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Growth of Lu₂O₃ and HfO₂ Based High Melting Temperature Single Crystals by Indirect Heating Method Using Arc Plasma

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Abstract: A novel single-crystal growth method was developed, using arc plasma and metal melt, for a quick survey of high melting point materials. Single crystals of Yb-doped Lu₂O₃, Lu_{0.388}Hf_{0.612}O_{1.806}, and Lu_{0.18}Hf_{0.82}O_{1.91}, with melting points of 2460, 2900, and 2840 °C, respectively, were grown by an indirect heating method using arc plasma. We refer to this indirect heating growth method as the core heating (CH) method. The CH-grown Yb1%-doped Lu₂O₃ sample showed a full width at half maximum of 286 arcsec in the X-ray rocking curve. This value is better than the 393 arcsec obtained for the crystal grown by the micro-pulling-down (μ -PD) method. The Yb charge transfer state (CTS) emission was observed at 350 nm in the Yb1%-doped Lu₂O₃ and Lu_{0.18}Hf_{0.82}O_{1.91}. In the case of the μ -PD method, using a rhenium (Re) crucible, absorption due to Re contamination and a resulting reduction in the Yb CTS emission were confirmed. However, contamination did not influence the properties observed in the crystals grown by the CH method.

Keywords: single-crystal growth; oxides; core heating method; high melting point materials; scintillators

1. Introduction

Inorganic scintillators play a major role in radiation detection in many fields, including medical imaging, security, astrophysics, and well logging. In these applications, a heavy scintillator composed of high effective atomic number ions is required. For example, Lu₂O₃ has a high density of 9.42 g/cm³ and contains ions of Lu with its high effective atomic number of 71. Moreover, HfO₂ has attracted attention because of its high density of 9.7 g/cm³, high effective atomic number of Hf (72), and its negligible intrinsic background. These materials and their compounds could be promising host materials for scintillator applications. However, Lu₂O₃ and HfO₂ have relatively high melting temperatures of 2460 and 2700 °C, respectively. Solid solutions of two oxides, (LuHf)O_x, also have extremely high melting points, >2900 °C at 44% of Lu (Figure 1) [1]. Conventional growth techniques using an Ir

crucible, such as the Chochralski (Cz), Bridgman–Stockbarger (BS), and micro-pulling-down (μ -PD) methods, are widely used for the production of single crystals with high melting temperature. However, high-melting-point crystals, exceeding the melting point of the crucible material, cannot be produced by such means. Consequently, a quick materials survey using single crystals is necessary in order to discover novel scintillators. The μ -PD method is a quick and economical way of surveying materials. To date, single-crystal growths by the μ -PD method of undoped, Tm-, and Yb-doped Lu_2O_3 have been reported [2–4]. The use of rhenium (Re) as a crucible material, with a melting point of 3158 °C, made it possible to grow Lu_2O_3 . However, the Re crucible becomes very worn and Re contamination becomes a problem for optical applications. Furthermore, Re crucibles are difficult to process, very expensive, cannot be recast, and are currently difficult to purchase. A crucible-free growth technique, such as the skull melting method, can be adapted to high-melting-temperature materials, but this technique is not suitable for exploring and screening various materials quickly because of its need for a large amount of raw material and very long growth time. The floating zone (FZ) method is another crucible-free technique [5], but it requires consuming, sintering, and preparing the raw materials. Difficulty in crystal growth control and heating for high-transmittance crystals against FZ beams are also disadvantages for a quick material survey.

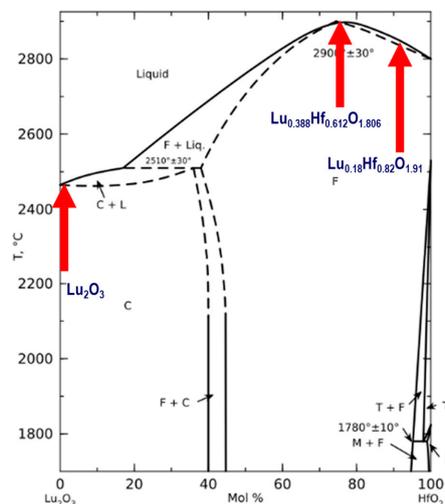


Figure 1. Phase diagram between Lu_2O_3 and HfO_2 [1]. The chemical compositions of the crystals grown in this study are indicated by red arrows.

In this study, we propose a novel single-crystal growth method using arc plasma and metal melt for a more rapid materials survey relative to the μ -PD and FZ methods. Single-crystal growth of Yb-doped Lu_2O_3 , $\text{Lu}_{0.388}\text{Hf}_{0.612}\text{O}_{1.806}$, and $\text{Lu}_{0.18}\text{Hf}_{0.82}\text{O}_{1.91}$, with melting points of 2460, 2900, and 2840 °C, respectively, was demonstrated. Single crystals were grown by an indirect heating growth method using arc plasma. We herein refer to this indirect heating growth method as the core heating (CH) method. Crystal phase and chemical composition analysis, as well as optical and luminescence properties measurements of the grown crystals were also performed.

2. Experimental

2.1. Crystal Growth

A stoichiometric mixture of 4N purity HfO_2 , Yb_2O_3 , and Lu_2O_3 powders was used as the starting material. Solid solutions between HfO_2 and Lu_2O_3 were thought of as Lu substitution in HfO_2 . So, they could be written as $\text{Hf}_{1-x}\text{Lu}_x\text{O}_{2-x/2}$; for example, the chemical composition of 24.1% Lu_2O_3 , 75.9% HfO_2 was written as $\text{Lu}_{0.388}\text{Hf}_{0.612}\text{O}_{1.806}$. Nominally, starting powders were prepared according to the formulas of $(\text{Yb}_{0.01}\text{Lu}_{0.99})_2\text{O}_3$, $\text{Yb}_{0.01}\text{Lu}_{0.378}\text{Hf}_{0.612}\text{O}_{1.806}$, and $\text{Yb}_{0.01}\text{Lu}_{0.17}\text{Hf}_{0.82}\text{O}_{1.91}$.

Crystals were grown by the CH method using an arc plasma furnace (GES-300A, GES Corp., Sendai, Japan). The furnace was equipped with a tungsten electrode with a 300 A power supply. A schematic diagram of the crystal growth set up is shown in Figure 2. Mixed powder was compressed into the bottom of a water-cooling copper hearth that was 40 mm in diameter and 15 mm deep. An iridium (Ir) pellet, about 25 mm in diameter, was placed on the compressed powder to contact with the copper hearth in order to maintain electrical conduction. The chamber was evacuated to ca. 20 Pa by a rotary pump. Argon gas was fed into the chamber to about 0.97 atm. The Ir pellet was heated by an arc plasma from the tungsten electrode to obtain Ir metal melt. The temperature of the Ir pellet was controlled by the power supply, and the compressed starting powder was heated by the Ir metal melt. The arc plasma power was increased until the starting powder around the Ir metal melt was completely melted. After confirming expansion of the melt area, the power was decreased to zero over a 20 minute period. After the temperature of the Ir pellet had decreased to room temperature, the chamber was opened and the grown crystal was extracted. The Ir pellet could be reused after acid cleaning.

2.2. Characterizations

Plates of about 2–5 mm square \times 1 mm thick were cut and polished for optical and luminescence spectra measurements. Pieces of the grown crystals were crushed and ground into powders using a pestle and mortar. Powder X-ray diffraction (XRD) analysis for phase identification was carried out in the 2θ range of 10–80° using an X-ray diffractometer (D8 Discover, Bruker, Berlin, Germany). A Cu $K\alpha$ X-ray source was used, and the accelerating voltage and beam current were 40 kV and 40 mA, respectively. To evaluate the crystallinity of the obtained crystals, an X-ray rocking curve (XRC) measurement was performed using the Rigaku-ATX (Rigaku, Akishima, Japan) at the $\langle 222 \rangle$ peak. The slit size was 0.5 mm \times 0.5 mm. The Cu $K\alpha$ X-ray at 40 kV and 30 mA irradiated a cross section of the sample. Quantitative chemical analysis of Hf, Yb, and Lu in the crystals was performed by electron probe microanalysis (EPMA) using the JXA-8621MX system (JEOL, Tokyo, Japan). Chemical composition analysis of Cu, Re, Ir, and W ions as possible contaminants was carried out by inductively coupled plasma–mass spectrometry (ICP-MS) using the Agilent 8800 (Agilent Technologies, Santa Clara, CA, USA). Transmittance spectra were measured by a 3101PC spectrometer (Shimadzu, Kyoto, Japan) in the 190–700 nm range. Radioluminescence spectra at room temperature were measured by the Spectrofluorometer 199S (Edinburgh Instrument LTd., Livingston, UK) using an X-ray tube (operated at 35 kV and 16 mA, with a Mo cathode) for the excitation.

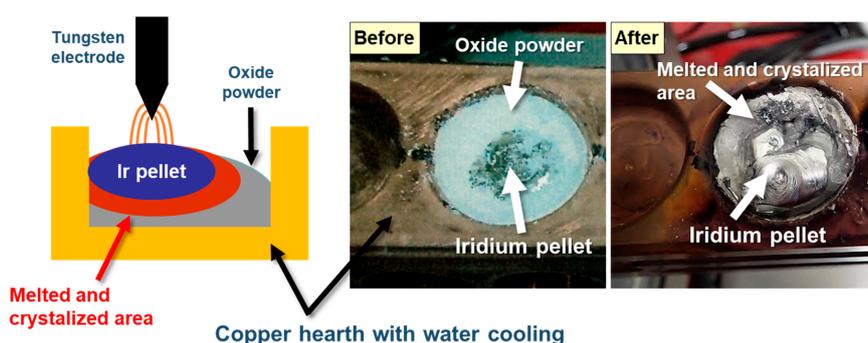


Figure 2. Schematic drawing of the core heating (CH) method at left, and photographs taken before and after crystal growth.

3. Results and Discussion

3.1. Crystal Growth

The arc-melting technique is generally applied for conductive metals. Conductive metals are directly heated and melted by the arc plasma. However, since oxide materials are not conductive at room temperature, they cannot be directly heated by the arc plasma. Therefore, our procedure

was designed so that the starting oxide materials were indirectly heated by a high-temperature metal melt, and in this study Ir was selected to be heated by the arc plasma to form a metal melt. In this way, we succeeded in melting oxide materials with high melting points. Undoped and Yb1%-doped Lu_2O_3 , $\text{Lu}_{0.388}\text{Hf}_{0.612}\text{O}_{1.806}$, and $\text{Lu}_{0.18}\text{Hf}_{0.82}\text{O}_{1.91}$ crystals were grown by the CH method. The total processing time, including material preparation, evacuation, heating, and cooling, was about 1 h for each crystal. Crystallized parts about 2 mm thick were obtained around the Ir pellet. The grown Yb1%: Lu_2O_3 samples removed from the Ir pellet are shown in Figure 3a. Plates of Yb1%-doped Lu_2O_3 , $\text{Lu}_{0.388}\text{Hf}_{0.612}\text{O}_{1.806}$, and $\text{Lu}_{0.18}\text{Hf}_{0.82}\text{O}_{1.91}$, about 2–5 mm square \times 1 mm thick, after cutting and polishing, are shown in Figure 3b, 3c, 3d, respectively. All plates were colorless and transparent despite some cracks in the plates.

Powder XRD patterns of the grown Yb-doped crystals are shown in Figure 4. The Yb1%: Lu_2O_3 sample is related to the Sm_2O_3 -type (Ia3) cubic phase. All the observed peaks can be identified by powder diffraction file (PDF) 43-1021 of Lu_2O_3 . Yb1%-doped $\text{Lu}_{0.388}\text{Hf}_{0.612}\text{O}_{1.806}$ and $\text{Lu}_{0.18}\text{Hf}_{0.82}\text{O}_{1.91}$ correspond to the CaF_2 -type (Fm3m) cubic phase without the presence of any secondary phases. All the observed peaks can be identified by PDF 70-2831 of HfO_2 . Lattice constants of 10.3971, 5.1370, and 5.1163 Å were obtained for the Yb1%-doped Lu_2O_3 , $\text{Lu}_{0.388}\text{Hf}_{0.612}\text{O}_{1.806}$, and $\text{Lu}_{0.18}\text{Hf}_{0.82}\text{O}_{1.91}$ samples, respectively. The lattice constants of the Yb1%: $\text{Lu}_{0.388}\text{Hf}_{0.612}\text{O}_{1.806}$ and $\text{Lu}_{0.18}\text{Hf}_{0.82}\text{O}_{1.91}$ increased with an increase in the Lu concentration, and were compared to the previously reported 5.08 Å of HfO_2 itself [6]. The ionic radii of Lu^{3+} (VI) = 0.861 Å and Yb^{3+} (VI) = 0.868 Å are larger than that of Hf^{4+} (VI) = 0.71 Å [7], and substitution by a larger ion can expand the crystal lattice. Hf, Yb, and Lu distributions in the Yb1%: $\text{Lu}_{0.388}\text{Hf}_{0.612}\text{O}_{1.806}$ along the growth direction, measured by EPMA, are shown in Figure 5. The effective segregation coefficients of the Hf, Yb, and Lu ions in the solid area were 0.96, 0.88, and 1.06, respectively. XRC measurement was performed for the Yb1%: Lu_2O_3 sample. The CH-grown sample showed a full width at half maximum (FWHM) of 286 arcsec in the XRC as shown in Figure 6. This value is better comparing with the 393 arcsec obtained for Yb1%: Lu_2O_3 grown by the μ -PD method [4].

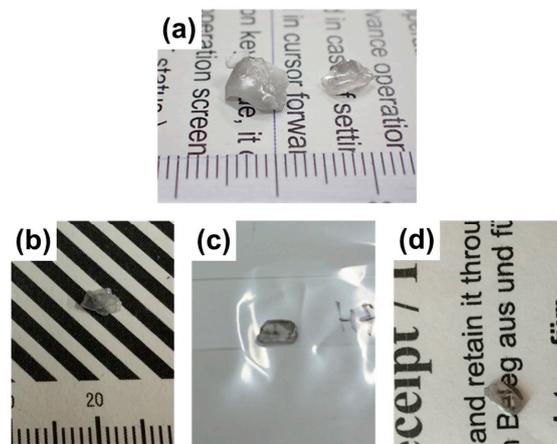


Figure 3. Photographs of (a) as-grown Yb1%: Lu_2O_3 , (b) Yb1%: Lu_2O_3 , (c) Yb1%: $\text{Lu}_{0.388}\text{Hf}_{0.612}\text{O}_{1.806}$, and (d) Yb1%: $\text{Lu}_{0.18}\text{Hf}_{0.82}\text{O}_{1.91}$ after cutting and polishing.

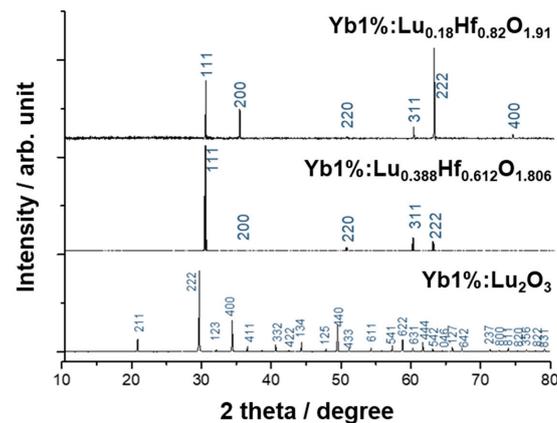


Figure 4. Results of powder X-ray diffraction (XRD) of the grown Yb1%:Lu₂O₃, Yb1%:Lu_{0.388}Hf_{0.612}O_{1.806}, and Yb1%:Lu_{0.18}Hf_{0.82}O_{1.91}.

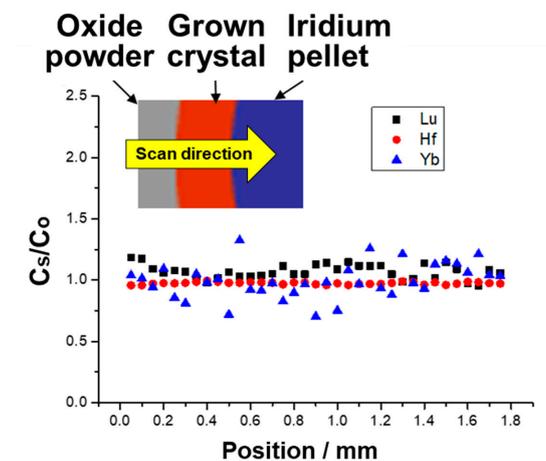


Figure 5. Hf, Yb, and Lu distributions in the grown Yb1%:Lu_{0.388}Hf_{0.612}O_{1.806}.

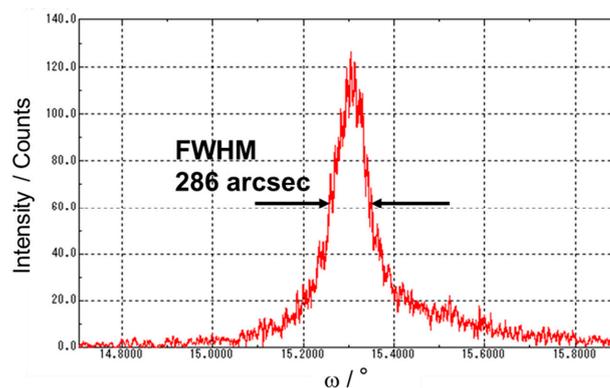


Figure 6. X-ray rocking curve (XRC) of the CH-grown Yb1%:Lu₂O₃ sample. ($2\theta = 29.66^\circ$ $\langle 2\ 2\ 2 \rangle$, slit size: 0.5 mm \times 0.5 mm). Cu K α (40 kV, 30 mA).

3.2. Optical and Luminescence Measurements

Figure 7 shows in-line transmittance measurements of the CH-grown undoped Lu₂O₃, Yb1%-doped Lu₂O₃, and Lu_{0.18}Hf_{0.82}O_{1.91} compared with measurement for a Yb1%:Lu₂O₃ sample grown by the μ -PD method with a Re crucible. The CH-grown Yb1%-doped Lu₂O₃ and Lu_{0.18}Hf_{0.82}O_{1.91} showed absorption at around 270 nm because of the Yb charge transfer state (CTS). The μ -PD-grown

Yb1%:Lu₂O₃ showed broad absorption around the 250–500 nm range. This absorption can be ascribed to the effect of Re contamination [2–4]. Radioluminescence spectra of the grown Yb1%-doped Lu₂O₃, Lu_{0.388}Hf_{0.612}O_{1.806}, and Lu_{0.18}Hf_{0.82}O_{1.91} compared with the μ -PD-grown Yb1%:Lu₂O₃ measured under X-ray irradiation are shown in Figure 8. The expected Yb CTS emission was observed at 350 nm in the Yb1%-doped Lu₂O₃ and Lu_{0.18}Hf_{0.82}O_{1.91}. If a large amount of trivalent Lu is substituted for a tetravalent Hf, then the band structure may change and generation of the Yb CTS is inhibited. The μ -PD grown Yb1%:Lu₂O₃ did not show any Yb CTS emission because of the above mentioned Re-related absorption. Table 1 shows the ICP-MS results of the CH- and μ -PD-grown Yb1%-doped Lu₂O₃ for Cu, Re, Ir, and W impurity ions. We observed 61.4 wt. ppm of Re contamination in the μ -PD-grown sample. This is good evidence for the existence of Re-related absorption. We observed 14.1 and 8.70 wt. ppm of Cu and Ir contaminations, respectively, in the CH-grown sample. These contaminations could have come from the copper hearth and Ir pellet. No significant influence of Cu or Ir contaminations was observed in the optical and luminescence properties. We observed 475 and 590 wt. ppm of W contaminations in the CH and μ -PD samples, respectively. This contamination may be derived from impurities in the Lu₂O₃ raw powders.

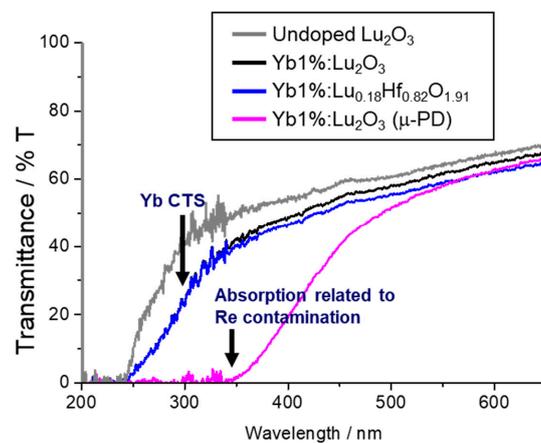


Figure 7. In-line transmittance of the CH-grown undoped Lu₂O₃, Yb1%:Lu₂O₃, and Yb1%:Lu_{0.18}Hf_{0.82}O_{1.91}, in comparison with μ -PD-grown Yb1%:Lu₂O₃.

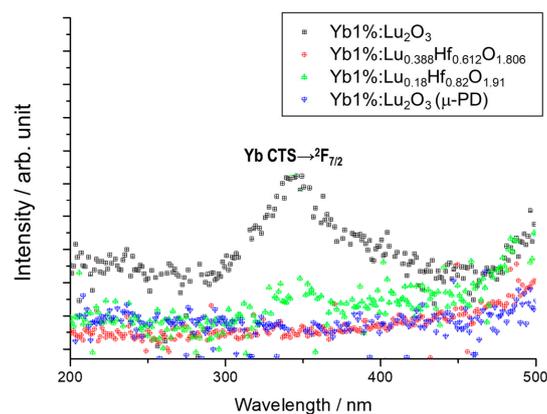


Figure 8. Radioluminescence spectra excited by X-rays (Cu K α 30 mV, 110 μ A). CTS: charge transfer state.

Table 1. ICP-MS results of the CH- and μ -PD-grown Yb1%-doped Lu_2O_3 on Cu, Re, Ir, and W ions.

Growth Method	Ions	Cu (wt. ppm)	Re (wt. ppm)	Ir (wt. ppm)	W (wt. ppm)
CH		14.1	N.D.	8.70	475
μ -PD		0.40	61.4	N.D.	590

N.D.: not detected.

The results of this study indicate that the CH method can be used to grow single crystals with a melting point of 2900 °C without using a precious crucible. Furthermore, contaminations from the Ir pellet or environment were not sufficiently high to affect the optical or luminescent characteristics. The CH method had a total crystal growth time of less than 1 h, which was shorter than that for the μ -PD method. Crystals with a better XRC value could also be obtained. The material of a pellet that can be used in the CH method is not limited to Ir. It is expected that cheaper metals such as molybdenum, tungsten, or platinum could be used if they do not react with the crystalline material and are stable during heating. This study provides evidence for the usefulness of a novel CH method for carrying out material surveys.

4. Conclusions

A novel single-crystal growth technique, referred to as the CH method, was proposed in this paper, using an arc plasma and Ir metal melt for a quick survey of materials. Undoped and Yb1%-doped Lu_2O_3 , $\text{Lu}_{0.388}\text{Hf}_{0.612}\text{O}_{1.806}$, and $\text{Lu}_{0.18}\text{Hf}_{0.82}\text{O}_{1.91}$ crystals were grown by this method. The CH-grown Yb1%-doped Lu_2O_3 sample showed an FWHM of 286 arcsec in the XRC. This value was better than that of the μ -PD grown crystal. The Yb CTS emission was observed at 350 nm in the Yb1%-doped Lu_2O_3 and $\text{Lu}_{0.18}\text{Hf}_{0.82}\text{O}_{1.91}$. In the case of the μ -PD method, using a Re crucible, absorption due to Re contamination and reduction in the Yb CTS emission were both confirmed. However, contamination from experimental materials such as Cu and Ir was so small that no influence on the optical and light emission characteristics was observed in the crystals grown by the CH method. These results provide evidence that the developed CH method is useful for quick material surveys.

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Conflicts of Interest: The authors declare no conflicts of interest.

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