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Pressureless sintering of highly transparent AlON ceramics with $CaCO_3$ doping

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ABSTRACT

Employing $CaCO_3$ as sintering additive, highly transparent aluminum oxynitride (AlON) ceramics were pressurelessly fabricated from AlON powder at 1870 °C during150 min. The transmittance of the AlON doped with 0.3–0.4 wt% $CaCO_3$ is up to 83–85% at ~3700 nm for 2 mm thickness samples, and their transmittances are consistently higher than that of the AlON doped with the ideal amount of Y_2O_3 at wavelength ranging from 200 nm to 6000 nm. The AlON doped with $CaCO_3$ exhibits the transmittance of 71% at 4800 nm (typical band for infrared targeting), which is higher by 6% than that of the doped Y_2O_3.

Transparent aluminum oxynitride (AlON) ceramics are one of the most promising transparent ceramic materials for infrared/visible windows used in severe environments, such as high temperature, abrasion, corrosion, etc., due to their excellent optical transparency properties, high strength and hardness, and good chemical inertness [1–4]. AlON ceramics can be sintered by pressureless sintering, hot pressing sintering, hot isostatic pressing, spark plasma sintering, etc. [5–8]. Among those methods, pressureless sintering is a preferred technology due to its significant advantage in fabricating large size and complicated components.

Generally, sintering additive is always required to fabricate transparent AlON ceramics. Currently, Y_2O_3, La_2O_3 and MgO have been chosen as sintering additives to accelerate the densification process of AlON ceramics [5,9–13]. Among these additives, Y^{3+} is believed to enhance the mobility of grain boundaries and accelerate grain growth, and 0.5 wt% Y_2O_3 was reported to be the ideal doping amount to obtain AlON ceramics with high transparency [9,14]. At the same time, La^{3+} and Mg^{2+} can inhibit the abnormal grains growth [9,13,15]. Consequently, La_2O_3 and MgO are usually selected as grain growth inhibiters to co-dope with Y_2O_3 to fabricate transparent AlON ceramics [13,15]. It is commonly recognized that high densification and reducing the amount of scattering and refracting sources are all a must to ensure the optical quality of fabricated AlON ceramics. To further improve the properties of transparent AlON ceramics, it is necessary to find more sintering additive candidates.

Recently, it was reported that proper amount of CaO dopant can promote densification and grain growth of $MgO\cdot1.5Al_2O_3$ and YAG ceramics at a suitable sintering temperature [16,17]. It is understandable that it is Ca^{2+} that is being used as dopant for fabrication of $MgO\cdot1.5Al_2O_3$ and YAG ceramics, which implies that it is highly possible that Ca^{2+} can also induce positive properties in the densification process of AlON ceramics. It is well known that CaO is easy to react with H_2O to form $Ca(OH)_2$ at room temperature, which means a non-ignorable small amount of $Ca(OH)_2$ may exist in CaO additive during fabrication process. This $Ca(OH)_2$ is decomposed into CaO and H_2O at ~1200 °C, where H_2O is incompatible with sintering furnace environment. To avoid the risk induced by unexpected H_2O, $CaCO_3$ was mixed with AlON powder to fabricate transparent AlON ceramics in this study. As a matter of fact, $CaCO_3$ decomposes into CaO and CO_2 at ~825 °C. More importantly, the decomposition temperature of $CaCO_3$ is much lower than the starting temperature of AlON ceramics sintering (~1300 °C) [6]. Therefore, it is still CaO that is employed to be a sintering additive, i.e., Ca^{2+} is being used as a dopant for sintering AlON ceramics.

Table 1
Effects of doping amount of $CaCO_3$ on the relative density of AlON ceramics.

Doping amount of $CaCO_3$ (wt%)	0.2	0.3	0.4	0.5
Relative density (%)	99.70	99.92	99.94	99.62

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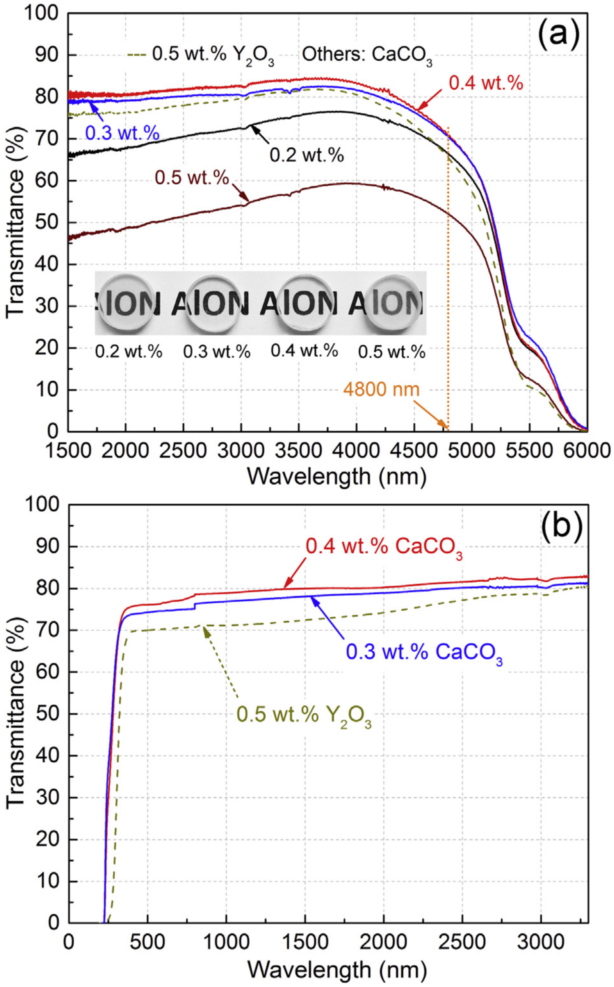

Fig. 1. Transmittance of the transparent AlON ceramics doped with 0.2–0.5 wt% $CaCO_3$ and 0.5 wt% Y_2O_3 at 1500–6000 nm (a), doped with 0.4 wt% $CaCO_3$ and 0.5 wt% Y_2O_3 at 190–3300 nm (b). Insert: photographs of AlON ceramics doped with 0.2–0.5 wt% $CaCO_3$.

The pure AlON powder was firstly synthesized by carbothermal reduction and nitridation (CRN) method (detailed fabrication process is described in Ref. [18]), then 0.2 wt%, 0.3 wt%, 0.4 wt% and 0.5 wt% $CaCO_3$ (99.99%; Macklin, China) were added into the obtained AlON powder, respectively. Using Si_3N_4 ball as milling media, mixture of the powders of AlON and $CaCO_3$ were grinded in absolute ethyl alcohol at 170 rpm for 24 h. The obtained slurry was fully dried and sieved to obtain the starting mixed powder. Then, 1.4 g of mixed AlON powder was packed into pellets of 13 mm in diameter under 50 MPa. The pellets were pressureless sintered within a graphite furnace in an atmosphere of 0.1 MPa N_2. All samples were heated to 1870 °C at a heating rate of 40 °C/min, the heating system was shut down after holding for 150 min. The sintered specimens were then grinded and polished at both sides to a thickness of 2 mm for the optical transmittance measurement.

The phase assemblage of the sintered samples was characterized by X-ray diffractometry (XRD; D/Max-ULtima1, Rigaku, Tokyo, Japan) using Co $K_{\alpha 1}$ radiation. The microstructure of the sintered samples was observed by field-emission scanning electron microscopy (FESEM; supra 55, Zeiss, Jena, Germany). Micrograph observation of the polished samples hot etched at 1640 °C for 40 min was performed using a metallurgical microscope (GX51, OLYMPUS, Japan). The grain area and the average grain size of AlON were statistically calculated, where the average grain size was proportional to the average value of diameters passing through the objects' centroid. Then, based on the calculated average grain size, the grain number was counted for every 36 μm as a group to analyze the grain size distribution. The bulk density of the sintered samples was measured by the Archimedes method. Optical transmittance of the samples in the wave range of 1500–6000 nm was recorded by the Fourier transform infrared spectroscopy (FTIR; Frontier, PE, USA). The transmittance of AlON ceramics at the wave range of 190–3300 nm was measured with a spectrophotometer (Cary 5000, Varian, USA).

The XRD pattern of all the samples after holding for 150 min at 1870 °C showed that only the AlON crystalline phase was detected. The absence of secondary phases means that the AlON grains were below its solubility limit [12]. Relative densities of all the sintered samples measured by the Archimedes principle are ≥99.62%, as listed in Table 1. It indicates that the AlON powder was fast densified to achieve a high

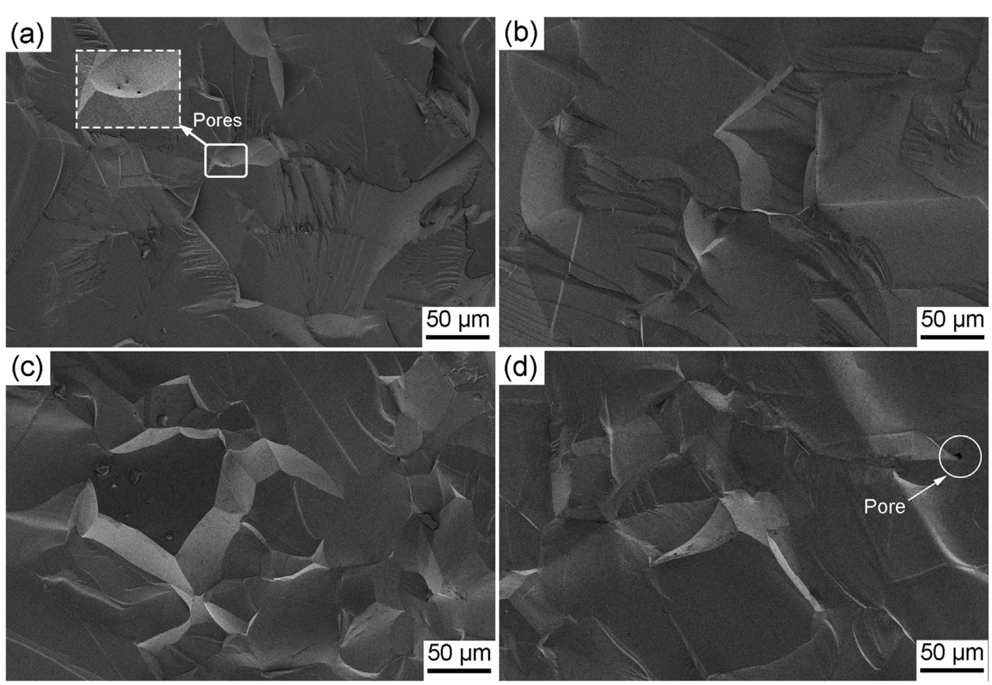

Fig. 2. SEM images of the fracture surfaces of the AlON ceramics with $CaCO_3$ doping: (a) 0.2 wt%, (b) 0.3 wt%, (c) 0.4 wt% and (d) 0.5 wt%.