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Short communication

The effect of non-stoichiometry on microstructure and selected properties of YAG polycrystals

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Abstract

Using modified citrate process three materials were prepared: the one of stoichiometric Al/Y ratio corresponding to YAG composition, another one with aluminum deficit and the third one containing surplus amount of aluminum. Typical microstructure of single-phase body reveals stoichiometric material. The one of aluminum deficit shows YAP inter-crystalline inclusions. Material of Al/Y ratio higher than the YAG stoichiometry shows inter/intra α-Al_2O_3 inclusions. Stoichiometry of the system influences mechanical properties of the material.

Keywords: YAG polycrystals; Non-stoichiometry; Microstructure

1. Introduction

In the Al_2O_3–Y_2O_3 system, apart from the end-member phases, three compounds stable at room temperature are known: $Y_3Al_5O_{12}$ (YAG), $YAlO_3$ (YAP), and $Y_2Al_4O_9$ (YAM). Yttrium-aluminum garnet (YAG) has received much attention because of its interesting optical and mechanical properties. Rare-earth doped YAG single crystals have been used as a laser host material. Attempts to synthesize polycrystalline transparent YAG ceramics for laser application have been reported in [1–3]. Another application of rare-earth doped YAG in the powder form as phosphor for displays, due to its good stability to high electron irradiation, should be mentioned [4]. High temperature creep resistance is an attractive YAG property. A study presented in [5] revealed that creep rate of polycrystalline YAG at 1400 °C is three times slower than that of alumina.

The factor of utmost importance for the properties of the final material is stoichiometry of the starting powder. Aim of the present study was to find the effect of Y/Al ratio discrepancy from the YAG composition on the sintered material microstructure and selected mechanical properties.

2. Experimental

The starting powders were prepared according to the modified citrate process elaborated by us [6]. So it is sufficient here to show only basic steps of the process. Aluminum nitrate of analytical quality and yttria (4 N) were used. Yttria was dissolved in nitric acid (1:1) of analytical purity. The solution was added to the aluminum nitrate aqueous solution. Mutual solution of both nitrates was treated with citric acid and 2-propanol in the proportion of 5 mole of both additives per 1 mole of (Al + Y). Drying of this solution and thermal treatment at 300 °C for 0.5 h resulted in a stiff body. By this method three compositions were prepared; one of stoichiometric Y/Al ratio, another one showing 5% Al deficit and third one of Al content higher by 5% compared to the YAG stoichiometry. Each sample was calcined at 900 °C for 1 h in air atmosphere. The resulting powders were uniaxially compacted under 250 MPa. Disc samples of 8 mm diameter and about 3 mm thickness were sintered in air atmosphere at 1700 °C for 5 h.

The X-ray diffraction (CuK_1 radiation, X'PertPro, Panalytical) was used to determine phase composition of the samples. Their Vickers hardness was measured using Future Tech (Japan) equipment and 3 kgf load. Higher load of 10 kgf allowed us to determine fracture toughness (K_{Ic}) with Palmqvist cracks and Niihara relation [7]. Apparent densities were determined by the hydrostatic weighing technique.

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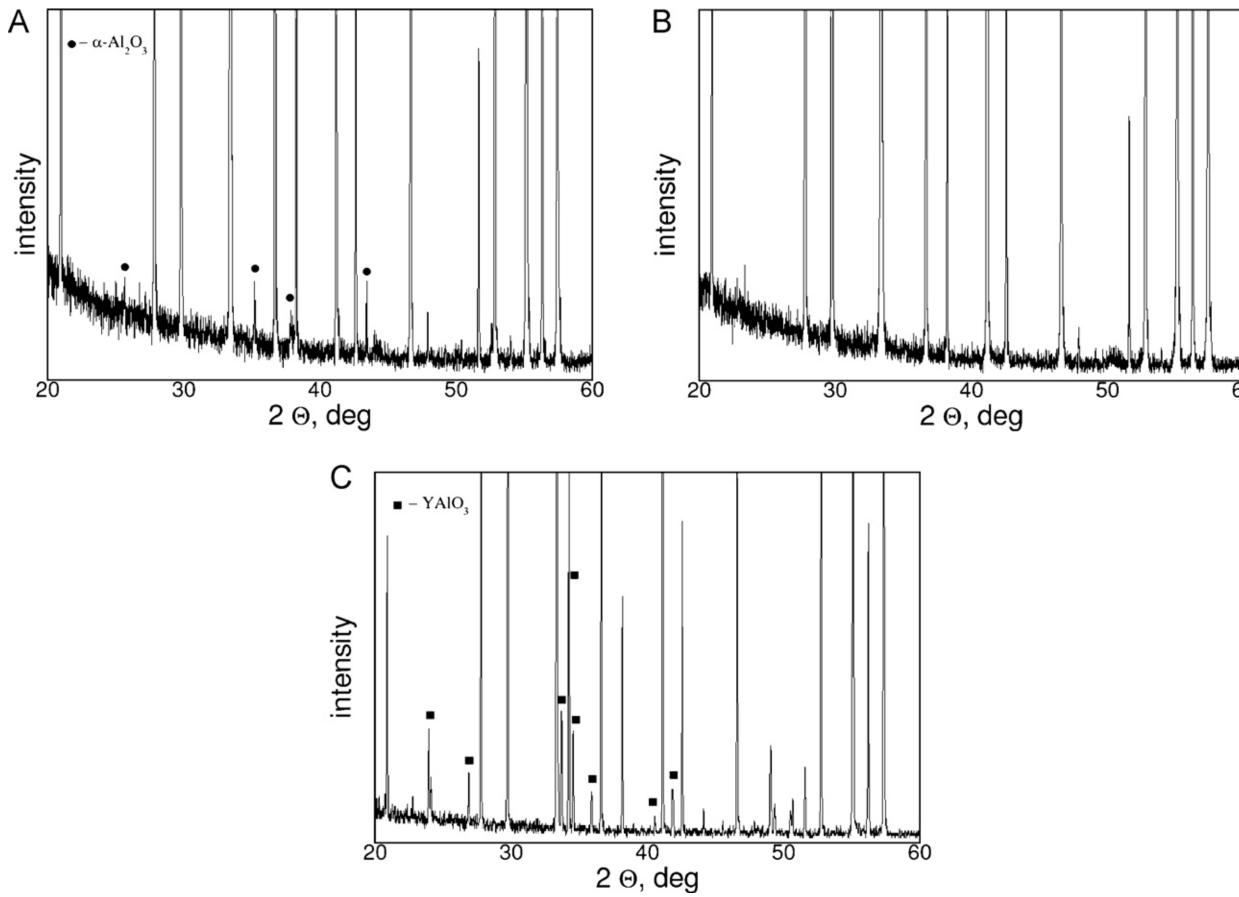

Fig. 1. X-ray diffraction patterns of the materials. CuKα irradiation. (A) Sample "+5%"; (B) sample "O"; (C) sample "−5%".

3. Results and discussion

Fig. 1 shows diffraction patterns of the samples. The one of stoichiometric composition (designed "0") shows YAG as the only component. Samples of Al deficit (designed −5%), except of YAG, shows also presence of $YAlO_3$ *of hexagonal symmetry* (h-YAP). Material with surplus amount of Al (designed +5%) demonstrates presence of α-Al_2O_3. Phase compositions of the materials differing from stoichiometry agree with the phase diagram of the Y_2O_3–Al_2O_3 system [8] confirmed later by the neutron diffraction [9].

Basing of the known chemical compositions of the materials under study fractions of h-YAP and α-Al_2O_3 were assessed. It was assumed that in the +5% material surplus aluminum amount results in the α-Al_2O_3 formation and hence its fraction corresponds to 4.12 weight%. In the −5% material surplus yttrium leads to the 3.85 weight% YAP crystallization. Assuming YAG, YAP and α-Al_2O_3 densities of 4.55, 5.55 and 3.99 g/cm^3, respectively physical densities of +5% and −5% should be equal to 4.52 and 4.58 g/cm^3, respectively. These values were applied to calculate relative densities of the sintered materials. Results are summarized in Table 1 together with hardness and fracture toughness of the materials.

Fig. 2 shows the microstructures of the materials. They differ substantially from each other. Material of the stoichiometric composition (0) shows typical microstructure of the single-phase ceramic. Inter-granular inclusions of YAP occur in the sample −5% and inter/intra α-Al_2O_3 inclusions are observed in the +5% material. Identification of inclusion phases is corroborated by the shown chemical EDS analyses at indicated points. Limited resolution of the method is responsible for revealed yttrium in the alumina inclusions.

Table 1
Properties of the materials sintered at 1700 °C for 5 h.

Material	Apparent density (g/cm^3)	Relative density (%)	Hardness (GPa)	K_{Ic} (MPa $m^{0.5}$)
−5%	4.47 ± 0.02	97.60	10.69 ± 0.67	3.59 ± 0.54
0	4.42 ± 0.02	97.14	12.03 ± 0.35	2.88 ± 0.28
+5%	4.46 ± 0.670.02	98.67	12.29 ± 0.35	2.36 ± 0.28

±: confidence interval at confidence level of 0.95.

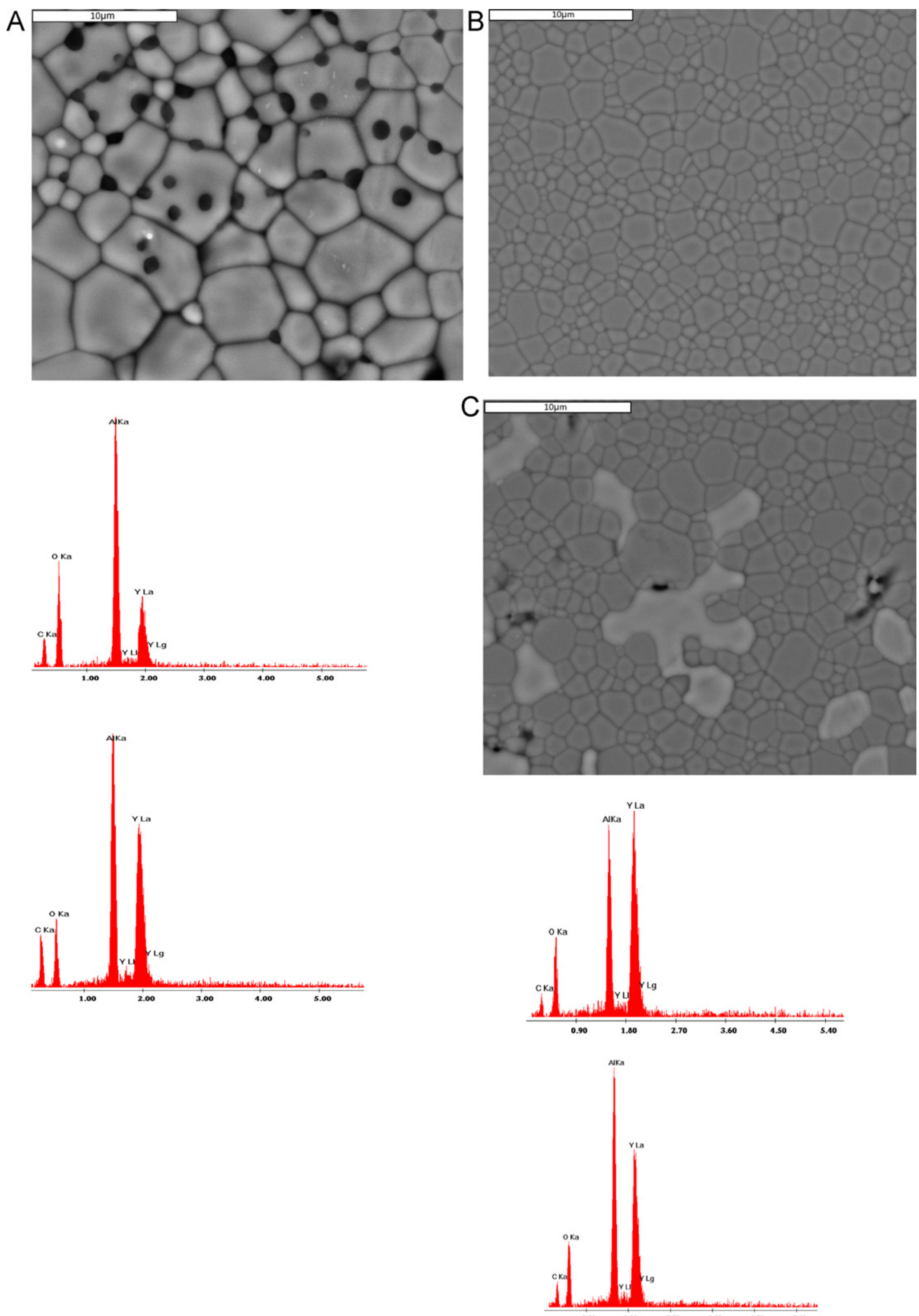

Fig. 2. SEM micrographs of the materials. Indicated EDS chemical analyses are shown. (A) Sample "+5%"; (B) sample "O"; (C) sample "−5%".

4. Conclusions

Presented results indicate that hardness of the stoichiometric material and that one containing alumina inclusion is higher than the material with aluminum deficit, i.e. which shows YAP inclusions. Reverse tendency could be observed as for fracture toughness, the highest values occur in case of the material with aluminum deficit, containing YAP inclusions.

References

[1] G. de With, H.J.A. van Dijk, Translucent $Y_3Al_5O_{12}$ ceramics, Mater. Res. Bull. 19 (1984) 1669–1674.

[2] C.A. Mudler, G. de With, Translucent $Y_3Al_5O_{12}$ ceramics: electron microscopy characterization, Solid State Ionics 16 (1985) 81–86.
[3] M. Sekita, H. Haneda, T. Yanagutani, S. Shirasaki, Induced emission cross section of Nd:YAG, J. Appl. Phys. 67 (1985) 453–458.
[4] I. Matsubara, M. Parathaman, S.W. Allison, M.R. Cates, D.L. Beshears, D.E. Holacomb, Preparation of Cr-doped $Y_3Al_5O_{12}$ phosphors by heterogeneous precipitation methods and their luminescence properties, Mater. Res. Bull. 35 (2000) 217–224.
[5] T.A. Parthasarathy, T. Mah, H. Keller, High-temperature deformation behaviour of polycrystalline yttrium–aluminum garnet (YAG), Ceram. Eng. Sci. 12 (1991) 1767–1773.
[6] M. Zarzecka, M.M. Bućko, J. Brzezińska-Miecznik, K. Haberko, YAG powder synthesis by the modified citrate process, J. Eur. Ceram. Soc. 27 (2007) 593–597.
[7] K. Niihara, A fracture mechanics analysis of indentation-induced Palmqvist crack in ceramics, J. Mater. Sci. Lett. 2 (1983) 221–223.
[8] R.S. Roth, Phase Equilibria Diagrams for Ceramics, vol. XI,, The American Ceramic Society, Westville, OH, 1995, p. 107.
[9] M. Madraj, R. Hammond, M.A. Parvez, R.A.L. Drew, W.T. Thompson, High temperature neutron diffraction study of the Al_2O_3–Y_2O_3 system, J. Eur. Ceram. Soc. 26 (2006) 3515–3524.