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Reactive Spark Plasma Sintering of $Y_3Al_5O_{12}$-$MgAl_2O_4$ Composites

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ABSTRACT

In this study, $Y_3Al_5O_{12}$-$MgAl_2O_4$ (YAG-Spinel) composites, with different molar ratios (1:1 and 1:3), were in-situ fabricated using Reactive Spark Plasma Sintering (RSPS) technique. To this end, Al_2O_3, MgO, and Y_2O_3 powders were used as the starting materials. In-situ formation of YAG-Spinel composites was investigated based on the reaction 3.5 Al_2O_3 + MgO + 1.5 Y_2O_3 → $Y_3Al_5O_{12}$ + $MgAl_2O_4$. Both synthesis and densification processes were accomplished using a single-cycle RSPS with one-step heating. The RSPS process was performed at a sintering temperature of 1300 °C for 30 min hold time with a maximum uniaxial pressure of 90 MPa under vacuum conditions. The synthesized phases and microstructures were investigated by X-ray diffraction and field emission scanning electron microscopy. The unwanted phases such as YAP ($YAlO_3$) in a composite microstructure were removed using LiF additive. LiF was used as a sintering aid in the process of sintering. The in-situ synthesized YAG-Spinel composites exhibited no internal infrared transmittance over the infrared wavelength ranges of 2.5-25 µm.

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1. INTRODUCTION

In recent years, infrared technology is widely used in military and civil applications, and the development of infrared transmitting materials is a requirement of this technology [1]. Optical infrared windows that can transmit infrared wavelengths well have many applications [2]. Some of the transparent ceramics used in this field include Al_2O_3, Y_2O_3, MgO, YAG, $MgAl_2O_4$ spinel, and AlON [3]. In recent years, many studies have been conducted on optically transparent ceramics such as Al_2O_3, Spinel, Y_2O_3, and YAG due to their good optical, mechanical, and thermal properties [4,5]. Most researches on transparent ceramics have focused on single phases, and only a few researches can be found on making transparent ceramic composites [4]. A ceramic composite can be made transparent if the refractive indexes of different phases very closely match each other [6]. Nevertheless, it was found that a normally translucent ceramic can be made transparent when the grain size is far less than the wavelength (one-twentieth wavelength) [4,6-8]. The first research on transparent composites pertains to the Y_2O_3-MgO system [6]. It was reported that Y_2O_3-MgO composite with a grain size of

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about 400 nm exhibited good infrared transmission. In this composite, the solubility of each phase in the other phase is quite low.

As shown, obtaining a transparent ceramic material implies sintering with a high theoretical density, very close to ≥ 99.9 %, and keeping few pores left. As a result, the sintering method gains significance in achieving this objetive [9]. RSPS is a newly developed method for obtaining fully-dense transparent ceramics at low temperatures within short-time durations. In this method, the sintering time is short due to the simultaneous formation and synthesis in one step [10].

YAG and $MgAl_2O_4$ spinel ceramics are both infrared transparent materials. In addition, both of these materials have a medium wavelength cut-off and, consequently, are used as an infrared transmission window [11,12]. An important issue may arise here, that is, 'whether YAG-Spinel composites can exhibit a transmission for an IR-wavelength'. To the best of the authors' knowledge, no published study has been carried out on the fabrication of YAG-Spinel composites. The main objecive of this study is to investigate the microstructural and optical properties of YAG-Spinel composites.

2. MATERIALS AND METHODS

Al_2O_3 (purity of 99.9 %, average particle size of 50 nm, US Research Nanomaterials, Inc.), MgO (purity of 99.9 %, average particle size of 20 nm, US Research Nanomaterials, Inc.), and Y_2O_3 (purity of 99.9 %, average particle size of 1 µm, Henan Huier Nano Technology Co.) were selected as the starting materials to prepare the YAG-Spinel composites with different compositions. The molar composition of YAG: Spinel composites was 1:1 and 1:3. Further, Al_2O_3, Y_2O_3, and MgO powder mixtures were ball milled for six hours in a polymer cup with alumina balls using ethanol as a dispersion medium. In the next step, the powder mixtures were dried in an oven at 100 °C for two hours. The dried powders were placed in a cylindrical graphite die with an inner diameter of 40 mm and consolidated into bulk specimens using the SPS system (SPS-20T-10, Easy Fashion metal products trade Co., China). The average heating rate during the SPS process was about 50 °C/min. During the SPS process, the temperature was monitored by an optical pyrometer focused on the small hole on the surface of the die. In the SPS process, a pressure of 20 MPa was initially applied to the specimen that increased to 90 MPa at the maximum temperature. The specimens were sintered at 1300 °C for 10-30 min. The specimens' codes for 1 mol % YAG-1 mol % Spinel and 1 mol % YAG-3 mol % Spinel were abbreviated as Y1S and Y3S, respectively.

The phase composition was determined by the XRD of specimens using a Philips-PW3710 operating at 40 kV and 30 mA using Cu Kα radiation (λ = 0.15406 nm). The microstructure of the gold-coated specimens was characterized by a field emission scanning electron microscope (FESEM, MIRA3 TESCAN operating at 15 kV) equipped with Energy Dispersive Spectroscopy (EDS). The in-line transmittance of the polished samples with a thickness of 1.5 mm was evaluated using Fourier-Transform Infrared Spectrometer (FTIR) (Vector 33, Bruker Bio spin Corp, USA) in the wavelength range of 2.5-25 µm.

3. RESULTS AND DISCUSSION

To prepare the Y1S composite, the mixture of Al_2O_3-MgO-Y_2O_3 powders was subjected to the SPS at 1300 °C for 15 min. The X-ray analysis of this sample shows that in addition to the spinel and YAG phases, the unreacted YAP and Y_2O_3 phases are also present in the structure (Figure 1).

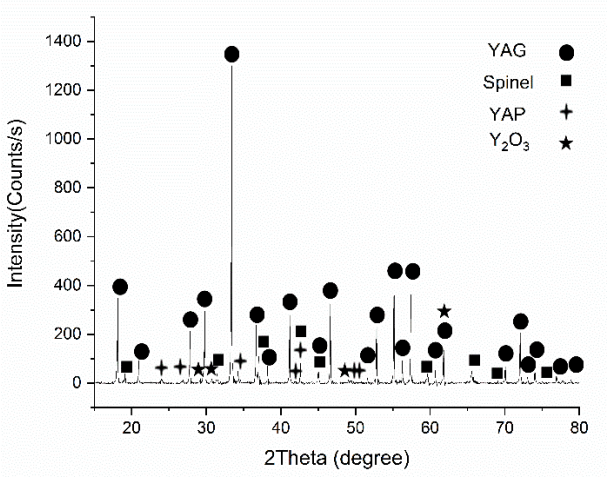

Figure 1. X-ray diffraction pattern of Y1S specimen sintered at 1300 °C for 15 min

The microstructure of the Y1S SPS-ed specimen is shown in Figure 2. The regions marked with the letters A, B, and C represent the phases Y_2O_3, YAG, and Spinel, respectively. This sample has no infrared transmission due to the presence of the YAP phase in the microstructure. Although many of the physical properties of this phase are similar to those of the YAG phase, its structure is orthorhombic and non-isotropic in terms of optical properties [13].

To prepare the Y3S composite, the mixture of Al_2O_3-MgO-Y_2O_3 powders was subjected to SPS at 1300 °C for 10 min. The microstructure of the SPS-ed sample is depicted in Figure 3. According to this figure, in addition to the YAG and Spinel phases, the unreacted YAP and Y_2O_3 phases are also present in the structure. The regions marked with A, B, C, and D represent the Spinel, YAG, Y_2O_3, and YAP phases, respectively.

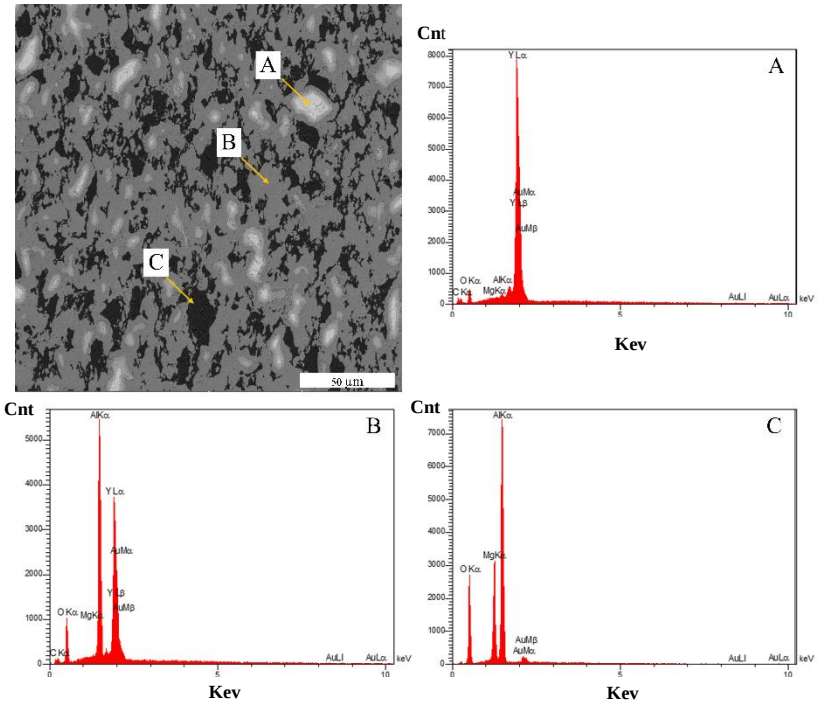

Figure 2. FESEM micrograph of the Y1S specimen sintered at 1300 °C for 15 min

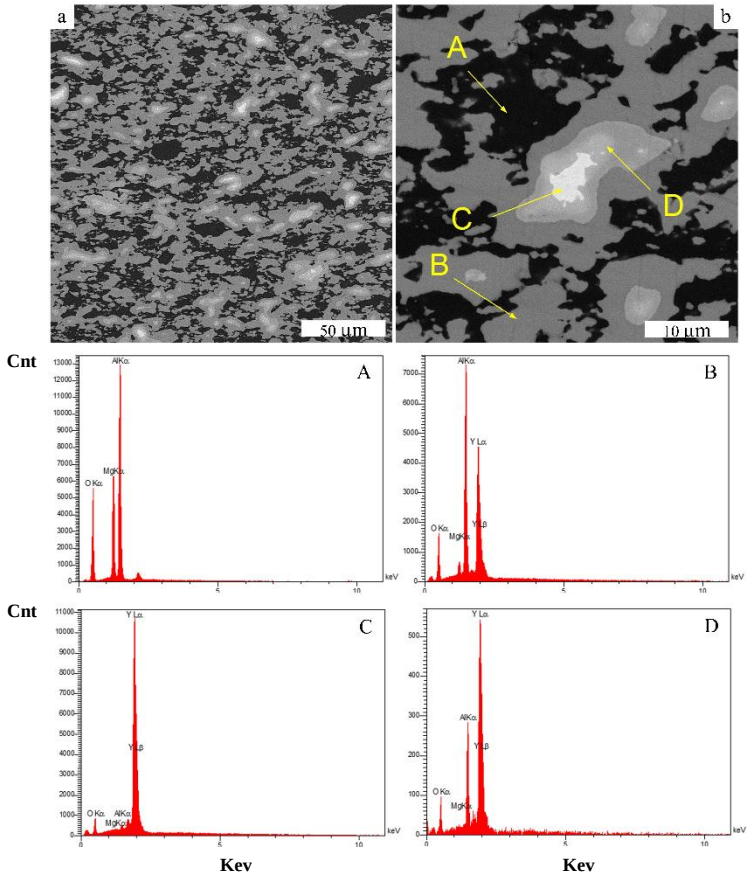

Figure 3. FESEM micrograph of the Y3S specimen sintered at 1300 °C for 10 min: (a) low and (b) high magnifications

The presence of Y_2O_3 and YAP phases in the structure indicates that the sintering time or temperature is not sufficient. In this regard, increasing the sintering time can contribute to the complete diffusion of the elements in raw materials and as a result, the target phase will be easier to consider. For this purpose, sintering time increases from 10 min to 30 min. According to the X-ray analysis of the SPS-ed sample for 30 min, the main peaks belong to the YAG and Spinel phases and the interphase peaks of YAP are visible in the spectrum (Figure 4).

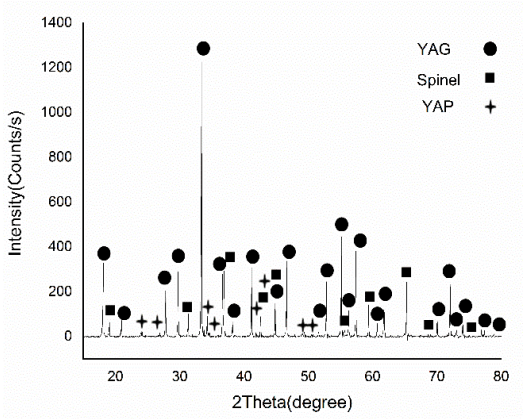

Figure 4. X-ray diffraction pattern of Y3S specimen sintered at 1300 °C for 30 min

Of note, there was no unreacted yttria in the structure, indicating that the sintering time of 10 min was not appropriate for the reaction of yttria with alumina to form the YAG and spinel phases. The annealing process at 1300 °C for 10 h as well as a temperature increase up to 50 °C did not affect the residual phase removal process of YAP and other solutions should, therefore, be considered. Until now, many researchers have used LiF as a sintering aid in the process of sintering Spinel [14-16], Y_2O_3 [17], and MgO [18], mainly because it enjoys several advantages: reducing the sintering temperature, faster diffusion of elements and thus better sintering, reducing the grain size, increasing the density of the liquid phase during sintering, and improving the optical transmittance [15,19]. In this study, 1 % wt. of LiF sintering aid was used in the mixture of initial powders, and the mixture of Al_2O_3-MgO-Y_2O_3 powders was subjected to the SPS at 1300 °C for 30 min. Temperature-Time-Displacement-Pressure behavior of this sample is shown in Figure 5. Displacement changes in the positive direction of the graph mean contraction as well as the negative direction mean sample expansion. The densification of the sample during the SPS process was evaluated based on the displacement of punch rods caused by shrinkage of the specimen. According to the figure, before reaching the approximate temperature of 500 °C, no change in displacement was observed; however, upon increasing temperature, some displacement in the positive direction was observed. The abrupt displacement of approximately 0.3 mm in the sample is indicative of the initiation of spinel synthesis. In fact, the synthesis began with the reaction of MgO and Al_2O_3, and an increase in volume during sintering is caused by the volume difference between unit cells of reactant material with spinel. During synthesis and formation of the spinel phase, volumetric expansion between 5-7 % has been reported [20]. This displacement continued up to the approximate temperature of 1050 °C, and with a gradual increase in the temperature, the displacement rate increased gradually and remained unchanged at the stable temperature of 1300 °C.

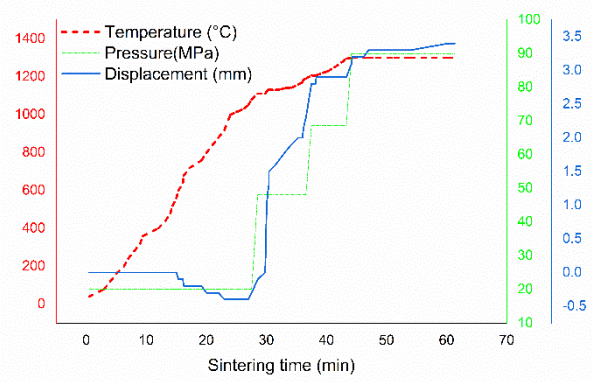

Figure 5. Temperature-time-displacement-pressure behavior during the SPS process of the Y3S specimen using LiF additive

The X-ray analysis of the sample is illustarted in Figure 6. As shown earlier, all peaks belong to the two phases of YAG and Spinel. In this case, the LiF sintering aid permeates the components faster to form the YAG and spinel phases; in other words, it performs well, leaving no residual and unwanted phases such as YAP in the sample.

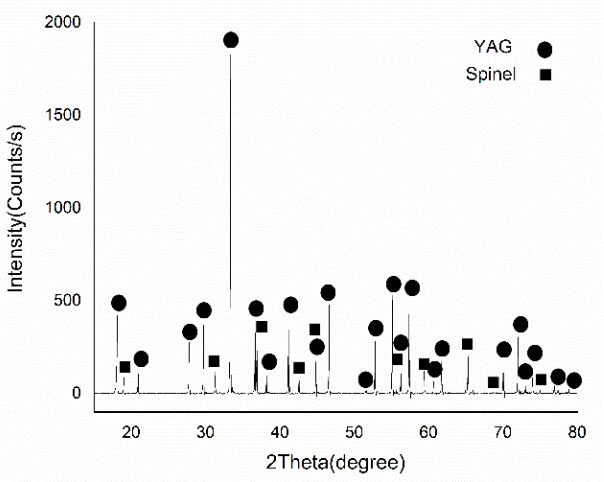

Figure 6. X-ray diffraction pattern of Y3S specimen using LiF additive sintered at 1300 °C for 30 min

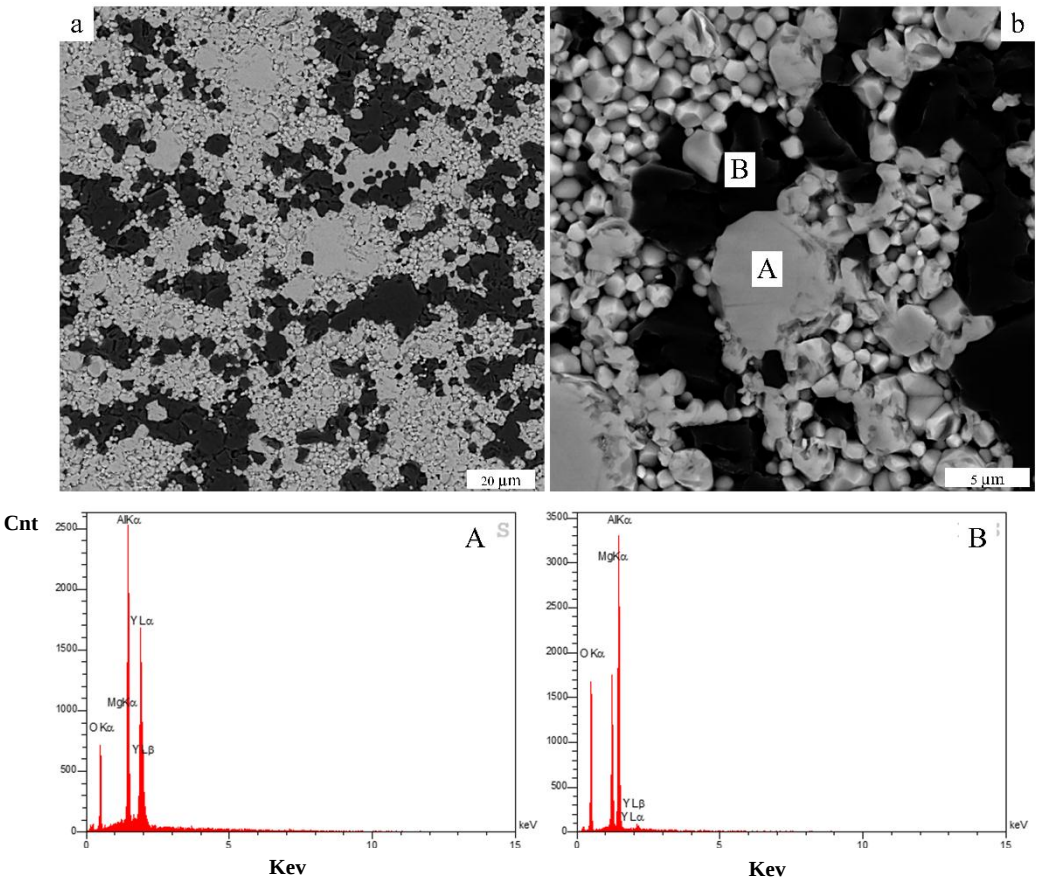

Figure7. FESEM micrograph of the Y3S specimen ,using LiF additive, sintered at 1300 °C for 30 min

Figure 6 and X'Pert HighScore Plus software (version 3.0 e, developed by PANalytical BV Company, Almelo, Netherlands) were employed to calculate the quantitative phase identification result of the YAG and Spinel based on Rietveld refinement method which were 59.13 and 40.67 wt. %, respectively. The real density value of the spark plasma sintered Y3S measured through Archimedes method was 4.087 g/cm^3, and the relative density was 99.98 %. The density value tends to approach the theoretical density (ρ_{theo}= 4.086 g/cm^3). According to the microstructure of this sample, the two phases of YAG and Spinel were the only phases shown in Figure 7 by letters A and B, respectively. Visible transparency of the sample is given in Figure 8. As observed, the sample exhibits no transparency. Figure 9. shows the in-line transmittance (T_{in}) of the sintered Y3S as a function of wavelength. Internal transmittance examination of IR waves from this sample exhibited no internal transmittance over the infrared wavelength of 2.5-25 µm. According to the findings, this transparent ceramic cannot be used as an optical mid-IR-window. Among the reasons why there is no transmittance, we can refer to the difference between the refractive indexs of two components in the composite. Refractive index for Spinel in the wavelength range of 0.35-5.5 µm is 1.7488-1.5722, and for YAG is 1.8608-1.7219 [21]. The difference between the refractive indexs of two-phase YAG and Spinel is between 0.11 and 0.15, which is significant for this composite system. However, the presence of porosity can be another reason for the lack of IR transmittance.

Figure 8. Picture of the Y3S specimen disc, 40 mm in diameter and 2 mm thick, consolidated by SPS

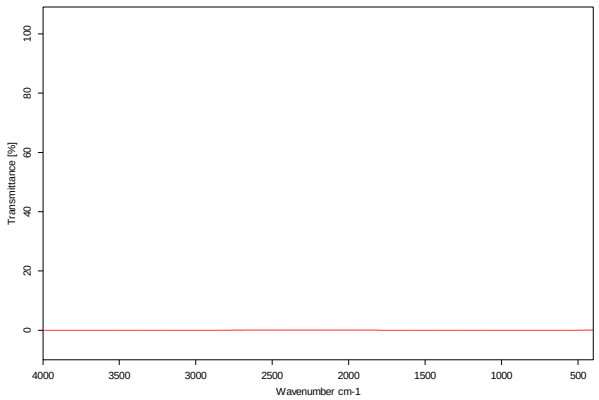

Figure 9. Optical transmission of a Y3S sample as a function of the incident light wavelength

4. CONCLUSION

In-situ synthesis and sintering of YAG-$MgAl_2O_4$ composites with molar ratios of 1:1 and 1:3 were performed using alumina-yttria-magnesia raw materials through the reactive spark plasma sintering method. The unwanted phases such as YAP in composite microstructure were removed using LiF additive in the mixture of starting materials. The results showed that two phases of YAG and Spinel, each of which revealed transparency, led to the formation of composites with no internal transmittance in the infrared wavelength range.

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