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Letter

Melt-casting of $Y_3Al_5O_{12}$ (YAG) ceramics by combustion synthesis under high gravity with the addition of glass

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ABSTRACT

Bulk YAG-based ceramics have been prepared by melt-casting under high gravity with the addition of glass. The glass helps to reduce the porosity and grain size of the casted ceramics. In the casting process, the glass melt can feed the shrinkage cavities produced during fast solidification of YAG. With the addition of glass, the grain boundary migration of YAG is pinned and thus grain growth is limited. The effect of the glass strongly depends on its chemical composition and crystallization behavior, where a higher SiO_2 content is necessary to avoid devitrification.

1. Introduction

In contrast to metals and alloys, which are generally produced by casting from melts, polycrystalline ceramics are mainly fabricated by sintering from fine powders. For the melt-casting of ceramics, two technical obstacles are involved. At first, it is difficult to get stable and homogeneous ceramic melts because most ceramic materials have high melting points or decompose before melting. Secondly, during the solidification of ceramic melts exaggerate grain growth will happen and impair mechanical properties. Conventionally, the melt-casting of ceramic materials is realized by directional solidification or micro-pulling-down techniques, which often involves laser or induction heating followed by rapid cooling [1–4].

Recently, a new approach to the melt-casting of ceramics has been reported, which is known as combustion synthesis under high gravity [5–7]. In this technique, highly exothermic combustion reactions are utilized to achieve high temperature and produce ceramic and metal melts, and a high-gravity field is introduced to improve the separation of the two melts and removal of pores. By this means, bulk ceramics can be prepared by melt-casting like metal materials.

For the melt-casting of ceramics, it is important to reduce the porosity and grain size in the ceramic ingots to improve their properties. It has been proved that a stronger high-gravity field can accelerate the separation and removal of pores from ceramic melts [8]. Besides the pores, shrinkage cavities are often produced in the center part of an ingot during fast solidification. After solidification, these shrinkage cavities can only be compensated by plastic deformation. However, owing to the high yield stress and short duration at high temperature, the plastic deformation in the ceramic ingots is very limited, even in a strong high-gravity field of 5000 × *g*. Consequently, the shrinkage cavities can hardly be removed, which remain in the casted samples and lower the density.

In contrast to enhancing the high-gravity field, this paper reports an alternate way to increase the relative density of melt-casted ceramics, where a glass melt is introduced to feed the shrinkage cavities during fast solidification. As an example, dense YAG ceramics are prepared here with the addition of aluminosilicate glass. The effects of the glass on the densification and grain growth during melt-casting of YAG are discussed. After doping with proper cations (Ce3+, Eu3+, Dy3+, Tb3+, etc.), the prepared YAG-based samples can be used as phosphors in LED lighting [9,10] or in the field of thermometry and thermography [11,12].

2. Experimental

Commercial powders of Al, NiO, Y_2O_3, Al_2O_3, SiO_2, MgO, and CaO were used as raw materials. The Al powder has a purity >99% and an average particle size of $2\sim3\,\mu m$, the Y_2O_3 powder has a purity >99.99%, and the other oxides were analytical-grade reagents. The Al, NiO, and Y_2O_3 powders were used to produce YAG ($Y_3Al_5O_{12}$) by the reactions of $2Al + 3NiO = Al_2O_3 + 3Ni$ and $5Al_2O_3 + 3Y_2O_3 = 2Y_3Al_5O_{12}$. The Al_2O_3, SiO_2, MgO, and CaO powders were used to produce glass melts with the compositions listed in Table 1. The compositions were selected from the low eutectic points in SiO_2–Al_2O_3–MgO and SiO_2–Al_2O_3–CaO ternary phase diagrams, and their melting temperatures varied in the range of 1170–1500 °C. In each sample, the proportion of glass additives was 10 wt%, in expectation of repairing the porosity of 9% for pure YAG samples (Table 1).

The raw materials were mixed in ethanol and homogenized by planetary ball milling for 1 h, and then dried at 80 °C for 8 h. The reactant powder was cold-pressed into a compact with a porosity of 50%. The compact was loaded into a graphite

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Table 1
The densities and phase assemblages of the prepared samples with different additives.

Sample no.	Composition to produce YAG	Composition of additives	Density (g/cm^3)	Apparent porosity (%)	Phase assemblage
0#	13.0%Al + 54.3%NiO + 32.7%Y_2O_3	No additive	4.14	9	YAG
1#	13.0%Al + 54.3%NiO + 32.7%Y_2O_3	21%Al_2O_3–54%SiO_2–25%MgO	4.27	4	YAG + spinel ($MgAl_2O_4$) + glass
2#	13.0%Al + 54.3%NiO + 32.7%Y_2O_3	20%Al_2O_3–70%SiO_2–10%CaO	4.20	2	YAG + glass
3#	13.0%Al + 54.3%NiO + 32.7%Y_2O_3	15%Al_2O_3–62%SiO_2–23%CaO	4.16	3	YAG + glass + anorthite ($CaAl_2Si_2O_8$)
4#	13.0%Al + 54.3%NiO + 32.7%Y_2O_3	53%Al_2O_3–10%SiO_2–37%CaO	3.94	8	YAG + mayenite ($Ca_{12}Al_{14}O_{33}$)

crucible with an inner diameter of 30 mm, which was mounted into a reaction chamber to perform combustion synthesis under high gravity. The chamber was evacuated to a vacuum of ~100 Pa. A high-gravity field with an acceleration of $900 \times g$ was induced by centrifugation, where g means the gravitational acceleration. By passing an electric current through a tungsten coil closely above the sample, combustion reaction was triggered. During the reaction, a large amount of heat was produced and made the products melted. In a high-gravity field, the ceramic and metal melts were separated because of their density difference. After the solidification of the melts, bulk ceramic and metal ingots were obtained. The ceramic ingot was machined and polished for later characterization.

The bulk density was measured according to the Archimedes principle. The phase composition was identified by X-ray diffraction (XRD; D8 Focus, Bruker, Germany) with a step of 0.02° and a scanning rate of 6°/min. The microstructure was examined by scanning electron microscopy (SEM; S-3400, Hitachi, Japan).

3. Results and discussion

Fig. 1 shows the XRD pattern of 0# sample, in which only the diffraction peaks of YAG are observed. This indicates that the aluminothermic reaction between Al and NiO is complete and the resultant Al_2O_3 has fully reacted with Y_2O_3 to form YAG. Ni is not found in the sample, verifying a thorough separation of the ceramic melt from the metal melt under high gravity. For 1–4# samples with glass-forming oxide additives, the phase assemblage depends on the nominal chemical composition of the glass, as shown in Table 1. With a higher content of SiO_2, only amorphous glass is obtained other than YAG major phase. When the content of SiO_2 is reduced and more MgO or CaO is added, crystalline secondary phases are produced. This should be attributed to the different roles of the oxide additives. In the structure of silicate glass, SiO_2 is a glass-forming agent, with $[SiO_4]^{4-}$ tetrahedron as the fundamental subunit of the whole network. MgO and CaO are glass-modifying oxides, which will break up the network by reducing the amount of bridge-oxygen. Therefore, with the decrease of SiO_2 and increase of MgO or CaO content, the network structure of glass can no longer be preserved and crystallization occurs.

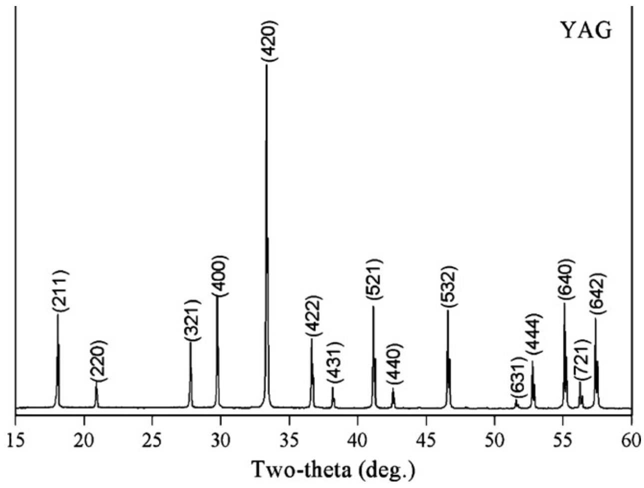

Fig. 1. XRD pattern of melt-casted YAG ceramics by combustion synthesis under high gravity (0# sample).

The densities of the casted samples are listed in Table 1. An evident increase in relative densities of the samples is observed with the addition of glass. It is also noticed that, the relative densities depend on the chemical composition of the glass, and a higher SiO_2 content is desirable. By the addition of Si–Al–Ca–O glass, a relative density of 98% is reached in 2# sample, compared with 91% in 0# sample with no addition of glass.

Fig. 2 shows the SEM images of casted samples. In 0# sample without glass addition, very coarse YAG grains larger than 200 μm are observed. Among these grains, large cavities up to 100 μm exist, which may be responsible for the lower relative density (91%) of the sample. In 1–4# samples with the addition of glass, the cavities among YAG grains are filled by glass or crystalline secondary phases, leading to higher relative densities. At the same time, by the addition of glass, the average grain size of YAG is reduced. In 2# and 3# samples, the average grain size is nearly 10 μm, which is smaller by a magnitude than that in 0# sample.

From the above results, the addition of glass melt brings two effects on the melt-casting of YAG ceramics: (1) to improve the densification; and (2) to limit grain growth.

The porosity in the melt-casted ceramics comes from two sources. One is the residual pores existing in the ceramic melt, which will be inherited in the ingots after solidification. The other is the shrinkage cavities produced during fast solidification. The densities of YAG solid and melt are 4.552 and 4.31 g/cm^3, respectively. In this way, the solidification of YAG melt is accompanied by a volume shrinkage of 5%. Because the solidification starts from the edge of an ingot, the shrinkage cavities in the center part can hardly be compensated, especially for a fast solidification process associated with a short lifetime of melt. As a result, most shrinkage cavities remain in the final ceramic ingots. Such shrinkage cavities can be compensated by the addition of glass. With a melting point much lower than YAG, the glass still keeps a liquid state with good flowability when the solidification of YAG is over. In this case, the glass melt can readily feed into the shrinkage cavities and increases the relative density of the YAG ingot.

Besides improving densification, the presence of a glass secondary phase can limit grain growth and reduce grain size. At high temperatures, the glass melt intersects the ceramic melt and divides the latter into smaller localized sections. During solidification, the mass transport among these sections by the flowing of melt is blocked by the glass barrier. Accordingly, grain growth is restricted into a smaller volume. In each localized section, YAG grains are coated and separated by the glass melt, as shown in Fig. 2. Accordingly, the grain boundary migration of YAG is pinned by the glass phase and grain growth is depressed. With the decrease of temperature, the glass melt solidifies and exists in the gaps among YAG grains, either as amorphous glass or as a crystalline secondary phase. Compared with the matrix glass, the crystalline secondary phase is rich in alkali-earth elements such as Mg or Ca, as revealed by EDS analysis. In addition, EDS results reveal that some Y element exists in the grain boundary region. This is probably caused by slight reaction of YAG grains with the glass phase at grain boundaries.

The effect of glass is closely related to its composition and crystallization behavior. With a higher SiO_2 content, the glass melt is inclined to keep amorphous after solidification. In this solidifica-

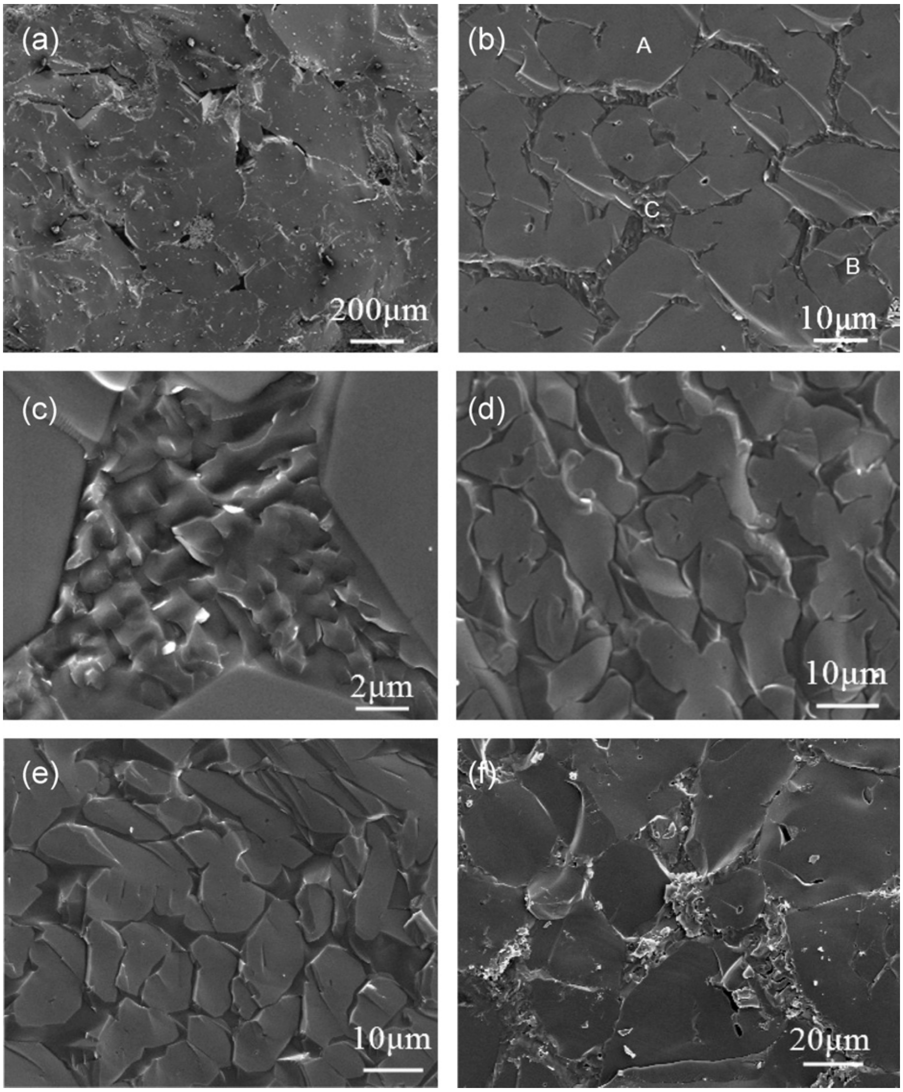

Fig. 2. SEM images of the casted samples: (a) 0#; (b) and (c) 1#; (d) 2#; (e) 3#; (f) 4#. From EDS analysis, the chemical compositions of the areas of "A", "B", and "C" in (b) are Mg:Al:Si:Y = 0.03:1:0.08:0.71, Mg:Al:Si:Y = 0.14:1:0.31:0.51, and Mg:Al:Si:Y = 0.24:1:0.29:0.08, respectively (in molar ratio).

tion process, the volume change is continuous, which will not cause cracks or cavities. With the decrease of SiO_2 and increase of alkali-earth oxide (such as CaO) content, the devitrification trend of the glass is enhanced and crystallization happens. The crystallization process is accompanied with an abrupt volume change, leading to the formation of cracks or shrinkage cavities. Therefore, a glass composition with more SiO_2 is desirable to improve the densification and limit grain growth in the melt-casting of YAG. This is verified by the experimental results for 2# and 4# samples (Table 1 and Fig. 2), where a higher SiO_2 content results in a higher relative density and smaller grain size.

4. Conclusion

Dense YAG ceramics were prepared by melt-casting under high gravity with the addition of glass. The compositions of the glass additives were selected from the low eutectic points in SiO_2–Al_2O_3–MgO and SiO_2–Al_2O_3–CaO ternary phase diagrams. The addition of glass was effective to improve the densification and limit grain growth of YAG. During fast solidification of YAG, the glass melt could feed in the shrinkage cavities and reduce the porosity. With the presence of glass, the grain boundary migration of YAG was pinned and thus grain growth was limited. The effect of the glass additives was closely related to their chemical composition and crystallization behavior, where a higher SiO_2 content was necessary to avoid devitrification. In addition, slight reaction of YAG grains with the glass phase at grain boundaries occurred during combustion synthesis.

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