

Effect of Y_2O_3 , La_2O_3 and MgO Co-Doping on Densification, Microstructure and Properties of ALON Ceramics

J. Zhang¹, J. Lei^{1, 2}, Y. Shi^{*1}, J. Xie¹, F. Lei¹, L. Zhang¹

¹Department of Electronics and Information Materials, School of Material Science and Engineering, Shanghai University, Shanghai 200444, China

²Ceramic Department, Shanghai FRP Research Institute Co.Ltd., Shanghai 201404, China

received December 6, 2016; received in revised form January 29, 2017; accepted February 10, 2017

Abstract

The densification of transparent ALON ceramics was investigated with the aid of Y_2O_3 , La_2O_3 and MgO as sintering agents. It was found that the density of the ALON ceramics obtained after co-doping with Y_2O_3 and La_2O_3 could be further improved with the addition of a small amount of MgO . The relative density of the ALON ceramic reached 99.9 % when it was co-doped with 0.08 wt% Y_2O_3 + 0.02 wt% La_2O_3 + 0.2 wt% MgO after undergoing pressureless sintering at 1900 °C for 24 h. It is argued that Y^{3+} and Mg^{2+} can decelerate grain boundary mobility, suppress grain growth and promote the elimination of pores.

Keywords: Transparent γ -ALON ceramics, pressureless sintering, co-doping

I. Introduction

Cubic-structured spinel aluminum oxynitride (γ -ALON) exhibits superior optical, chemical and mechanical properties. Thanks to its outstanding and comprehensive performance, ALON transparent ceramic is considered a most promising optical material for military and commercial applications (e.g. windows, domes and transparent armors) ^{1,2}.

It has been established that various microstructural sites in ceramics scatter light; these include grain boundaries, impurities and residual pores within grains and at grain boundaries ³. It is suggested that the residual pores are the main factor impairing the transparency of optical ceramics. Those pores resulting from the sintering of ALON ceramics can be reduced and eliminated with the introduction of a small amount of rare earth oxide sintering aids, such as Y_2O_3 , La_2O_3 and MgO ^{4–7}. Mg^{2+} has a similar ionic radius to that of Al^{3+} in ALON (ionic radii are 0.65 and 0.50 Å for Mg^{2+} and Al^{3+} , respectively), Y^{3+} and La^{3+} have the same quantivalence as Al^{3+} . Jun Wang *et al.* obtained ALON ceramics co-doped with 0.12 wt% Y_2O_3 and 0.09 wt% La_2O_3 with a relative density over 99 %, the in-line optical transmittance at four microns being up to 80.3 %. The mechanism by which the dopants influence the densification of ALON ceramics has also been discussed ⁸. It was confirmed by X Li *et al.* ⁹ that the microstructure of γ -ALON ceramics is further densified by means of doping with Y_2O_3 . Shen Qi *et al.* investigated the influence of Y_2O_3 and MgO additions on the grain size and residual porosity of ALON ceramics. When 0.02 wt% MgO and 0.16 wt% Y_2O_3 are added, the resulting grain size and porosity are finer and less than

that of pure ALON ceramics ¹⁰. Furthermore, MgO as a raw material for MgALON has been researched in previous papers ^{11–12}. However, the effect of co-doping of MgO combined with Y_2O_3 and La_2O_3 on the densification of ALON ceramics has received limited attention.

In this study, single-phase ALON powders with sub-micron particle size for pressureless sintering of ceramics were synthesized by means of carbothermal reduction and nitridation. The effects of the MgO concentration (range of 0.05–0.3 wt%), Y_2O_3 and La_2O_3 on ALON densification and transparency were investigated. The grain boundaries of ALON co-doped with 0.08 wt% Y_2O_3 , 0.02 wt% La_2O_3 and 0.2 wt% MgO were observed by means of high-resolution transmission electron microscopy.

II. Experimental Procedure

Monophase γ -ALON powders were prepared from γ - Al_2O_3 (> 99 %, 0.01 μm , M-100, Shanghai Fenghe Ceramic Co. Ltd, China) and micron carbon powders (> 97 %, 1.679 μm , Shanghai CABOT Chemical Co. Ltd, China) with the carbothermal reduction and nitridation (CRN) method. 5.6 wt% micron carbon powders and 94.4 wt% γ - Al_2O_3 were mixed in ethanol by means of high-energy ball milling for 1 h. After being dried and passed through a 60-mesh sieve, ALON powders were synthesized by calcinating the $\text{Al}_2\text{O}_3/\text{C}$ mixture precursor in an alumina crucible at 1750 °C for 2 h in a flowing N_2 atmosphere. The as-synthesized powders were then calcined at 750 °C in air for 10 h to remove possible carbon residue.

MgO , Y_2O_3 and La_2O_3 (these three reagents were all from Sinopharm Chemical Reagent Co. Ltd, Shanghai, China) were chosen as sintering aids for addition to the ALON powders. The un-doped and doped synthet-

* Corresponding author: yshi@shu.edu.cn

ic AlON powders were milled with absolute ethyl alcohol by means of high-energy ball milling for 1 h. The weight ratio of alumina balls to powder was 10:1. The slurry was dried at 60 °C and screened through a 80-mesh sieve to obtain ultrafine powders. The as-prepared powders were subsequently pressed uniaxially into pellets at 2 MPa and cold-isostatically-pressed at 200 MPa for 2 min. To remove organic matter, the AlON green body pellets were calcined at 700 °C in air. The samples were placed in a BN crucible, embedded in AlON and BN mixture to undergo pressureless sintering at 1900 °C for 24 h in a flowing N₂ atmosphere. Finally, the sintered AlON samples were ground and polished on both sides to the thickness of 1 mm.

A laser diffraction particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd, UK) was employed to determine the particle size distribution and the specific surface areas of the high-energy-milled AlON powders. The morphology of the synthetic powders was directly observed using a field-emission scanning electron microscopy (FESEM, JSM-6700F, JOEL Ltd. Tokyo, Japan). Densities of sintered compacts were determined according to the Archimedes principle. In-line optical transmittance of the polished samples were measured using a UV-VIS spectrophotometer (UV-2501PC, Hitachi, Japan) in the wavelength range from 200 to 900 nm. The morphology of fracture surfaces of the sintered samples were observed with a Phillips XL 30 scanning electron microscope. HRTEM (High Resolution Transmission Electron Microscopy, 200keV, Tecnai G2 F20, FEI, USA) and HRTEM-EDS (Energy-Dispersive Spectroscopy) were performed on the ultra-thin AlON compact prepared by cutting, polishing, dimpling and argon ion-milling.

III. Results and Discussion

(1) The morphology of the AlON powders after ball-milling

Fig. 1 shows the scanning electron micrograph of high-energy-milled AlON powders with irregular shape and submicron particle size. As shown in Fig. 2, the particle size of the milled AlON powders exhibited a typical particle trimodal distribution, and the value of mean particle size decreased from 57.289 μm to 0.717 μm , the specific surface areas increased from 0.233 m^2/g to 12.600 m^2/g . High-energy ball milling is an effective way to refine particle size and enhance the sintering activity of AlON powders.

(2) Effect of dopants on the microstructure and densification of AlON

The sintering-aid-dependent fracture microstructures of AlON samples sintered at 1900 °C for 24 h are shown in Fig. 3. The AlON sample without sintering additives had small amounts of residual pores (marked by circles) located in the region of grains and boundary (Fig. 3(a)). The diameter of residual pores is observed to be around 1 micrometer. Fig. 3(b) shows the smaller grain size (around 20 μm) of the AlON sample doped with 0.08 wt% Y₂O₃, pores could hardly be seen. It indicates Y³⁺ can decelerate grain boundary mobility, suppress grain growth and

promote the elimination of pores. As shown in Fig. 3(c), unfortunately, there were many closed pores in the AlON sample doped with 0.08 wt% Y₂O₃ and 0.02 wt% La₂O₃, which indicates that La³⁺ has a negative effect on the elimination of pores during the sintering process. This result is inconsistent with the research results by Fang *et al.*¹³ that Y₂O₃ and La₂O₃ segregate to the alumina grain boundaries and reduce the coarsening and densification rate, promoting the density of alumina ceramics. Compared with Fig. 3(d), residual pores were eliminated with the addition of Mg ions.

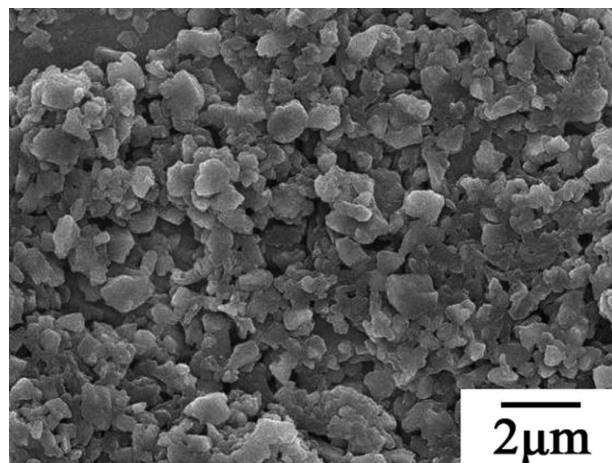


Fig. 1: Scanning electron micrographs of high-energy-milled AlON powders.

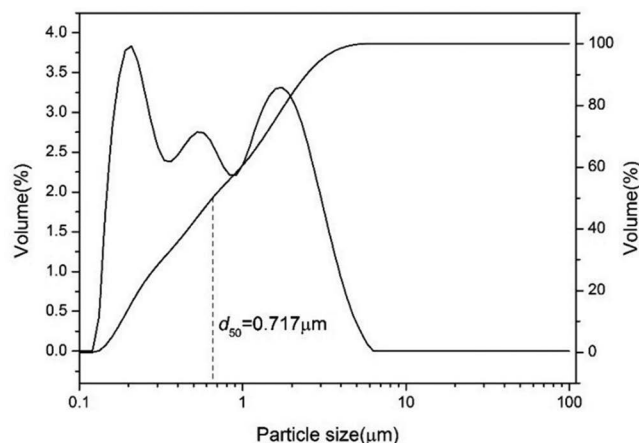


Fig. 2: Particle size distribution of high-energy-milled AlON powders.

Relative densities of AlON ceramics sintered at 1900 °C for 24 h with different sintering aids are listed in Table 1. The results are in good agreement with SEM observation of ceramics fracture surfaces. AlON ceramics with finer grain size and lower porosity were obtained by doping 0.08 wt% Y₂O₃ or 0.08 wt% Y₂O₃ + 0.02 wt% La₂O₃ + 0.1 wt% MgO. The density of 0.08 wt% Y₂O₃ + 0.02 wt% La₂O₃ + 0.1 wt% MgO co-doped AlON ceramics attained 99.7 % of theoretical density.

Light transmittance is one of the main parameters for evaluating the optical properties of AlON ceramics. Fig. 4 illustrates the in-line optical transmittance curve of the doped AlON samples sintered at 1900 °C for 24 h. The data of the sample with no additive is also displayed. Com-

pared with Table 1, the transmittance increased with increasing density of ALON compact. The in-line optical transmittance of ALON ceramics with 0.08 wt% Y_2O_3 + 0.02 wt% La_2O_3 + 0.1 wt% MgO additive reach 55 % at 900 nm, whereas the ALON ceramics without any sintering additives only attain 25 % at 900 nm.

Table 1: Relative density of ALON ceramics sintered at 1900 °C for 24 h with different sintering aids. The results were expressed as the mean $\pm$ SD.

Sintering additives	Relative density (%)
no additive	99.2 $\pm$ 0.3
0.08 wt% Y_2O_3	99.5 $\pm$ 0.4
0.08 wt% Y_2O_3 + 0.02 wt% La_2O_3	98.6 $\pm$ 0.5
0.08 wt% Y_2O_3 + 0.02 wt% La_2O_3 + 0.1 wt% MgO	99.7 $\pm$ 0.2

(3) Effect of MgO concentration on densification of Y-La-Mg co-doped ALON ceramics

Fig. 5 shows the relative density and in-line optical transmittance of ALON doped with 0.08 wt% Y_2O_3 + 0.02 wt% La_2O_3 and different concentration of MgO. The relative density of ALON was increased from 98.9 % to the peak value of 99.9 % as the MgO concentration were

raised from 0.05 wt% to 0.2 wt%. However, the relative density of ALON dropped to approx. 99.3 % as the MgO concentration increased further to 0.3 wt%. Bruke^{14,15} suggested a mechanism to explain the role of MgO during the LucaloxTM (pore-free aluminum oxide ceramic by GE company) sintering process. Mg^{2+} inhibited grain boundary dissolution and grain growth, decelerated grain boundary migration, prevented the separation of pores and grain boundaries, which resulted in a full elimination of pores.

(4) HRTEM observation of Y-La-Mg co-doped ALON grain boundary

Optical scattering of polycrystalline ALON ceramics can be reduced significantly by minimizing grain boundary defects. Doping even very low levels of additives may cause grain boundary enrichment. Measured by Lior Miller and Wayne D. Kaplan¹⁶, the solubility limits of Y, La and Mg in ALON were respectively 1775 ± 128 ppm, 498 ± 82 ppm and over 4000 ppm. Fig. 6 shows a transmission electron micrograph of ALON sample co-doped with 0.08 wt% Y_2O_3 + 0.02 wt% La_2O_3 + 0.2 wt% MgO. The inset is a high-magnification lattice image of a grain boundary between adjacent ALON grains. The (111) and the (200) lattice planes in each ALON grain were connected to the grain boundary, demonstrating that the grain boundary in ALON with 0.08 wt% Y_2O_3 + 0.02 wt% La_2O_3 + 0.2 wt% MgO is very clear, no amorphous phase or second phase was observed along the boundary.

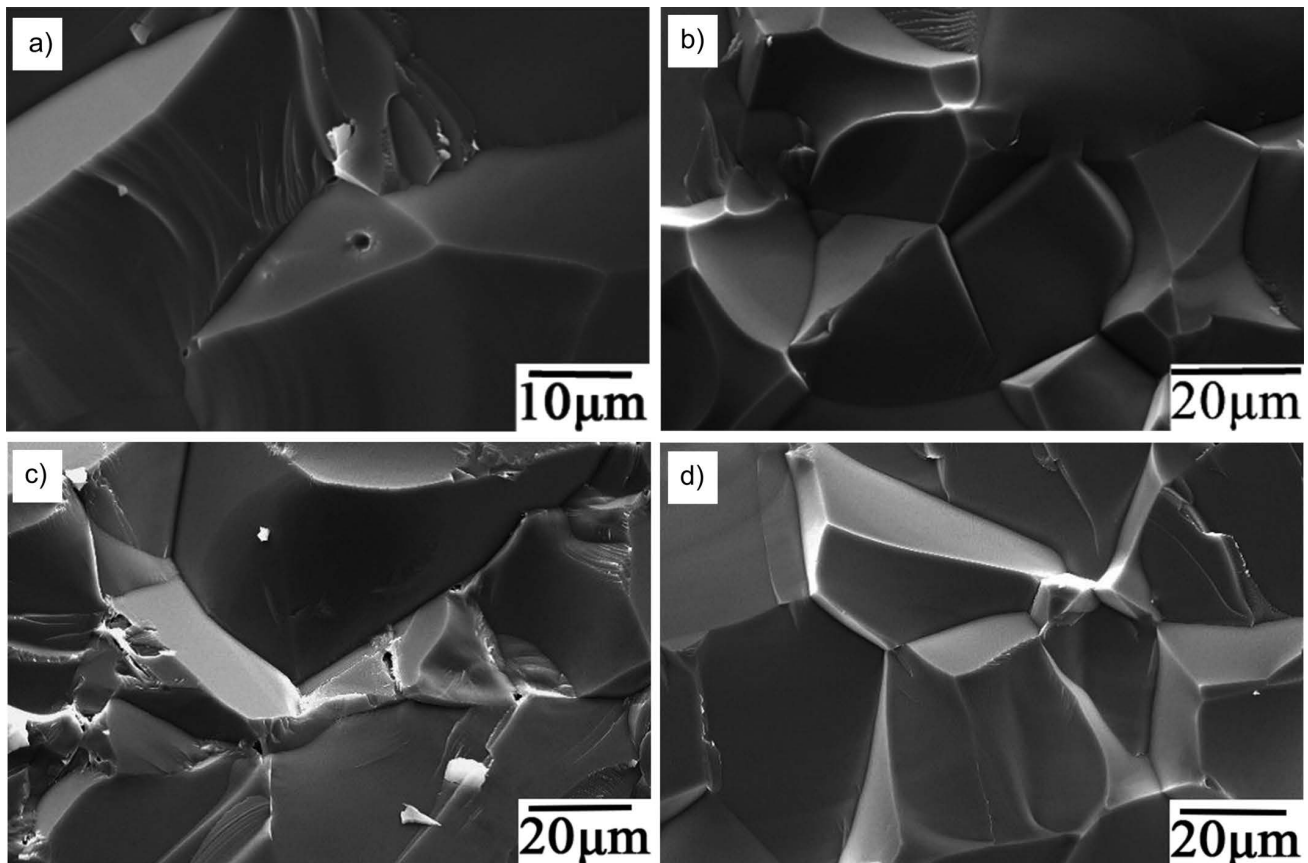


Fig. 3: Microstructures of the fracture surface of ALON ceramics sintered at 1900 °C for 24 h with different sintering aids: (a) no additive (b) 0.08 wt% Y_2O_3 (c) 0.08 wt% Y_2O_3 + 0.02 wt% La_2O_3 (d) 0.08 wt% Y_2O_3 + 0.02 wt% La_2O_3 + 0.1 wt% MgO.

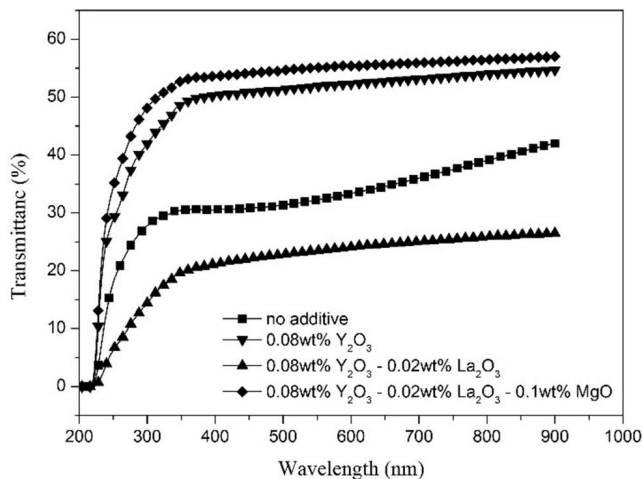


Fig. 4: The in-line transmittance spectra of the un-doped and doped ALON samples.

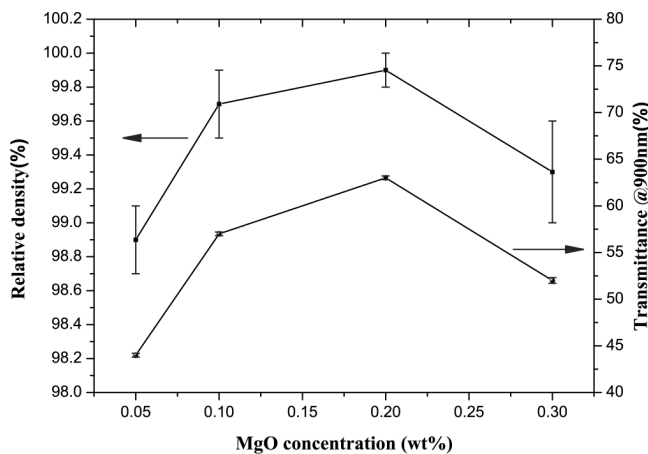


Fig. 5: Effect of MgO concentration on the relative density and in-line transmittance of ALON ceramics. All samples were sintered at 1900 °C for 24 h. Data of the relative density are shown as mean $\pm$ SD.

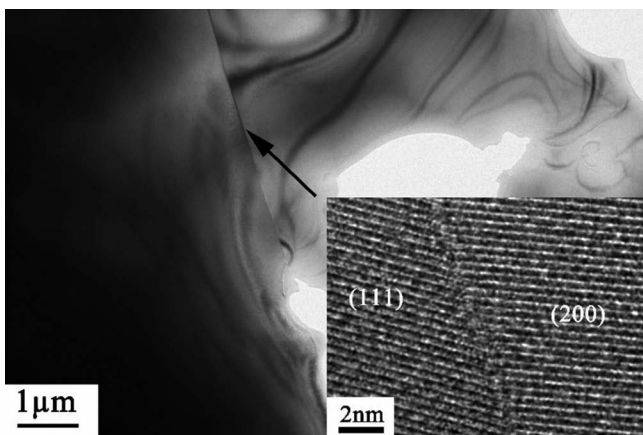


Fig. 6: Transmission electron micrograph of the grain boundary between adjacent grains. Insert: High-magnification lattice image of the selected area.

Fig. 7 shows EDS spectra obtained from the grain boundary in 0.08 wt% Y_2O_3 + 0.02 wt% La_2O_3 + 0.2 wt% MgO co-doped ALON. No lanthanum, yttrium or magnesium

was detected at the grain boundary, indicating that no second phase or rare earth sintering additives existed in the region of grain boundary after densification. It is implied that three sintering additives we chose could form a solid solution with the ALON phase and enhance the densification of ALON effectively.

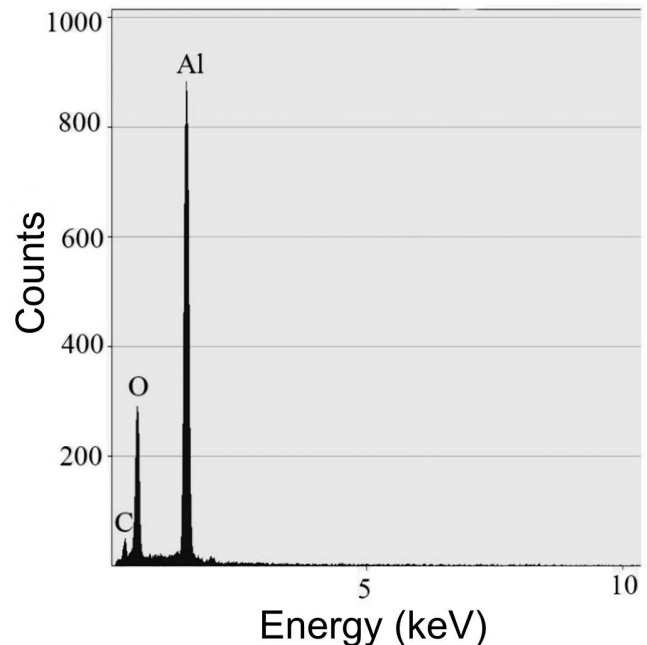


Fig. 7: EDS spectra of the grain boundary of ALON co-doped with 0.08 wt% Y_2O_3 + 0.02 wt% La_2O_3 + 0.2 wt% MgO.

IV. Conclusions

The relative density of sintered ALON ceramic reached approx. 99.9 % when co-doped with 0.08 wt% Y_2O_3 , 0.02 wt% La_2O_3 and 0.2 wt% MgO with pressureless sintering under 1900 °C for 24 h. Meanwhile, the in-line optical transmittance of ALON ceramics reaches 63 % at 900 nm. HREM observation proved that no second phase existed in the region of grain boundary. Y^{3+} and Mg^{2+} can decelerate grain boundary mobility, suppress grain growth and promote the elimination of pores.

Acknowledgement

This work is supported by National Science Foundation of China under Grant No. 61475097.

References

- Corbin, N.D.: Aluminum oxynitride spinel: a review, *J. Eur. Ceram. Soc.*, **5**, 143–154, (2009).
- Wahl, J.M., Hartnett, T.M., Goldman, L.M.: Recent advances in ALON optical ceramic. In: Window and Dome Technologies and Materials IX. Orlando, Florida, 2005.
- Ikesue, A., Aung, Y.L.: Ceramic laser materials, *Nat. Photonics*, **2**, 721–727, (2008).
- Martin, C., Cales, B.: Synthesis and hot pressing of transparent aluminum oxynitride. In: Window and Dome Technologies and Materials. Orlando, Florida, 1989.
- Cheng, J., Agrawal, D., Zhang, Y., Roy, R.: Microwave reactive sintering to fully transparent aluminum oxynitride (ALON) ceramics, *J. Mater. Sci. Lett.*, **20**, 77–79, (2001).

- ⁶ Maguire, E.A., Hartnett, T.M., Gentilman, R.L.: Method of producing aluminum oxynitride having improved optical characteristics. U.S. Patent Application 4,686,070, (1987).
- ⁷ Chen, F., Zhang, F., Wang, J., Zhang, H.L., Tian, R., Zhang, Z., Wang, S.W.: Hot isostatic pressing of transparent ALON ceramics with Y_2O_3/La_2O_3 additives, *J. Alloy. Compd.*, **650**, 753–757, (2015).
- ⁸ Wang, J., Zhang, F., Chen, F., Zhang, J., Zhang, H.L., Tian, R., Wang, Z.J., Liu, J., Zhang, Z., Chen, S., Wang, S.W.: Effect of Y_2O_3 and La_2O_3 on the sinterability of γ -ALON transparent ceramics, *J. Eur. Ceram. Soc.*, **35**, 23–28, (2015).
- ⁹ Li, X., Lu, J., Feng, Z.: Microstructural characteristics and oxidation behavior of Y_2O_3 -doped γ -ALON, *J. Mater. Sci.*, **50**, 7097–7103, (2015).
- ¹⁰ Qi, S., Mao, X., Chai, B.: Reaction sintering of transparent aluminum oxynitride (ALON) ceramics using MgO and Y_2O_3 as co-additives, *Key Eng. Mater.*, **697**, 7–11, (2016).
- ¹¹ Dai, W., Yamaguchi, A., Lin, W.: Oxidation behavior of magnesium aluminum oxynitride with different composition, *J. Ceram. Soc. Jpn.*, **115**, 409–413, (2007).
- ¹² Liu, X., Wang, H., Tu, B.: Highly transparent $Mg_{0.27}Al_{2.58}O_{3.73}N_{0.27}$ ceramic prepared by pressureless sintering, *J. Am. Ceram. Soc.*, **97**, 63–66, (2014).
- ¹³ Fang, J., Thompson, A.M., Harmer, M.P.: Effect of yttrium and lanthanum on the final-stage sintering behavior of ultrahigh-purity alumina, *J. Am. Ceram. Soc.*, **80**, 2005–2012, (1997).
- ¹⁴ Burke, J.E.: Control of grain boundary mobility. In: Symposium on Sintering of Advanced Ceramics Cincinnati, Ohio, 1988.
- ¹⁵ Burke, J.E.: Lucalox alumina.: Lucalox alumina: the ceramic that revolutionized outdoor lighting, *MRS Bulletin*, **21**, 61–68, (1996).
- ¹⁶ Miller, L., Kaplan, W.D.: Solubility limits of La and Y in aluminum oxynitride at 1870 °C, *J. Am. Chem. Soc.*, **91**, 1693–1696, (2008).

