FABRICATION OF TRANSPARENT $MgAl_2O_4$ SPINEL CERAMICS BY PECS PROCESSING OF COMBUSTION - SYTHESIZED NANOPOWDERS

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Abstract
Transparent $MgAl_2O_4$ ceramic could be found in a wide range of applications for both military and civil sector due to its high melting point, good mechanical properties, small refractive index (1.71) and its ability to allow light in range from UV to mid-IR to pass through. In the present work, transparent $MgAl_2O_4$ spinel ceramics were fabricated from metal nitrates via two steps. Firstly, the $MgAl_2O_4$ nanopowder was synthesized via solution combustion synthesis from the metal nitrates. Secondly, the powder was then consolidated by Pulsed Electric Current Sintering (PECS) technique to fabricate transparent ceramic. XRD patterns of the obtained powder showed the peaks of only $MgAl_2O_4$ phase. Besides, the atomic compositions of magnesium, aluminium and oxygen determined by EDX analysis were approximately corresponded to 1:2:4 of the molecular formula of $MgAl_2O_4$. After deagglomerating for 48 hours using soft ball-milling, the powder had the average particle of 27 nm. Transparent $MgAl_2O_4$ samples, which were sintered with two-step sintering mode of 1050ºC/60 minutes-1400ºC/20 minutes, permitted the transmission of visible and infrared light with the transmittance up to 80%, Vickers hardness of 14.2 GPa, and fracture toughness of 1.1 $MPa.m^{1/2}$. The results are a critical step toward fabrication of high-quality transparent ceramics from metal nitrates.

Keywords: $MgAl_2O_4$, transparent ceramic, combustion synthesis, PECS, two-step sintering

1 Introduction

Magnesium Aluminate ($MgAl_2O_4$) spinel is one of the most outstanding transparent ceramics due to its unique optical and mechanical properties, even at high temperatures [1,2]. Furthermore, such material can allow light to pass through in a wide range from ultraviolet to mid-infrared wavelength (0.2 - 6 μm) [1]. Transparent $MgAl_2O_4$ spinel ceramics have a variety of application such as solid-state lasers, scintillators, armours, optical devices, electro-optical devices, biomaterials etc. [1, 2].

Powder fabrication and sintering play a vital role in transparency of final $MgAl_2O_4$ products since they are directly responsible for the density and the purity of materials. For powder fabrication, chemical synthesis methods have been recently considered as an effective approach

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to prepare powders with high purity and nanoscale particles. Among chemical synthesis methods, solution combustion synthesis has been received an increasing attention due to low temperature requirement, homogeneous products, and low-cost precursors [3]. Various recent studies have reported that solution combustion synthesis have been effective for preparation of ultrafine $MgAl_2O_4$ powders [4, 5]. However, deagglomeration was often required to isolate the nanoparticles.

Recently, PECS has emerged as an efficient method to produce transparent ceramics [6-9], especially transparent $MgAl_2O_4$ [10, 11]. This method can assist in increasing bulk density and reducing grain size in $MgAl_2O_4$ ceramics, which improve both the mechanical properties and the transparency of the materials. Morita et al. [12] successfully demonstrated the densification of a fine-grained transparent spinel only for a 20 minutes holding time at a low temperature of 1300°C with a pressure of 80 MPa by employing a low heating rate ≤ 10°C/min. It is proposed that a slow heating rate can satisfy high density and fine grain size at a low sintering temperature; however, it takes a prolonged time for sintering process. To overcome the issues, two-step sintering technique was applied because this method not only prohibits grain growth but also shortens sintering duration [13]. In this method, the first stage is performed at a relatively low temperature and is followed by a higher temperature stage. Feasibility of two-step sintering method has been reported [14, 15], however, there are few reports on the combination of two-step sintering and PECS [16, 17, 18].

In this work, the feasibility of transparent $MgAl_2O_4$ ceramics fabrication from metal nitrates via solution combustion synthesis and two-step PECS sintering was investigated.

2 Experimental procedure

The starting materials were $Al(NO_3)_3.9H_2O$ and $Mg(NO_3)_2.6H_2O$ as oxidizers, and an urea (CH_4N_2O) as fuel. These materials have purity of 99% and were purchased from Xilong Scientific Co. Ltd., China. Precursor mixture was stoichiometrically balanced by a molar ratio of 3:6:20, and then dissolved in distilled water. Subsequently, the solution was placed in an electric resistance furnace (Linn HT1300, Germany) and it was heated at 500°C. The combustion reaction occurred according to the following reaction [2] to form a voluminous product.

$$3Mg(NO_3)_2\,(aq) + 6Al(NO_3)_3\,(aq) + 20CH_4N_2O\,(aq)$$
$$\rightarrow 3MgAl_2O_4(s) + 20CO_2(g) + 40H_2O(g) + 32N_2(g) \qquad (1.)$$

The synthesized product was deagglomerated for 48 hours in a highly pure ethanol solution using alumina balls with ball-powder mass ratios of 20/1. The milled powder was dried at 120°C for 24 hours and then calcined at 1100°C for 2 hours. As-received powders were fine but not showed spherical shape like other alloys [19]. The obtained powder was sintered by PECS machine (LABOX 1550i75S, Japan) in a graphite die with diameter of 10 mm, with a heating rate of 100°C/min and a uniaxial pressure of 100 MPa. Two-step sintering profile was applied with first-step temperature of 1050°C for 60 minutes and second-step temperature of 1400°C for 20 minutes. After sintering, samples were ground and polished by a slurry of Al_2O_3 powder with particle size of 0.05 μm for 80 hours.

The phase analysis was carried out by X-ray diffraction (Siemens D5000, Germany) using Cu Kα radiation. Morphology was characterized by a field-emitting scanning electron microscope (Hitachi S4800, Japan). The particle size and the size distribution were determined by ImageJ software through SEM images. Energy dispersive analysis (EDX) was performed to identify the elements that present in synthesized powders. Transmission spectrum was investigated by

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ultraviolet-visible (UV-Vis) spectrophotometer (Shimadzu UV-1800, Japan) and Fourier-transform infrared (FTIR) spectrophotometer (Jasco FT/IR 4600, Japan). The Vickers hardness was tested by micro hardness tester (Struers Duramin 2, Germany).

3 Results and discussion

XRD patterns of combustion-synthesized product before and after annealing at 1100°C in air for 2 hours are shown in **Fig. 1**. The pattern of combustion-synthesized product before annealing shows 4 peaks at 2θ of 36.81°, 44.79°, 59.38°, 65.24° corresponding to magnesium aluminate spinel phase as given in the ICDD 01-082-2424 file. The broaden peaks reveal a poor crystallinity of combustion-synthesized product. After annealing, almost all the main $MgAl_2O_4$ reflections appeared in the XRD pattern are detected at 2θ of 31.29°, 36.81°, 38.52°, 44.79°, 56.21°, 59.38° and 65.24°. The peaks of $MgAl_2O_4$ phase are more intensive and well-defined indicating a good crystallinity of the annealed product. In addition, no peaks of impurities observed implies that the combustion synthesis process was operated in a well-controlled condition.

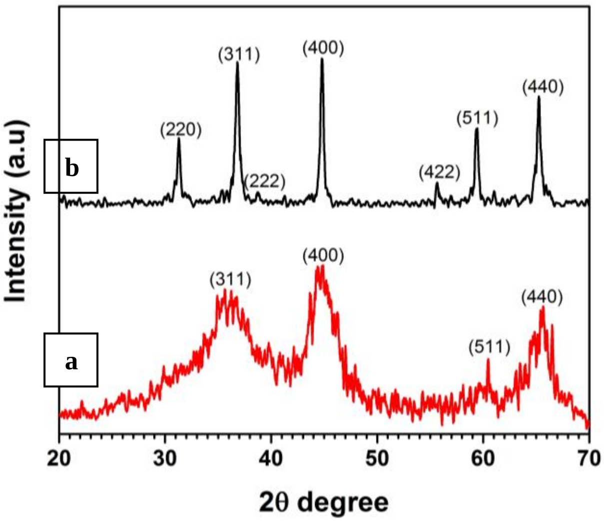

Fig. 1 XRD patterns of combustion-synthesized products before (a) and after (b) annealing at 1100°C in air for 2 hours

The morphology of the combustion-synthesized $MgAl_2O_4$ product characterized by SEM observation appeared in the form of large agglomerates of fine spherical particles (**Fig. 2a,b)**. The average sizes of particles and agglomerates are 20 nm and 8 μm, respectively. EDX pattern (**Fig. 2c**) acquired at the agglomerates shows that magnesium, aluminium and oxygen were the only detected elements with an atomic ratio of approximately 1:2:4. It is concluded that combustion-synthesized product possesses a relative high purity.

Soft-ball-milling is often required to isolate the $MgAl_2O_4$ particles. **Fig. 3a** shows SEM image of the $MgAl_2O_4$ powders milled for 48 hours with ball-powder mass ratio of 20/1. The milling process has a great influence on deagglomeration of particles. After milling, the amount of particle agglomerates significantly decreases. The agglomerate-size distribution and the percentage of particle volume of the $MgAl_2O_4$ powders milled is presented in **Fig. 3b**. The

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milling process reduced the agglomerate proportional volume; hence the size distribution becomes uniform. The average agglomerate size is approximately 27 nm.

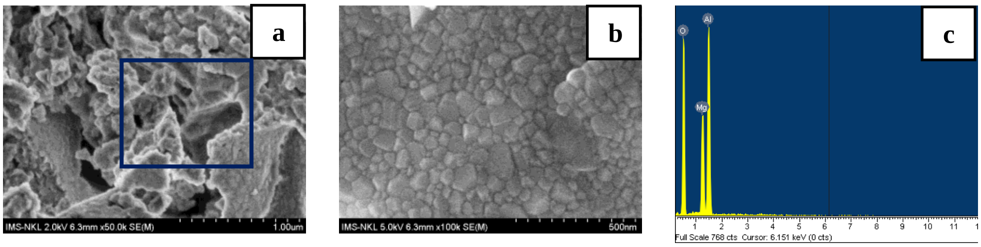

Fig. 2 SEM images of $MgAl_2O_4$ product before annealing at different magnifications of (a) 50kX and (b) 100kX and (c) corresponding EDX spectrum

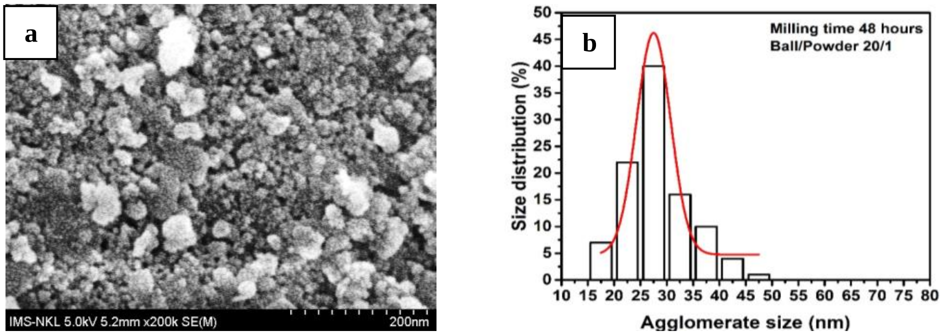

Fig. 3 SEM image (a) and agglomerate-size distribution (b) of $MgAl_2O_4$ powder milled for 48 hours with ball-powder ratio of 20/1

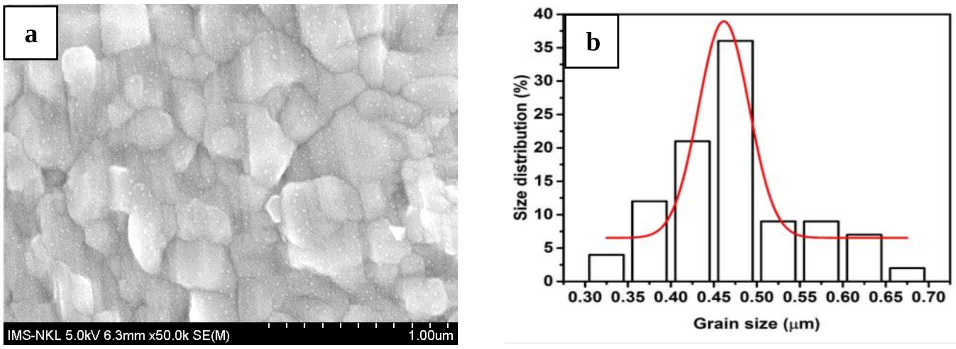

Fig. 4 SEM image (a) and grain size distribution (b) of $MgAl_2O_4$ sample sintered via two - step sintering mode of 1050°C/60 minutes - 1400°C/20 minutes

PECS process was carried out on the obtained nanopowders via two-step sintering mode of 1050°C/60 minutes-1400°C/20 minutes. Morphology of the sintered $MgAl_2O_4$ sample showed no residual pores on the thermal-etched polished surface (**Fig. 4a**). Moreover, most of the grains were in submicron sized and the interparticle necks were not occurred in comparison with sintered alloys [20]. Grain sizes distribute in a narrow range from 0.3 μm to 0.7 μm with the average value of 0.48 μm (**Fig. 4b**).

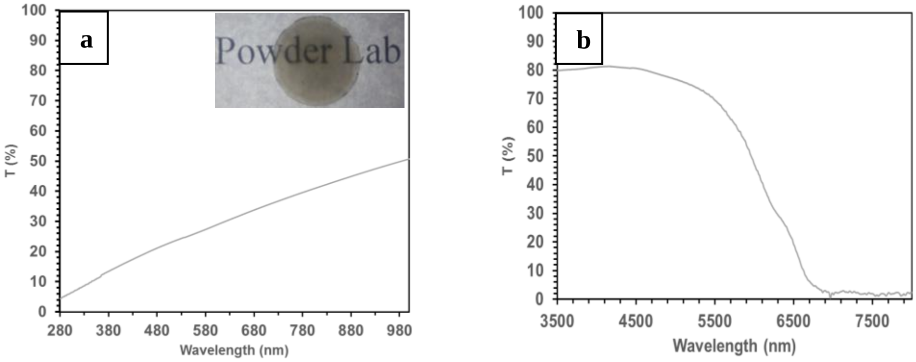

Fig. 5 Transmission spectrum of transparent $MgAl_2O_4$ ceramic samples in (a) ultraviolet-visible range (280-1000 nm) and (b) infrared range (3500-8000 nm)

The appearance of $MgAl_2O_4$ samples produced by PECS via sintering mode of 1050°C/60 minutes-1400°C/20 minutes (inset of **Fig. 5a)** showed a good transparency by naked eyes. **Fig. 5** represents transmission spectrum of $MgAl_2O_4$ samples in ultraviolet-visible range (wavelength, λ = 280-1000 nm) and infrared range (3500-8000 nm) with the thickness converted into 1 mm. The samples have poor transmittances in ultraviolet range. At visible wavelength, the transmittance values linearly increase, and reach the maximum value up to 80% in infrared range, which is close to the theoretical maximum of transmission (87%) [3]. Additionally, the transmittance begins to drop dramatically at 5500 nm and decreases to 0% at 7000 nm. The transmission evaluated at wavelengths of 700 nm (T_{700}) and 4000 nm (T_{4000}) are about 40% and 80%, respectively. The values of the Vickers hardness with a load of 20N and the fracture toughness K_{IC} calculated by using impression diagonals from Vickers hardness tips [21] of $MgAl_2O_4$ samples are 14.2 GPa and 1.1 MPa.m$^{1/2}$, respectively.
In general, transparent $MgAl_2O_4$ ceramics have been successfully fabricated from metal nitrates by the combination of two processes: solution combustion synthesis and spark plasma sintering via two-step temperature profile. The results obtained by this method are favourable compared with the previous results obtained for single-step-SPS processing. For a 20 nm co-precipitated powder, which is quite similar to the one in the present study, transparent $MgAl_2O_4$ spinel ceramics were achieved by single-step-SPS processing at 1550°C for 3 minutes under an applied pressure of 50 MPa and a heating rate of 100°C/min [22]. Transmittances of sintered samples are about 46% at 550 nm and 83% in the infrared range. Benaissa et al. proposed that sintering temperature can be reduced by using a low heating rate [23]. The commercial high purity powder with an average particle size of 50 nm (S30R, France) was single-step-SPS-sintered at 1300°C under a pressure of 73 MPa with various steps of heating rate, i.e. 100°C/min to 800°C then 10°C/min up to 1100°C and 1°C/min up to the final temperature. The transmission reached 70% at λ=550 nm and 78% at λ=1100 nm. The Vickers hardness and fracture toughness reached 18 GPa and 2.2 MPa.m$^{1/2}$, respectively. Their results presented a higher transmittance than in the present case. It might be caused by purity or agglomerate size distribution of the combustion synthesized powders. The control of $MgAl_2O_4$ nanopowders characteristics could be obtained by optimizing the elaboration conditions.

4 Conclusions

Transparent $MgAl_2O_4$ were successfully fabricated from metal nitrates via two-step process including solution combustion synthesis and PECS processing. The product obtained from

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combustion reactions existed only single phase of $MgAl_2O_4$ and presented. Microstructure was in the form of large agglomerates of the fine spherical particles. After milled for 48 hours with ball-powder ratio of 20/1, $MgAl_2O_4$ powder had homogeneous distribution with a nanoscale average size (27 nm). Transparent $MgAl_2O_4$ ceramics was sintered via two-step sintering mode of 1050ºC/60 min-1400ºC/20 min using the combustion-synthesized nanopowders. Their microstructure showed submicron grain size (480 nm) with narrow size distribution. The optical transmittance of sintered $MgAl_2O_4$ ceramics was up to 40% at visible range and 80% at infrared range. Furthermore, sintered samples exhibited good mechanical properties, i.e. the Vickers micro-hardness of 14.2 GPa and the fracture toughness of 1.1 MPa.m$^{1/2}$.

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