. SrS was doped with Ce either together with co-activator (F, Cl, Br, I in a form of NH_4F , NH_4Cl , NH_4Br , NH_4I , LiCl , NaCl , KCl) or without any co-activator. Concentration of Ce was varied from 0.01 to 5 mol.%. Concentration of co-activator was varied in the range of 0.97–6.5 mol.%. The annealing atmosphere was also controlled. Luminophor was protected from oxidation by sulphur vapours either completely or partly, with a restricted atmospheric oxygen access. The condition of limited oxygen access enhances the probability of creation of cation vacancies, because the oxygen is readily incorporated into

sulphides instead of sulphur, being more active to compose oxides than sulphur composes sulphides of alkaline earth metals. Thus, a lack of alkaline earth metal arises in a form of cation vacancies. It is not yet completely clear, is the incorporated oxygen included into complex centres containing cation vacancies or not, it is rather sometimes but not always included (see below the discussion of [paper VII]).

The results obtained in [papers VII–IX] are briefly formulated below:

Two absorption bands in the range of 2–3 eV were observed in the diffuse reflectance spectra of SrS-Ce,F phosphors [paper VIII], first one at 2.88 eV, and the second one at 2.36 eV. The band at 2.36 eV was observed in SrS-F with no Ce added, while the absorption band at 2.88 eV was formed in the samples doped with Ce and increased essentially when both Ce and F were added to SrS. The intensity of the absorption band at 2.88 eV increased also when the added Ce concentration has been increased at fixed concentration of F impurity. The obtained data indicate that an absorption band at 2.36 eV is connected with some defects induced by incorporated into the lattice halogen ions. This absorption band was observed also with other halogenides (NH₄Cl, NH₄Br, NH₄I, LiCl, NaCl, KCl). What concerns the absorption band at 2.88 eV, it is obviously connected with a centre containing Ce impurity. The maximum of this absorption band coincides with the maximum of excitation spectrum of Ce³⁺ luminescence in SrS [102]. However, the presence of halogen co-activator increases the absorption band at 2.88 eV. This indicates that there are most probably complex centres, containing both Ce³⁺ and halogen. This is possible when they both are situated close to the same cation vacancy – this way the charge compensation is performed. The same conclusion was derived in [paper IX] from the studies of luminescence spectra of SrS-Ce³⁺ doped with different halogen ions as co-activators. The luminescence spectra do not depend on the kind of halogen used as co-activator. Besides the compensation of positive charge of Ce³⁺ in cation position, a cation vacancy provides a movable electron cloud of sulphide anions. Hence, it is probable that the absorption at 2.88 eV is connected also with a charge-transfer transition in a complex Hal–V_C–Ce³⁺. The excitation of Ce³⁺ luminescence through a charge-transfer mixed state of Ce³⁺ with sulphide anions is an intracentre process, with almost the same efficiency and speed as direct transitions 4f–5d. The solubility of Ce₂S₃ in SrS is rather high, and halogen ions are not so necessary to facilitate the diffusion of as low amount as 0.1 mol.% of Ce³⁺ into the lattice of SrS. EPR data [103] confirm, that there are different Ce³⁺ ions in SrS luminophor, both isolated ones and aggregated with other defect, most probably, cation vacancy. Hence, it is possible that, by some reasons, the isolated Ce³⁺ ions are less efficient in luminescence. It is interesting to note that the excess of halogen ions causes the degradation of the two-humped luminescence band of Ce³⁺ in SrS. However, another pair of weaker luminescence bands at longer wavelengths appear only in case of SrS-Ce,F luminophors doped with high fluorine concentrations [paper IX]. These bands possess about twice slower decay characteristics than

normal luminescence bands of Ce^{3+} . The model of compensated by interstitial F^- ions Ce^{3+} is suggested to explain these shifted luminescence spectrum. This is also indirectly proved by the SrF_2 phase arising in SrS at high fluorine concentrations. Interstitial ions demonstrate a first step to a separate phase formation. The other halogen ions have too large ionic radii, and no analogous luminescence bands were detected with high concentrations of other halogen ions. The shifted luminescence bands (however, towards higher energies) were observed also in the samples prepared with a limited oxygen access [**paper VII**]. Besides the ordinary pair of bands at 2.31 and 2.57 eV, an additional pair of luminescence bands at 2.73 and 3.15 eV was observed. Fast decay characteristics of these bands enable one to connect them with Ce^{3+} . Either they are direct emission transitions in the influenced by a changed due to oxygen crystal field Ce^{3+} , or probably, the decay characteristics are explained by the fast energy transfer through some charge-transfer state in a complex luminescence centre where oxygen is included together with cation vacancy and Ce^{3+} .

The idea of charge transformations of dopants and transfer of charge carriers (electrons or holes) through conduction band or valence band was taken from the models suggested previously for the well-known storage luminescent materials SrS:Eu,Sm and SrS:Ce,Sm . Nevertheless, our recent studies demonstrated the absence of charge transformations of Eu and Sm impurities in the luminophor SrS:Eu,Sm during storage and release of stored energy [**paper X**]. The results were obtained with very sensitive SQUID magnetometer and demonstrated very negligible variations of magnetic susceptibility after storage and release of stored excitation (see Table 5).

Table 5. Variations of Curie-Weiss constant ($\chi=C(T-\theta)+\chi_0$) due to excitation and IR-irradiation of storage phosphor SrS:Eu,Sm Nr. 274.

	C	θ	χ_0
Unexcited	308.66±1.91	0.120±0.026	-1.82±0.08
Excited	304.58±1.41	0.085±0.020	-1.80±0.06
IR-emptied	295.32±3.77	-0.026±0.042	-1.15±0.22
Excited once more	308.73±6.75	0.177±0.076	-1.95±0.39

The variations did not correlate with the old model, and were even more pronounced in a sample without storage properties. We connect the processes of storage and release of energy in SrS:Eu,Sm with the excited charge-transfer state formed on the basis of complex composed by a pair of Eu^{3+} and Sm^{3+} around a common cation vacancy. This model is evidenced indirectly from the fact that no storage properties were observed in the sample of the same composition but different order of doping with the same impurities. Only simul-

taneously introduced Eu and Sm are bound in mixed pairs around a common cation vacancy. To enhance this effect, a special synthesis technology was designed which included simultaneous reduction of added portion of SrSO_4 and re-crystallisation of SrS mixed with this additional SrSO_4 and both activators. As was mentioned above, trivalent rare earth dopants produce required for charge compensation cation vacancies in AES. This is a common way of charge compensation. Also, the covalent bond of a rare earth metal with sulphur is better realised (the electron density can be shifted to a large extent towards a rare earth impurity) when the cation vacancy is the closest neighbour to an impurity ion. When a pair of two different rare-earth impurities is situated around a common cation vacancy, the asymmetrical redistribution of electron cloud occurs giving a minimum of lattice potential energy. However, some special technological efforts are required to realise this configuration to a maximum extent. This charge-transfer state of the complex centre has at least two excited states, the upper excited state and partially relaxed one. The energy is transferred to Eu^{3+} only from the upper excited state with phonon absorption required to overcome an additional barrier. This excited state relaxes soon back to lower energy level, and IR quantum is required again to obtain this upper excited state back. This explains a low emission rate at IR stimulation when temperature is low enough. When the excited state of Eu^{3+} eventually appears from the charge transfer upper excited state, the forbidden f-f transitions are not realised. The excitation of Eu^{3+} is finally deactivated with the resonance energy transfer to Eu^{2+} ion emitting a wide luminescence band in red region.

3.2.2. Sulphates of alkaline earth and alkaline metals and their luminescence properties

Despite of extensive studies of electron excitations and excitation transfer in sulphates, there are still many unknown features limiting the forecasts concerning their application as host materials for commercial luminophors. The main difficulty of luminescence studies is connected with very low intensity of intrinsic luminescence bands compared with various emission bands of impurities and radiation-induced defects. The intrinsic luminescence bands can be suppressed in the presence of very small amounts of impurities. Hence, the study of different luminescence processes using intrinsic luminescence bands as the reference is possible only with the samples of very high purity grade, with no undesired and with controlled amount of desired impurities and intrinsic lattice defects.

We have succeeded to develop the preparation technique and to produce the luminescent materials satisfying these requirements. We have prepared CaSO_4 -Dy, SrSO_4 , SrSO_4 -Eu, BaSO_4 , Na_2SO_4 , K_2SO_4 , Rb_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, Cs_2SO_4 . These materials were used to study excitation and luminescence spectra both at pulse and at steady excitation in the temperature range of 4–400 K. The results

of physical investigations of these materials are published in **papers [I,II]** and discussed below.

a) “slow” luminescence bands (with τ about 10^{-6} s):

there are two spectral ranges in all sulphates where slow luminescence bands are observed, namely, at 3.6–4.5 eV, and at 2.5–3.3 eV. The luminescence band at a shorter range of wavelengths is effectively excited by the quanta with energies starting from 7.6–9.3 eV and coinciding with excitonic absorption band. The nature of luminescence is connected with the emission of autolocalised exciton. Low luminescence intensity is explained by the fact that the excited state of a sulphate-anion $(\text{SO}_4)^{2-*}$ is efficiently decaying non-radiatively but yielding radicals $(-\text{O}-\text{SO}_2-)$, $(-\text{SO}_2-)$, etc. When the effective luminescence centres are introduced (Dy^{3+} or Eu^{2+}), the efficiency of energy transformation into luminescence increases due to radiative recombination of charge carriers released by heat or light [**papers I,II**].

The luminescence bands at a longer range of wavelength (2.5–3.3 eV) are excited mostly by quanta with energies close to the fundamental absorption edge of the lattice. This means that these luminescence bands are connected with lattice defects, either intrinsic or radiation-induced ones. This is concluded from the fact that the intensity of these luminescence bands increases with the radiation dose, with the initial intensity being dependent on the preparation of luminescent material.

b) “fast” intrinsic luminescence bands:

an emission with rather complex spectral constitution and short decay time (τ shorter than $2 \cdot 10^{-9}$ s) is discovered in undoped pure sulphates K_2SO_4 , Rb_2SO_4 , Cs_2SO_4 , SrSO_4 , BaSO_4 . The study of excitation spectra showed that this emission band is excited only by quanta with energies above 15 eV [**paper I**]. This emission band is similar by its’ properties to the well-known in other materials (e.g., CsCl , BaF_2 , etc. [104]) cross-luminescence, which is excited by quanta with energies exceeding the energy of creation of cationic excitons. The cross-luminescence occurs due to creation and annihilation a hole in the filled cationic valence band after the electron from the cationic valence band was released into a conductive band. A hole in the cationic valence band is then annihilated at recombination with another electron coming from an anionic valence band. This results in a very fast cross-luminescence. However, systematic studies of different sulphates revealed that the spectral range of fast luminescence excitation starts in different sulphates at about 15 eV, while the structure of excitation spectrum depends on the nature of a cation in the lattice. Also, this fast intrinsic luminescence is observed only in those sulphates where a broad oxygen valence band is split by the crystal field. All these facts lead one to a conclusion that the exciting quanta with energies above 15 eV are transferring electrons from a lower oxygen valence band into a conductive band. The spectrum of fast luminescence band represents how the densities of states are distributed in the upper part of the split valence band, while the

excitation spectrum in the range of 15–25 eV represents both the distribution of the densities of states in the lower part of the valence band and also the imposing states of cations like Cs 5d (15 eV), Ba 5d (18 eV), or K (25 eV).

Besides the structured fast luminescence band, sulphates demonstrate also a fast unstructured luminescence band. In case of sulphates with non-split valence band (Na_2SO_4 , CaSO_4), the short wavelength edge of this unstructured luminescence band lies out of the spectral range of the installation used for measurements ($h\nu \geq 7$ eV). The intensity of this unstructured luminescence is decreasing in the range of 6.1–6.6 eV in case of sulphates with a split valence band (K_2SO_4 , Rb_2SO_4 , Cs_2SO_4 , SrSO_4 , BaSO_4). This unstructured fast luminescence band can be connected with the radiative transitions inside the oxygen valence band.

3.2.3. Luminescent materials on the basis of CaF_2

The luminescent materials on the basis of calcium fluoride attract the attention of researchers due to multiple possible applications: as the dosimeters of ionising radiation [105,106,58], as the model objects for studying energy transfer in solids [58–60,107], and also as materials for short-wavelength laser optics [61,62].

However, there are only two papers [66,108] where the processes of luminescence excitation were studied with photon energies above 6 eV. This means that very essential problems remained unexplored till present days. High-energy excited states of impurities were not studied well, and also, the processes of electron-hole and exciton energy transfer to luminescence centres. The mechanisms of transformation of host lattice excitation into elementary excitations (electron-hole pairs, excitons) transporting energy to luminescence centres were also poorly studied in CaF_2 .

The spectral measurements in the VUV range require the samples of very high purity, without the traces of oxygen or casual impurities. These samples were prepared by co-precipitation of MnF_2 together with CaF_2 using the technology briefly described above in a previous section. The concentration of Mn was varied in the initial solutions, with the resulting Mn concentration being determined in a separate study [**paper III**]. The resulting Mn concentration in luminophors varied from 0.01 to 2.47 wt. %. The high quality of the samples was confirmed by spectral measurements — neither the luminescence of oxygen-related centres nor other luminescence bands of casual impurities were revealed [**paper IV**].

Main results of the study of luminescence excitation of CaF_2 -Mn are the following:

1. The impurity-bound excitons are created at 9.4 eV and at 10.1 eV, the mobile excitons are generated at 11.2 eV, and the band-to-band transitions are observed above 12 eV.

2. There are three ineffective mechanisms of Mn^{2+} excitation in CaF_2 : reabsorption of light, direct transport of mobile excitons to Mn^{2+} , and electron recombination processes (capturing by neutral centre first hole, then electron).
3. There are two effective mechanisms of Mn^{2+} excitation in CaF_2 : resonance energy transfer from excitons due to good overlapping of exciton emission with absorption spectra of Mn^{2+} , and also hole recombination process (capturing first electron then hole).
4. The most effective is the hole recombination mechanism, when Mn^{2+} ion is first capturing an electron, and then a hole (migrating freely at temperatures above 130 K) recombines captured electron. The energy is stored at irradiation as a result of decay of impurity-bound excitons into a pair of Frenkel defects, $F_A(\text{Mn})$ (F-centre in a close vicinity of Mn^{2+}), and H-centre going away to lattice defects. Hence, the stability and preservation of stored dose information depends in $\text{CaF}_2\text{-Mn}$ on the stability of lattice defects resulted from this process of exciton decay.

4. CONCLUSIONS

Main results of the present work are briefly presented below:

- The co-precipitation method was developed and optimized to obtain thermoluminophors $\text{CaSO}_4\text{-Dy}$ with suitable sensitivity and TL curve. The optimum TLD on the basis of $\text{CaSO}_4\text{-Dy}$ was obtained from $\text{Ca}(\text{NO}_3)_2$ and H_2SO_4 solutions with a large excess of H_2SO_4 ($[\text{Ca}^{2+}]:[\text{SO}_4^{2-}] = 1:15$). After final annealing, the sensitivity to gamma- or Roentgen radiation was close to that of $\text{CaSO}_4\text{-Dy}$ synthesised by re-crystallisation of CaSO_4 with Dy doping agent in hot H_2SO_4 . The co-precipitation is much easier to carry out, because there is no necessity to work with a highly concentrated hot H_2SO_4 . Also, the product obtained by co-precipitation method has a homogeneous and small grain size making easier to produce TLD detectors in a form of tablets.
- A nice thermoluminophor $\text{SrSO}_4\text{-Eu}$ with a single TL peak at 493 K (220°C) was obtained by a similar to used for $\text{CaSO}_4\text{-Dy}$ co-precipitation process, except the lower excess of sulphate anions ($[\text{Sr}^{2+}]:[\text{SO}_4^{2-}] = 1:2$).
- The technique used for additional refinement of both CaSO_4 and SrSO_4 was suitable to obtain the pure luminescent materials without masking luminescence bands. The obtained samples were used to study the intrinsic luminescence in different sulphates. Several groups of luminescence spectra were observed. The most interesting are “fast” intrinsic luminescence bands, an emission with rather complex spectral composition and short decay time (τ shorter than $2 \cdot 10^{-9}$ s) is discovered in undoped pure sulphates K_2SO_4 , Rb_2SO_4 , Cs_2SO_4 , SrSO_4 , BaSO_4 . The study of excitation spectra showed that this emission band is excited only by quanta with energies above 15 eV. Systematic studies of different sulphates revealed that the spectral range of fast luminescence excitation starts in different sulphates at about 15 eV, while the structure of excitation spectrum depends on the nature of a cation in the lattice. Also, this fast intrinsic luminescence is observed only in those sulphates where a broad oxygen valence band is split by the crystal field. All these facts lead one to a conclusion that the exciting quanta with energies above 15 eV are transferring electrons from a lower oxygen valence band into a conductive band. The spectrum of fast luminescence band represents how the densities of electronic states are distributed in the upper part of the split valence band, while the excitation spectrum in the range of 15–25 eV represents both the distribution of the densities of states in the lower part of the valence band, and also the imposing states of cations.
- A technology of synthesis of $\text{Li}_2\text{B}_2\text{O}_7\text{-Mn,Si}$ thermoluminophor with suitable for TLD characteristics was developed, including synthering of TLD in a form of tablets.
- The samples of stable against oxidation and free of oxygen traces $\text{CaF}_2\text{-Mn}$ were studied. Samples were produced by co-precipitation of Ca^{2+} and Mn^{2+} from acidic solution containing hydrofluoric acid. The shape of TL curve

was studied depending on the actual concentration of Mn determined in the luminophor. The main TL curve maximum occurs at higher temperatures (about 570 K, or 300°C) when the actual Mn concentration is close to 2 % m/m. High purity of the host material and absence of oxygen-related luminescence bands helped to study luminescence properties and energy transfer mechanisms in the CaF₂-Mn luminophor. The energies of creation of impurity-bound excitons were determined (9.4 eV and 10.1 eV), also the energy of creation of mobile excitons (11.2 eV), and the energy band-to-band transitions (12 eV). The effective and ineffective mechanisms of Mn²⁺ excitation and energy storage were studied. Very wide range of linear response to dose makes this material suitable to monitor the extreme cases of radiation accidents.

- The technology of alkaline earth sulphides was further developed in order to obtain complex thermoluminescent systems with both linear and non-linear effects. The essential role of interaction of impurities in solid solutions was found. The final structure of complex centres was shown to depend on the consecution of impurity set introduction into the lattice, and not only on the composition of luminophor. Non-linear dose response and mechanical dose storage effects were studied in CaS-Bi thermoluminophors destined for dosimetry of fast neutrons (recoil protons).
- Some of known TLD were checked against the possibility of readout using optically stimulated afterglow (OSA) method. The basic requirements are formulated for the luminophors intended for OSA method application. Thermoluminophor CaSO₄-Dy is shown to be very suitable for OSA method employment.
- The conditions of formation of complex luminescent centres in SrS-Ce and SrS-Eu,Sm luminophors were studied. The essential role of cation vacancies was revealed. On the analogy with non-linear dosimetric materials, the mechanisms of complex defects formation are shown to depend on consecution the impurities are introduced into the host lattice. The absorption bands of Ce³⁺ impurity and halogen impurity were found. The shifted emission bands of Ce³⁺ were observed in samples with excess of fluorine, the emission bands of Ce³⁺ are shifted towards red due to probable influence of crystal lattice field. Another pair of shifted but into ultraviolet luminescence bands is observed in the samples with a limited oxygen access. Possible role of charge-transfer states is discussed. The storage phosphor SrS-Eu,Sm is studied at SQUID-magnetometer. The proper charge transformations of Eu²⁺ and Sm³⁺ were not detected after the storage and release of excitation. The alternative model of luminescence and storage properties was suggested to explain the observed results. The model is based on the transitions between excited states of charge-transfer complex composed of rare earth ions and electron clouds of sulphide-ions near a cation vacancy.

REFERENCES

1. Mihaltsenko, G.A. Radiation physics, **1967**, 5, 103 (Riga "Zinatne")
2. Schvarts, K.K.; Grant, Z.A. Luminescent receivers and transformers of ionising radiation, **1974**, Proceedings of All-Union symposium, p. 94 (Moscow, MNIIRRI, 1974).
3. Lushchik, Ch.B. *Proceedings of Inst. of Physics of Est. Acad. Sci.* **1961**, 15, 103.
4. Savikhin, F.A. *Proceedings of Inst. of Physics of Est. Acad. Sci.* **1974**, 42, 137.
5. Niewiadomski, T.; Bilski, P.; Budzanowski, M.; Olko, P.; Ryba, E. *Nukleonika* **1996**, 41(2), 93.
6. Prokic, M. *Radiat. Prot. Dosim.* **1996**, 66(1–4), 153.
7. Ohera, M.; Fiala, E.; Valasek, J. *Jaderna Energie* **1992**, 38(11), 393.
8. Scabo, P.P.; Feher, I.; German, E. *Radiat. Prot. Dosim.* **1990**, 34(1–4), 191.
9. Tae-Jin Choi, Do-Sung Kim, Shi-Hong Do et al *New Physics (Korean Physical Society)* **1986**, 26(6), 507.
10. Matthews, R.J.; Stoebe, T.G. *J. Phys. C.* **1982**, 15, 6271.
11. Spurny, Z.; Novotny, J. The third International Conference on Luminescence Dosimetry, Risø, Denmark, 11–14 October, 1971. Proceedings, *Risø Rept.* No. 249, p. 132, **1971**.
12. Nambi, K.S.V.; Bapat, V.N.; Ganguly, A.K. *J. Phys. C.* **1974**, 7, 4403.
13. Lakshmanan, A.R. *Phys. Stat. Sol. A* **2001**, 186, 153.
14. Kher, R.S.; Pandey, R.K.; Dhoble, S.J.; Khokhars M.S.K. *Radiat. Prot. Dosim.* **2002**, 100(1–4), 281.
15. Banshi, A.K.; Pradhan, A.S.; Sristava, K.; Kolambe, D.H. *Radiat. Prot. Dosim.* **2002**, 100(1–4), 293.
16. Yang, J.S.; Kim, J.L.; Kim, S.Y.; Chang, Y.M.; Nam, Y.M.; Park I.W. *Radiat. Prot. Dosim.* **2002**, 100(1–4), 337.
17. Erfurt, G.; Krbetschik, M.R. *Radiat. Prot. Dosim.* **2002**, 100(1–4), 403.
18. Grossi, F.H.; Campos, L.L. *Radiat. Prot. Dosim.* **2002**, 100(1–4), 421.
19. Cruz-Zaragosa, E.; Ramos-Bernal, S.; Negron-Mendoza, A.; Azorin, J. *Radiat. Prot. Dosim.* **2002**, 100(1–4), 447.
20. De Jesus, E.F.O. *Radiat. Prot. Dosim.* **2002**, 100(1–4), 553.
21. Zapasskiy, V.S.; Feofilov, P.P. in Collection of articles: *Spectroscopy of Crystals* **1975**, 85.
22. Belskiy, A.N.; Kamenskikh, I.A.; Mikhailin, V.V.; Shpinkov, I.N.; Vasilev, A.N. *Phys. Scripta* **1990**, 41(4), 530.
23. Kutomi, Y.; Takuchi, N. *J. Mat. Sci. Lett.* **1986**, 5, 51.
24. Balarin, M.; Hübner, K. *Cryst. Res. Technol.* **1985**, 20(9), 231.
25. Hübner, K.; Prokert, K. *Kernenergie* **1983**, 26, 118.
26. Lakshmanan, A.R.; Aqyanger, K. Proc. of National Symposium on Thermo-luminescence and its Applications, Kalpakkam, Madras, **1975**, 446.
27. Soares, C.; Ehrlich, M. *Med. Phys.* **1979**, 6, 312.
28. Burgkhart, B.; Herrera, R.; Piesch, E. In: Proceedings of The 5th International Conference on Luminescence Dosimetry (Ed.: A. Scharmann, Gießen), Sao Paolo, Brasil, 14–17 February **1977**: 75 (**1977**).
29. Prokic, M. *Radiat. Prot. Dosim.* **1990**, 33(1–4), 99.
30. Draaisma, F.S.; Verhagen, H.W. *Radiat. Prot. Dosim.* **2002**, 101(1–4), 293.
31. Veinot, K.G.; Hertel, N.E. *Radiat. Prot. Dosim.* **2001**, 95(1), 25.

32. Vilaithong, T.; Wanwilairat, M.; Rhodes, M.; Hoffmann, W.; Messarius, T. *Radiat. Prot. Dosim.* **2002**, 100(1–4), 211.
33. Takenaga, M.; Yamamoto, O.; Yamashita, T. US Patent No. 4,248,731 (**1981**).
34. Furetta, C.; Sanipoli, C.; Scacco, A.; Somaiah, K. *Radiat. Prot. Dosim.* **1996**, 65(1–4), 339.
35. Watanabe, S.; Chinaglia, E.F.; Nascimento, M.L.F.; Matsuoka M. *Radiat. Prot. Dosim.* **1996**, 65(1–4), 79.
36. Martini, M.; Meinardi, F.; Kovacs, L.; Polgar, K. *Radiat. Prot. Dosim.* **1996**, 65(1–4), 343.
37. Miljanic, S.; Knezevic, Z.; Stuhec, M.; Ranogajec-Komor, M.; Krpan, K.; Vekic, B. *Radiat. Prot. Dosim.* **2003**, 106(3), 253.
38. Prokic, M. *Radiat. Prot. Dosim.* **2002**, 100(1–4), 265.
39. Zarate-Morales, A.; Buentil, A.E. *Health Phys.* **1996**, 71, 358.
40. Vehl, D.L.; Muron, D.I.; Suijka, R.R.; Vehar, D.W.; Lorence, L.I.; Westfall, R.L.; Jones, S.C.; Sweet, I.A.; Braunlich, P. *Rev. Sci. Instrum.* **1994**, 65, 3243.
41. Nicolae, M.; Lazar, M. *Rev. Roum. Phys* **1985**, 30, 207.
42. Environmental Radiation Data Report 75. US Environmental Protection Agency, Office of Radiation. **1993**.
43. Miller S.D. PCT WO94/152227, **1994**.
44. Schulman, J.R.; Ginther, R.J.; Kirk, R.D.; Goulart, H.S. *Nucleonics* **1960**, 18, 92.
45. Puite, K.J.; Arends, J. The third International Conference on Luminescence Dosimetry, Risø, Denmark, 11–14 October, 1971. Proceedings, *Risø Rept.* No. 249, p. 680, **1971**.
46. Prokert, K.; Sommer, M. *Rad. Prot. Dosim.* **1998**, 78(2), 249.
47. Chakrabati, K.; Sharma, J.; Mathur, N.K. *Rad. Prot. Dosim.* **1993**, 47, 155.
48. Miller, S.D.; McDonald, J.; Eichner, F.N.; Tomeraasen, P.L. US Patent No. 4,954,707 (**1990**).
49. Puite, K.J. *Intern. J. Appl. Radiat. Isot.* **1968**, 19(4), 397.
50. Da Rosa, L.A.R.; Nette, H.P. *Appl. Radiat. Isot.* **1988**, 39(3), 191.
51. Miller, S.D. US patent No 5,272,348 (**1993**).
52. Miller, S.D.; McDonald, J.C.; Eicner, F.N.; Tomeraasen, L.P. US Patent No. 5,025,159 (**1991**).
53. Miller, S.D. US Patent No. 5,196,704 (**1994**).
54. Gasiot, J.; Braunlich, P.F.; Fillard, J.P. US Patent No. 4,507,562 (**1985**).
55. McKeever, S.W.S.; Akselrod, M.S.; Markey, B.G. US Patent No. 5,962,857 (**1997**).
56. Braunlich, P.F.; Tetzlaff, W. US Patent No. 4,906,848 (**1990**).
57. Miller, S.D. US Patent No. 5,569,927 (**1996**).
58. Jassemnejad, B.; Abbundi, R.J.; Brown, M.D. et.al *Phys. Stat. Sol. A.* **1988**, 108(2), 753.
59. Sen, S.C.; Bose H.N. *Z. Phys.* **1967**, 201(4), 368.
60. Bozhevolnov, V.E.; Ivanov, L.N.; Kozlov, V.K. et al *Phys. Stat. Sol. B* **1976**, 78(2), 483.
61. Mizuguchi, M.; Hosono, H.; Kawazoe, H. et al *J. Vac. Sci. Technol. A.* **1998**, 16(5), 3052.
62. Denks, V.; Maarroos, A.; Nagirnyi, V. et al *J. Phys. C* **1999**, 11(15), 3115.
63. Alonso, P.J.; Alcala R. *J. Lumin.* **1981**, 22(3), 321.
64. Lewandowski, A.C.; Wilson T.M. *Phys. Rev. B* **1994**, 50(5), 2780.

65. Lira, A.; Munder, A.; Dagdug, L. et al *Phys. Stat. Sol. B* **1999**, 212(1), 199.
66. Lushchik, N.E.; Soovik, K. in Collection of articles: *Spectroscopy of Crystals* M. Nauka, **1970**, 258 (Russ.).
67. Klatt, V.; Lenard, P. *Wied. Ann.* **1889**, 38, 90.
68. Title, R.S., *Phys. Rev. Lett.*, **1959**, 3, 273.
69. Lehmann, W. *J. Lumin.* **1972**, 5, 87.
70. Pham-Thi, M. *Jpn. J. Appl. Phys.*(Part 1) **1992**, 31, 2811.
71. Pham-Thi, M. *J. Alloys Comp.* **1995**, 225, 547.
72. Pham-Thi, M.; Ruelle, N.; Tronc, E. et al *Jpn. J. Appl. Phys.*(Part 1) **1994**, 33, 1876.
73. Shanker, V.; Fukada, H.; Maesono, M.; Ohmi, K.; Tanaka, S.; Kobayashi, H. *J. Soc. Info. Displ.*, **1998**, 6, 35.
74. Benalloul, P.; Barthou, C.; Benoit, J.; Garcia, A.; Fouassier, C.; Soininen, E. *Eur. Phys. Journ., Appl. Phys.* **2000**, 9, 19.
75. Morishita, T.; Matsuyama, H.; Matsui, M.; Tonomura, S.; Wakihara, M. *Appl. Surf. Sci.* **2000**, 157, 61.
76. Hua, Z.; Salamanca-Riba, L.; Wuttig, M.; Soltani, P.K. *J. Opt. Soc. Am., B (Opt. Phys.)* **1993**, 10, 1464.
77. Lee, Y.H. Ju, B.K.; Yeom, T.H.; Kim, D.H.; Hahn, T.S.; Choh, S.H.; Oh, M.H. *J. Appl. Phys.* **1994**, 75, 1754.
78. Xin, Y.B.; Tong, W.; Park, W.; Chaichimansour, M.; Summers, C.J. *J. Appl. Phys.* **1999**, 85, 3999.
79. Gruzintsev, A.N. *J. Lumin.* **1997**, 71, 207.
80. Seeman, V.; Danilkin, M.; Must, M.; Ots, A.; Pung, L. *Phys. Stat. Sol. (b)* **2003**, 238(1), 102.
81. Kim, Chang-Hong; Pyun, Chong-Hong; Choi, Han; Kim, Sung-Jin *Bull. Korean Chem. Soc.* **1999**, 20(3), 337.
82. Ruan, H.; Gan, F.; Xu, J.; Chang, Y. *Mat. Sci. & Engin. B (Sol.-Stat. Mat. for Adv. Techn.)* **2000**, 76, 73.
83. Nanto, H.; Sato, T.; Miyazaki, M.; Imai, A.; Komori, H.; Douguchi, Y.; Kusano, E.; Nasu, S.; Kinbara, A. Proc. Advanced Optical Data Storage: Materials, Systems, and Interfaces to Computers — Conf., Denver, CO, USA, 20–22 July 1999; *Proc. of the SPIE* **1999**, 3802, 258.
84. Gode, G. Synthesis of borates. I. Riga, LU rotaprint, **1971**, 31.
85. Schmid, W.F.; Mooney, R.W. *J. Electrochem. Soc.* **1963**, 110, 340.
86. Ginther, R.J. *J. Electrochem. Soc.* **1954**, 101, 248.
87. Lust, A. "Method of synthesis of CaF₂:Mn thermoluminescent material and detectors", **1997**, M.Sci. Thesis, University of Tartu.
88. Frank, M., Herforth, J. *Kernenergie* **1962**, 5, 173.
89. Smith, A.L. *J. Electrochem. Soc.* **1954**, 101, 189.
90. Ginther, R.J.; Kirk, R.D. Rep. Pf NRL Progress, **1956**, Sept., p.12.
91. Ginther, R.J.; Kirk, R.D. *J. Electrochem. Soc.* **1957**, 104, 365.
92. Erdey, L.; Kasa, I.; Kovacs, L. *Periodica Polytechnica* **1965**, 9, 223.
93. Palmer, R.C.; Blasé, E.F.; Poirier, V.D. *Int. J. Appl. Rad. Isot.* **1965**, 16, 737.
94. Palmer, R.C.; Poirier, V.D.; Blasé, E.F. Patent of France Nr. 1365883, cl. C01f, G01j; 3.07.1964.
95. Niewiadomski, T. *Nukleonika* **1967**, 12, 281.

96. Pedak, E.J.; Allsalu, M.-L.J.; Kanter, M.J. *Zhurnal Priklad. Khimii* **1972**, 45, 2619 (Russ).
97. Wirsching, F. Calcium Sulfate, in Ullmann's Encyclopedia of Industrial Chemistry, 4th ed. **1985**, vol. A4, pp. 555–584.
98. Jaek, I.V., "Selective dosimetry of fast neutrons by means of AII-BVI crystals" **1975**, Doct. Sci. Thesis, Tartu (Russ.).
99. Seeman, V.; Pung, L.; Danilkin, M.; Kerikmäe, M. *Proc.Univ.Tartuensis* **1993**, 964, 37.
100. Tohda, T.; Okajima, M.; Jamamoto, M.; Matsuoka, T. *Jpn. J. Appl. Phys.* **1991**, 30, 2786.
101. Tanaka, S. *J. Cryst. Growth* **1990**, 101, 958.
102. Allsalu, M.-L.J.; Mikhailin, V.V.; Nelipa, V.V.; Pedak, E.J. *Vestn. Mosk. Univ., ser. 3 Fiz. Astron.* **1984**, 25, 78 (Russ.).
103. Seeman, V. Private communication.
104. Lushchik, A.; Feldbach, E.; Frorip, A.; Ibragimov, K.; Savikhin, F.; Lushchik, Ch. *J. Lumin.* **1995**, 63, 273.
105. Agrawal, M.D.; Rao, K.V. *Phys. Stst. Sol. A* **1970**, 3(1), 153.
106. McMaster, D.W.; Jassemnejad, B.; McKeever, S.W.S. *J. Phys. D.: Appl. Phys.* **1987**, 20(3), 1182.
107. Patel, J.L.; Cavenett, B.C.; Davies, J.J.; Hagston, W.E. *Phys. Rev. Lett.* **1974**, 33(21), 1300.
108. Bagai, R.K.; Warriar, A.V.R.; *Phys. Stat. Sol. B*, **1976**, 73(2), K123.

SUMMARY IN ESTONIAN

Käesoleva töö peamised tulemused on lühidalt alljärgnevad:

1. Arendati ja optimeeriti aktivaatori kaasasadestamise meetodit, et saada sobivate karakteristikutega termoluminofoorid $\text{CaSO}_4\text{-Dy}$ alusel. Optimaalne TLD-materjal saadi $\text{Ca}(\text{NO}_3)_2$ ja H_2SO_4 lahustest suure H_2SO_4 liia korral ($[\text{Ca}^{2+}]: [\text{SO}_4^{2-}]=1:15$). Peale selliste kaasasadestatud aktivaatoriga luminofoori aluste kuumutamist oli nende tundlikkus gamma- ja röntgenkiirgusele lähedane proovidele, mis olid saadud CaSO_4 ja Dy- soola klassikalisel ümberkristalliseerimise meetodil kuumast kontsentreeritud väävelhapest. Kaasasadestamine on tehniliselt lihtsam, kuna ei ole vajadust töötada kuumast kontsentreeritud happega. Selliselt saadud produkt oli homogeenne ja ühtlase kristalli tera suurusega, mis kergendas TLD-detektorite valmistamist tableti vormis.
2. Ainsa TL- maksimumiga 493 K juures termoluminofoor $\text{SrSO}_4\text{-Eu}$ saadi kasutades $\text{CaSO}_4\text{-Dy}$ sünteesile analoogilist kaasasadestamise meetodit. Optimaalseks osutus väiksem sulfaadi liig ($[\text{Sr}^{2+}]: [\text{SO}_4^{2-}]=1:2$).
3. CaSO_4 ja SrSO_4 kõrghastusele analoogiline tehnoloogia võimaldas saada puhtad luminesentsmaterjalide alused ilma segavate luminesentsribadeta. Saadud proove kasutati struktuurse omaluminesentsi uurimisel erinevates sulfaatides. Uuriti mitmeid luminesentsspektrite gruppe. Kõige huvitavamad olid “kiired” omaluminesentsi ribad üsna komplekse spektraalse koostisega ja lühikese kustumisajaga ($\tau < 2 \cdot 10^{-9}$ s), mis avastati aktiveerimata puhastes sulfaatides K_2SO_4 , Rb_2SO_4 , Cs_2SO_4 , BaSO_4 , SrSO_4 . Nende objektide ergastusspektrid näitasid, et emissioonriba ergastus ainult üle 15 eV energiat omavate kvantidega. Sellisel ergastusel saadud spektri struktuur oleneb kationist võres. Põhivõre luminesents leiti ainult nendel sulfaatidel, kus lai hapniku valentsriba on eraldatud kristallvõre poolt. Kõik need faktid viisid järeldusele, et üle 15 eV energiaga ergastavad kvandid kannavad üle elektrone hapniku madalamast valentstsoonist juhtivustsooni. Kiire luminesentsi spekter näitab, kuidas elektronolekute tihedused on jaotunud eraldatud valentstsooni ülemistes osades. Ergastusspekter 15–25 eV vahemikus selgitab nii olekute tiheduse jaotust valentstsooni madalamatel osadel, kui ka kattuvaid kationide olekuid.
4. Töötati välja sobivate TLD karakteristikutega $\text{Li}_2\text{B}_4\text{O}_7\text{-Mn, Si}$ sünteesi tehnoloogia, kaasa arvatud detektorite süntees tableti vormis.
5. Töös uuritud $\text{CaF}_2\text{-Mn}$ proovid olid sünteesitud mangaani kaasasadestamisel CaF_2 -ga. Täpne Mn kontsentratsioon luminofooris määrati ja seostati TL kõvera kuju sõltuvus kontsentratsioonist. TL kõvera põhimaksimum asub 570 K juures mangaani kontsentratsioonil umbes 2 % m/m. Sünteesitud luminofoor ei sisalda hapniku jälgi ja on vastupidav oksüdatsioonile. Lai lineaarsuse piirkond teeb materjali sobivaks ekstreem-monitooringus. Kõrge puhtusastmega alusmaterjal ja hapnikuga seotud luminesentsribade puudu-

mine kergendas luminesentsomaduste ja energia ülekande mehhanismide uurimist luminofooris. Lisanditega seotud eksitonide moodustumise energiaks leiti 9,4 eV ja 10,1 eV. Mobiilsete eksitonide moodustumise energia väärtuseks leiti 11,2 eV ja ribalt-ribale ülemineku energia oli 12 eV. Uuriti Mn^{2+} ergastuse efektiivseid ja mitteefektiivseid mehhanisme.

6. Töötati välja leelismuldmetallide sulfiidide sünteesi tehnoloogia, et saada kompleksed termoluminestsetssüsteemid nii lineaarsete kui mittelineaarsete efektidega. Leiti lisandite eriline vastasmõju tahketes lahustes. Komplektsentrite lõplik struktuur sõltub tõenäoliselt ka lisandite võresse viimise järjekorrast ja mitte ainult luminofoori koostisest. Kiirete neutronite dosimeetriaks ette nähtud CaS-Bi luminofooridel uuriti mitte-lineaarset doosist sõltuvust ja mehhaanilise toime mõju informatsiooni salvestamisel.
7. Kontrolliti mõnede TLD-de võimalikku kasutamist lugemi võtmiseks optiliselt stimuleeritud järelhelenduse meetodil (OSA). Formuleeriti peamised nõuded luminofooridele, millised sobivad lugemi võtmiseks OSA meetodil. Termoluminofoor $CaSO_4$ -Dy näib kõige rohkem sobivat selleks otstarbeks.
8. Uuriti ka SrS -Ce ja SrS -Eu,Ce luminofoorides komplektsentrite moodustumise tingimusi. On ära toodud katioonvakanside eriline osa. Analoogiliselt mittelineaarsete dosimeetriliste materjalidega, kompleksdefektide moodustumise mehhanismid sõltuvad lisandite sisseviimise järjekorrast põhivõresse. Leiti Ce^{3+} ja halogeeni lisandi absorptsioonribad. Ce^{3+} emissioonribad olid nihkunud kõrgema lainepikkuse poole floori sisaldavatel proovidel kristallvõre välja oletatava mõju tõttu. Teine nihutatud paar leiti ultravioletse luminesentsriba juures proovidel limiteeritud hapniku juurdepääsuga. On arutletud laengukandjate võimalikke olekuid. Salvestavat SrS -Eu,Sm luminofoori uuriti SQUID magnetomeetriga. On soovitatud luminesentsi- ja salvestusomaduste alternatiivne mudel saadud tulemuste selgitamiseks. Mudeli aluseks on üleminekud haruldaste muldmetallide ioonidest moodustunud laengu-ülekande komplekside ergastatud olekute ja katioonvakansi läheduses sulfiidioonide elektronpilvede vahel.

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PUBLICATIONS

Molecular excitons and electron-hole processes in K_2SO_4 and $CaSO_4$,
Tokbergenov, I.; Feldbach, E.; Kerikmäe, M.; Lushchik, A.; Nagimyi, V.;
Nurakhmetov, T.; Savikhin, F.; Vasilchenko, E.
Radiation Effects and Defects in Solids, **1999**, 150, 103–107.

Electronic excitations and luminescence in some alkaline earth metal sulphates,
Tokbergenov, I.; Savikhin, F.; Rakhimov, D.; Myrzakhmet, M.; Nurakhmetov, T.;
Kerikmäe, M. 12th International conference on radiation physics and
chemistry of inorganic materials, September 23–27, **2003**, Tomsk, Russia.
Proceedings, p.p. 466–469. Tomsk Polytechnic University, 2003 (*in Russian*).

Determination of manganese in thermoluminescent materials
by inductively coupled plasma atomic emission spectrometry and spectrophotometry,
Lust, A.; Paama, L.; Kerikmäe, M.; Must, M.; Perämäki, P. *Proc. Estonian Acad. Sci.*
Chem., **2002**, 51(2), 126–133.

Photoluminescence of Concentration Series
of $CaF_2:Mn$ Phosphors Excited by VUV Radiation,
Denks, V.P.; Kerikmäe, M.P.; Lust, A.L.; Savikhina, T.I.
Solid State Physics, **2000**, 42(2), 261–269.

The formation of Compton-electron traces in thermoluminescent detectors,
Allsalu, M.-L.; Kerikmäe, M.; Pung, L.; Savikhin, F.; Seeman, V.
Luminescent receivers and transformers of ionizing radiation,
All-Union Symposium, 1987, Proceedings,
p.p. 29–36, Tartu University, **1987** (*in Russian*).

Optically Stimulated Luminescence of Some Thermoluminescent Detectors
as an Indicator of Absorbed Dose, Jaek, I.; Kerikmäe, M.; Lust, A.
Radiation Protection Dosimetry, **2002**, 100(1–4), 459–462.

Investigation of a New Emission Band of $SrS-Ce$ Phosphor,
Rammo, I.; Kerikmäe, M.; Lepist, M.; Matisen I.
Journal of Applied Spectroscopy (Minsk), **1995**, 62(3), 165–168.

Impurity Absorption of $SrS-Ce$ Phosphors,
Rammo, I.; Kerikmäe, M.; Lepist, M.; Matisen I.; Pung, L.; Ritslaid, K.
Journal of Applied Spectroscopy (Minsk), **1997**, 64(4), 542–544.

Studies of the Structure of Ce^{3+} Centres in SrS Phosphors,
Rammo, I.; Kerikmäe, M.; Lepist, M. Matisen I., Pung, L; Ritslaid, K.; Haav, A.
Journal of Applied Spectroscopy (Minsk), **1997**, 64(2), 173–178.

Energy Transfer and Storage Mechanism
in Infrared Sensitive Storage Phosphor SrS:Eu,Sm,
Danilkin, M.I.; Kerikmäe, M.P.; Klimonsky, S.O.; Kuznetsov, V.D.;
Makarov, E.F.; Permyakov, J.V.; Primenko, A.E.; Seeman, V.O.
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1. I. Rammo, M. Kerikmäe, M. Lepist, I. Matisen. Investigation of the Nature of New Band SrS-Ce Phosphors. *Journal of Applied Spectroscopy*, 1995, vol. 62, no. 3, 165–168.
2. I. Rammo, M. Kerikmäe, M. Lepist and other. Supplementary Absorption in the SrS:Ce Phosphors. *Journal of Applied Spectroscopy*, 1997, vol. 64, no. 3, pp. 542–544.
3. I. Rammo, M. Kerikmäe, M. Lepist, L. Matisen. Structure of the Ce³⁺/Centres in SrS Phosphors. *Journal of Applied Spectroscopy*, 1997, vol. 64, no. 2, pp. 173–178.
4. Tokbergenov I., Feldbach, E., Kerikmäe M., et.al. Molecular excitons and electron-hole processes in K₂SO₄ and CaSO₄. *Radiat. EFF DEFECTS* 150, 1999, (1–4), pp. 103–107.
5. V. P. Denks, M. P. Kerikmäe, A. L. Lust and T. I. Savikhina. Photoluminescence of Concentration Series of CaF₂: Mn Phosphors Excited by VUV Radiation. *Physics of the Solid State*, 2000, vol. 42, no. 2, pp. 261–269.
6. I. Jaek, M. Kerikmäe and A. Lust. Optically Stimulated Luminescence of Some Thermoluminescent Detectors as an Indicator of Absorbed Dose. *Radiation Protection Dosimetry*, 2002, vol. 100, no. 1–4, pp. 459–462.
7. M. I. Danilkin, M. P. Kerikmäe, S. O. Klimonsky, V. D. Kuznetsov, E. F. Makarov, J. V. Permyakov, A. E. Primenko, V. O. Seeman. Energy Transfer and Storage Mechanism in Infrared Sensitive Storage Phosphor SrS:Eu,Sm. NIMA. (2004), accepted for publication.
8. Aime Lust, Lilli Paama, Mihkel Kerikmäe, Mare Must and Paavo Perämäki. Determination of Manganese in Thermoluminescence Materials by Inductively Coupled Plasma Atomic Emission Spectrometry and Spectrophotometry. *Proc. Estonian Acad. Sci. Chem.*, 2002. Vol. 51, no. 2, pp. 126–133.

CONFERENCES AND SYMPOSIUMS

1. M. Kerikmäe et al. The method of the thermoluminescent detector preparation from powder mixture. Author Certificate no 803672, 1980.
2. M. Kerikmäe et al. The method of the thermoluminescent detector preparation. Author Certificate no 1169446, 1985.
3. Savihhin F. A., Allsalu M.-L. J., Pung L. A., Seeman V. O., Kerikmäe M. P. The conditions of formation of compton-electrons. *Proc. of the V SU Symposium on Luminescent Acceptors and Converters of Ionizing Irradiation*. Tallinn, 1985, pp. 62.
4. V. Seeman, L. Pung, M. Danilkin, M. Kerikmäe V-Centres in Plastically Deformed CaS. *Proc. Univ. Tartuensis*, 1992, pp. 88–89.

5. V. Seeman, L. Pung, M. Danilkin, M. Kerikmäe. V-Centres in Plastically Deformed CaS. *Proc. Univ. Tartuensis*, 1993, no 964, pp. 37–46.
6. V. Seeman, L. Pung, M. Danilkin, M. Kerikmäe. V-Centres in Plastically Deformed CaS and SrS Polycrystals. *Proc. of the XII International Conference on Insulating Materials*. Ed. O. Karnet and I. M. Spaeth. World Scientific, Singapore, New Jersey, London, Hong Kong, 1993, vol. 1, pp. 523–525.
7. I. Rammo, M. Kerikmäe, M. Lepist, L. Matisen. Investigation of the new band of the emission spectrum of the SrS-Ce. *Proc. of the International Conference on Luminescence*. 22–24.11.1994. Moscow, pp. 12.
8. I. Rammo, M. Kerikmäe, M. Lepist, L. Matisen, L. Pung. Investigation of the 3,15 eV Luminescence Band of SrS-Ce Phosphors. 3rd Baltic ALE Symposium, Nov. 23–24, 1995, Helsinki.
9. M. Kerikmäe. Thermoluminescence Detectors (TD) for Registration of Ionizing Radiation. 17th Estonian Chemistry Days, April 18–20.1996, Tartu, Estonia. Abstracts of Scientific Conference, Tartu, 1996, p. 73.
10. M. Kerikmäe, A. Lust, M. Orav, A. Ratas, I. Riiv. Thermoluminescence Detectors (TD) for Registration Ionizing Irradiation. 23th Estonian Chemistry Days. Abstracts of Scientific Conference, Tallinn, Estonia, 1997, p. 49.
11. M. Danilkin, M. Kerikmäe, A. Lust, M. Must, E. Pedak, E. Pärnoja, I. Riiv, V. Seeman. Synthesis and Characteristics of CaS:Eu Luminophors 23th Estonian Chemistry Days, Abstracts of Scientific Conference. May 7–9, 1997, p. 26, Tallinn, Estonia.
12. M. Kerikmäe, M. Danilkin, A. Lust. The Specification of TLD Detectors of $\text{Li}_2\text{B}_4\text{O}_7\text{:Mn}$ on Base of IEC 1066. 24th Estonian Chemistry Days, Abstracts of Scientific Conference, May 7–8, 1998. p. 28, Tartu, Estonia.
13. I. Tokerbenov, E. Feldbach, M. Kerikmäe, A. Luschchik, V. Nagirnyi, T. Nukrakhmetov, F. Savikhin and E. Vasilchenko Molecular excitons and electron-hole processes in K_2SO_4 and CaSO_4 . Abstracts Europhysical Conference on Detects in Insulating Material, Eurodim 98, Keele, UK-1998.
14. M. Danilkin, M. Kerikmäe, E. Klestin, M. Must, E. Pedak, E. Pärnoja, V. Seeman. Luminescence Kinetics of CaS:Eu Luminophors. 25th Estonian Chemistry Days, Abstracts of Scientific Conference. Nov. 24–26, 1999, p. 26. Tallinn, Estonia.
15. A. Lust, L. Paama, M. Kerikmäe. The Effect of Concentration of Activator on Thermoluminescent Characteristics of Thermoluminophor $\text{CaF}_2\text{:Mn}$ 26th Estonian Chemistry Days, Nov. 16–18, 2000, Tallinn, Estonia. Abstracts of Scientific Conference, Tallinn, 2000, p. 82.
16. M. Danilkin, M. Kerikmäe, A. Lust, V. Seeman. Light Sensitivity of $\text{Li}_2\text{B}_4\text{O}_7\text{:Mn}$. 26th Estonian Chemistry Days, Nov. 16–18, 2000, Tallinn, Estonia. Abstracts of Scientific Conference, Tallinn, 2000, p. 24.
17. I. Jaek, M. Kerikmäe and A. Lust “OSL of some TL-detectors as the indicator of obsorbed radiation dose”. Abstracts of the 13th International

- Conference on Solid State Dosimetry, 9–13 July 2001, Athens, Greece, p. 130.
18. M. I. Danilkin, M. P. Kerikmäe, S. O. Klimovsky, V. D. Kuznetsov, E. F. Makarov, Ju. V. Permyakov, A. E. Primenko, V. O. Seeman. Energy transfer and storage mechanisms in IR-sensitive storage phosphor SrS:Eu,Sm. 7th International Conference on Inorganic Scintillators and Industrial Applications SCINT 2003, Vallencia-Spain, p. 64.

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1. I. Rammo, M. Kerikmäe, M. Lepist, L. Matisen. Investigation of the Nature of New Band SrS-Ce Phosphors. *Journal of Applied Spectroscopy*, 1995, vol. 62, no 3, pp 165–168.
2. I. Rammo, M. Kerikmäe, M. Lepist and other. Supplementary Absorption in the SrS:Ce³⁺ Phosphors. *Journal of Applied Spectroscopy*, 1997, vol. 64, no 3, pp. 542–544.
3. I. Rammo, M. Kerikmäe, M. Lepist, L. Matisen. Structure of the Ce³⁺/centres in SrS Phosphors. *Journal of Applied Spectroscopy*, 1997, vol. 64, no 2, pp. 173–178.
4. Tokbergenov I., Feldbach, E., Kerikmäe, M., et al. Molecular excitons and electron-hole processes in K₂SO₄ and CaSO₄. *Radiat. EFF DEFECT S* 150, 1999, (1–4), pp. 103–107.
5. V. P. Denks, M. P. Kerikmäe, A. L. Lust and T. I. Savikhina. Photoluminescence of Concentration Series of CaF₂:Mn Phosphors Excited by VUV Radiation. *Physics of the Solid State*, 2000, vol. 42, no. 2. pp. 261–269.
6. I. Jaek, M. Kerikmäe and A. Lust. Optically Stimulated Luminescence of Some Thermoluminescent Detectors as an Indicator of Absorbed Radiation Dose. *Radiation Protection Dosimetry*, 2002, vol. 100, nos 1–4, pp. 459–462.
7. M. I. Danilkin, M. P. Kerikmäe, S. O. Klimonsky, V. D. Kuznetsov, E. F. Makarov, J. V. Permyakov, A. E. Primenko, V. O. Seeman. Energy Transfer and Storage Mechanisms in Infrared Sensitive Storage Phosphor SrS:Eu,Sm. *NIMA*, (2004), vastu võetud publitseerimiseks.
8. Aime Lust, Lilli Paama, Mihkel Kerikmäe, Mare Must and Paavo Perämäki. Determination of Manganese in Thermoluminescence Materials by Inductively Coupled Plasma Atomic Emission Spectroscopy and Spectrophotometry. *Proc. Estonian Acad. Sci. Chem.*, 2002, **51**, 2, pp. 126–133.

KONVERENTSID JA SÜMPOOSIUMID

1. M. Kerikmäe et. al. The method of the thermoluminescent detector preparation from powder mixture. Author Certificate no 803672, 1980.
2. M. Kerikmäe et. al. The method of the thermoluminescent detector preparation. Author Certificate no 1169446, 1985.
3. Savihhin F. A., Allsalu M.-L. J., Pung L. A., Seeman V. O., Kerikmäe M. P. Kompton-elektronide formeerumise tingimused. Ettekannete teesid. V Üleliiduline sümpoosium luminesentsvastuvõtjatest ja ioniseeriva kiirguse muunduritest. Tallinn, 1985, 62.

4. V. Seeman, L. Pung, M. Danilkin, M. Kerikmäe V-Centres in Plastically Deformed CaS. Proc. Univ. Tartuensis, 1992, 88–89.
5. V. Seeman, L. Pung, M. Danilkin, M. Kerikmäe. V-Centres in Plastically Deformed CaS. Proc. Univ. Tartuensis, 1993, no 964, pp. 37–46.
6. V. Seeman, L. Pung, M. Danilkin, M. Kerikmäe. V-Centres in Plastically Deformed CaS and SrS Polycrystals. Proc. of the XII International Conference in Insulating Materials. Ed. O. Karnet and I. M. Spaeth. World Scientific., Singapore, New Jersey, London, Hong Kong, 1993, vol. 1, pp. 523–525.
7. I. Rammo, M. Kerikmäe, M. Lepist, L. Matisen. SrS - Ce luminofoori uue kiirgusriba uurimine. Luminestsentsialane rahvusvaheline konverents. Konverentsi teesid. 22–24.11.1994. Moskva, lk. 12.
8. I. Rammo, M. Kerikmäe, M. Lepist, L. Matisen, L. Pung. Investigation of the 3,15 eV Luminescence Band of SrS-Ce Phosphors. 3rd Baltic ALE Symposium, Nov. 23–24, 1995, Helsinki.
9. M. Kerikmäe. Thermoluminescence Detectors (TD) for Registration of Ionizing Radiation. 17th Estonian Chemistry Days, April 18–20.1996, Tartu, Estonia. Abstracts of Scientific Conference, Tartu, 1996, p. 73.
10. M. Kerikmäe, A. Lust, M. Orav, A. Ratas, I. Riiv. Thermoluminescence Detectors (TD) for Registration Ionizing Irradiation. 23th Estonian Chemistry Days. Abstracts of Scientific Conference, Tallinn, Estonia, 1997, p. 49.
11. M. Danilkin, M. Kerikmäe, A. Lust, M. Must, E. Pedak, E. Pärnoja, I. Riiv, V. Seeman, Synthesis and Characteristics of CaS:Eu Luminophors 23th Estonian Chemistry Days, Abstracts of Scientific Conference. May 7–9, 1997, Tallinn, Estonia.
12. M. Kerikmäe, M. Danilkin, A. Lust. The Specification of TLD Detectors of $\text{Li}_2\text{B}_4\text{O}_7\text{:Mn}$ on Base of IEC 1066. 24th Estonian Chemistry Days, Abstracts of Scientific Conference, May 7–8, 1998. p. 28, Tartu, Estonia.
13. I. Tokerbennov, E. Feldbach, M. Kerikmäe, A. Luschchik, V. Nagirnyi, T. Nukrakhmetov, F. Savikhin and E. Vasilchenko Molecular excitons and electron-hole processes in K_2SO_4 and CaSO_4 . Abstracts Europhysical Conference on Detects in Insulating Material, Eurodim 98, Keele, UK-1998.
14. M. Danilkin, M. Kerikmäe, E. Kletsin, M. Must, E. Pedak, E. Pärnoja, V. Seeman. Luminescence Kinetics of CaS:Eu Luminophors. 25th Estonian Chemistry Days, Abstracts of Scientific Conference. Nov. 24–26, 1999, p. 26. Tallinn, Estonia.
15. A. Lust, L. Paama, M. Kerikmäe. The Effect of Concentration of Activator on Thermoluminescent Characteristics of Thermoluminophor $\text{CaF}_2\text{:Mn}$ 26th Estonian Chemistry Days, Nov. 16–18, 2000, Tallinn, Estonia. Abstracts of Scientific Conference, Tallinn, 2000, p. 82.
16. M. Danilkin, M. Kerikmäe, A. Lust, V. Seeman. Light Sensitivity of $\text{Li}_2\text{B}_4\text{O}_7\text{:Mn}$. 26th Estonian Chemistry Days, Nov. 16–18, 2000, Tallinn, Estonia. Abstracts of Scientific Conference, Tallinn, 2000, p.24.

17. I. Jaek, M. Kerikmäe and A. Lust “OSL of some TL-detectors as the indicator of absorbed radiation dose”. Abstracts of the 13th International Conference on Solid State Dosimetry, 9–13 July 2001, Athens, Greece, p. 130.
18. M. I. Danilkin, M. P. Kerikmäe, S. O. Klimovsky, V. D. Kuznetsov, E. F. Makarov, Ju. V. Permyakov, A. E. Primenko, V. O. Seeman. Energy transfer and storage mechanisms in IR-sensitive storage phosphor SrS:Eu,Sm. 7th International Conference on Inorganic Schintillators and Industrial Applications SCINT 2003, Vallencia-Spain, p.64.