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Journal of the European Ceramic Society 26 (2006) 3295–3299
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Fabrication of transparent ceramics through melt solidification of near eutectic compositions in HfO_2–Al_2O_3–$GdAlO_3$ system

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Received 27 June 2003; accepted 5 January 2004
Available online 5 October 2005

Abstract

Solidification of eutectic melts in multiple oxide systems can produce directionally solidified eutectic composites by slow cooling, while rapid cooling would give the formation of amorphous phases as super cooled liquids. We have successfully fabricated an amorphous bulk ceramics in the ternary system HfO_2–Al_2O_3–$GdAlO_3$ for the first time. It has the near eutectic composition of HfO_2 (14 mol%), Al_2O_3 (63 mol%) and Gd_2O_3 (23 mol%) and highly transparent, >85%, in the visible region after the cooling of around 200–500 K/s for 2–5 mm Ø globules. The sample had kept amorphous up to 1073 K but crystallized above 1273 K then lost the transparency. The formation of an amorphous phase could be discussed by the equilibrated temperature (T_0) lines in meta-stable phase diagram. The present study suggests possible formation of transparent bulk ceramics by the melt-solidification of eutectic melts in various ternary or multiple phase systems.

Keywords: Al_2O_3; Glass; Nanocomposites; Perovskites; Optical properties; Transparent ceramics; HfO_2; Al_2O_3; $GdAlO_3$

1. Introduction

Solidification of the eutectic melt can produce directionally solidified eutectic composites when the eutectic melt is solidified slowly. In 1997, Waku et al.[1] reported very innovative results where the Al_2O_3–gadolinium aluminum perovskite (GAP) eutectic grown composites have excellent structural and mechanical stability at very high temperatures. Since then a number of studies[2–6] have been published in those areas.

On the other hand, meta-stable liquid phase may be quenched when eutectic or near eutectic melts are rapidly cooled down below the glass transition temperature (T_g) for those super-cooled liquids.[7–10] This is, in fact, "melt-derived glass formation method" which has been applied for most of conventional glass containing SiO_2, B_2O_3, P_2O_5, GeO_2, etc. which are called Network Former oxides.[11,12] Many glass–ceramics have been fabricated in the multi-component oxide systems containing the network formers, where melts are cast in molds to give required shape and size and then annealed in appropriate manners to give crystallize phases as ceramics. This melt-casting process is rather common to fabricate shaped and sized materials for polymer/plastics and metals/alloys. However, most of ceramics have not been fabricated by melt-casting but by sintering of fine powders except for glasses containing network former oxides.

We are challenging to develop novel processing to fabricate shaped and sized ceramics without sintering of shaped powders.[13,14] In those regards, we have studied melt quenching of eutectic and/or near eutectic melts in binary and ternary systems non-containing network former oxides, that is, ZrO_2 (or HfO_2)–Al_2O_3–MO_X (M = rare earths etc.).[15–17] In their developments, we have found that transparent amorphous phases can be obtained by just simple solidification of near eutectic melts. Here, we report for the first time the fabrication of amorphous transparent materials in the ternary HfO_2–Al_2O_3–$GdAlO_3$ system. Those transparent materials should have wide applications for structural, and/or functional ceramics consisted of amorphous phase and/or nano-structured multi-phases by appropriate annealings.

2. Experimental

Starting materials were high purity HfO_2 (99.9%, Daiichi Kigenso Kagaku Kogyo Co., Ltd.), Al_2O_3 (99.99%, AKP-30,

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0955-2219/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2005.09.002

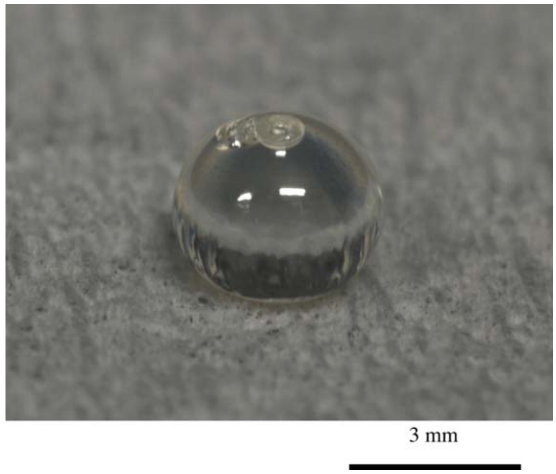

Fig. 1. Appearance of transparent HfO_2–Al_2O_3–$GdAlO_3$ sample by melt solidification.

Sumitomo Chemical Co., Ltd.) and Gd_2O_3 (99.99%, Shin-Etsu Chemical Co., Ltd.) powders. They were mixed to HfO_2 14 mol%–Al_2O_3 63 mol%–Gd_2O_3 23 mol% by dry and wet mixing in ethanol using an alumina mortar.

The mixed powders were placed on a copper plate cooled by water and melted in vacuum using an arc-image furnace by the radiation of a 10-kW Xe-lamp (Ushio UF-10001). Spherical melted specimens were quenched by sudden shut down of the Xe-lamp light. The cooling rate was estimated to be approximately 200–500 K/s.

After above processes, a transparent spherical sample was obtained (Fig. 1). The transparent samples were annealed at 1073, 1273, 1473 and 1673 K for 6 h in air.

All the samples were characterized by X-ray diffraction. Powder X-ray diffraction patterns were obtained after grinding using alumina mortar, using Cu Kα radiation in a curved graphite-beam monochromotor (MXP3VA, MAC Science, Tokyo, Japan). Fine structure of melted samples was studied by TEM (JEOL JEM-2000EX) by diamond polishing and ion milling before observation. Transmittance was measured by a spectrometry (JASCO U-570) for the wavelength 200–780 nm.

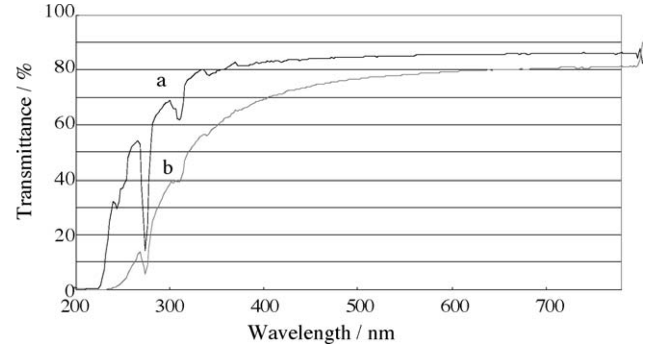

Fig. 3. Optical transmission spectra of HfO_2–Al_2O_3–$GdAlO_3$ ternary omposites. (a) As prepared, (b) after annealing (1273 K, 6 h). (diameter, 5 mm; thickness, 1 mm).

3. Results and discussion

In our previous reports,[15–17] fine structured composites have been fabricated by melt-solidification of eutectic melts in the ternary system of ZrO_2–Al_2O_3–Yttrium aluminum garnet (YAG), but transparent amorphous samples have never been obtained. However, the samples in the system of HfO_2–Al_2O_3–$GdAlO_3$ with near eutectic composition: HfO_2 14 mol%, Al_2O_3 63 mol% and Gd_2O_3 23 mol%, could give highly transparent ones without cracking when they were just cooled on a water-cooled Cu plate after melting as seen in Fig. 2. The sample size are changeable from ∼1 to ∼5 mm Ø, thus the cooling rates could be estimated 500–200 K/s because the molten sphere cooled down to dark color within 2–5 s after melting. It is noteworthy that it is not the rapid quenching with the

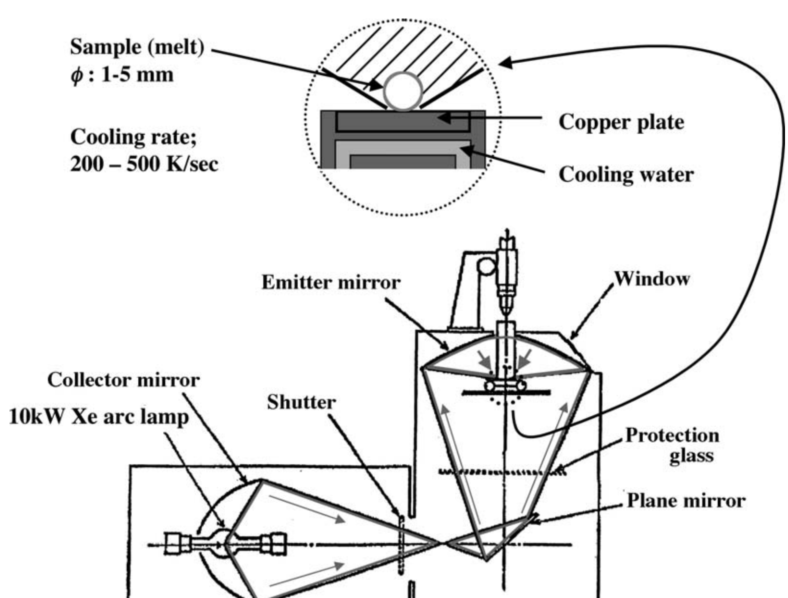

Fig. 2. Schematic illustration of the optical system of the arc-imaging furnace.

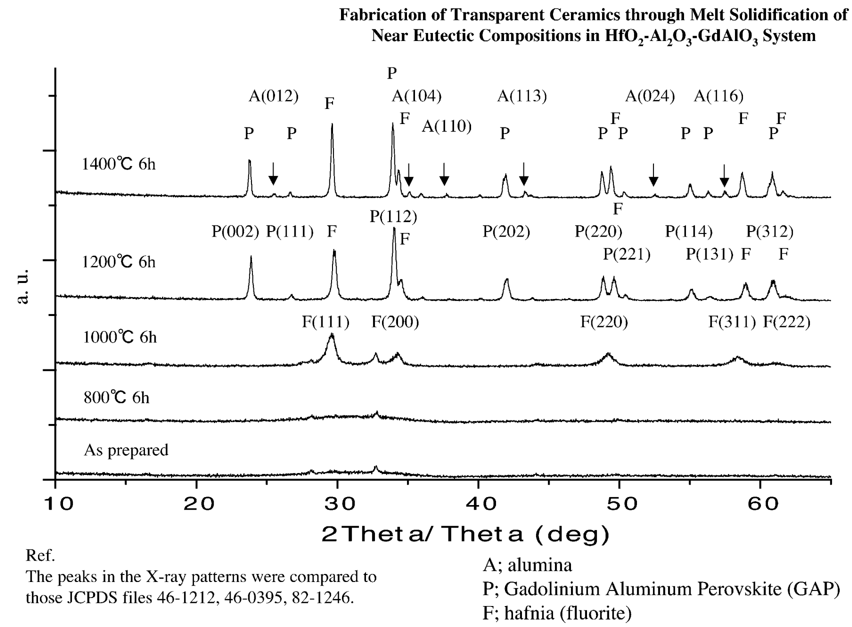

Fig. 4. XRD analysis for the HfO_2–Al_2O_3–$GdAlO_3$ composites with various annealing. Hafnia (F), perovskite (P) and corundum (A) phases crystallized above 1273 K.

cooling rates of 10^4–10^6 K/s, where molten samples must be in thin plates or films.[7–10] Thus, we can get bulk samples with at least mm size for those samples. The as-prepared sample showed a high transparency, >85% to fused silica for the visible region of light (Fig. 3). Some absorptions ∼274 and ∼308 nm in ultra violet region might be characteristic ones in the sample.

X-ray diffraction analysis indicated the as-prepared sample to be amorphous as seen in Fig. 4. Annealing at 1073 K for 6 h in air gave no change, but 1273 K annealing resulted in the crystallization of a fluorite phase, 1473 K a fluorite and a perovskite, and 1673 K a fluorite, a perovskite and corundum phases (Fig. 4). Therefore, crystallization of HfO_2, $GdAlO_3$ and Al_2O_3 can be controllable from amorphous to fully crystallized phases by appropriate annealing.

TEM observation clearly showed that the as-prepared transparent sample was amorphous, that was confirmed by its electron diffraction as shown in Fig. 5a. The sample had the precipitates of ∼10 nm crystallization in the matrix after the annealing at

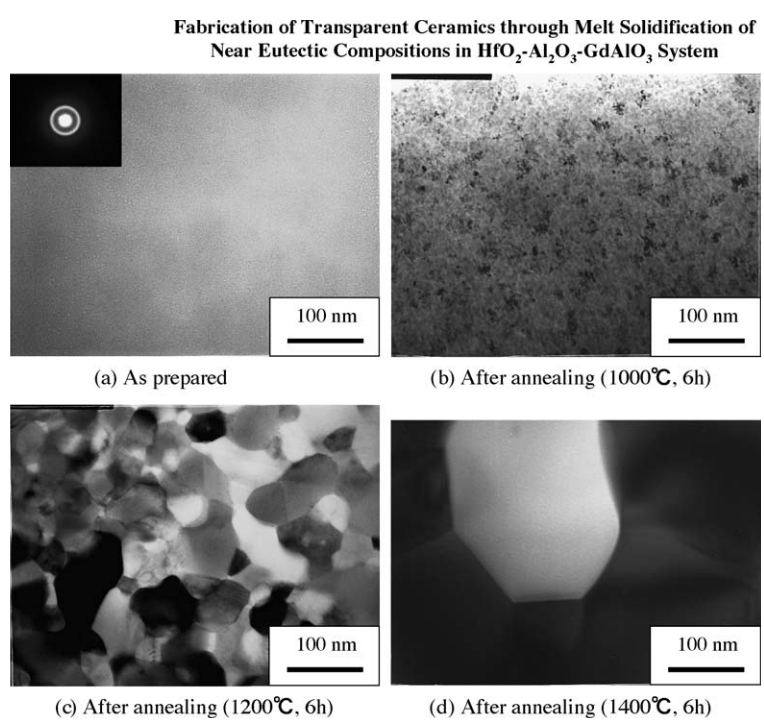

Fig. 5. TEM image of HfO_2–Al_2O_3–$GdAlO_3$ ternary composites (horizontally, ion milling with various annealing).

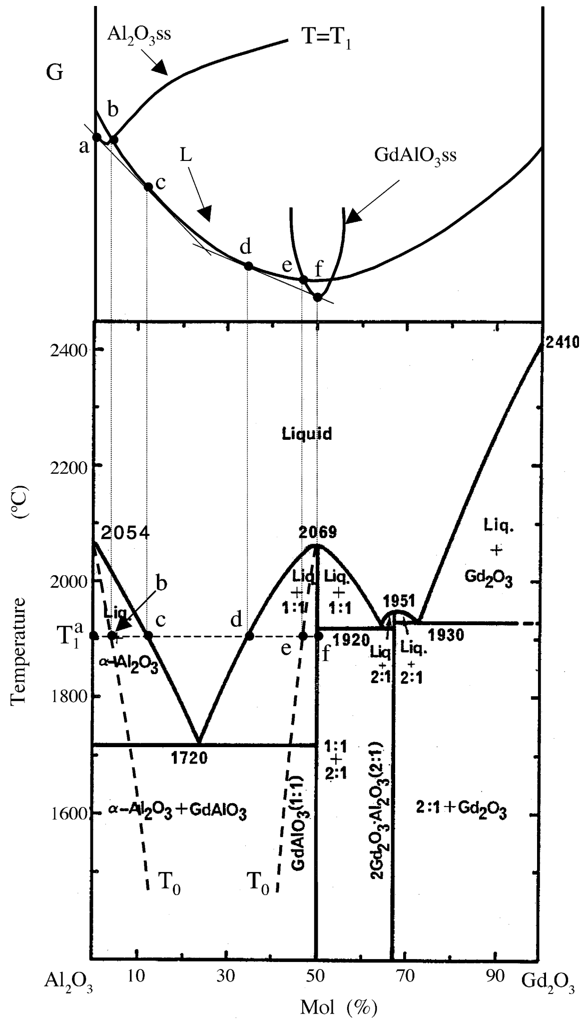

Fig. 6. Energy and phase diagrams of the system Al_2O_3–Gd_2O_3. They suggest possible formation of amorphous phases by quenching of eutectic liquids.

1273 K for 6 h (Fig. 5b), but it changed to a fully crystallized nano-composite of HfO_2–$GdAlO_3$–Al_2O_3 by the annealing of 1473 or 1673 K (Fig. 5c and d). The crystallite size increased from 50 to 100 nm at 1473 K to larger than 100 nm at 1673 K. Those samples lost their transparency after annealing above 1473 K. In addition, excess annealing might give a tendency of sample cracking. Therefore the annealing conditions must be carefully controlled to keep the transparent samples. Nevertheless such a difficulty, it should be noted that the present study demonstrates the possible fabrication of bulk transparent ceramics by simple solidification of the melts with the eutectic or near eutectic compositions in multiple phase systems where no network former oxides are included.

Here, we discuss the formation of amorphous phases by rapid cooling of eutectic melt, which is quite different from eutectic solidified composites that show excellent thermal and mechanical stability at high temperatures as demonstrated by Waku et al.[1–6] When Al_2O_3–Gd_2O_3 equilibrium phase diagram was given as Fig. 6,[18] a free energy diagram where all phases with every composition at every temperature should be considered although full thermodynamic data for all phases have not been available. The upper part of this figure is an illustration of the energy diagram for the Al_2O_3–Gd_2O_3 system in the Al_2O_3–$GdAlO_3$ region at a temperature ($T = T_1$). The energy curve for every phase is schematic but the positions a, c, d and f should be defined to be the cross section of the phase boundaries and $T = T_1$. In the two phases region of Al_2O_3 + liquid, Al_2O_3 with the composition [a] and the liquid phase with composition [c] should coexist at $T = T_1$ at the equilibrium, which is given by a common contact line [a]–[c]. If a liquid phase with a composition between a and c could so rapidly cooled down to $T = T_1$ that no phase separation by diffusion could be allowed, this liquid phase should either stay in the liquid phase or crystallize as the Al_2O_3 solid solution phase with that composition. Both of the phases must be meta-stable because their energies are always higher than the energy for the coexistence of two phases of a + c. Therefore, the composition [b] where the free energy of Al_2O_3ss is equal to that of the liquid phase at $T = T_1$ can be defined as the critical point where the super-cooled liquid (=amorphous phase) can be obtained by rapid solidification. The dotted line T_0 in the phase diagram, which is the trace of those compositions, is called to be "equilibrated temperature line" between Al_2O_3ss and the liquid phase.[14] This T_0 line can be regarded as the meta-stable phase boundary between Al_2O_3ss and liquid phases when the system might be ultra-rapidly cooled. Another similar T_0 line can be defined between the liquid phase and $GdAlO_3$ss phase as seen in Fig. 6. The region between two T_0 lines is possible formation one of amorphous phase by rapid cooling of melts in this system. Thus, the eutectic or near eutectic compositions would give amorphous phase by rapid cooling (quenching). There exist no data in the system Al_2O_3–$GdAlO_3$ as far as we know, but Weber et al.[19–21] reported amorphous formation in the system Al_2O_3–Y_2O_3 by rapid quenching.

In ternary eutectic systems, the eutectic temperature and the T_0 lines would drop to lower than in binary systems. We, therefore, have expected easier formation of the amorphous phase by relatively slower cooling in ternary systems than in binary ones. In fact, the amorphous transparent phase could be obtained by just solidification of the melts in the ternary system HfO_2–Al_2O_3–$GdAlO_3$ in the present work even though the exact eutectic point has not been determined yet in this ternary nor in the binary HfO_2–$GdAlO_3$ system. We are studying the complete equilibrium and non-equilibrium phase diagrams in the ternary system HfO_2–Al_2O_3–$GdAlO_3$ to establish the work related to the formation of transparent ceramics by melt solidification, first proposed in the present work.

4. Conclusions

Transparent bulk ceramics can be fabricated by a simple solidification of melts with eutectic or near eutectic compositions. We have succeeded to prepare a transparent bulk sample, 1–5 mm globule, in the ternary system HfO_2–Al_2O_3–$GdAlO_3$ for the first time. It is noteworthy that they have no network former oxides but kept amorphous by just cooling of 200–500 K/s. The possible formation of amorphous phase as super-cooled liquid could be discussed by the meta-stable phase boundaries in the phase diagram.

Note added in proof

This paper has been presented at the Workshop on Directionally Solidified Eutectic Ceramics, May 5–7, 2003, Paris, France. Since then related following papers have been published:

(1) Araki, S. and Yoshimura, M., Transparent nano-composites ceramics by annealing of amorphous phase in the HfO_2–Al_2O_3–$GdAlO_3$ system. *Int. J. Appl. Ceram. Technol.*, 2004, **1**(2), 155–160.
(2) Rosenflanz, A., Frey, M., Endres, B., Anderson, T., Richards, E. and Schardt, C., Bulk glasses and ultrahard nanoceramics based on alumina and rare earth oxides. *Nature*, 2004, **430**, 761–764.
(3) Calderon-Moreno, J. M. and Yoshimura, M., Al_2O_3-$Y_3Al_5O_{12}$(YAG)-ZrO_2 ternary composite rapidly solidified from the eutectic melt. *J. Euro. Ceram. Soc.*, 2005, **25**, 1365–1368.

Acknowledgments

We thank Professor Shuichi SHIBATA and Mr. Hidemi Yoshikawa (Tokyo Institute of Technology) for helping our measurements of optical data. We are also thankful to Dr. Tomoaki Watanabe, Dr. Jose M. Calderon-Moreno and Mr. Naonori Sakamoto for their help in experiments and discussion.

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