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The central role of oxygen on H^+-irradiated Lu_2SiO_5 luminescence

L.G. Jacobsohn*, B.L. Bennett, J.-K. Lee, R.E. Muenchausen, J.F. Smith, B.P. Uberuaga, D.W. Cooke

Materials Science & Technology Division, Los Alamos National Laboratory, MST-8 E546, Los Alamos, NM 87545, USA

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Abstract

The behavior of self-trapped defects (STDs) in ion-beam irradiated Lu_2SiO_5 (LSO) crystal has been investigated via temperature-dependent radioluminescence (RL) measurements. Production of oxygen vacancies is the major effect of H^+ irradiation on luminescencent properties of this phosphor. Luminescence centers for self-trapped exciton (STE) and self-trapped hole emission are assigned to oxygen vacancies and oxygen ions, respectively. Ion-induced structural damage modifies the thermal stability of the STDs and creates perturbed STEs. A striking effect of ion irradiation is the approximate factor-of-two enhancement of STE RL intensity that results from implantation of only a thin (~250 nm) surface layer of LSO. This enhancement is attributed to ion-beam modification of a surface dead layer.

Keywords: Ion irradiation; Lu_2SiO_5; Oxygen; Radioluminescence; Self-trapped exciton; Self-trapped hole

1. Introduction

Ion irradiation is a powerful tool for modifying optical properties of materials for specific applications [1], although creation of structural damage is a direct, and not necessarily desired, consequence of the implantation process. Vacancies and interstitials are created either by the momentum transferred from the projectile to the host matrix or within the subsequent collision cascade. If the amount of transferred energy from the projectile to an atom of the network is larger than a given threshold value, known as the displacement energy, then an interstitial and a vacancy are created. Typical values are ca. 15 and 25 eV for elemental metals and semiconductors, respectively [2]. Very often, and depending on the initial energy of the incoming projectile, the interstitial itself can have enough energy to produce other interstitials, thus initiating a collision cascade with creation of other structural defects. The process of direct energy transfer from the projectile to the atoms of the host matrix is known as the nuclear energy-loss mechanism. Conversely, the dominant energy-loss mechanism for beams of low atomic number projectiles possessing high energy is energy transfer from the projectile to the electrons of the host material either by excitation or by ionization. Of particular interest is the formation of self-trapped defects (STDs), *viz.* excitons (STEs) and holes (STHs). While the process of creation of vacancies and interstitials by ion irradiation is well understood [2], much less is known about formation of STDs. With the exception of the alkali halides [3], creation and dynamics of STDs in most materials is not well understood.

In previous work we examined the effects of ion irradiation on radioluminescence (RL) of STDs in Lu_2SiO_5 (LSO), but did not provide a model that adequately described all of the observations [4]. Although we identified STE and STH emission bands, we lacked sufficient insight to elucidate the origin of luminescence centers associated with STE and STH emission. In the present work, we describe a model that incorporates the structural damage

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*Corresponding author. Tel.: +1 55 505 667 8011; fax: +1 55 505 665 5849.
E-mail address: lgjacob@lanl.gov (L.G. Jacobsohn).

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induced by H^+ irradiation, oxygen ions and vacancies as STH and STE luminescence centers, and a surface dead layer to explain the RL results.

2. Experimental procedures

LSO crystals were synthesized by the Czochralski method without any intentional rare-earth doping. Secondary ion mass spectrometry measurements revealed rare-earth ion contamination, including Ce, to be in the ppm level. The presence of rare-earth impurities is also indicated by the presence of emission bands in the region from 370 to 500 nm. The characteristics of these bands are in good agreement with those obtained from an intentionally Tb-doped LSO crystal [5], suggesting Tb^{3+} substitution for Lu^{3+} to be the origin of these emission bands. Sample surfaces were polished to an optical quality and were ion irradiated at room temperature using a 40 keV H^+ beam with dose 2×10^{16} atoms/cm^2, yielding a projected range + straggling of 250 + 100 nm as determined by application of the SRIM 2003 code [6]. Detailed Monte Carlo calculations of the H^+ irradiation of LSO that take into account all collisional damage created in the cascades were also carried out using the SRIM 2003 code. In these calculations, the displacement energy values for Lu, Si and O were 25, 15 and 28 eV, respectively.

RL measurements were made in vacuum from room temperature to liquid He using a Mo-target X-ray source operating at 50 kV and 40 mA. The effective X-ray energy was ~25 keV and the dose rate at the sample was 1.75 Gy/s. An exposure time of 10 s was used to obtain RL spectra at each selected temperature. Typical luminescence intensity experimental error was 10%.

3. Results and discussion

Fig. 1 shows the temperature-dependent RL behavior of LSO that has not been subjected to H^+ irradiation. Of importance are the two bands centered at 256 (4.84 eV) and 315 nm (3.91 eV) that correspond to STE and STH emission, respectively. These assignments follow the observation that in all yttrium- and lutetium-based crystals STE and STH bands exhibit maxima near 250 and 315 nm [7,8]. Notice that the intensity of these two bands decreases for higher temperatures, but at quite different rates. The intensity of the STH band decreases faster than the STE band and is nearly extinguished by 80 K. In contrast, the STE band, albeit weak, is still present at room temperature.

The RL results obtained from an LSO crystal irradiated with 40 keV H^+ ions (2×10^{16} atoms/cm^2) are presented in Fig. 2. Similar to RL behavior of the pristine sample, the STH band of irradiated LSO decreases faster than the STE band for higher temperatures with weak STE emission still evident at room temperature. However, in this case the STH band vanishes at a slightly higher temperature, viz. ~100 K.

The thermal behavior of the two bands, before and after ion irradiation, is summarized in Fig. 3. The STE curve for the irradiated sample is shifted to lower temperatures relative to the unirradiated one, has an inflection point at T^*~75 K, and exhibits two-fold increase in emission intensity. In contrast, following ion irradiation the STH band shifts to higher temperatures with no change in emission intensity and no evidence for an inflection point.

As explained in the introduction, creation of electronic and structural defects is the primary effect of ion irradiation. Since STDs in LSO are not stable at room temperature (cf. Figs. 1 and 2), the retained damage must consist only of vacancies and interstitials. Fig. 4 shows the absolute and relative concentrations of O, Si and Lu vacancies as obtained from Monte Carlo simulations of 40 keV H^+ irradiation of LSO using the SRIM 2003 code. The number of oxygen vacancies comprises nearly 50% of the total number of vacancies, which is of the order of

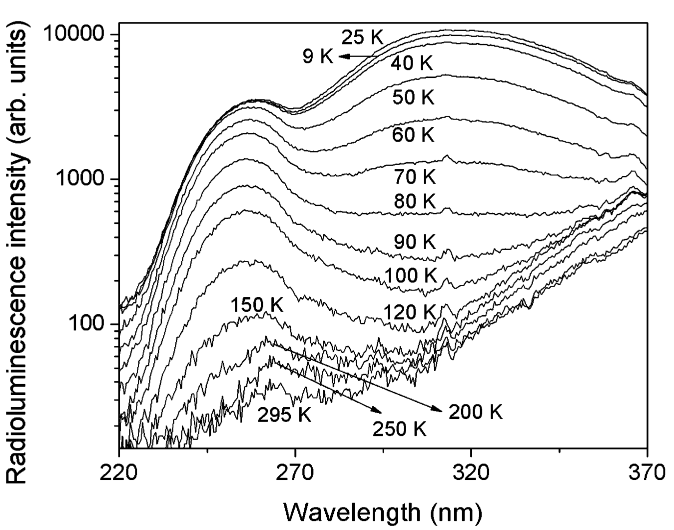

Fig. 1. Radioluminescence measurements of pristine LSO crystal as a function of temperature.

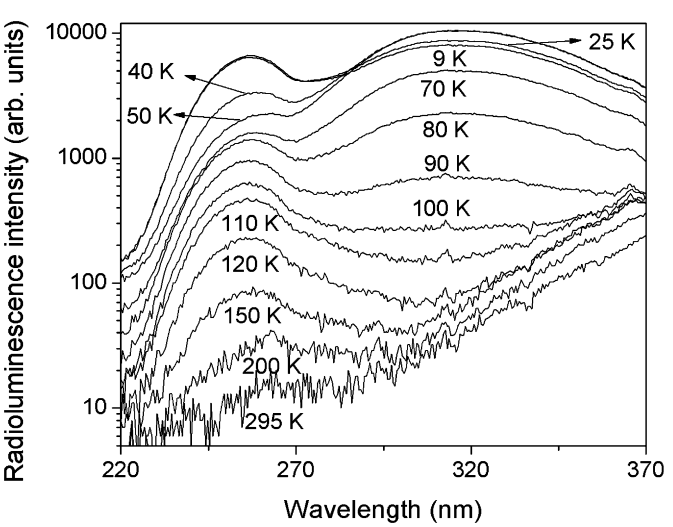

Fig. 2. Radioluminescence measurements of 2×10^{16} atoms/cm^2 40 keV H^+-irradiated LSO crystal as a function of temperature.