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Optical properties and electronic structure of Lu_2SiO_5 crystals doped with cerium ions: Thermally-activated energy transfer from host to activator

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ABSTRACT

This paper reports on the optical properties of cerium-doped lutetium oxyorthosilicate (LSO:Ce) crystals. The reflection and X-ray photoelectron spectra are measured, and compared to the electronic structure calculated by a discrete variational $X\alpha$ method. A sharp exciton band originating from $\text{O } 2p \rightarrow \text{Lu } 5d$ transition is observed at 7.27 eV at 6 K, with the band-gap energy of 7.52 eV. Luminescence measurements have also been performed in a wide temperature range of 6–300 K. The intensity of Ce luminescence arising from the $5d \rightarrow 4f$ transition is temperature-independent under the direct excitation of Ce^{3+} ions, but it is enhanced at around 50 K under the excitation of host LSO crystals. This enhancement is found to anti-correlate with a thermal quenching of the intrinsic luminescence due to self-trapped excitons. The present results provide a piece of evidence that thermally-activated energy transfer from host to activator takes place efficiently in LSO:Ce.

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1. Introduction

Better understanding of luminescence phenomena in condensed matter is essential for development of scintillator and display devices [1–4]. Cerium-doped lutetium oxyorthosilicate ($\text{Lu}_2\text{SiO}_5\text{:Ce}$ or LSO:Ce) is an excellent scintillation material, and its luminescence property has been widely studied for the past two decades [5–10]. The host crystal of LSO consists of isolated ionic SiO_4 tetrahedral units and non-Si-bonded O atoms surrounded by four Lu atoms in a distorted tetrahedron [11]. This OLu_4 tetrahedra form edge-sharing infinite chains along the crystallographic c axis. Lu^{3+} ions occupy two crystallographically different sites coordinated with either six or seven oxygen atoms. In LSO:Ce crystals, Ce^{3+} ions substitute for Lu^{3+} ions, and consequently have two Ce sites, called Ce1 and Ce2.

Mechanisms of excitation energy transfer are a main subject of long-standing studies for wide-band-gap scintillators [2,12,13]. Despite extensive investigations of luminescence properties of LSO:Ce [5–10], energy transfer processes from host LSO crystal to Ce^{3+} impurities are still under discussion. Furthermore, optical properties and electronic structure of LSO are less studied. In the

present work, we have measured reflection and luminescence spectra of LSO:Ce crystals in a temperature range between 6 and 300 K by using synchrotron radiation as a light source. The inter-band excitation with ultraviolet light could bring us useful information on elementary processes of the energy transfer from host to activator, i.e. host-sensitization, in scintillation materials. X-ray photoelectron spectroscopy (XPS) has also been performed. The results obtained are discussed with the help of the electronic structure of LSO investigated by a relativistic molecular orbital calculation. Existence of a thermally-activated energy transfer process is confirmed through an analysis of temperature dependences of the intensities of Ce luminescence and intrinsic luminescence.

2. Experiment

The crystals of LSO:Ce used in the present experiment were obtained from Zecotek Photonics, Inc. in Canada. The concentration of Ce^{3+} ions was 0.25 mol%. The specimens, which were polished to optical grade over all surfaces, having a size of $3 \times 3 \times 15 \text{ mm}^3$, were mounted on the copper holder in a closed-cycle He optical cryostat working in the temperature range between 6 and 300 K.

Measurements of reflection, luminescence, and luminescence-excitation spectra were performed with the use of synchrotron

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radiation from the UVSOR storage ring in Okazaki. The light beam was monochromatized through a 1 m VUV monochromator, with a typical resolution of 0.5 nm. The reflected light was detected under near-normal incidence by a photomultiplier tube coated with sodium salicylate phosphor. Luminescence emitted from the sample surface was measured by a liquid-nitrogen-cooled CCD camera (Princeton, 1100PBVISAR) after passing through a monochromator (Acton SpectraPro 2300i), with a resolution of 5 nm. No correction of the spectral response of the detection system was made for the luminescence spectra. The excitation spectra were corrected for the intensity distribution of the incident light.

Decay kinetics of Ce luminescence was examined under the excitation with the fourth harmonics (266 nm) of a Q-switched Nd:YAG laser (Continuum Minilite II), with a pulse duration of 7 ns. The decay curves were displayed on a digital storage oscilloscope.

Measurement of XPS spectra was carried out by an ESCA spectrometer (AXIS-NOVA, Kratos/SHIMADZU), with an excitation source of Al anode ($K\alpha$: 1486.6 eV). An electron flood gun was used to compensate for the sample charging under X-ray irradiation. The overall resolution was about 1 eV under our experimental condition.

3. Experimental results

Fig. 1 shows the reflection spectra of LSO:Ce measured in the energy region below 30 eV at $T=6$ and 300 K. A sharp lowest-energy band is observed at around 7.2 eV. The peak energy is determined to be 7.27 eV at 6 K and 7.19 eV at 300 K. Four distinct peaks appear in the 8–11 eV region. In the high-energy region, a broadband is observed at around 21 eV.

XPS spectra of LSO:Ce is presented in Fig. 2, in which the binding energy is given relative to the top of the valence band. The valence band consists of two prominent bands at 5.19 and 6.45 eV, superimposed on a weak basic structure in the 0–10 eV region. In the high-binding-energy region, three bands are observed at 18.9, 25.1, and 31.2 eV.

The contour plot of three-dimensional luminescence-excitation spectrum of LSO:Ce at $T=6$ K is shown in Fig. 3. The dominant luminescence, with two peaks at 396 and 423 nm, arises from the $5d \rightarrow 4f$ transition within the Ce^{3+} manifold at Ce1 sites, in which the ground state of $4f^1$ configuration splits into $^2F_{5/2}$ and $^2F_{7/2}$ by the spin-orbit interaction. The Ce2 luminescence peaking at 460 nm [5] is much weaker and not well resolved in our experiment. The $5d$ excited state of Ce^{3+} ions splits into several components due to the crystal field effect of host LSO. Among them, three $5d$ subbands are clearly recognized in the excitation spectrum, with peaks at 264, 296, and 354 nm.

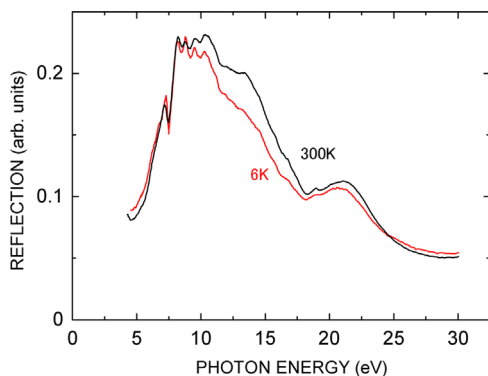


Fig. 1. Reflection spectra of LSO:Ce measured in the energy region up to 30 eV at $T=6$ K (red line) and 300 K (black line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

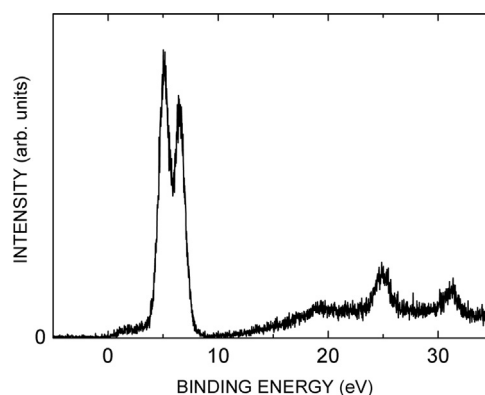


Fig. 2. XPS spectrum of LSO:Ce. The binding energy is given relative to the top of the valence band.

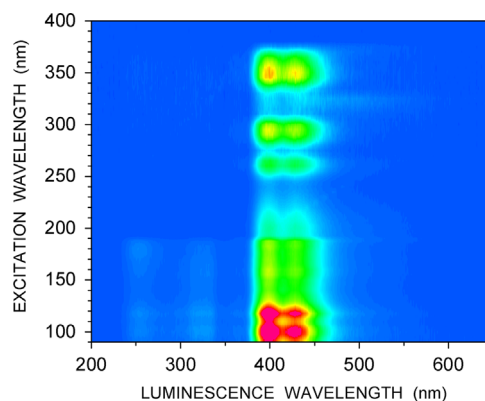


Fig. 3. The luminescence intensity of LSO:Ce at $T=6$ K is plotted as functions of excitation and luminescence wavelengths.

In Fig. 3, one may recognize two weak, but appreciable, luminescence bands at 256 and 320 nm. They are both excited with ultraviolet light in the wavelength region shorter than 190 nm (or > 6.52 eV), which corresponds to the onset of the fundamental absorption of LSO. The 256 nm luminescence is attributed to the radiative annihilation of a self-trapped exciton (STE), as suggested by Cooke et al. [8]. The 320 nm luminescence is probably associated with lattice perturbations induced by substitution of larger Ce^{3+} ion (1.01 Å) for host Lu^{3+} ion (0.86 Å) [8]. This “perturbed” STE luminescence is not discussed in the present paper. The result of Fig. 3 is in good agreement with previously published data [7,10].

The luminescence spectrum in the 225–350 nm region overlaps with the absorption bands due to Ce^{3+} ions. Therefore, there may be a possibility that its spectral shape and intensity are perturbed by the reabsorption in the Ce^{3+} bands. However, since the “hole” at around 280 nm in the luminescence spectrum has also been observed in undoped LSO [8], the spectral shape of Fig. 3 is supposed to be likely free from the reabsorption effect. On the other hand, the emission intensity may be influenced by the reabsorption. Furthermore, the quantum efficiencies of STE luminescence and Ce luminescence are expected to be quite different to each other. It is thus difficult to compare the intensity of STE luminescence with that of Ce luminescence quantitatively.

Fig. 4 shows the luminescence spectra excited with 150 nm (8.26 eV) light at different temperatures. The peak intensity at $T=300$ K is normalized to unity. A double-peak structure of Ce luminescence would overlap and combine into a single broadband at 300 K. A striking feature of Fig. 4 is that the intensity of Ce luminescence increases more than twice when T goes from 6 to 300 K. On the other hand, intrinsic STE luminescence at 256 nm

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