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Sintering Studies of Transparent Yttria Ceramics

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Abstract

In the present work, transparent yttria ceramics were prepared by hot pressing using lithium fluoride as a sintering aid. The influence of lithium fluoride concentration (0.1 to 1.5 wt%) and sintering parameters (temperature, pressure) on properties of the ceramic were evaluated. The best transmittance was obtained for 1 wt% addition of LiF and sintering temperature of 1450°C. It was found that the appropriate temperature of pressure application, related to the temperature of LiF melting and further reaction between Y_2O_3 and LiF are the crucial points for good sintering effects.
Keywords: Transparent ceramics, Y_2O_3, Optical properties, Microstructure - final

BADANIA NAD SPIEKANIEM PRZEŹROCZYSTEJ CERAMIKI TLENKU ITRU

W zaprezentowanej pracy przygotowano przeźroczystą ceramikę tlenku itru wykorzystując prasowanie na gorąco i fluorek litu jako dodatek do spiekania. Oznaczono wpływ stężenia fluorku litu (0.1 to 1.5 % mas.) i parametrów spiekania (temperatura, ciśnienie) na właściwości ceramiki. Najlepszą transmitancję otrzymano w przypadku dodatki LiF wynoszącego 1 % mas. i temperatury spiekania 1450°C. Stwierdzono, że kluczowymi dla spiekania są odpowiednia temperatura przyłożenia ciśnienia, związana z temperaturą topienia LiF, oraz reakcja pomiędzy Y_2O_3 i LiF.
Słowa kluczowe: ceramika przeźroczysta, Y_2O_3, właściwości optyczne, mikrostruktura finalna

1. Introduction

Yttria (Y_2O_3) has excellent physical and chemical properties, such as chemical stability, high melting point (2430 °C), broad transmittivity from 280 nm to 8 μm, heat and corrosion resistance and high thermal conductivity. The applications of yttria include chemically stable substrates, crucible material for melting reactive metals, nozzle material for jet casting of molten rare earth-iron magnetic alloys and cutting tools [1, 2].

Transparent yttria ceramics have found potential applications, such as luminous pipes for high-intensity-discharge lamps, heat-resistive windows and transparent armours due to their excellent properties, such as high corrosion resistivity, thermal stability and transparency over a wide wavelength region from violet to infrared light [3]. Recently, transparent yttria ceramics were extensively studied as a host material for scintillators [4] and solid-state lasers [5]. Similarly as other transparent polycrystalline materials, yttria ceramics have an advantage over single crystals owing to easier mass production, possibility of fabrication large size elements, lower preparation cost and higher doping concentration in the case of laser materials.

Transparent yttria can be produced by several methods, including pressure-free sintering of nanometric powders [6] or combination of pressure-free sintering followed, by hot isostatic pressing (HIP) [7, 8]. There are also several reports on hot-pressing (HP) of transparent/translucent yttria without additives [9] or with LiF, serving as a sintering aid [10, 11]. The last method seems to be interesting while it is technologically simple and reproducible. Despite some works showing very good transmittance of yttria ceramics prepared by HP with LiF [10], there are still many unanswered questions which appear in relation to this process. The present work was aimed at studies of impact of hot-pressing conditions (temperature, pressing schedule) and LiF content on the optical properties of yttria ceramics.

2. Experimental procedure

Commercial yttria powder of high purity (99.999 %) purchased from Metal Rare Earth Ltd. (China) was used. SEM picture of the powder is presented in Fig. 1. LiF powder was used (Aldrich, 99.995 % purity, precipitated) as a sintering aid.

The Y_2O_3-LiF mixtures were prepared by 30 minutes milling in an attritor with alumina balls and ethanol. The powder mixture was dried in air and crushed in an agate mortar.

All sintering experiments were conducted using the hot press (Astro Division, Thermal Technology Inc.) with graphitic interior and Ar (99.99 % purity) atmosphere. The 25.4 mm diameter die was lined with graphite foil, and foil disks were cut to fit at the ends of punches. Instead of the loose powder,

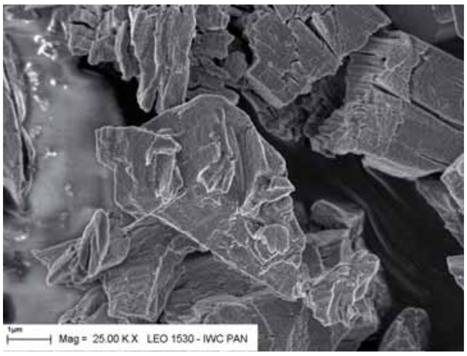

Fig. 1. Scanning electron micrograph of yttria powder used in the study.

pressed pellets of about 12 g (120 MPa, isostatic pressing) were put into the graphite die. This operation was aimed to avoid contamination of interior part of samples by graphite particles from the die or foil. A uniaxial load was applied during hot-pressing process. Maximum pressure used was 30 MPa.

After sintering, the pellets were ground to 1 mm thickness and double side polished. Total transmittance measurements in the infrared light range were performed using FT-IR spectroscopy (Bruker IFS 113v). For microscopic observations the samples were chemically etched (20 % HCl, 3 min). The average grain sizes were calculated via AXIOVERT 40MAT Zeiss, KS RUN.

X-ray diffraction measurements were performed on powder samples, using a Siemens D500 diffractometer in Bragg-Brentano geometry, equipped with high-resolution, semiconductor Si:Li detector and CuKα radiation. The diffraction pattern was recorded in a $\theta/2\theta$ step-scanning mode with a 2θ step of 0.05°, counting time of 4 sec/step and 2θ range 10-70°. The experimental data were analyzed by the XRAYAN phase analysis program and ICDD PDF4+ 2008 data base package.

3. Results and discussion

LiF is commonly used as a sintering aid for hot-pressing of many materials, *e.g.*, MgO, $BaTiO_3$ or $SrTiO_3$ [12-14]. Recent works devoted to the studies of magnesium aluminate ($MgAl_2O_4$) ceramics showed that this compound during HP process not only forms liquid phase which helps to reorganize the particles, but also reacts with spinel grains and it promotes another densification mechanisms [15, 16]. To check if a similar process takes place in the case of yttria,

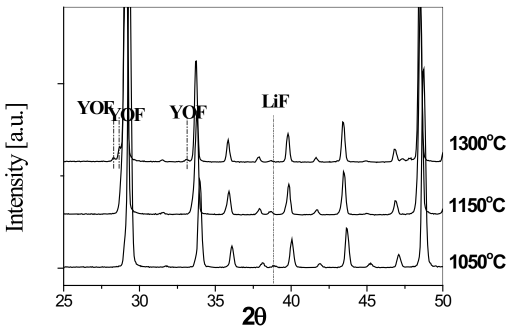

Fig. 2. XRD spectra of the Y_2O_3–5wt% LiF powder mixtures annealed for 5 min at temperatures 1050 to 1300°C.

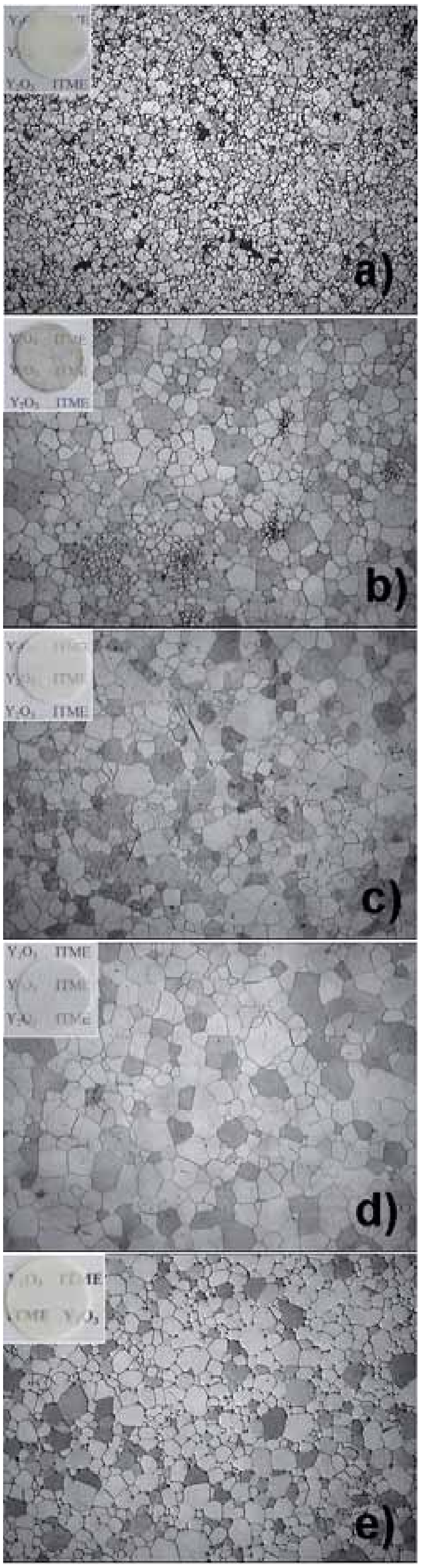

Fig. 3. Photographs of 1 mm thick polished yttria samples and optical micrographs of its microstructures prepared by HP sintering (1450°C/2h) with 1 wt% LiF and temperature of pressure application of: a)1100°C, b)1170°C, c) 1250°C, d) 1300°C, e) 1350°C.

Y_2O_3-5 wt% LiF mixtures were heated to 1050, 1100 and 1300°C. XRD results of the obtained samples are presented in Fig. 2.

On the XRD pattern collected from the sample heated to 1300°C besides Y_2O_3 and LiF peaks a new crystalline phase of YOF can be detected. Its appearance proves that during sintering the reaction between lithium fluoride and yttria takes place. In order to check the influence of this phenomenon on the sintering of yttria several HP processes were conducted with different temperatures of maximum pressure application. 1 wt% LiF-Y_2O_3 mixture, sintering temperature of 1450°C and 2 h dwelling time were chosen for the studies. In all the cases minimum pressure (of 5 MPa) was applied at 900°C (just above the melting point of LiF which is 870°C). The heating rate was constant (10°C/min). The pressure was increasing with different velocities to reach its maximum value at 1100°C to 1350°C. The photographs of sintered ceramics and their microstructures are presented in Fig. 3. As it can be seen, the temperature at which maximum pressure was applied has a great impact on microstructure of ceramics. Both porosity content and the grain size are strongly affected. Changes of yttria grain size with temperature of maximum pressure application are collected in Table 1.

Table 1. Grain size dependence on temperature of pressure application during HP sintering (1450°C/2h) with 1 wt% LiF addition.

Temperature of maximum pressure application [°C]	Average grain size [µm]
1100	15.9 ± 7.9
1170	32.0 ± 22.1
1250	36.0 ± 14.5
1300	42.2 ± 20.9
1350	57.0 ± 25.0

HP sintering of yttria with LiF at the same temperature and identical heating rate leads to the ceramics of significantly different grains sizes if the maximum pressure is applied at another temperature.

The changes of ceramic microstructure are followed by differences in transmittance (Fig. 4.). The best transmittance of 81 % at 6 µm was measured for the ceramics prepared with maximum pressure application at the highest temperature (1350°C). However, this material showed strong transmittance decrease during shifting to lower wavelengths (at 2 µm the transmittance value is only of about 66 %). On the contrary, the HP process with maximum pressure application at a slightly lower temperature of 1300°C (but when the reaction between LiF and Y_2O_3 already took place as was presented in Fig. 2) leads to quite stable transmittance values (79 % and 72 % at 6 µm and 2 µm, respectively) in the whole measurement range. The lowest transmittance (below 1 %) was obtained for the HP process, when the pressure was applied at the lowest temperature. The sample prepared in this case was opaque and porous (Fig. 3a).

The results presented suggest that during hot pressing of yttria LiF acts not only as a liquid phase which enables easier particles movement, but also helps in grain accommodation due to particles etching. This way is important to apply the pressure at the appropriate temperature, when the reaction between Y_2O_3 and LiF already starts.

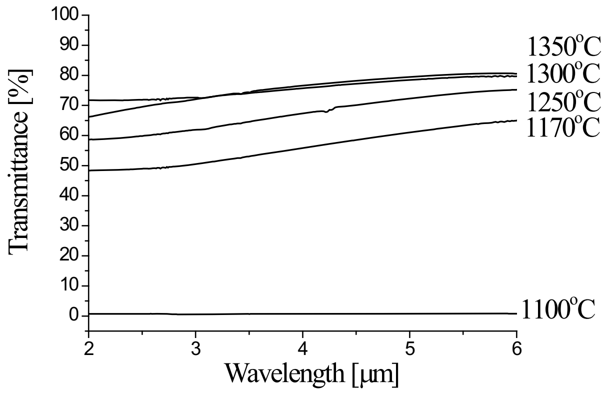

Fig. 4. Transmittance of yttria ceramics sintered at 1450°C with 2 h dwelling, maximum pressure of 30 MPa applied at 1100–1350°C.

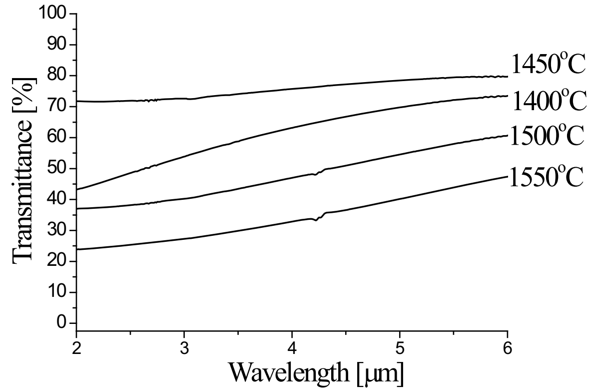

Fig. 5. Transmittance of yttria ceramics sintered by HP with maximum pressure of 30 MPa applied at 1300°C, 1 wt% LiF content and 2 h dwelling at temperatures ranging from 1400–1550°C.

The influence of final sintering temperature and LiF content on samples transmittance was also studied. In this case the maximum pressure was applied at 1300°C. Fig. 5. presents the relation between sintering temperature and transmittance of obtained ceramics. The best transmittance was found at 1450°C.

In Fig. 6, the influence of LiF content on the transmittance of yttria ceramics hot-pressed at 1450°C for 2 h was presented. The results show that for the studied powder and the mixing method used the best amount of LiF occurred to be 1 wt%. Both the higher and the lower content leads to the decrease of ceramics transmittance.

4. Conclusions

In the present work yttria ceramics transparent in the infrared light region was prepared by hot pressing of commercial micropowder of high purity (Metall Rare Earth Ltd., 5N), using lithium fluoride as sintering aid. The influence of lithium fluoride concentration (0.1 to 1.5 wt%) and sintering parameters on ceramic properties were evaluated. The best transmittance of ceramics was obtained for hot pressing of yttria powder with 1 wt% of LiF at 1450°C. It was found that the appropriate temperature of maximum pressure application is crucial for ceramic transmittance. The best transmittance was obtained for ceramics fabricated when the minimum pressure (5 MPa) was applied at 900°C, and then the pressure was increased to reach the maximum value of 30 MPa at 1300°C.

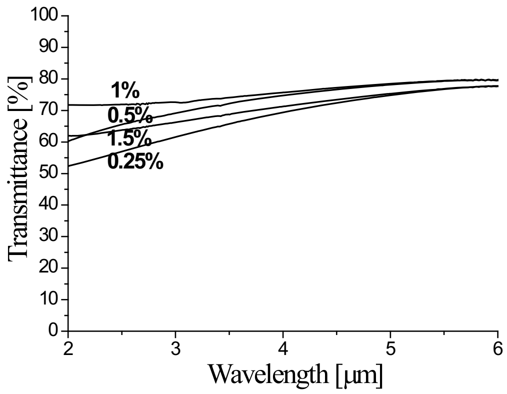

Fig. 6. Transmittance of yttria ceramics sintered by HP with 2 h dwelling at 1450°C, maximum pressure of 30 MPa applied at 1300°C, LiF content ranging from 0.25 wt% to 1.5 wt%.

As found, this condition can be related to the temperature of LiF melting and further reaction between Y_2O_3 and LiF.

Acknowledgements

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