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Crystal structure of Ce-doped $(La,Gd)_2Si_2O_7$ grown by the Czochralski process

Rikito Murakami [a, b, *], Shunsuke Kurosawa [c, d, **], Hisanori Yamane [e], Takahiko Horiai [b], Yasuhiro Shoji [a, b], Yuui Yokota [c], Akihiro Yamaji [b], Yuji Ohashi [b], Kei Kamada [a, c], Akira Yoshikawa [a, b, c]

[a] C&A Corporation, 6-6-40 Aramaki Aza-aoba, Aoba-ku, Sendai, Miyagi, Japan
[b] Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi, Japan
[c] New Industry Creation Hatchery Center, Tohoku University, 6-6-10 Aoba, Aramaki, Aoba-ku, Sendai, Miyagi, Japan
[d] Faculty of Science, Yamagata University, Kojirakawa-machi 1-4-12, Yamagata 990-8560, Japan
[e] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

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ABSTRACT

Single crystals of $(La_{0.25}Gd_{0.75})_2Si_2O_7$ and $(La_{0.235}Ce_{0.015}Gd_{0.75})_2Si_2O_7$ were grown by the Czochralski method. Structure analysis of the single crystals by X-ray diffraction (XRD) revealed that $(La_{0.25}Gd_{0.75})_2Si_2O_7$ and $(La_{0.235}Ce_{0.015}Gd_{0.75})_2Si_2O_7$ crystalize in monoclinic cells (space group $P2_1/c$), $a = 5.3905(8)$ Å, $b = 8.5605(11)$ Å, $c = 13.957(2)$ Å, $\beta = 112.223(6)°$, and $a = 5.3921(7)$ Å, $b = 8.5688(10)$ Å, $c = 13.9172(14)$ Å, $\beta = 111.980(5)°$, respectively. One of the two different rare-earth sites is preferentially occupied by La and Gd atoms or by La, Ce and Gd atoms, and the other is occupied by Gd atoms only. Peaks attributed to the 4f-4f transitions ($^8S_{7/2}$–$^6G_{7/2}$ and $^8S_{7/2}$–^6I_x) of Gd^{3+} and 4f-5d transitions of Ce^{3+} were observed in the absorption spectra of $(La_{0.25}Gd_{0.75})_2Si_2O_7$ and $(La_{0.235}Ce_{0.015}Gd_{0.75})_2Si_2O_7$ single crystals.

1. Introduction

Rare-earth pyrosilicates ($RE_2Si_2O_7$) are of great interest for their favorable luminescence properties. In addition, magnetic properties such as spin frustration, which is drawing attention in inorganic and hybrid systems have been studied [1,2]. In particular, Ce-doped Gd-based pyrosilicate-type scintillators were found to be promising candidates for oil well logging, medical imaging and other applications in radiation monitoring. A pyrosilicate-type compound, Ce-doped $(La,Gd)_2Si_2O_7$ (Ce:La-GPS) has been recently investigated and it has shown sufficient light output and good energy resolution [3–7], and outperformed conventional silicate compounds such as Ce:Gd_2SiO_5 (Ce:GSO) [8] and other pyrosilicate-type compounds (Ce:$Lu_2Si_2O_7$ and Ce:$Gd_2Si_2O_7$). Up to now, Gd pyrosilicate crystals admixed with 9–50% of La have been grown, and it has been found that $(La_{0.235}Ce_{0.015}Gd_{0.75})_2Si_2O_7$ shows the highest light output of $42{,}000 \pm 2000$ photons/MeV [5]. A 2-inch diameter single crystal of this composition has been successfully grown without cracks [7].

The structural and luminescent properties of rare-earth pyrosilicates have become of interest because of their various polymorphs, which amount to eight types (at normal pressure) depending on the preparation conditions [9,10]. Although a large number of studies on the polymorphs of single rare-earth pyrosilicates have been conducted, further crystallographic investigation of the complex rare-earth pyrosilicates is still required. $Gd_2Si_2O_7$ usually has two types of polymorphs; orthorhombic at high temperature and triclinic at low temperature. For the mixture of $Gd_2Si_2O_7$ and $Ce_2Si_2O_7$, three types of polymorphs have been reported so far: orthorhombic, monoclinic and triclinic. Besides these polymorphs, a tetragonal structure was reported for a sparse Ce-containing system [11,12]. Since Ce and La have similar chemical properties and $Ce_2Si_2O_7$ and $La_2Si_2O_7$ have the same crystal

* Corresponding author. C&A Corporation, 6-6-40 Aramaki Aza-aoba, Aoba-ku, Sendai, Miyagi, Japan.
** Corresponding author. New Industry Creation Hatchery Center, Tohoku University, 6-6-10 Aoba, Aramaki, Aoba-ku, Sendai, Miyagi, Japan.,
E-mail addresses: r_murakami@imr.tohoku.ac.jp (R. Murakami), kurosawa@imr.tohoku.ac.jp, kurosawa@sci.kj.yamagata-u.ac.jp (S. Kurosawa).

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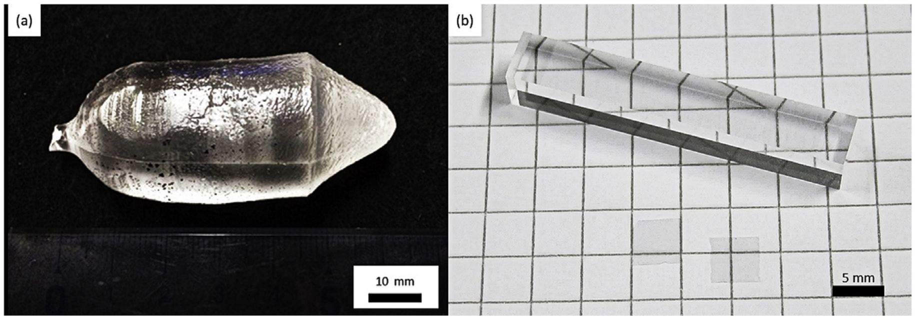

Fig. 1. A single crystal of $(La_{0.235}Ce_{0.015}Gd_{0.75})_2Si_2O_7$ (a) and a polished bar and square platelet specimens with a thickness of 0.08 mm (b).

structure, it has been expected that the crystal structure of $(La,Gd)_2Si_2O_7$ is similar to that reported in the previous study of $(Ce,Gd)_2Si_2O_7$. Specifically, the $Gd_2Si_2O_7$ admixed with 20–60% of La was expected to belong to triclinic system [7] similarly to as the $Gd_2Si_2O_7$ admixed with 20–60% of Ce, which showed triclinic structure. Concerning $La_2Si_2O_7$-$Gd_2Si_2O_7$ system, only the following crystal systems have been reported: orthorhombic, monoclinic, triclinic, and tetragonal [12,13]. The present paper reports the crystal structures of $(La_{0.25}Gd_{0.75})_2Si_2O_7$ and $(La_{0.235}Ce_{0.015}Gd_{0.75})_2Si_2O_7$ analyzed by single-crystal X-ray diffraction. Absorption spectra of these crystals which may be affected by the coordination environments around Gd^{3+} and Ce^{3+} atoms were measured.

2. Experimental

$(La_{0.25}Gd_{0.75})_2Si_2O_7$ and $(La_{0.235}Ce_{0.015}Gd_{0.75})_2Si_2O_7$ single crystals were grown by the Czochralski (Cz) method (Cyberstar, Oxypuller 05–03). Starting materials were powders of La_2O_3, CeO_2, and Gd_2O_3 (99.99% purity) and granules of SiO_2 (99.995% purity). All raw material powders were calcined at the air atmosphere before mixing (>500°C, 5 h). A mixture of the powders and granules was

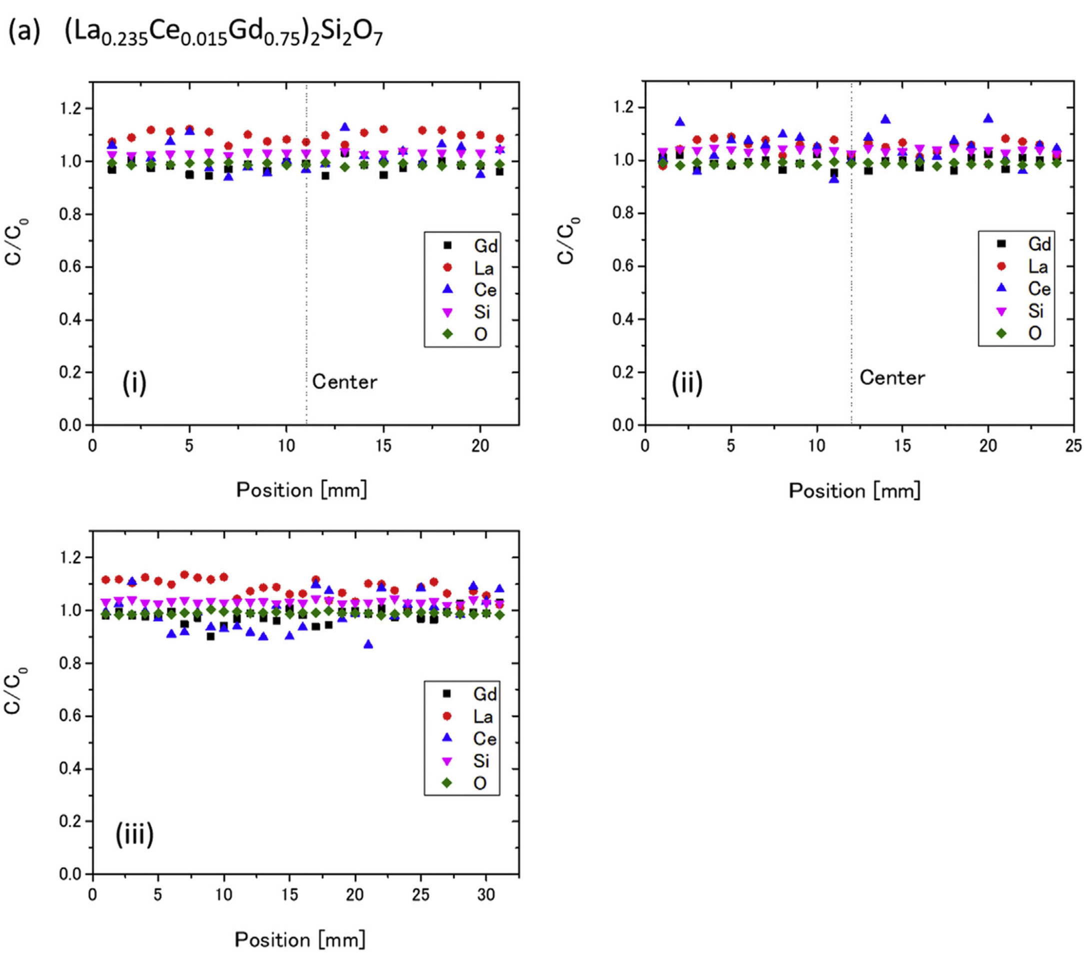

Fig. 2. The WDX results of the grown crystals with the chemical composition of (a) $(La_{0.235}Ce_{0.015}Gd_{0.75})_2Si_2O_7$ and (b) $(La_{0.25}Gd_{0.75})_2Si_2O_7$. (i) and (ii) show the distribution of the constituents in radial direction at seed side and tail side, respectively. (iii) shows the distribution of the constituents along the growth direction.