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Crystal growth and structural characterizations of Ce-doped $Gd_{9.33}(SiO_4)_6O_2$ single crystals

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ABSTRACT

A new type of scintillator crystal, Ce-doped $Gd_{9.33}(SiO_4)_6O_2$ (Ce:GSAP), was grown by the micro-pulling-down (μ-PD) method. Single-crystal structural analysis coupled with X-ray absorption near-edge structure (XANES) analysis clearly implied the preference of Ce^{3+} at the 6h site in the Ce:GSAP structure. The X-ray excited luminescence spectra showed a peak around 410 nm originating from the Ce^{3+} 5d–4f transition. The corresponding decay time estimated was about 25 ns.

1. Introduction

Single-crystal scintillators are widely applied for the X-rays or γ-rays detectors in medicine, industry and fundamental researches, and a variety of scintillators based on lanthanide-containing materials have been developed in the last decades in order to satisfy many requirements for various application fields. Among them, some of the Ce-doped crystals are well recognized as the promising scintillator materials due to their fast scintillation response dominated by the several tens of ns decay time enabled by the 5d–4f radiative transition of Ce^{3+} [1–3]. At the same time, Gd-containing materials attract a particular interest because of their high luminescent efficiency activated with suitable activators. Recently, a series of $RE_{9.33}(SiO_4)_6O_2$ (RE = La and Gd) single crystals have been successfully grown and well characterized [4,5] and these results allow us to expect that $Gd_{9.33}(SiO_4)_6O_2$ (hereafter abbreviated as GSAP) can be counted as an appreciated host for scintillator materials with Ce^{3+}.

In this study, we will report the optimization of growth conditions for undoped and Ce-doped GSAP crystals using the conventional micro-pulling-down (μ-PD) method, and discuss their structural and optical features including the valence state of Ce.

2. Experimental procedure

2.1. μ-PD method

Single crystals of undoped and Ce-doped GSAP were grown by the μ-PD method using an iridium crucible [6]. The starting materials were prepared from stoichiometric mixtures of Gd_2O_3(4N), CeO_2(3N) and SiO_2(4N) powders (High Purity Chemicals Co., Ltd.), according to the chemical formula $(Ce_x,Gd_{1-x})_{9.33}(SiO_4)_6O_2$ ($x = 0.0$, 0.001, 0.005, 0.010, 0.030, 0.050 and 0.100). After the solid state reaction at 1400 °C for 24 h, each sample was ground into fine powders and charged in an iridium crucible (16 mmϕ and 38 mm in height) with a hole of about 0.5 mmϕ at the crucible bottom. The crucible was heated inductively at a frequency of 20 kHz and the growth atmosphere was controlled using N_2 gas to avoid the oxidation of the crucible. It may be added that an iridium rod was used as a seed and pulling rate operated was 0.03 mm/min.

2.2. Structural and chemical analysis

Single-crystal X-ray diffraction data were collected by using the monochromatic MoKα radiation (Rigaku R-AXIS RAPID). The resultant data set was corrected for Lorentz, polarization and absorption effects [7]. The structure model was refined by the least-squares software SHELXL-97 [8]. Morphological quality such

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as inclusions, heterogeneity, etc. of the obtained crystals was examined by the backscattered electron microscopy (HITACHI S-530T). Chemical compositions were analyzed by electron microprobe analysis (EPMA; JEOL JXA-8900L). The distribution of Ce in the single-crystal samples was measured along the growth axis and perpendicular to the growth axis, in particular.

2.3. Ce L_{III} edge XANES spectra

X-ray absorption near-edge structure (XANES) spectra were examined in order to investigate the oxidation state of Ce incorporated in the present GSAP samples. The Ce L_{III} XANES spectra were measured in the fluorescence mode at the BL-12C at the Photon Factory, High Energy Accelerator Research Organization (KEK-PF) in Tsukuba, Japan. The reference spectra were also measured by using the appropriate mixtures of chemical reagents $CeCl_3 \cdot 7H_2O$ (3N) and $Ce(SO_4)_2 \cdot 4H_2O$ (purity $>99.5\%$) diluted with hexagonal boron nitride. The experimental details of the XANES analysis for the determination of Ce^{3+}/Ce^{4+} ratio were similar to those for our previous study [9].

2.4. Optical analysis

The grown crystals were sliced perpendicular to the growth direction with the thickness of about 1 mm. The prepared sample disks were polished by using abrasive papers and alumina abrasives for the following optical measurements. Radioluminescence (RL) spectra were measured at room temperature by a Tokyo Instruments #77441 FICS spectrometer, and X-ray from an ordinary Cu X-ray tube operated at 40 kV and 40 mA was used for an excitation source. The photoluminescence decay time was measured on the Edinburgh Instruments, FLS920 equipped by a hydrogen steady-state flash-lamp as an excitation source.

3. Results and discussions

3.1. Crystal growth

We have succeeded to grow transparent and crack-free undoped and Ce-doped GSAP single crystals by the μ-PD method as shown in Fig. 1. The subsequent observation by the backscattered electron imaging analysis readily rejects any inhomogeneous region of a secondary phase in the present samples. It may be added that the transparent yellow colors of the obtained single crystals become deeper with increasing in Ce concentrations. Although the chemical analysis of EPMA implied that the concentration of Ce was constant along the growth direction, the concentration along the radial direction was increased gradually from the center to the rim of the crystal specimens. Similar radial concentration dependence was reported in the case of Pr-doped Y_2SiO_5 single crystals [10] and these features were attributed to the thermocapillary Marangoni convection at the high-temperature meniscus liquid produced by the μ-PD method [11].

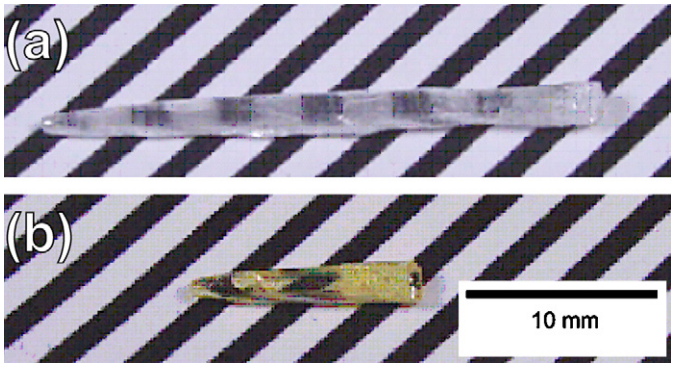

Fig. 1. Photographs of (a) GSAP and (b) 1.0% Ce:GSAP crystals grown by the μ-PD method.

3.2. Structural characterization

The experimental details of the single-crystal structural analysis for the GSAP and 10% Ce:GSAP samples are summarized in Table 1. The final atomic coordinates and equivalent isotropic temperature factors are listed in Table 2. For the structural analysis of 10% Ce:GSAP, the distribution model for Ce was introduced and the corresponding occupation parameters were refined by the ordinary least-squares procedure with a constraint of the chemical composition. The structure contains two distinct RE sites. The RE1 position at the 6h site (Wyckoff notation) is fully occupied and coordinated by seven oxygen atoms, with an average bond length shorter than that of another RE2 site. This feature

Table 2
Atomic coordinates and occupancies of undoped and 10.0% Ce-doped GSAP

Sample	GSAP	10% Ce:GSAP
RE1 (6h), (*x*,*y*,1/4)		
x	0.00830(4)	0.00845(4)
y	0.24005(4)	0.24036(4)
Occupation (Gd/Ce)	1.0/0.0	0.850/0.15
U(eq.)	0.0090(1)	0.0095(2)
RE2 (4f), (2/3,1/3,*z*)		
z	−0.0005(1)	−0.0003(1)
Occupation (Gd/Ce)	0.833/0.0	0.826/0.007
U(eq.)	0.0154(2)	0.0164(2)

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z	−0.0005(1)	−0.0003(1)
Occupation (Gd/Ce)	0.833/0.0	0.826/0.007
U(eq.)	0.0154(2)	0.0164(2)
Si (6h), (*x*,*y*,1/4)		
x	0.4004(3)	0.4003(2)
y	0.3722(3)	0.3719(2)
U(eq.)	0.0091(4)	0.0084(4)
O1 (2*a*), (0,0,1/4)		
U(eq.)	0.022(2)	0.026(3)
O2 (6h), (*x*,*y*,1/4)		
x	0.3194(9)	0.3183(9)
y	0.4869(8)	0.4850(9)
U(eq.)	0.023(1)	0.025(1)
O3 (6h), (*x*,*y*,1/4)		
x	0.5257(7)	0.5261(7)
y	0.1234(7)	0.1233(7)
U(eq.)	0.019(1)	0.019(1)
O4 (12*i*), (*x*,*y*,*z*)		
x	0.3423(7)	0.3428(7)
y	0.2505(6)	0.2510(5)
z	0.0631(7)	0.0627(7)
U(eq.)	0.026(1)	0.029(1)