

## Thermoluminescent dosimeter $\text{Li}_2\text{B}_4\text{O}_7:\text{Mn},\text{Si}$ – a false-dose problem

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**Abstract.** The false-dose effects are investigated in the thermoluminescent detectors of ionizing radiation based on  $\text{Li}_2\text{B}_4\text{O}_7:\text{Mn},\text{Si}$ . To reveal the mechanism of daylight sensitivity, thermoluminescence, EPR, and luminescence excitation studies and technological experiments were undertaken. A 400 nm light was shown to be most effective to store the dose and to excite the luminescence band near 600 nm. A charge-transfer complex of a casual titanium impurity is supposed to be responsible for daylight false-dose storage. Another mechanism of a false-dose storage is supposed to be caused by a thermally induced stress, which yields a high-temperature thermoluminescence of  $\text{Li}_2\text{B}_4\text{O}_7:\text{Mn},\text{Si}$  detectors. Increasing the temperature of the sintering of tablets eliminates both false-dose effects. Possible models of energy storage are discussed.

**Key words:** thermoluminescence, dosimetry, false dose, lithium tetraborate, daylight sensitivity, luminescence spectra, EPR spectra.

### INTRODUCTION

Lithium tetraborate is a promising material for non-linear optics and piezoelectric devices. These applications imply extensive studies of  $\text{Li}_2\text{B}_4\text{O}_7$  single crystals [1]. However, this material is also important for an older application: when doped with impurities such as Cu, Mn, or Eu, it is known to be suitable to produce thermoluminescent detectors (TLD) of ionizing radiation.  $\text{Li}_2\text{B}_4\text{O}_7$  ceramics has a good tissue-equivalence for the absorption of ionizing radiation dose. Ideally, the atomic number,  $Z$ , of the dosimetric material should match as

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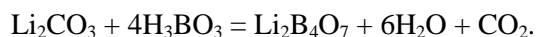
closely as possible that of the biological tissue ( $Z_{eff} = 7.42$ ) to be irradiated and so the measurement becomes independent of the photon energy. The tissue equivalence becomes very important when the incident  $\gamma$ - or X-radiation energy is in the region between 20 and 100 keV. At these energies, the photoelectric interaction is predominant and depends on the third power of the atomic number; so, in that region of energies there is an over-response in the case of materials having a higher atomic number [2].  $\text{Li}_2\text{B}_4\text{O}_7:\text{Mn}$  ceramics has an effective atomic number  $Z_{eff} = 7.40$ , very close to that of biological tissue. When  $\text{Li}_2\text{B}_4\text{O}_7:\text{Mn}$  is co-doped with a small amount of  $\text{SiO}_2$ , the exact value of  $Z_{eff} = 7.42$  of the biological tissue can be achieved. The excellent tissue equivalence makes this material very useful as TLD, in particular in clinical applications such as radiological examinations and therapeutic treatments.  $\text{Li}_2\text{B}_4\text{O}_7:\text{Mn},\text{Si}$  is now available commercially – for instance, from Bicron under the name TLD-800 [3]. Nevertheless, there are several unsolved problems limiting wider applications of this TLD material. The thermoluminescence (TL) mechanism of  $\text{Li}_2\text{B}_4\text{O}_7:\text{Mn}$  is not clear yet, and this fundamental problem results in several technical issues, such as a problem of false dose caused by daylight sensitivity or by some other reasons.

TLD should measure the integral dose of the ionizing radiation but not the integral dose of daylight. The effect of daylight decreases the accuracy of measurements and decreases the lower threshold of the sensitivity of TLD. The IEC-1066 Standard restricts the light sensitivity of TLD. According to this document, the  $\text{Li}_2\text{B}_4\text{O}_7:\text{Mn},\text{Si}$  detectors should not exceed a false dose of 1 mSv when irradiated for 24 h under normal conditions by a luminous energy flux of  $1000 \text{ W/m}^2$  in the spectral range 295–769 nm.

Here we report the results of thermoluminescence, electron paramagnetic resonance (EPR), and luminescence excitation studies of TLD  $\text{Li}_2\text{B}_4\text{O}_7:\text{Mn},\text{Si}$  produced in our laboratory. We discuss the nature of the daylight sensitivity of detectors. One more mechanism of a false-dose storage is connected with a thermally induced stress, which causes a high-temperature TL of  $\text{Li}_2\text{B}_4\text{O}_7:\text{Mn},\text{Si}$  detectors in some special cases. Increasing the temperature of final annealing has eliminated both false-dose effects. Possible models of energy storage are discussed.

## EXPERIMENTAL

Lithium tetraborate was prepared from lithium carbonate (Aldrich, A.C.S.) and boric acid (Merck, pure pro anal.) by wet reaction at continuous stirring and heating in order to evaporate extra water:



Activators and co-activators were added during the reaction in proper amounts. The product was dried, and then heated in a flow of protective nitrogen

at a temperature of 823 K for 120 min. This preliminary annealing completely removes water and carbon dioxide from the product. Then the tablets were pressed, and the final annealing was performed in the inert gas atmosphere at a temperature close to the melting point. The resulting amount of manganese in the samples was shown to be almost the same as the introduced one – there were no essential manganese losses during the synthesis. The concentration of manganese in finished samples (TLD) was determined by means of the ICP-AES method (Inductively Coupled Plasma Atomic Emission Spectroscopy). The details of the analysis technique were described previously [4]. The procedure differed only slightly in the case of  $\text{Li}_2\text{B}_4\text{O}_7:\text{Mn}$ . A TLD tablet ( $0.026\text{--}0.028 \pm 0.0002$  g) was dissolved in a quartz crucible with diluted 1 : 1 nitric acid (Merck, suprapur). The sample was heated until a complete dissolution was achieved. The solution was allowed to cool down, then transferred into a 25 mL volumetric flask, where it was coupled to a volume of 25 mL with deionized water. Then the ICP-AES technique was applied exactly as described in [4]. The EPR spectra of  $\text{Mn}^{2+}$  were studied using two X-band EPR spectrometers (8.87 GHz with a 100 kHz magnetic field modulation and 9.1 GHz with a 975 kHz magnetic field modulation). The spectra were measured both at room temperature (295 K) and at the temperature of liquid nitrogen (77 K).

The TL curves were measured with a semiautomatic TLD reader based on thermocontroller OMRON E5CK and a photomultiplier tube with a current-frequency converter. Both the thermocontroller and the data acquisition system were connected to a computer. The measurements were performed at a constant heating rate (0.5 K/s).

The TL materials were irradiated with a  $^{60}\text{Co}$   $\gamma$ -radiation source (doses up to 25 Gy) to study radiation effects, TL curves, and other manifestations of stored dose information. The reference dose irradiator 6527B (Sweden) equipped with a  $^{90}\text{Sr}/^{90}\text{Y}$   $\gamma$ -radiation source was used to give lower doses (0.1–1.0 Gy). To irradiate samples with  $\alpha$ -particles, a 0.006 GBq  $^{239}\text{Pu}$  radiation source was used, which gives approximately  $6.10^5$   $\alpha$ -particles per second. Also, an installation equipped with a Roentgen tube (18 mA, 45 kV, W-anode) was used for X-raying the samples, especially for EPR measurements.

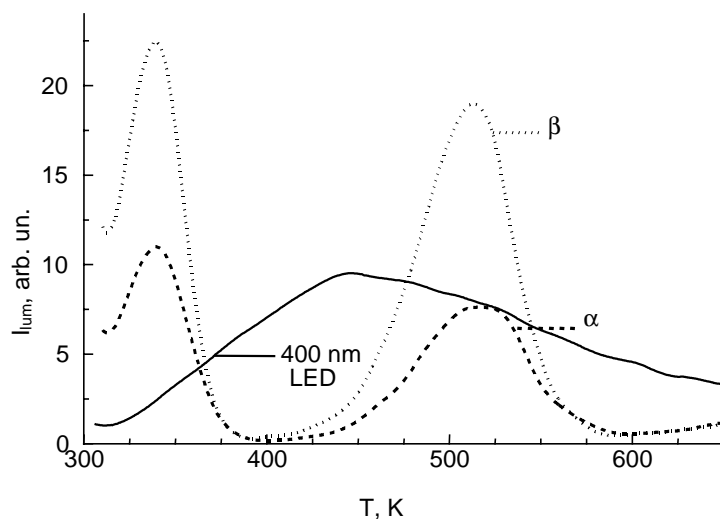
Luminescence spectra and luminescence excitation spectra were measured at room temperature with a HITACHI 650-60 spectrofluorimeter connected through a data acquisition system to a computer.

## RESULTS AND DISCUSSION

The problem of the sensitivity of  $\text{Li}_2\text{B}_4\text{O}_7$ -based TLD to daylight was known previously [5–7], especially for  $\text{Li}_2\text{B}_4\text{O}_7:\text{Cu}$ . The effect of light on the dose stored in  $\text{Li}_2\text{B}_4\text{O}_7:\text{Mn}$  detectors was mentioned in two publications [8, 9]. However, neither explanations nor models were suggested. We had encountered the daylight induced false dose in the case of only a few samples among a large set of

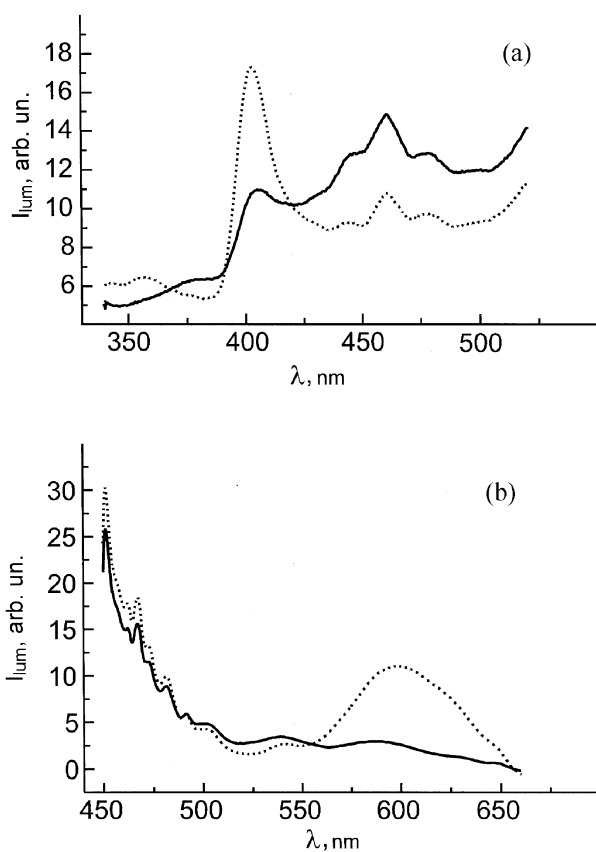
detectors, but the situation repeated steadily from one set to another. Thermoluminescence studies demonstrated that both light-sensitive and light-insensitive samples have the same TL curve when excited by either  $\beta$ - or  $\alpha$ -particles. As to the excitation by light, a 400 nm light emitting diode (LED) was found to be the most efficient to excite TL. However, the TL curve excited by 400 nm is very different from that excited by ionizing radiation (see Fig. 1). The TL curve induced by light is very wide, it covers all the temperature range from 320 K to 650 K, having a broad maximum at about 440 K. Some samples demonstrated a still broader curve, showing a strong afterglow at room temperature. The TL curves induced either by  $\beta$ - or  $\alpha$ -particles are very similar: both have two peaks, one of them (near 510 K) being always used for dose measurements. Light is completely ineffective to excite these two TL peaks, giving instead a broad curve. Hence, the mechanisms of energy storage should be completely different in the cases TL is excited by light or by ionizing radiation.

We studied photoluminescence and photoluminescence excitation spectra of different samples of  $\text{Li}_2\text{B}_4\text{O}_7:\text{Mn}$ : either with a pronounced sensitivity to daylight or without any daylight sensitivity. The spectra are shown in Fig. 2. The luminescence of  $\text{Mn}^{2+}$  is excited in an activator band equally poorly in light-sensitive and light-insensitive samples. This is natural for the intracentre transitions of  $\text{Mn}^{2+}$ , which are both spin and parity forbidden. However, light-sensitive samples show a luminescence band at 600 nm that is easily excited in the narrow peak at 400 nm. This luminescence band is similar to the  $\text{Mn}^{2+}$  spectrum but is noticeably shifted towards longer wavelengths compared with  $\text{Mn}^{2+}$  in  $\text{Li}_2\text{B}_4\text{O}_7$ . This luminescence band could belong to either  $\text{Mn}^{2+}$  located somewhere in the



**Fig. 1.** Thermoluminescence curves of a light-sensitive  $\text{Li}_2\text{B}_4\text{O}_7:\text{Mn},\text{Si}$  detector excited by different means:  $\alpha$ -particles (about  $1.8 \times 10^7$  particles),  $\beta$ -particles (0.25 Gy), a 400 nm light-emitting diode (about  $1.5 \times 10^{19}$  photons).

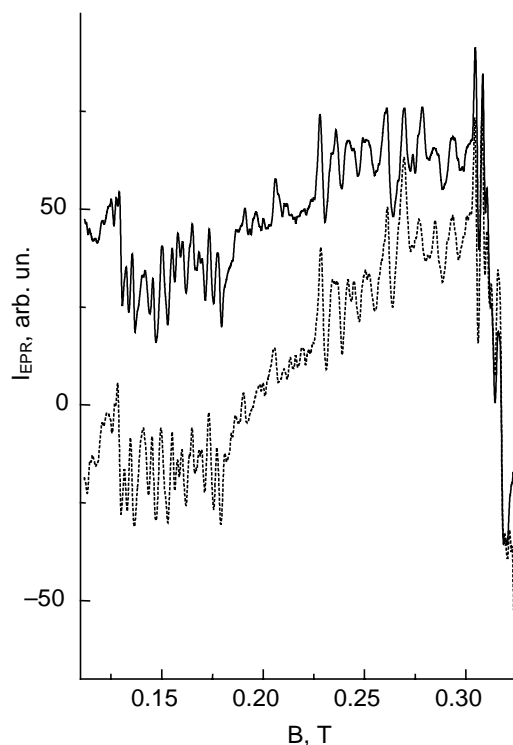
other crystal field or to some impurity like a transition metal ion. When the samples are excited in the band at 400 nm, the luminescence of some oxygen complex (in the region of 460–470 nm; probably, borate clusters) is also observed in both cases, in light-insensitive and light-sensitive material. The excitation at 400 nm of a luminescence band with a maximum near 600 nm cannot occur through band-to-band transitions. We can suppose that we are dealing with a charge-transfer excitation of some impurity, where the electron is taken from the closest coordinated anion complex. This means that the samples with light sensitivity have such close coordination, while the light-insensitive samples have not. However, the information is still insufficient to decide what impurity is involved in the complex coordination. It is essential to note that energy storage occurs in the light-sensitive samples just after the excitation in the narrow band at 400 nm where the luminescence of this unknown complex is excited. Hence, this is not simply a coincidence.



**Fig. 2.** Luminescence excitation (a) spectra at  $\lambda_{\text{lum}} = 600$  nm and luminescence (b) spectra excited at  $\lambda_{\text{exc}} = 400$  nm of light-insensitive (—) and light-sensitive (.....) samples of  $\text{Li}_2\text{B}_4\text{O}_7$ : Mn,Si.

To understand the reason of such behaviour, we studied EPR spectra of  $\text{Mn}^{2+}$  in  $\text{Li}_2\text{B}_4\text{O}_7:\text{Mn}$  samples, both sensitive and insensitive to daylight. The EPR spectra measured at room temperature are shown in Fig. 3. Two groups of  $\text{Mn}^{2+}$  hyperfine structure lines are seen: a low-field group (0.13–0.17 T) and the central one (0.22–0.33 T). Each group should contain 6 lines, due to the nuclear spin 5/2 of  $^{55}\text{Mn}$ , a single isotope of 100% natural abundance with magnetic moment 3.4532. However, there are several sets of 6 lines in each group, with the lines of different sets being mixed together. The presence of several sets of lines is connected probably with anisotropy of the g-factor and the fine structure of  $\text{Mn}^{2+}$ . A super-hyperfine structure of either B or Li could be expected but was not found. The additional groups of lines could not be detected either in lower or in higher magnetic fields. If the two groups of lines represent a broad-spaced anisotropic fine structure, the  $\text{Mn}^{2+}$  ions should be situated in a low-symmetry crystal field in  $\text{Li}_2\text{B}_4\text{O}_7$ . It is difficult to decide at once from the observed spectrum whether manganese is situated in low-symmetry crystals of lithium tetraborate or in glass-like ceramics. The exact position of  $\text{Mn}^{2+}$  in the crystal lattice cannot be recognized because the analysis of the complex EPR spectra is not effective in low-symmetry polycrystals. One could suppose two different positions of  $\text{Mn}^{2+}$  in  $\text{Li}_2\text{B}_4\text{O}_7$  lattice (probably, in ceramics, too), in which case each of the two positions gives rise to its own group of lines in the EPR spectrum. The central group of lines corresponds to a g-factor close to 2.0. This is a very common situation for  $\text{Mn}^{2+}$  in different crystal lattices. A low-field group of lines corresponds to the region of a g-factor close to 4.0. This unusual scene is characteristic of manganese in glasses [10] and does not occur in crystals with a high symmetry of lattice. The following comparison of light-sensitive and light-insensitive samples can be made on the basis of our EPR studies:

1. After X-raying the samples (18 mA, 45 kV, W-anode) neither variations of the spectra of  $\text{Mn}^{2+}$  nor correlation of spectra with light sensitivity were detected. Hence,  $\text{Mn}^{2+}$  seems not to change its charge state in the process of dose accumulation and release, being the luminescence centre only. In the TL process,  $\text{Mn}^{2+}$  accepts the excitation either through a charge transfer mechanism from some complexes-donors, or probably, by a resonance energy transfer.
2. EPR spectra of  $\text{Mn}^{2+}$  are almost identical in samples of both kind (light-sensitive and light-insensitive) except of the intensity being slightly higher (up to 30%) in the light-sensitive material. Besides the lines of  $\text{Mn}^{2+}$ , a broad line is observed both in the light-sensitive and the light-insensitive sample; however, the broad line is much less pronounced in the light-insensitive sample. Some components of the spectrum in the central region ( $g \approx 2$ ,  $B = 0.24\text{--}0.26$  T) are resolved slightly better in the case of the light-sensitive sample. Also, the higher intensity of EPR lines observed for the light-sensitive sample is more pronounced in the central region than in the low-field part of the spectrum.



**Fig. 3.** EPR spectra of  $Mn^{2+}$  in low-symmetry field of  $Li_2B_4O_7:Mn,Si$ . The spectra show no basic difference between light-sensitive (...) and light-insensitive (-) samples.

To understand the obtained results, we should mention the physical characteristics of the studied detectors. Sintering proceeds at a temperature very close to but not exceeding the melting point. So, we have both polycrystals and glass in the same tablet: the micro-crystals of  $Li_2B_4O_7$  are dispersed in a glass-like ceramics. The divalent manganese is distributed among two phases, glass and crystals. The results of EPR studies indicated that light-insensitive samples were probably treated at a higher temperature, which was closer to the melting point, and the amount of glass increased at the expense of the crystal phase. The experimental check gave a confirmation – the sensitivity to daylight disappeared after increasing the sintering temperature. Thus, a problem has been eliminated but not solved completely, because the nature of light-sensitive complexes is still unknown.

The information on the dose of ionizing radiation is stored at trapping centres in the crystal phase, and the glass phase does not take part in the dose information storage. This fact was confirmed by simple experiments in which completely molten samples were found to be insensitive to ionizing radiation. It could be supposed that the daylight sensitivity appears somewhere at the surface of micro-crystals or in the glass phase, where the absorbed energy of ionizing

radiation cannot migrate so easily as in crystals. Also, a wide, almost shapeless TL curve excited by light shows that the trapping energy should have a wide continuous range of values, which could be realized either at the surface of crystals or at low-symmetry sites in glass. The impurity involved in light sensitivity was discovered by chance when the configuration was changed in the furnace used for sintering. The false dose of daylight disappeared completely when we removed a support made of titanium and changed it for quartz. To check this fact, we tried different means of doping TLD with titanium compounds. Sometimes we obtained only a small increase in luminescence excitation in the narrow band near 400 nm and a very negligible sensitivity to daylight. It is possible that titanium forms optically active complexes with borate (or, probably, silicate) only at the moment when a partial melting of the material of the tablet starts. This explains why the sensitivity to daylight disappeared when the sintering temperature was increased. An increased temperature caused a faster overcoming of the critical temperature range where reactions with a casual impurity could occur.

The experiments with different sintering temperatures revealed one more false-dose effect, which has not been studied and published earlier. The samples sintered at lower temperatures demonstrated sometimes a false-dose effect caused by lattice stress. The TL appeared at temperatures higher than the working peak of TLD, and could be increased by rapidly cooling down the sample after readout. This effect seems to be similar to mechanically induced thermoluminescence or triboluminescence. The thermal expansion coefficients are different for  $\text{Li}_2\text{B}_4\text{O}_7$  crystal and glass phases. The samples sintered at lower temperatures contain more crystal and less glass phase. Micro-crystals could be in tight contact and exert deformation and stress due to thermal expansion. The discovered false-dose effect is much smaller than the daylight sensitivity; nevertheless it also decreases the accuracy of measurements. Both false-dose effects disappear when the sintering temperature is increased.

As for the mechanism of energy storage in  $\text{Li}_2\text{B}_4\text{O}_7:\text{Mn},\text{Si}$  TL detectors, we can say that manganese seems to be the luminescence centre only, and the energy is stored somewhere else in the host material. Manganese does not change its charge state during dose information storage and release. To reveal the exact mechanism of energy storage in  $\text{Li}_2\text{B}_4\text{O}_7$ , some additional investigations will be undertaken, including the study of other impurities in this material.

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## REFERENCES

1. Kuznetsov, A. Yu., Isaenko, L. I., Kruzhalov, A. V., Ogorodnikov, I. N. & Sobolev, A. B. Electronic structure of single crystals of lithium tetraborate  $\text{Li}_2\text{B}_4\text{O}_7$ . Cluster calculations and Roentgen photoelectron spectroscopy. *Fizika Tverdogo Tela*, 1999, **41**(1), 57–59 (in Russian).
2. Kitis, G., Furetta, C., Prokic, M. & Prokic, V. Kinetic parameters of some tissue equivalent thermoluminescence materials. *J. Phys. D: Appl. Phys.*, 2000, **33**, 1252–1262.
3. Mahesh, K., Weng, P. S. & Furetta, C. *Thermoluminescence in Solids and Its Applications*. Nuclear Technology, Ashford, UK, 1989.
4. Lust, A., Paama, L., Kerikmäe, M., Must, M. & Perämäki, P. Determination of manganese in thermoluminescent materials by inductively coupled plasma atomic emission spectrometry and spectrophotometry. *Proc. Estonian Acad. Sci. Chem.*, 2002, **51**, 126–133.
5. Prokic, M. Dosimetric characteristics of  $\text{Li}_2\text{B}_4\text{O}_7$ :Cu,Ag,P solid TL detectors. *Radiat. Prot. Dosim.*, 2002, **100**(1–4), 265–268.
6. Takenaga, M., Yamamoto, O. & Yamashita, T. Preparation and characteristics of  $\text{Li}_2\text{B}_4\text{O}_7$ :Cu phosphor. *Nucl. Instrum. Methods*, 1980, **175**, 77–78.
7. Sristava, J. K. & Supe, S. J. The thermoluminescent characterisation of  $\text{Li}_2\text{B}_4\text{O}_7$  doped with Cu. *J. Phys. D*, 1989, **22**, 1537–1543.
8. Christensen, P. Manganese activated lithium borate as a thermoluminescent dosimetry material. *Risó Rep.* 161, 1967.
9. Gesell, T. F. Environmental monitoring with thermoluminescence dosimetry. *IEEE Trans. Nucl. Sci.*, 1982, **NS-29**(3), 1225–1232.
10. Griscom, D. L. & Griscom, R. E. Paramagnetic resonance of  $\text{Mn}^{2+}$  in glasses and compounds of the lithium borate system. *J. Chem. Phys.*, 1967, **47**(8), 2711–2722.

## Termoluminestsentsdosimeeter $\text{Li}_2\text{B}_4\text{O}_7$ :Mn,Si: pseudodoosi probleem

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On uuritud pseudodoosiefekte  $\text{Li}_2\text{B}_4\text{O}_7$ :Mn,Si alusel sünteesitud termoluminestsentsdetektoritel (TLD). Selgitamaks valgustundlikkuse mehhanismi, on läbi viidud termoluminestsentsi (TL), EPR-i ning luminestsentsergastuse uuringud ja mitu tehnoloogilist eksperimenti. 400 nm lainepikkusega ergastav valgus näib kõige efektiivsemalt salvestavat doosi ja ergastavat luminestsentsriba 600 nm läheduses. Juhusliku lisandi (nt Ti) laenguülekandekompleks on oletatavasti seotud päeva valgusest tingitud pseudodoosi salvestumisega. Teine pseudodoosi salvestumise mehhanism on arvatavasti tingitud termilisel kuumutamisel tekkinud pingetest, mis põhjustavad  $\text{Li}_2\text{B}_4\text{O}_7$ :Mn,Si detektoritel kõrgetemperatuurse termoluminestsentsi. Detektorite sünteesi temperatuuri tõstmine elimineerib mõlemad pseudodoosiefektid. Töös on toodud võimalikud energia salvestamise mudelid.