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Fabrication of amorphous bulk and multi-phase ceramics by melting method in the HfO_2-Al_2O_3-Gd_2O_3-Eu_2O_3 system

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Abstract Ceramics have generally been fabricated from powders by shape forming & sintering methods except for glasses and glass ceramics. Glasses and glass ceramics can be fabricated by melting methods. The melting method has not only higher productivity but also higher shape forming ability than powder processes via forming & sintering methods. Thus we have reinvestigated melting methods in binary and ternary oxides systems to fabricate amorphous bulk ceramics and bulk nano composites. We have successfully fabricated amorphous phases by simple melt solidification methods in ternary eutectic melts in the HfO_2-Al_2O_3-Gd_2O_3 system. The present study demonstrates the formation of the amorphous phases in quaternary systems HfO_2-Al_2O_3-Gd_2O_3-Eu_2O_3. Furthermore, we have also succeeded to fabricate nano-structured bulk ceramics, which consisted of constituent oxide grains with 20–100 nm in size, by post annealing of the amorphous phase.

Keywords Amorphous · Melting · $GdAlO_3$ · HfO_2 · Al_2O_3

1 Introduction

Recently ceramics attract attention as wear-resistant, heat-resistant, chemically stable and various functional characteristic materials. However, ceramic materials have a difficult problem how they can be made and fixed their shapes because of their brittle nature, which is apparently contrasting with plastics, polymers even metals.

Generally melting process is not common for ceramics except for so-called "Glass-Ceramics". In the cases of "Glasses" and "Glass-Ceramics" network former oxides like SiO_2, B_2O_3, GeO_2, P_2O_5, etc. have been included as a major component. Most of other ceramics have been fabricated from powders by shape forming & sintering but not by melting. Since the melting method have higher productivity and shaping ability [1–6], we have reinvestigated the melting method particularly for binary and ternary ceramic systems of multi oxides [1–4]. We have succeeded in obtaining an amorphous phase in the HfO_2-Al_2O_3-Gd_2O_3 system, not by rapid quenching [5, 6] but by simple melt solidification [2–4]. In their developments we have found out that the amorphous phase is easier to obtain from quaternary melts than from ternary melts.

This report deals with amorphous phase formation in the quaternary HfO_2-Al_2O_3-Gd_2O_3-Eu_2O_3 system by simple melt solidification. Multi-phase ceramics nano composites were successfully fabricated by post annealing those amorphous samples.

2 Experimental

High purity HfO_2 (99.9%, Daiichi Kigenso Kagaku Kougyou Co., Ltd.), Al_2O_3 (99.99%, AKP-30, Sumitomo Chemical Co., Ltd.), Gd_2O_3 (99.99%, Shin-Etsu Chemical Co., Ltd.), and Eu_2O_3 (99.99%, Shin-Etsu Chemical Co., Ltd.) powders were weighed in molar ratios of $HfO_2/Al_2O_3/Gd_2O_3/Eu_2O_3 = 14/63/18/5$. A homogeneous mixed powder of them was obtained by dry and wet mixing in ethanol using an alumina mortar and pestle. After drying the mixed powder was placed

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on a copper plate cooled by water, and melted using an arc-image furnace by the radiation of 10-kW Xe-lamp (Ushio UF-10001). Melted samples were solidified on the water-cooled copper plate by sudden shut down of the Xe-lamp radiation. The cooling rate of the sample was estimated to be approximately 200–500 K/s. Detailed procedures have been reported elsewhere [1, 2].

Subsequently the solidified samples were annealed at 1273 K and 1473 K for 6 h in air.

Both annealing temperatures were above crystallization temperatures of the sample, which were measured by using TG-DTA (2000/Control model TAPS-1000, MAC Science, Tokyo Japan). TG-DTA measurement under temperature range from room temperature to 1473 K at 10 K/min was conducted after grinding the solidified sample using an alumina mortar. To trace the thermal expansion of the sample by using TD (TD5000SA, Brucker axs, Yokohama, Japan), the solidified sample was cut into a columnar shape. All samples prepared by grinding using alumina mortar were characterized by Powder X-ray diffraction patterns using CuKα (MXP3VA, MAC Science, Tokyo, Japan). The microstructure of annealed sample at 1273 K-6 h was studied by HRTEM (H-9000, HITACHI Co., Ltd. Tokyo, Japan) by diamond polishing and ion milling before observation.

3 Results and discussion

3.1 Amorphous bulk ceramics

Samples melt-solidified by the arc-image furnace became a sphere by the surface tension of melts as seen in Fig. 1(a). Since the sample melting was carried out on a water-cooled copper plate, the bottom part of samples was non-melted or crystallized. However, completely transparent samples were obtained by cutting the center part of samples into a disk, Fig. 1(b). The X-ray diffraction pattern of these transparent samples indicates to be amorphous as shown in Fig. 1(c). A halo peak around $2\theta \approx 30°$($d \approx 0.29$ nm) which is common in many oxide-based amorphous phases indicates a large population of Metal-Oxygen-Metal bondings.

It is interesting to note that amorphous bulk materials could be fabricated for those multi-components systems containing only refractory oxides like Al_2O_3, HfO_2 and rare earth oxides. In our previous study, the size of fabricated amorphous bulk ceramics in the ternary HfO_2-Al_2O_3-Gd_2O_3 system by the arc-image furnace was limited to about 5 mm in diameter, whereas this HfO_2-Al_2O_3-Gd_2O_3-Eu_2O_3 quaternary system enables it to increase to about 7 mm. It may be realized due to the easy formation of the amorphous phase by adding Eu_2O_3 to the ternary system.

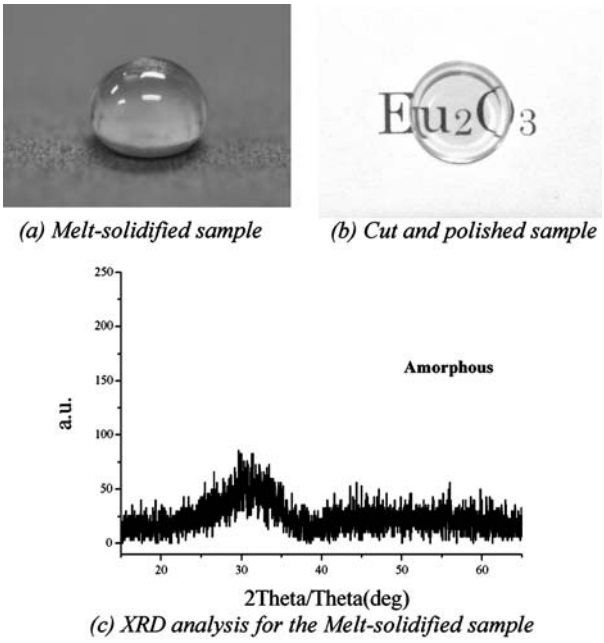


Fig. 1 Transparent HfO_2-Al_2O_3-Gd_2O_3-Eu_2O_3 sample as prepared by the solidification of the eutectic melt

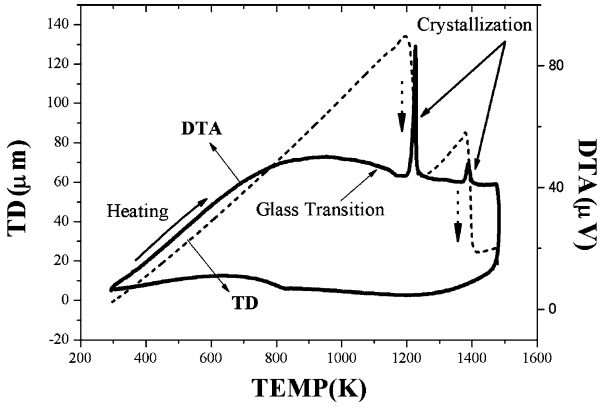


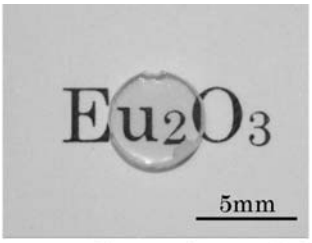
Fig. 2 DTA and TD curves of HfO_2-Al_2O_3-Gd_2O_3-Eu_2O_3 sample

3.2 Multi-phase ceramics

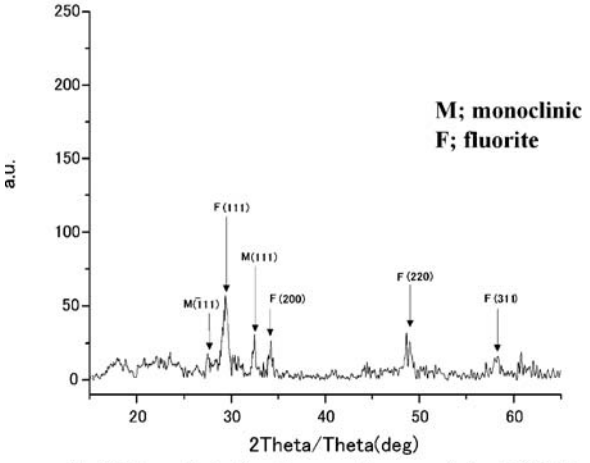
To investigate the crystallization from the amorphous matrix of those samples, the crystallization path was examined by DTA and TD (Fig. 2). After the glass transition around 1200 K, two exothermic signals at around 1226 K and 1388 K were observed. They are well correspond to two sharp shrinkages in TD, which are indicating that the crystallization occurs by two steps in those amorphous samples.

To confirm these crystallization paths in detail, melt-solidified samples were annealed at 1273 K or 1473 K for 6 h both above the crystallization temperatures.

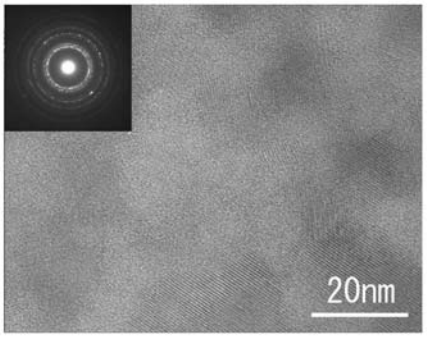
Figure 3 shows the result after annealing at 1273 K for 6hours. According to the result of X-ray diffraction, the first crystallization was identified to be the crystallization of hafnia phases. Figure 3(b) shows only hafnia phases, which



(a) Appearance of the sample annealed at 1273K

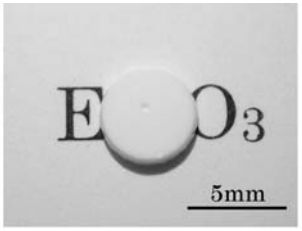


(b) XRD analysis for the sample annealed at 1273K

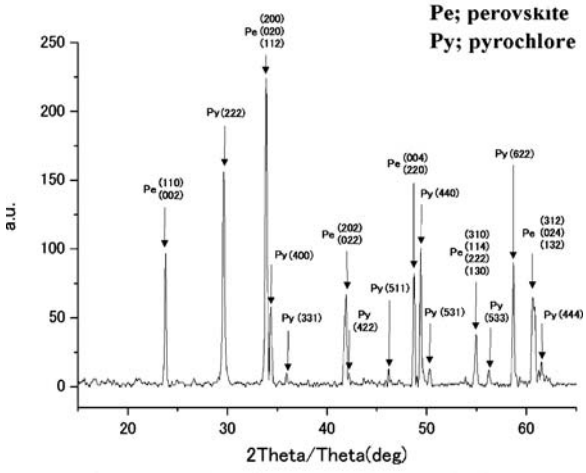


(c) High-resolution TEM image of the sample

Fig. 3 HfO_2-Al_2O_3-Gd_2O_3-Eu_2O_3 samples annealed at 1273 K for 6 h



(a) Appearance of the sample annealed at 1473K



(b) XRD analysis for the sample annealed at 1473K

Fig. 4 HfO_2-Al_2O_3-Gd_2O_3-Eu_2O_3 samples annealed at 1473 K for 6 h

can be identified as monoclinic and fluorite-related pseudo-cubic hafnia phases. Although the sample was crystallized, its transparency was still quite high as shown in Fig. 3(a). Probably the microstructure consisting of the small crystallite grains of 5–10 nm in size and the fully dense with no pores (Fig. 3(c)) do not contribute in the light scattering. It is also interesting that transparent bulk nano-composite(s) can be prepared by the present procedures.

The second step of the crystallization might be caused by the crystallization of a perovskite phase, because the perovskite peaks were appeared in the sample annealed at 1473 K as seen in Fig. 4(b). The perovskite phase might be Eu substituted $GdAlO_3$: $(Gd_{0.78}Eu_{0.22})AlO_3$ assuming complete solid solubility between Eu and Gd which are just neighbor in the Periodic Table. The composition can be calculated to be 22 mol%Eu because we have added 5 mol%Eu_2O_3 to 18 mol%Gd_2O_3, $5/(18 + 5) = 0.22$. The XRD patterns in Fig. 4(b) are also showing the existence of a pyrochlore phase. It can be described as $(Gd_{0.78}Eu_{0.22})_2Hf_2O_7$ as assumed as the complete solid solubility of Eu and Gd. The formation of the pyrochlore phase from rare earth containing hafnia phases can be considered due to the structural similarity between them, which can be regarded as fluorite-related structures. The details must be studied more carefully.

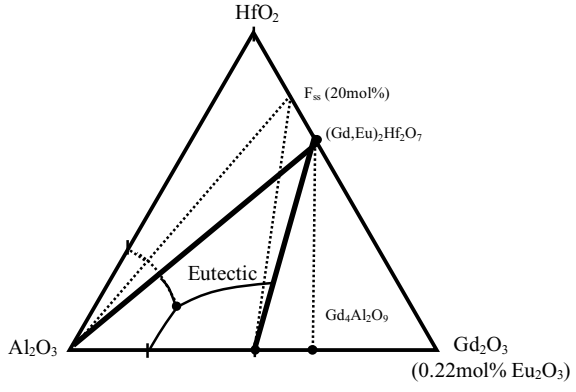


Fig. 5 Pseudo-ternary phase diagram [2]

The sample annealed at 1473 K became opaque as shown in Fig. 4(a) due to the light scattering probably caused by the grain growth of the crystallites.

If Eu can dissolve with Gd completely, the present result can be summarized using a pseudo-ternary phase diagram, Fig. 5, which is similar to the ternary system HfO_2-Al_2O_3-Gd_2O_3 [2]. The eutectic melt could give amorphous products upon melt-solidification. Those amorphous products start to precipitate first rare earth dissolved hafnia phases upon annealing. In the second step crystallization, a perovskite phase, (Eu doped Gd)AlO_3 has crystallized. A pyrochlore phase, (Eu doped Gd)$_2Hf_2O_7$ could form upon annealing at 1473 K. Apparently more detailed works are required to establish the phase diagrams.

4 Conclusions

We have succeeded to obtain amorphous phases by simple melt solidification even without containing network former oxides.

Amorphous bulk ceramics seem to be easier to prepare in HfO_2-Al_2O_3-Gd_2O_3-Eu_2O_3 quaternary system than in HfO_2-Al_2O_3-Gd_2O_3 ternary system. Those amorphous ceramics can be changed into nano-composites upon appropriate annealing.

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