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Dosimetric features of strontium orthosilicate (Sr_2SiO_4) doped with Eu^{2+}

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HIGHLIGHTS

- New efficient phosphor material was found for luminescence dosimetry.
- Linear themoluminescent (TL) response was observed in wide range of beta doses.
- Trap parameters were determined by glow curve analysis.
- Isothermal TL measurements were performed and significant TL fading is reported.

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ABSTRACT

Thermoluminescence (TL) of strontium orthosilicate doped with Eu^{2+} has been investigated in the range RT-750 K. Trap parameters of a TL peak at 450 K established by means of glow curve analysis suggest the possibility of applying this sensitive peak for TL dosimetry. The thermal stability test shows that the 450 K peak is partially unstable. The isothermal decay experiments reveal that the traps responsible for this peak can be emptied by a competitive way that is efficient during storage at a constant temperature, and is characterized by lower values of activation energy and frequency factor.

1. Introduction

Orthosilicate $Sr_2SiO_4:Eu^{2+}$ has attracted great interest mostly as an efficient phosphor suitable for WLED (white light emitting diodes) (Sun et al., 2008; Zhi-Jun et al., 2009; Yong and Sung, 2010). In this contribution the applicability of $Sr_2SiO_4:Eu^{2+}$ for dosimetric purposes is presented. To the best of our knowledge, no reasonable studies have been carried out on dosimetric characteristics of Sr_2SiO_4 doped with rare earth ions up to the present moment. In our investigations, a strong thermoluminescence (TL) signal in the range from room temperature to 750 K has been detected for strontium silicate synthesized using the solid state reaction method and doped with 2–4 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 the glow curve depends on the concentration of Eu ions. The highest TL intensity is observed for Sr_2SiO_4 with 2 mol% Eu. Two peaks – about 350 and 450 K – dominate in the glow curve of this sample. The 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 fitting the sum of first-order curves to experimental curves. The lifetimes estimated using these parameters allow the supposition that the TL peak at 450 K can be used for radiation dose measurement. This peak appears in all samples and, as has been demonstrated, its intensity increases linearly with a dose over four orders of magnitude. Detailed investigations, however, showed that this peak partially fades faster than 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 mechanism of the 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.

2. Experimental

2.1. Material

Strontium orthosilicate Sr_2SiO_4 occurs in two phases: low temperature monoclinic form β (space group $P21/c$) and high

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temperature orthorhombic form α′ (space group Pmab) (Catti et al., 1983a, 1983b). The temperature of the phase transition is (~358 K), and α′ form can exist also at temperatures lower than 358 K if a small amount of Ba2+ or Eu2+ is added to the Sr_2SiO_4 lattice (Catti et al., 1983a, 1983b; Sun et al., 2008; Yong and Sung, 2010).

β-Sr_2SiO_4 and α′-Sr_2SiO_4 have very similar crystal structures (Fig. 1). In both phases, Sr^{2+} ions occupy two kinds of inequivalent sites, SI and SII, which occur in the lattice in the same amount. Sr^{2+} ion is coordinated with ten oxygen ligands in the SI site, and with nine oxygen ligands in the SII site. In β→α′ phase transition a small rotation of SiO_4 tetrahedra causes appearance of a (1 0 0) symmetry plane, which is absent in the β form, but the average Sr–O distances stay almost unchanged: for the 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 (Catti et al., 1983a, 1983b; Sun et al., 2008; Yong and Sung, 2010).

Since Eu^{2+} has an ionic radius very similar to Sr^{2+} and much larger than Si^{4+}, dopant ions Eu^{2+} substitute Sr^{2+} in a crystal lattice in two different sites (SI and SII). Besides dopant ions, other defects present in Sr_2SiO_4 lattice are vacancies. Synthesis in an inert atmosphere provide the Sr_2SiO_4:Eu^{3+} where the excess positive charge of 2 Eu^{3+} ions is most likely compensated by Sr^{2+} vacancies that form electron traps. To obtain Sr_2SiO_4:Eu^{2+} annealing in reducing atmosphere is performed, which produces oxygen vacancies - hole traps.

For the purpose of this work we investigated samples of strontium silicate Sr_2SiO_4 nominally doped with 2–4 mol% 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 a 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). The material obtained was grounded and again calcined at 1250 C for 4 h in a reducing atmosphere using a mixture of hydrogen (5 vol%) and nitrogen (95 vol%) in an electrical tubular furnace. Samples of Sr_2SiO_4:Eu^{2+} have a powdered form with grain diameters ranging from 0.3 to 1.5 μm. These grains tend to aggregate and form large secondary particles, which is common in phosphors obtained via the solid state synthesis method. The quality and purity of these samples were examined with the X-ray diffraction method (XRD). Morphology of the samples was examined with a Scanning Electron Microscope TM—1000 (Hitachi). We estimated that in sample two Sr_2SiO_4 phases coexist: 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 were scattered onto stainless steel discs that had previously been covered with a thin layer of silicon oil.

2.2. Experimental equipment

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 (2 mm) and Schott BG 3 (3 mm) filters. $^{90}Sr/^{90}Y$ beta sources (beta dose rate calibrated for quartz—about 40 mGy/s) have been used for TL excitation (Przegietka and Chruścińska, 2014).

3. Results and discussion

TL measurements were carried out for two spectral windows of the optical detection. Fig. 2 presents results obtained for the two samples A and C (for sample B results are analogous to results for sample C) using a wide filter BG-39 and a much narrower BG-3. Eu^{2+} ions occupying the SI and SII sites are affected by different crystal field that results in two broad bands in the emission spectrum of Sr_2SiO_4:Eu^{2+}: the green one related to $4f^65d \rightarrow 4f^7$ transitions in Eu^{2+}(SI) and the orange one related to the same transition in Eu^{2+}(SII) (Kim et al., 2005; Zhi-Jun et al., 2009;

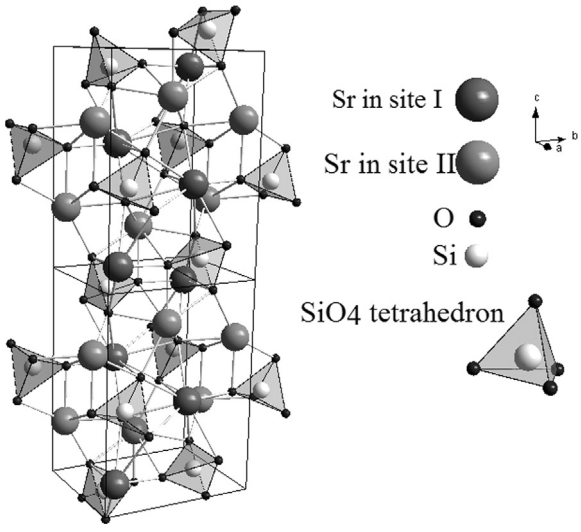

Fig. 1. Crystal structure of the high temperature orthorhombic form α′ of strontium orthosilicate. Phases β-Sr2SiO4 and α′-Sr2SiO4 have very similar crystal structure.

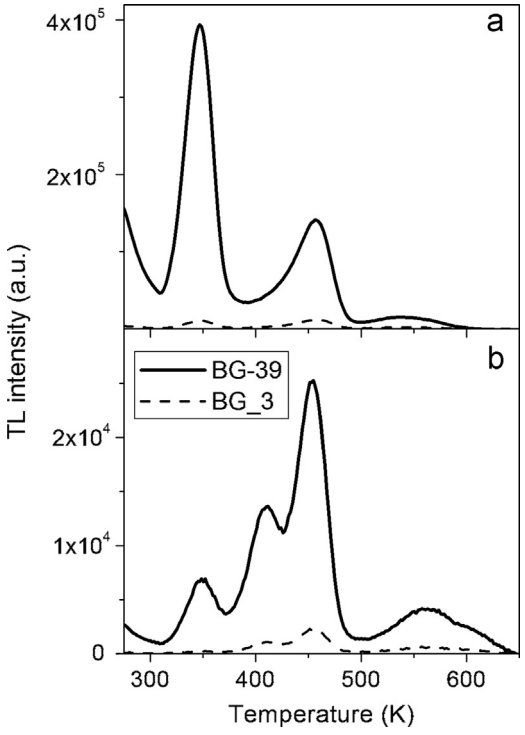

Fig. 2. Glow curves of sample A (a) and C (b) (results for sample B are analogous to curves for sample C) measured using filters BG-39 and BG-3. Irradiation time 5 s.