Dosimetric features of strontium orthosilicate (Sr$_2$SiO$_4$) doped with Eu^{2+}

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Introduction

Strong thermoluminescence (TL) signal in the range from room temperature to 750K has been detected for strontium silicate synthesized using the solid state reaction method and doped with 2 mol%, 3 mol% and 4 mol% Eu^{2+}. It can be excited by UV, X and beta radiation. The TL emission spectrum extends from about 400 to 700 nm. The shape of glow curve depends on the concentration of Eu ions. The highest TL intensity is observed for Sr$_2$SiO$_4$ with 2mol% Eu. Two peaks – about 350 and 450 K dominate in the glow curve of this sample. Less intensive TL of two other samples is more complex. One can easily distinguish three peaks around 350, 410 and 450 K and a wide maximum above 470 K. The trap parameters were established by various heating rate method and by fitting the sum of first-order curves to experimental curves. The lifetimes estimated using these parameters allow to suppose that the TL peak at 450 K can be used for radiation dose measurement. This peak appears in all samples and, as it has been showed, its intensity increases linearly with dose over four orders of magnitude. Detailed investigations, however, showed that this peak fades partially faster than it could be inferred from the values of trap parameters determined by means of the TL measurements. The TL intensity, even after fading, is still high. The aim of this study is to establish the mechanizm of fading process. The TL isothermal decay has been investigated at different temperatures. The trap parameters obtained from these experiments have been compared with parameters obtained by means of the glow curve analysis.

Experimental

For purpose of this work we investigated samples of strontium silicate Sr$_2$SiO$_4$ nominally doped with 2 mol% (sample A), 3 mol% (sample B) and 4 mol% (sample C) Eu^{2+}. All samples where synthesized using the solid state reaction method. Strontium carbonate (Merck, optipure), silica (Aldrich 99.999%) and europium oxide (Aldrich 99.99%) were used as starting materials. The mixture of a proper ratio of starting materials was thoroughly mixed for 1.5 h using tempered steel planetary ball mill with a rotating speed of 400 rpm (Fritsh, Pulverisette 6). After milling the mixture was firstly calcined at 1250°C for 4 h in an inert gas atmosphere (Ar). Obtained material was grounded and again calcined at 1250°C for 4 h in a reducing atmosphere using the mixture of hydrogen (5 vol.%) and nitrogen (95 vol.%) in an electrical tubular furnace. Samples of Sr$_2$SiO$_4$:Eu^{2+} have a form of powder with grains diameters from 0.3 µm to 1.5 µm. Grains tend to aggregate and form the large secondary particles, what is common in phosphors obtained via solid state synthesis method. Quality and purity of the samples were examined with X-ray diffraction method (XRD). Morphology of the samples was examined with Scanning Electron Microscope TM – 1000 (Hitachi). We estimated that in sample A coexist two Sr$_2$SiO$_4$ phases: 77% of α' and 15% of β. In sample B 83% of α' and 6% of β and in sample C 91% of α'. In all samples a small amount of SrSiO3 (8% in sample A, 10% in sample B and 6% in sample C) exists as an impurity phase

For TL experiments 2 mg portions of each sample have been scattered onto stainless steel discs that have been covered previously by the thin layer of silicon oil. All measurements were carried out using Risø TL/OSL System TL-DA-12 equipped with the EMI 9235QA photomultiplier in the temperature range from RT to 733 K in the argon atmosphere. The TL curves were obtained with the heating rate 2 K/s unless other values are given. TL has been detected in different spectral windows using Schott BG-39 (2mm), Schott BG-3 (3 mm) filters. ^{90}Sr/^{90}Y beta source (beta dose rate calibrated for quartz - about 40 mGy/s) have been used for TL excitation.

Tab.1	Activation energy (meV)	
Sample	fast component	slow component
A	58±12	215±118
B	394±80	228±27
C	390±105	168±27

Tab.1 Tab. 1 Activation energies estimated by applying the linear regression to the plot of lnτ versus 1/T (see the inset of Fig. 8), where τ is a lifetime determined from isothermal decay measurement at a defined temperature T.

Crystal structure legend:
– Sr In site I
– Sr in site II
– O
– Si
– SiO$_4$ tetrahedron
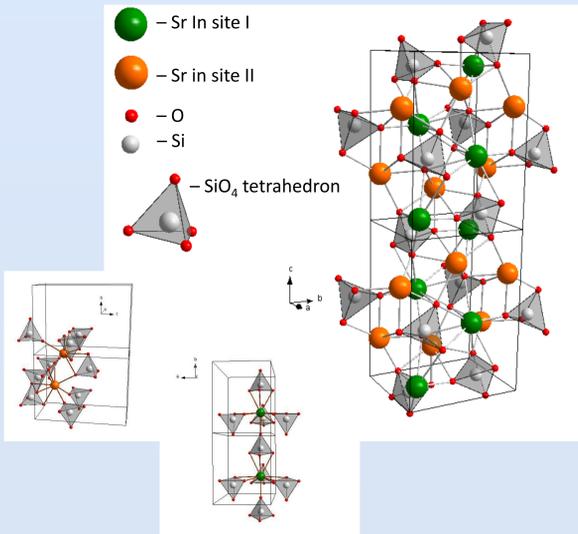
Crystal structure

Strontium orthosilicate Sr$_2$SiO$_4$ occurs in two phases: low temperature monoclinic form β (space group P2$_1$/c) and high temperature orthorhombic form α' (space group Pmab). The temperature of the phase transition is (~358 K), and α' form can exist also at temperature lower than 358 K if small amount of Ba^{2+} or Eu^{2+} is added to the Sr$_2$SiO$_4$ lattice.

β-Sr$_2$SiO$_4$ and α'-Sr$_2$SiO$_4$ have very similar crystal structure. In both phases Sr^{2+} ions occupy two kinds of inequivalent sites, SI and SII, that occur in the lattice in the same amount. Sr^{2+} ion in SI site is coordinated with ten oxygen ligands, and in SII site - with nine oxygen ligands. In β → α' phase transition a small rotation of SiO$_4$ tetrahedra causes appearance of (100) symmetry plane, which is absent in the β form, but the average Sr-O distances stay almost unchanged: for SI site the average Sr-O distance is equal to 2.852 Å in α' phase and 2.850 Å in β phase, and for SII site the average Sr-O distance is equal to 2.698 Å in α' phase and 2.709 Å in β phase.

Since Eu^{2+} has ionic radius very similar to Sr^{2+} and much larger than Si^{4+}, dopant ions Eu^{2+} substitute Sr^{2+} in crystal lattice in two different sites SI and SII. Besides of dopant ions, other defects present in Sr$_2$SiO$_4$ lattice are vacancies. Synthesis in an inert atmosphere provide the Sr$_2$SiO$_4$:Eu^{3+} where the excess positive charge of 2 Eu^{3+} ions is most likely compensated by Sr^{2+} vacancies that form hole traps. To obtain Sr$_2$SiO$_4$:Eu^{2+} annealing in reducing atmosphere is performed, that produce oxygen vacancies - electron traps.
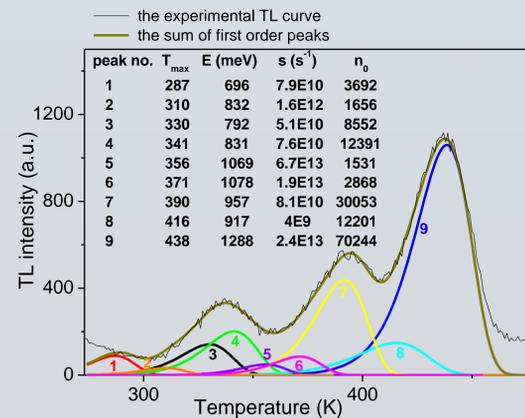
Fig.5 An example of fitting results for sample C. Experimental glow curve has been measured with the heating rate of 0.5 K/s after 5 seconds of excitation.

peak no.	T$_{max}$	E (meV)	s (s^{-1})	n$_0$
1	287	696	7.9E10	3692
2	310	832	1.6E12	1656
3	330	792	5.1E10	8552
4	341	831	7.6E10	12391
5	356	1069	6.7E13	1531
6	371	1078	1.9E13	2868
7	390	957	8.1E10	30053
8	416	917	4E9	12201
9	438	1288	2.4E13	70244

- the experimental TL curve
- the sum of first order peaks
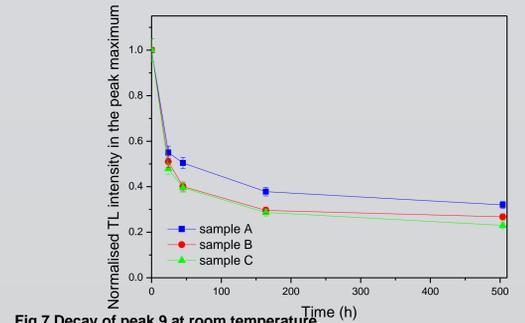
Fig.7 Decay of peak 9 at room temperature.

- sample A
- sample B
- sample C
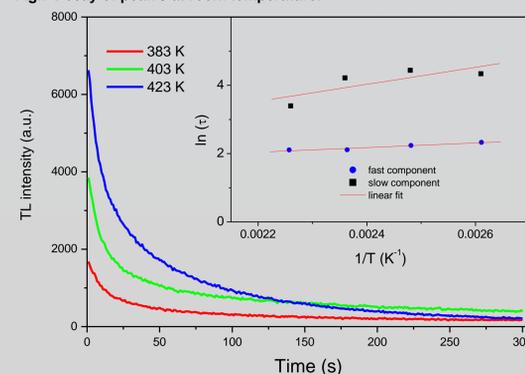
Fig.8 Isothermal decay of TL at different temperatures for sample A . Inset shows the plots that allow to establish activation energies using formula (2).
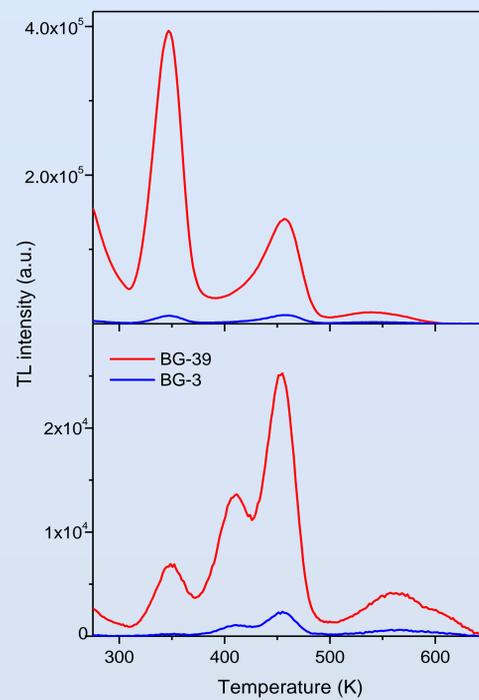
Fig.2 Glow curves of sample A and C (results for sample B are analogous to curves for sample C) measured using the filter BG-39 and BG-3. Excitation time – 5 s.
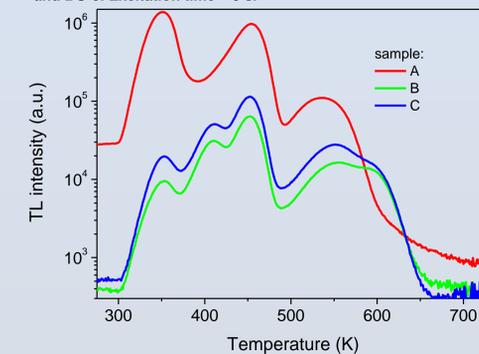
- BG-39
- BG-3

Fig.3 Glow curves for all investigated samples measured with the filter BG-39. Irradiation time 1000 s.
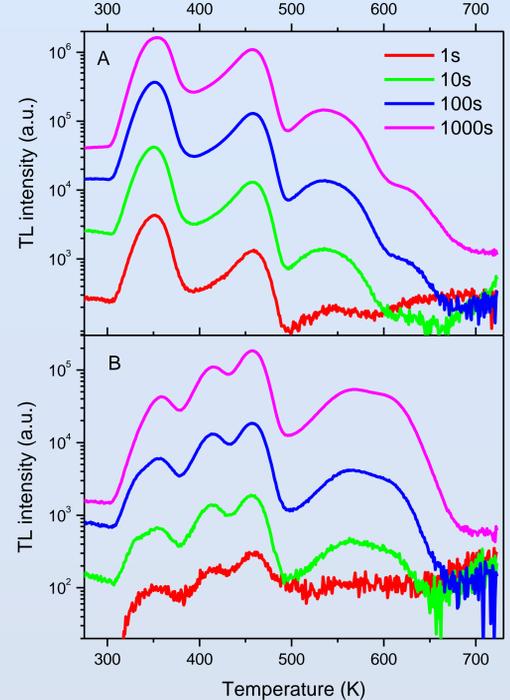
sample:
- A
- B
- C

Fig.4 The dependence of TL curves of sample A and B on the excitation dose.

- 1s
- 10s
- 100s
- 1000s
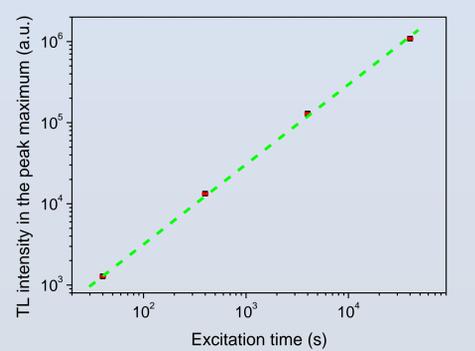
Fig.6. The dose dependence of the TL intensity in the peak maximum for peak 9.

Results and discussion

TL measurements were carried out for two spectral windows of the optical detection. Fig. 2 presents results obtained for two samples A and C (sample B show results analogous to sample C) using the filter BG-39 and BG-3. Eu^{2+} ions occupying SI and SII sites are affected by different crystal field that results in two broad bands in emission spectrum of Sr$_2$SiO$_4$:Eu^{2+}, green one related to 4f^{6}5d→4f^7 transitions in Eu^{2+}(SI) and orange one related to the same transition in Eu^{2+}(SII). The comparison of TL curves measured with different filters indicates that the orange band dominates the TL spectrum.

Fig. 3 presents TL curves for all investigated samples measured in the wide spectral range of the filter BG-39. In all glow curves three temperature ranges of TL signal can be distinguished – below 380K, range 380-480 K and above 480. In each of these ranges a TL broad maximum is observed. The complexity of the band above 480 K is obvious. A single peak between 400 and 480 K observed for sample A clearly corresponds to the double peak seen for samples B and C, so one can suppose that this peak is also a complex one. Fig. 4 shows the TL curves of sample A and B obtained after applying some different excitation doses. The position of peak maxima does not change with the dose. Such behaviour of TL peaks is characteristic for the TL process of first order kinetics. From the point of view of the dosimetric application, the lifetime of the carriers in the trap (τ) is the essential parameter. It is determined by the trap depth E (or thermal activation energy of trap) and frequency factor s:

$$\tau = \frac{1}{s} \exp(E/kT), \quad (1)$$

where k is the Boltzmann constant. Trap depth as well as frequency factor can be estimated by TL curve analysis. The fitting of the sum of first order curves to experimental glow curves is recently one of the most popular methods. Fig. 5 shows an example of fitting outcome for sample C together with the peak parameters. It is worth noting that the very close values of E and s have been obtained for sample A and B. As can be seen, nine different peaks can be distinguished. It is important, however, to know that not every peak is related to a real trap existing in the material. Although the TL kinetics can be supposed to be of first order because of the stable peak positions with the changes of initial trap population, one should not forget that the first order is an approximation that uses the assumption of low retrapping probability and this is valid only for high trap populations. During the TL process, especially for complex glow curves one can expect some effects connected with retrapping in traps that are just almost empty. This breaking of first order assumption introduces some TL curve deformations that lead to the presence of additional peaks of lower intensity in fitting results. In this case (Fig. 5) peak 2, 5, 6 and 8 can be candidates for such suspicion. The peak no. 9 with the temperature of the peak maximum at 438 K (for heating rate of 0.5 K/s, about 460 K for heating rate of 2 K/s) is clearly related to a specific kind of trap. Its E and s values obtained by the fitting allow to estimate the value of 10^9 s (about 32 years) for its lifetime at room temperature what could make this peak suitable for dosimetric applications. Fig. 6 presents a growth curve, the dependence of TL intensity on dose, for peak at 438 K in the range of four orders of magnitude.

The stability of peak 9 at room temperature has been tested and it turned out that it decays much faster that one can expect for the parameters obtained from glow curve analysis. Fig. 7 shows outcomes of this test for all three samples. In accordance with these results additional experiments have been carried out. Isothermal decay curves of TL are presented at Fig. 8. The measurements have been performed after 5 s of preheat at 383 K. The analysis of these decay curves allow to estimate two exponential components of the TL signal for each sample. Both of these components have lifetimes much shorter than the lifetimes calculated earlier on the basis of glow curve analysis. Using the temperature dependence of the lifetime (equation (1)) one can draw a plot of logarithm of lifetime versus 1/T and determine the activation energy from the linear regression in accordance with the following formula:

$$\ln\tau = \frac{E}{kT} - \ln s; \quad (2).$$

An example of the above mentioned plot is shown in the inset of Fig. 8. Tab. 1 presents the activation energy values obtained in results of such approach for all three samples. The s values that can be estimated by this method are burdened with a significant error but one can observe that they are extremely low for both components of TL decay. Although the activation energies given in Tab.1 should be treated cautiously because of the complexity of the TL process in the temperature range of isothermal decay measurements (383 – 423 K), their values are undoubtedly much lower than trap depth determined for peak 9 by glow curve fitting. Such observation suggests that in the TL process during heating the main way of carrier transfer is via conduction band whereas the localised transition of the electron directly to the luminescence centre without the transport through the conduction band takes place in the stable temperature conditions. The reason of such behaviour is the high dependence of the TL peak position on the heating rate. In this case because of the very low values of the frequency factor for the process of the direct electron transition to the luminescence centre the maximum of trap depopulation by means of such mechanism during heating would appear in the temperature higher than maximum temperature for peak 9 that is produced by process with the transfer via conduction band. So it cannot be observed in the glow curves.