ISSN: 0974 - 7486

Volume 10 Issue 10



Materials Science An Indian Journal Review

MSAIJ, 10(10), 2014 [403-409]

Preparation of rare-earth aluminate glasses by powder sintering and nano-ceramics by glass crystallization: A mini-review

Guanghua Liu*, Jiangtao Li, Lin Mei, Lili Wang, Gang He Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, (CHINA) E-mail:liugh02@163.com

ABSTRACT

Rare-earth aluminate glasses and ceramics have good chemical stability and unique optical properties, and are attractive for a large variety of applications. Rare-earth aluminate glasses can be produced by melt casting, but the sample size is strictly limited because of the high cooling rate required. Recently, a new method of powder sintering has been developed to prepare rare-earth aluminate glasses with much larger sample sizes. Furthermore, by crystallization of the rare-earth aluminate glasses, highlydense and transparent nano-ceramics have been obtained, which is a great challenge for conventional crystalline powder sintering. This article gives a brief review on the preparation of rare-earth aluminate glasses and nanoceramics by powder sintering and glass crystallization. Several examples are presented to show the processing and applicability of the new method. © 2014 Trade Science Inc. - INDIA

KEYWORDS

Glasses: Nano-ceramics; Rare-earth aluminates; Transparent.

INTRODUCTION

Rare-earth aluminate glass and ceramic materials are attractive for a large variety of applications because of their good chemical and thermal stability, acceptable mechanical strength and hardness, and unique optical properties^[1,2]. Rare-earth aluminate glasses are usually prepared by melt casting, where an extremely high cooling rate is required to avoid devitrification. In this case, only small glass spheroids or fine glass fibers can be produced^[3,4], and it is difficult to obtain bulk glass samples larger than 1 cm.

For the preparation of rare-earth aluminate ceramics, the conventional method is sintering of high-purity and ultrafine polycrystalline powders^[5,6]. In order to produce highly-dense and even transparent samples with a

very low porosity, a higher sintering temperature is necessary. At a high sintering temperature, however, fast grain growth usually takes place, and nano-sized grains are hardly preserved. In this case, highly-dense ceramics with nano-sized grains can only be produced under an ultra-high mechanical pressure on the magnitude of GPa^[7].

Recently, a new method has been developed for preparing rare-earth aluminate glasses and ceramics, which is powder sintering and glass crystallization^[8-11]. By powder sintering, rare-earth aluminate glasses with a much larger sample size can be produced in contrast to the melt-casting approach. By crystallization of rareearth aluminate glasses, highly-dense transparent ceramics with nano-sized grains can be obtained, which is difficult for conventional crystalline powder sintering.

Review

At the same time, the temperature for preparing rareearth aluminate glasses and ceramics is evidently decreased by using the new method. With the above merits, the new method may provide a more effective and practical way to produce rare-earth aluminate glasses and ceramics.

This article gives a brief review on the preparation of rare-earth aluminate glasses and highly-dense nanoceramics by powder sintering and glass crystallization. Several examples are presented to show the processing and applicability of this method.

EXPERIMENTAL

High-purity powders of Al_2O_3 , Re_2O_3 , and M_xO_y were used as raw materials, where Re_2O_3 means a rareearth oxide (e.g. Y_2O_3 and La_2O_3), and M_xO_y means the third oxide (e.g. SiO_2 , ZrO_2 , and HfO_2) to lower the melting point and increase the glass-forming ability of the Al_2O_3 - Re_2O_3 - M_xO_y system. The raw materials were mixed and homogenized by ball-milling in absolute ethanol with 1.5 wt% polyvinyl alcohol as binder. The obtained slurry was spray-dried into spherical granules with sizes in the range of 10-100 µm. The granules were fed into a C_2H_2/O_2 flame with a maximum temperature of >3000°C and then quenched into water. During water-quenching, amorphous microspheres were obtained by abrupt cooling with a cooling rate on the magnitude of $10^{3\circ}$ C/s.

The amorphous microspheres were loaded into a graphite die and consolidated by hot-pressing. The sintering temperature (T_s) is determined within the kinetic window of the microspheres ($\Delta T=T_x-T_g$), where T_g is the glass transition temperature and T_x is the onset crystallization temperature. For most Al₂O₃-Re₂O₃-M_xO_y systems discussed here, the sintering temperature was in the range of 850-1000°C. After hot-pressing, transparent bulk glasses were produced. By post-annealing and crystallization of the glasses, highly-dense and transparent nano-ceramics were obtained.

The glass transition temperature (T_g) and onset crystallization temperature (T_x) of the glass microspheres were measured by differential thermal analysis (DTA; STA 449C, Netzsch, Germany) with a heating rate of 10°C/min. The phase assemblage was determined by X-ray diffraction (XRD; D8 Focus, Bruker, Germany)

using Cu K α radiation. The microstructure was examined by field emission scanning electron microscopy (FESEM; S-4300, Hitachi, Japan) equipped with energy dispersive spectroscopy (EDS; INCA, Oxford Instrument, UK) and transmission electron microscopy (TEM; JEM 2100F, JEOL, Japan). The in-line transmittance spectra were obtained using an UV-VIS-NIR Spectrophotometer (Cary5000, Varian, USA) for 175-2000 nm and a fourier transform infrared spectra (FTIR; Excalibur 3100, Varian, USA) for 2-25 µm. The density of the bulk samples was measured according to the Archimedes method. The hardness (H_v) and fracture toughness (K_{ic}) were measured by the Vickers indentation method (HXD-1000TM, Shanghai, China).

RESULTS AND DISCUSSION

Preparation of rare-earth aluminate glasses by powder sintering

In the preparation of rare-earth aluminate glasses by melt casting, an extremely high cooling rate is usually required to avoid devitrification, and accordingly the size of glass samples that can be produced is strictly limited. During melt casting, the cooling rate gradually decreases from the surface to the center of the melt (Figure 1). For large volume of melt, the cooling rate in the center part may be below the critical value, and crystallization will take place. For this reason, it is difficult to produce large rare-earth aluminate glasses by melt casting. In fact, even with special melting techniques such as containerless melting by lasers, only small spheroids and thin fibers can be prepared^[3,4], and bulk



Figure 1 : A schematic illustration of the cooling of a molten droplet during quenching into water. $(dT/dt)_c$ means the critical cooling rate for glass formation with no crystallization.

405

glass samples larger than 1 cm have rarely been reported.

In contrast to melt casting, powder sintering offers a more feasible way to prepare large rare-earth aluminate glass samples. By powder sintering, glass microspheres smaller than 100 μ m are prepared at first and then consolidated into bulk glasses by hot-pressing. In this case, there is no intrinsic limitation for the sample size, which in principle only depends on the dimension of the die used for hot-pressing. Up to now, various rare-earth aluminate glasses have been prepared by powder sintering, and two examples are discussed here.

Al₂O₃-Y₂O₃-La₂O₃ glasses

The thermal stability of Al₂O₃-Y₂O₃-La₂O₃ glasses strongly depends on the molar ratio of La/Y^[12]. Figure 2 shows DTA curves of glass powders with chemical compositions of 62.5Al₂O₃-(37.5-x)Y₂O₃-xLa₂O₃ (in mol%, x=0, 5, 7, 10, 20), and quantitative data are listed in TABLE 1. With increasing La/Y ratio, the glass transition temperature (T_x) decreases but the onset crystallization temperature (T_x) increases, which results in a wider kinetic window (Δ T). The sintering temperature is usually selected within the kinetic window, and thus a larger Δ T is desired for preparation of bulk glasses by powder sintering.

From DTA results at different heating rates, the activation energy for the crystallization of Al_2O_3 - Y_2O_3 - La_2O_3 glasses has been calculated. The activation energy increases linearly with increasing La/Y ratio, which implies that the incorporation of more La_2O_3 enhances the stability of Al_2O_3 - Y_2O_3 - La_2O_3 glass. This result is consistent with previous reports suggesting that in Al_2O_3 - Y_2O_3 - La_2O_3 glass the substitution of Y^{3+} by larger La^{3+} cations will inhibit the transition from $[AlO_4]$ tetrahedron to $[AlO_6]$ octahedron and enhance the stability of the glass structure^[3].

To produce bulk glasses by powder sintering, a prerequisite is that the precursor glass powder has a wide kinetic window. For the $62.5Al_2O_3$ - $(37.5-x)Y_2O_3$ xLa_2O_3 glass powders with x=0 and x=5, the kinetic windows are 20 and 34 K, respectively, which are too narrow to realize full densification without devitrification. The glass powders with x≥7 show kinetic windows of ≥50°C and are acceptable for hot-pressing.

After hot-pressing at 905°C for 10 min under a



Figure 2 : DTA curves of Al_2O_3 - Y_2O_3 - La_2O_3 glass microspheres with compositions of 62.5 Al_2O_3 -(37.5-x) Y_2O_3 -x La_2O_3 (in mol%)^[12].

 $\label{eq:table_transform} \begin{array}{l} TABLE 1: DTA \ data \ of \ Al_2O_3-Y_2O_3-La_2O_3 \ glass \ microspheres \\ with \ compositions \ of \ 62.5Al_2O_3-(37.5-x)Y_2O_3-xLa_2O_3 \ (in \ mol\%)^{[12]} \end{array}$

x (mol%)	T _g (°C)	$T_x (^{o}C)$	$\Delta T = T_x - T_g (^{o}C)$
0	887	907	20
5	878	912	34
7	860	917	57
10	840	928	88
20	796	933	137

 T_g : glass transition temperature, T_x : onset crystallization temperature, ΔT : kinetic window width.

mechanical pressure of 60 MPa, bulk glasses were obtained for the compositions with x=10 and x=20. For the composition with x=7, however, crystallization took place with the formation of crystalline $Y_3A_5O_{12}$ (YAG) phase. The transmittance curves of the hot-pressed samples are shown in Figure 3. The samples with x=10 and x=20 exhibit the maximum transmittance of 66% and 69%, respectively. The sample with x=7 shows a much lower transmittance, which can be attributed to strong light scattering by the YAG crystallites.



Figure 3 : Transmittance spectra of Al_2O_3 - Y_2O_3 - La_2O_3 glasses with compositions of 62.5 Al_2O_3 -(37.5-x) Y_2O_3 -x La_2O_3 (in mol%) with a sample thickness of 1 mm^[12].

Al₂O₃-Y₂O₃-Ce₂O₃-SiO₂ glasses

In the Al₂O₃-Y₂O₃-Ce₂O₃-SiO₂ system, four compositions with fixed molar ratios of Al/Y=5/3 and Ce/ (Y+Ce)=0.05 but varying SiO₂ contents of 10, 20, 30, and 40 mol% were investigated. By flame spraying, glass powders were produced. DTA results revealed that, with increasing content of SiO₂, the glass transition temperature changed little but the crystallization temperature clearly increased^[13]. This means that the glass-forming ability of Al₂O₃-Y₂O₃-Ce₂O₃-SiO₂ glasses strongly depends on the content of SiO₂ and increases with the latter. Similar results were also reported for Al₂O₃-Y₂O₃-SiO₂ glasses prepared by melt casting, where a SiO₂ content of \geq 40 mol% is necessary to avoid devitrification^[14,15]. By flame spraying, Al₂O₃-



Figure 4 : XRD pattern and SEM micrograph (inset) of Al_2O_3 - Y_2O_3 -Ce₂O₃-SiO₂ glass microspheres with 10 mol% SiO₂^[13].

Materials Science An Indian Journal Y_2O_3 -Ce₂O₃-SiO₂ glass microspheres with much lower SiO₂ contents can be produced. For example, Figure 4 shows the XRD pattern and SEM micrograph of flame-sprayed Al₂O₃-Y₂O₃-Ce₂O₃-SiO₂ glass microspheres with 10 mol% SiO₂, where no crystalline phase is found.

After hot-pressing, transparent bulk glasses were produced (Figure 5) except for the sample with 10 mol% SiO₂, where devitrification occurred with the formation of YAG phase. Under excitation of 465 nm, the Al₂O₃-Y₂O₃-Ce₂O₃-SiO₂ glasses showed a broad emission band in the range of 500-600 nm, which is attributed to the f-f transition of Ce³⁺. It was noticed that, the emission peak shifted to long-wavelength and the emission intensity increased with decreasing content of SiO₂ in the glasses.



Figure 5 : Emission spectra of Al₂O₃-Y₂O₃-Ce₂O₃-SiO₂ glasses (λ_{ex} =465 nm). The inset shows the photos of the glass samples of 1, 2, 3, and 4 with 10, 20, 30, and 40 mol% SiO₂, respectively^[13].

Preparation of rare-earth aluminate nano-ceramics by glass crystallization

As many other oxide ceramics, rare-earth aluminate ceramics are generally produced by sintering of crystalline powders with a high purity and fine particle size. During sintering, densification occurs mostly by thermally-activated diffusion processes, and a higher sintering temperature is required to realize a high density. At high temperatures, however, fast grain growth often takes place and nano-sized grains can hardly be preserved. Because of the concomitant grain growth with densification, it is a great challenge to produce highly-dense nano-ceramics by crystalline powder sin-

407

Review

tering.

Compared with crystalline powder sintering, glass crystallization may provide a more feasible method to produce highly-dense nano-ceramics. By this method, highly-dense rare-earth aluminate glasses are prepared at first and then converted into nano-ceramics by post crystallization. Thus, the two processes of densification and grain growth are separated (Figure 6), which makes the preparation of highly-dense nano-ceramics possible. As an example, highly-dense and transparent LaAlO₃/ ZrO_2 nano-ceramics have been prepared by glass crystallization^[15,16], which is discussed in detail as follows.



Figure 6 : A comparison between crystalline powder sintering and glass crystallization with different densification and grain growth kinetics in the preparation of ceramics. A: highly-dense nano-ceramics; B: porous nano-ceramics; C: highly-dense submicron or micro-ceramics. In crystalline powder sintering, concomitant grain growth occurs with densification (grain size increases with increasing relative density), and it is difficult to realize both high density and nano-sized grains. By glass crystallization, the two processes of densification and grain growth are separated, where densification is completed at first and then grain growth takes place, thus offering the feasibility to prepare highly-dense nano-ceramics.

In the Al₂O₃-La₂O₃-ZrO₂ ternary system, the composition of $53Al_2O_3$ -20La₂O₃-27ZrO₂ (in mol%) was investigated. At first, glass microspheres were prepared by flame spraying (Figure 7 (a)). From DTA analysis, the glass transition temperature and onset crystallization temperature of the Al₂O₃-La₂O₃-ZrO₂ glass microspheres were 816 and 895°C, respectively. By



Figure 7 : (a) Al_2O_3 -La $_2O_3$ -ZrO $_2$ glass microspheres prepared by flame-spraying; (b) transparent Al_2O_3 -La $_2O_3$ -ZrO $_2$ bulk glass prepared by hot-pressing; (c) transparent LaAlO $_3$ /ZrO $_2$ nano-ceramic prepared by crystallization of the parent glass; (d) transmittance spectra of the Al_2O_3 -La $_2O_3$ -ZrO $_2$ glass and LaAlO $_3$ /ZrO $_2$ nano-ceramic. The sample thickness is 1 mm^[10].

sintering experiments, the most appropriate sintering temperature was determined to be 875°C.

After hot-pressing at 875° C under a pressure of 90MPa, highly-dense transparent glass was produced (Figure 7 (b)). It was confirmed by XRD analysis that the glass sample was fully amorphous with no crystalline phase. The density of the Al₂O₃-La₂O₃-ZrO₂ glass was 4.55 g/cm³ (99.8% TD), and SEM observation also indicated that the sample was highly-dense without pores. At the fracture surface, the sample showed a typical conchoidal feature commonly observed for glasses (Figure 8 (a)). The glass sample showed a good transparency in the range from 265 nm to 6.5 µm, and the maximum transmittance reached 75% in infrared region (Figure 7 (d)).

The hot-pressed Al_2O_3 - La_2O_3 - ZrO_2 glass can be converted into polycrystalline ceramics by post crystallization. To do this, the glass sample was annealed at





Figure 8: (a) SEM image of the Al₂O₃-La₂O₃-ZrO₂ glass; (b) TEM image of the LaAlO₃/ZrO₂ nano-ceramic^[10].

different temperatures in the range of 900-1300°C for 2 h. After annealing at 900°C, $La_2Zr_2O_7$ was precipitated. At 1000°C, the diffraction peaks of $La_2Zr_2O_7$ almost disappeared, and new crystalline phases of $LaAlO_3$ and ZrO_2 were produced. At 1100 and 1200°C, no $La_2Zr_2O_7$ remained and only LaAlO₃ and ZrO₂ existed. When the annealing temperature was further increased to 1300°C, minor $LaAl_{11}O_{18}$ phase was detected, and the diffraction intensities of LaAlO₃ and ZrO₂ changed little, implying that the crystallization was almost complete.

During annealing, both the crystallization fraction and the density of samples increased with increasing temperature. Particularly, after being annealed at 1200°C, the sample was almost fully-crystallized, and the grain size was smaller than 100 nm (Figure 8 (b)). That is to say, highly-dense LaAlO₃/ZrO₂ nano-ceramic was obtained. The nano-ceramic was transparent (Figure 7 (c)), and the maximum transmittance in infrared region reached ~70%, which was close to that of the parent glass before annealing (Figure 7 (d)). The LaAlO₃/ZrO₂ nano-ceramic showed a Vickers hardness of 19 GPa, which almost doubled that of the parent glass. The remarkable increase in hardness can be attributed to the large crystallization fraction and the nano-scale microstructure. With a combination of good optical and mechanical properties, the LaAlO₃/ZrO₂ nano-ceramics are attractive for a variety of applications.

In addition to $LaAlO_3/ZrO_2$, several other rare-earth aluminate transparent nano-ceramics have also been produced by glass crystallization, as shown in Figure 9. It appears that glass crystallization is an effective method to prepare highly-dense and transparent nano-ceramics.



Figure 9 : Transparent nano-ceramics prepared by glass crystallization: (a) LaAlO₃/ZrO₂; (b) 1.5%Er:LaAlO₃/ZrO₂; (c) 1%Nd:YAG/HfO₂; (d) 3%Nd:YAG/HfO₂^[11].

409

CONCLUSIONS

A new method of powder sintering and glass crystallization has been developed to prepare rare-earth aluminate glasses and nano-ceramics. By powder sintering, rare-earth aluminate glasses with a large sample size can be produced in contrast to the melt-casting approach where the sample size is strictly limited to be <1 cm. By glass crystallization, grain growth is separated from densification, and highly-dense rare-earth aluminate nano-ceramics can be prepared, which is difficult for crystalline powder sintering due to concomitant grain growth with densification. Moreover, by using the new method, the temperature for preparing rareearth aluminate glasses and ceramics is much decreased in comparison with the conventional techniques. In this case, the new method may provide a more effective and practical way to produce rare-earth aluminate glasses and ceramics. Finally, it should be pointed out that, the method of powder sintering and glass crystallization is not only limited in the production of rare-earth aluminate glasses and ceramics, but also applicable for preparing many other kinds of glasses and ceramics.

ACKNOWLEDGEMENTS

This work was supported by National Natural Science Foundation of China (Grant Nos. 50932006, 51002163), Beijing Natural Science Foundation (Grant No. 2112043), and Beijing Nova Program (Grant No. xx2013053).

REFERENCES

 J.Weber, J.Tangeman, P.Nordine, R.Scheunemann, K.Hiera, C.Ray; J.Non-Cryst Solids, 345, 359 (2004).

- [2] A.Ikesue, Y.L.Aung; Nat.Photon, 2, 721 (2008).
- [3] J.Weber, J.Abadie, A.Hixson, P.Nordine, G.Jerman; J.Am.Ceram.Soc., 83, 1868. (2000)
- [4] J.Weber, J.Felten, B.Cho, P.Nordine; Nature, **393**, 769 (**1998**).
- [5] A.Ikesue, T.Kinoshita, K.Kamata, K.Yoshida; J.Am.Ceram.Soc., 78, 1033 (1995).
- [6] H.Yagi, T.Yanagitani, K.Takaichi, K.Ueda, A.A.Kaminskii; Opt.Mater, **29**, 1258 (**2007**).
- [7] A.Podhorodecki, P.Gluchowski, G.Zatryb, M.Syperek, J.Misiewicz, W.Lojkowski, W.Strek; J.Am.Ceram.Soc., 94, 2135 (2011).
- [8] A.Rosenflanz, M.Frey, B.Enderson, E.Richards, C.Schardt; Nature, **430**, 761 (**2004**).
- [9] S.Araki, M.Yoshimura; Int.J.Appl.Ceram.Tech., 1, 155 (2004).
- [10] L.Mei, G.He, L.L.Wang; G.H.Liu, J.T.Li; J.Eur.Ceram.Soc., **31**, 1603 (**2011**).
- [11] L.Mei, G.H.Liu, G.He, L.L.Wang, J.T.Li; Opt.Mater, 34, 981 (2012).
- [12] L.L.Wang, L.Mei, G.He, G.H.Liu, J.T.Li, L.H.Xu, Z.J.Jiang; J.Eur.Ceram.Soc., 32, 3091 (2012).
- [13] L.L.Wang, L.Mei, G.He, J.T.Li, L.H.Xu; J.Am.Ceram.Soc., 11, 3800 (2011).
- [14] L.Wu, G.H.Liu, J.T.Li, B.He, Z.C.Yang, Y.X.Chen; Ceramics-Silikaty, 55, 228 (2011).
- [15] Z.C.Yang, G.H.Liu, J.T.Li, S.B.Guo, L.H.Xu; J.Am.Ceram.Soc., 95, 1799 (2012).

