Low-temperature irradiation effects in lithium orthosilicates

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Abstract

The emission spectra of lithium orthosilicates (Li_4SiO_4) ceramics have been measured in the range of 1.8–5.8 eV under irradiation by 6–30 eV photons or 1–30 keV electrons at 6–300 K. The tunnel recombination phosphorescence, as well as luminescence, stimulated by 1.5–2.5 eV photons has been detected in the sample preliminarily irradiated at 6 or 80 K. The main peaks of thermally stimulated luminescence (TSL) in the irradiated ceramics have been observed at 72, 118 and 265 K. The creation spectra of the 118 K TSL peak, as well as the excitation spectrum of photostimulated luminescence (PSL) span the region of the intrinsic absorption of a lithium orthosilicate (9–30 eV). The intensity of PSL and the TSL peaks in Li_4SiO_4 ceramics prepared in hydrogen/argon atmosphere is several times lower than that in the mainly investigated Li_4SiO_4 ceramics prepared in the atmosphere of dry argon. The optical characteristics of Li_4SiO_4 are compared with the ones known for Li_2O and SiO_2 . Low-temperature luminescent methods are promising for the investigation of electron–hole processes and radiation defects serving as the traps for tritium released in D–T fusion reactor blanket systems.

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1. Introduction

Lithium orthosilicate (Li_4SiO_4) is one of the most attractive candidates for solid tritium breeding materials in D–T fusion reactors [1–4] and as a lithium ion conductor [5]. A Li_4SiO_4 complex compound consists of SiO_4 tetrahedrons and small-radius Li atoms bonded to the oxygen atoms. The results of long-standing investigations of the physical processes in $\alpha\text{-SiO}_2$ crystals and other silicates [6–8], as well as in Li_2O single crystals and ceramics [9–12], will be useful for the study of lithium orthosilicates. The main applications of Li_4SiO_4 ceramics are expected at temperatures close to the melting point (1230 °C) of the material. Low-temperature optical and radiation processes in Li_4SiO_4 have obviously been insufficiently studied.

At the same time, the low-temperature investigations (2–80 K) of excitonic, electron–hole (e–h) and interstitial–vacancy (i–v) processes in simple lithium-containing materials (e.g. LiF) had a profound impact on the interpretation of the phenomena at room temperature and significantly higher temperatures (see, e.g. [13,14]).

The aim of the present study is to investigate the low-temperature (5–300 K) processes in lithium orthosilicate ceramics by means of up-to-date methods of vacuum ultraviolet (VUV) spectroscopy and highly sensitive methods of thermally or photostimulated luminescence (TSL and PSL).

2. Experimental

Ceramic samples of a Li_4SiO_4 complex oxide compound were prepared at the Institute of Physics, Tartu University, by a 4-h firing of pressed pellets of highly pure Li_4SiO_4 (99.9%, Alfa-Aesar Co.) in the atmosphere of dry argon

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or Ar/H₂ (10%) mixture at 1000 °C, and a subsequent rapid cooling of the sample in an argon stream. Further, these two types of samples will bear the names Li₄SiO₄-1 and Li₄SiO₄-2, respectively. To prepare a Li₄SiO₄-3 sample, about 1 mol% of GeO₂ was added to Li₄SiO₄ before its final firing in the argon atmosphere.

Cathodoluminescence (CL) was simultaneously detected by a two-channel system: (1) in the region of 4–12 eV, a double vacuum-grating monochromator and a photomultiplier Hamamatsu R6838; and (2) in the region of 1.5–6.0 eV, a double prism monochromator and a Hamamatsu H6240 photon-counting head. The CL spectra were measured at 6–300 K at the excitation by an electron gun (1–30 keV, 10–100 nA, spot size ~ 0.5 mm²). After the electron irradiation of a sample, it was possible to register the TSL (for different emissions selected through a double prism monochromator) by heating the irradiated sample with a constant rate of $\beta = 10$ K min⁻¹.

The PSL method for the study of e–h and i–v processes was earlier elaborated in Tartu and then applied also to synchrotron experiments with alkali halides [15], simple and complex oxides (e.g. MgO:Be [16]) and metal tungstates [17] at beamline BL52 at the MAX-Lab, Lund. Our preliminary experiments showed that the additional stimulation by visible or IR light of the Li₄SiO₄ ceramics, preliminarily irradiated at 8 or 80 K, causes the radiative recombination of carriers, i.e. the appearance of PSL. The spectroscopic experiments with synchrotron radiation were mainly performed at the SUPERLUMI station of HASYLAB at DESY, Hamburg (see [18] for details). The excitation spectra of various emissions (selected by a monochromator) were normalized to equal quantum intensities of incident synchrotron radiation.

3. Experimental results and discussion

Inset of Fig. 1 shows the emission spectra measured at 10 K at the excitation of Li₄SiO₄-1 by 11 or 23 eV photons, which form separated electrons and holes. The spectra consist of two main broad bands with the maxima at 2.9 and 3.8 eV and two weak emissions at ~ 2 eV and ≥ 4.7 eV. The emissions of 2.9 and ~ 2 eV dominate in case of the sample excitation by $h\nu_{\text{exc}} = 6.5$ eV. Two main emission bands at ~ 2.9 and ~ 3.8 eV are detected in the spectrum of CL of Li₄SiO₄-1 at 6 K. At room temperature, the 3.8-eV emission undergoes a strong thermal quenching. The emission band peaked at 3.8 eV is also drastically depressed in the CL spectrum measured at 6 K for a Li₄SiO₄-2 sample prepared in a reducing Ar/H₂ atmosphere. We failed to detect any emission in the region of 6–10 eV for the Li₄SiO₄ samples.

It is known that the emission of self-trapped excitons (STEs) has a maximum at 2.8 eV at the excitation of an α -SiO₂ crystal in the regime of two-photon absorption (ArF excimer laser, 2×6.4 eV) at 8 K [19], while the absorption maximum of a neutral oxygen vacancy (an F center) is located at 7 eV, i.e. in the region of the efficient excitation

Fig. 1. The emission spectra (1–4) and the excitation spectra of several emissions (5–8) measured for a Li₄SiO₄-1 sample at 10 K (1–3, 5–7) and 295 K (4, 8). The emission spectra are measured at the excitation by 6.5 eV (1), 23 (2) and 11 eV (3, 4), the excitation spectra are measured for 3.9 eV (5), 5.4 (6), 2.8 (7) and 2.3 eV (8) emissions.

of 5-eV emission [20]. In Li₂O single crystals at 9 K, two emission bands at 3.7 eV ($h\nu_{\text{exc}} = 6.8$ eV) and 4.75 eV ($h\nu_{\text{exc}} = 7.7$ eV) [11], as well as the 4-eV absorption band related to the so-called F⁺ centers (an electron in the field of an anion vacancy) [9,10] have been revealed. One might expect the analogous emissions of STEs, F and F⁺ centers in Li₄SiO₄ ceramics as well.

Fig. 1 also presents the excitation spectra of several emissions measured for Li₄SiO₄-1 using synchrotron radiation of 5–28 eV at 10 and 295 K. The efficiency of the 2.9- and 2.3-eV emissions is especially high at $h\nu_{\text{exc}} = 6$ –8 eV. A sharp increase of the efficiency of the 3.9- and 5.4-eV emissions occurs at $h\nu_{\text{exc}} = 9.5$ eV; the efficiency value remains high at 12–17 eV and it approximately doubles at 26–28 eV. Similar to other wide-gap dielectrics (including Al₂O₃ [21], Y₂SiO₄ and Zn₂SiO₄ [22], SiO₂ and aluminosilicates [8]), the phenomenon of the multiplication of electronic excitations (MEE) takes place in Li₄SiO₄ at $h\nu_{\text{exc}} \geq 23$ eV. Under MEE conditions, an absorbed exciting photon causes the creation of more than one electronic excitation.

An intense and prolonged phosphorescence was detected in Li₄SiO₄-1 after the end of a short irradiation by an electron beam (20 keV, 10 nA, 2 min). After the initial stage, comparable to the duration of irradiation, the phosphorescence exhibits distinctive features of tunnel recombination luminescence and its intensity drops with time by a power law $I \sim t^{-\alpha}$, where $\alpha = 0.696$. The band with the maximum at 2.8 eV dominates in the afterglow spectrum.

Fig. 2 shows the curve of low-temperature TSL for a Li₄SiO₄-1 sample irradiated by 20 keV electrons at 6 K.

Fig. 2. The TSL curves measured for 2.9 eV in Li_4SiO_4 -1 irradiated by 20 keV electrons at 6 K (1) or 11 eV photons at 10 K (2). $\beta = 10 \text{ K min}^{-1}$.

Two main TSL peaks at 72 (a nonelemental one) and 118 K have been detected for $(2.9 \pm 0.1) \text{ eV}$ emission at the heating rate of $\beta = 10 \text{ K min}^{-1}$. After several additional preheating of the irradiated sample up to 20, 50 and 60 K, it was possible to separate a weak TSL at 35–40 K against the background of the tunnel recombination phosphorescence. An additional study of this weak TSL peak is planned. Integral TSL has been detected also after selective irradiation of the sample by synchrotron radiation of 11, 14 and 19 eV. In all the cases, the TSL curves contained the same peaks as those after electron irradiation (see Fig. 2). Similar to LiF and SiO_2 materials with simpler structure (see, e.g. [13,14] and [6,7], respectively), the TSL in the region of 80–150 K, induced by electron or VUV irradiation, is caused mainly by e–h processes.

Fig. 3 shows the TSL curve measured after the irradiation of Li_4SiO_4 -1 by 1.5-keV electrons at 6 K. Such electrons are not able to create any defects due to the impact mechanisms in lithium orthosilicates. Nevertheless, the peaks at 72 and 118 K are detected for the 2.8-eV emission. Weak TSL peaks at 205 and 265 K can be registered for the 3.8-eV emission during heating of the irradiated sample from 160 to 390 K. The intensity of the 265 K peak is about 60 times as low as that of the TSL peak at 118 K. Fig. 3 also shows the TSL curve measured for the 2.8-eV emission

Fig. 3. The TSL curves measured for Li_4SiO_4 -1 (1, 1') and Li_4SiO_4 -3 (2) samples irradiated by 1.50 keV (1, 1') and 20 keV electrons (2) at 6 K. The TSL was measured for 2.8 (1, 2) and 3.8 eV (1') emissions, $\beta = 10 \text{ K min}^{-1}$.

after the 20-keV electron irradiation of a Li_4SiO_4 -3 sample containing GeO_2 . Intense TSL peaks at 72, 118 and 265 K and weak peaks at 180, 300 and 360 K were detected in this sample.

Fig. 4 demonstrates the TSL curve for a Li_4SiO_4 -1 sample irradiated by 20-keV electrons at 8 K and stored for 48 h under vacuum conditions at 295 K. Integral TSL of this irradiated sample was measured with the heating rate $\beta = 2.86 \text{ K s}^{-1}$ in the atmosphere of flowing nitrogen (System 310 TLD Reader). High-temperature TSL peaks at 430, 470, 545 and 670 K were detected.

In neutron-irradiated Li_4SiO_4 ceramics, the peaks of tritium release rate were observed in the region of 450–750 K [2]. These peaks were ascribed to the annealing of the charged defects that served as the traps for highly mobile tritium. An example of such traps is F^+ centers, which have been thoroughly studied in Li_2O crystals [9,10]. The spectrum of radiation-induced optical absorption consists of F^+ -band peaked at $\sim 4 \text{ eV}$ and a broad band at 1.7–2.3 eV. We made an attempt to complement a relatively low-sensitive absorption method of the investigation of the irradiated samples of Li_4SiO_4 by highly sensitive luminescent methods. The additional stimulation of Li_4SiO_4 -1 X-irradiated at 80 K by 1.6–2.4 eV photons (selected through a double prism monochromator) leads to the appearance of PSL in the region of 2.7–3.2 eV (selected through an optical filter).

The inset in Fig. 5 shows the integral TSL curve measured with $\beta = 10 \text{ K min}^{-1}$ for a Li_4SiO_4 -1 sample irradiated by 10.5-eV photons at 80 K. The 118 K peak (an activation energy of 180 meV) correlates well with the annealing of the PSL intensity measured in the regime of pulse heating: the stimulation by 1.8-eV photons at 80 K after the preheating of the sample up to a certain temperature $T_i = 90$ –140 K. After the photostimulation at 80 K, the intense secondary phosphorescence connected with a repeat localization and release of carriers from shallow traps (TSL at 72–75 K) was detected in Li_4SiO_4 -1.

Fig. 5 demonstrates the creation spectrum of PSL of $\sim 2.9 \text{ eV}$ measured for Li_4SiO_4 -1 irradiated by equal quantum doses of 7.5–28-eV photons at 10 K. When an

Fig. 4. The integral TSL measured for a Li_4SiO_4 -1 sample irradiated by 20 keV electrons at 8 K and stored for 48 h under vacuum conditions at 295 K. $\beta = 2.86 \text{ K s}^{-1}$.

Fig. 5. The integral TSL (1) and pulse annealing of the PSL (2.7–3.2 eV), stimulated by 1.8 eV photons (2), measured for a Li_4SiO_4 -1 sample irradiated by 10.5 eV photons at 80 K. The creation spectra of the PSL measured under VUV-irradiation of Li_4SiO_4 -1 at 10 K (3) and 80 K (4). The spectra of the 118 K TSL peak creation by VUV radiation at 80 K in Li_4SiO_4 -1 (5), Li_4SiO_4 -2 (6) and Li_4SiO_4 -2 preliminarily fired at 773 K (7).

additional stimulation of the VUV-irradiated sample is started, the PSL intensity slightly increases, reaches the maximum value, and then decreases. The rising stage is caused by a tunnel recharging of defects at 10 K that provides the increase of the number of centers responsible for PSL. The light sum detected during 15 s (since the maximum value was reached) was taken as a measure of the PSL efficiency. Before measuring the next point in the creation spectrum, a total deexcitation of the sample (the intensity of PSL approaches zero) was carried out by means of an intense stimulation by 1.8-eV photons. The efficiency of PSL sharply increases in the region of fundamental absorption at $h\nu_{\text{exc}} \geq 9$ eV as well as in the multiplication region of $h\nu_{\text{exc}} > 23$ eV (compare with Fig. 1). The intensity of PSL, measured in Li_4SiO_4 -1 5 min after the 10.5-eV photon irradiation at 80 K is stopped, sharply increases with the rise of the irradiation dose during 15 min and then linearly increases during 2 h.

Fig. 5 shows the creation spectra of PSL and the 118 K TSL peak by equal quantum doses of VUV radiation (7.0–11 eV) at 80 K in a Li_4SiO_4 -1 sample. The efficiency of PSL is close to zero at $h\nu_{\text{exc}} = 7.0$ –8.5 eV and then drastically increases in the region of up to $h\nu_{\text{exc}} = 11$ eV (limit of measurements with discharge VUV sources). The intensity of the 118 K TSL peak in Li_4SiO_4 -2 is about seven times lower than in Li_4SiO_4 -1. An additional firing of Li_4SiO_4 -2 in the argon atmosphere at 773 K for hydrogen release from the sample leads to the increase of the intensity of TSL and PSL in later irradiated sample by several times. It is not inconceivable that the investigation of Li_4SiO_4 -2-type orthosilicates will be useful to the preliminary study of the processes of the release of deuterium and tritium from Li_4SiO_4 without any complicated experiments under neutron irradiation.

4. Concluding remarks

The emission spectra of various Li_4SiO_4 ceramics have been measured in the range of 1.8–5.8 eV under irradiation by 6–30 eV photons or 1–30 keV electrons at 6–300 K. The tunnel recombination phosphorescence, as well as luminescence, stimulated by 1.5–2.5 eV photons has been detected in the sample preliminarily irradiated at 6 or 80 K. The creation spectra of the 118 K TSL peak, as well as the excitation spectrum of PSL, span the region of the intrinsic absorption of a lithium orthosilicate (9–30 eV). It is demonstrated that low-temperature, highly sensitive luminescent methods, based on the investigation of tunnel phosphorescence, TSL and PSL in lithium orthosilicates, have been very promising for the detailed investigation of e–h processes with the participation of defects that serve as the traps for tritium (see, e.g. [2]) in high-temperature commercial fusion reactors.

In our opinion, a detail comparison of the obtained results with the data on further investigation of Li_4SiO_4 irradiated by high-energy particles, which cause defect creation by the knock-out (impact) mechanism, will allow us to separate the nonimpact (electron–hole) mechanisms of radiation damage. Of particular interest are the processes of defect creation in a cation sublattice of a lithium orthosilicate. Small-radius interstitial Li^+ (and possibly Li^{2+}) ions can possess high mobility even at low-temperatures (8–80 K).

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