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Critical parameters to obtain Yb^{3+} doped Lu_2O_3 and ZnO transparent ceramics

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Abstract

Transparent ceramics of zinc oxide (ZnO) and 10% Yb^{3+} doped Lu_2O_3 (YLO) were fabricated by spark plasma sintering. The major sintering parameters to obtain transparent ceramics and their interdependency on each other are explained for cubic and non-cubic crystal structured transparent ceramics. Highly densified YLO and ZnO ceramics were obtained at 1250 °C and 850 °C, respectively. Postannealing of sintered YLO and ZnO ceramics at 1200 °C and 700 °C respectively removes discoloration and improves transparency. The 2 mm thick YLO ceramics prepared at 1700 °C with dwell time of 5 min and heating rate at 50 °C/min shows the maximum transmittance of 55% at a wavelength of 2 μm and the 2 mm thick ZnO transparent ceramics prepared at 1100 °C with dwell time of 20 min and heating rate of 10 °C/min shows maximum transmittance in the visible region with nearly 60% transmittance.

Keywords: A. Grain growth; A. Sintering; B. Grain size; B. Grain boundaries

1. Introduction

Transparent ceramics are widely studied owing to their versatility in various optoelectronic applications. Few cubic crystal system materials such as magnesium-aluminate spinel and sesquioxides have been realized in the form of transparent ceramics. Non-cubic crystal structures are mostly processed in the form of polycrystalline materials, as anisotropic grains could cause considerable light scattering around grain boundaries resulting in light absorption, inhibiting transparency in the fabricated ceramics. Non-cubic crystal structured materials need an equilibrium with various sintering parameters such as sintering temperature, dwell time, pressure and grain size to fabricate as transparent ceramics. To obtain transparent ceramics, consolidation of micro/nanograined powders is done at high temperatures with simultaneous application of high pressure (either by hot pressing (HP) or as hot isostatic pressing (HIP) [1–3]). Maximum transparencies up to 85% have been achieved with the aforesaid techniques either by addition of additives or with comparatively slower heating rates than spark plasma sintering.

Spark plasma sintering (SPS), is relatively a decade old technique which implements conjoint application of axial pressure at high temperature, initiated by DC pulses. The joule energy from the DC pulses enhances surface activation of grains by raising the temperature on the surface of each grain, which leads to highly densified samples at lower sintering temperatures and dwell time. Though SPS is currently being used for various groups of materials, its application in the field of transparent ceramics is limited [4]. Highly transparent ceramics with controlled microstructures by SPS have been prepared by a two-step pressure profile, i.e., a low pre-loading pressure at low temperatures and a high pressure at high temperatures [5]. The heating rate is another important sintering parameter for densification in the second and third stages. Although a fast heating rate > 30 °C/min is widely used in SPS, a low heating rate was applied to fabricate highly transparent Al_2O_3 [6] and $MgAl_2O_4$ [5]. SPS densified polycrystalline oxides generally fail to yield transmittance expected by theoretical inline transmittance, especially in the ultraviolet and low visible wavelengths. This optical behavior may be principally due to the presence of pores that are often observed at the grain

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junctions of ceramics subjected to SPS. In addition, another drawback is the reduction condition in SPS due to the presence of graphite at high temperature in vacuum. It has been reported that the combination of two-step profile and low heating rate can be more advantageous to obtain fine microstructure bodies with improved transparencies [7].

In the present work, we study about the various parameters yielding transparent ceramics of cubic crystal structured Yb^{3+} doped Lu_2O_3 (YLO) and non-cubic crystal structured (hexagonal) zinc oxide (ZnO) by SPS. Lu_2O_3 is a sesquioxide with cubic crystal structure which has applications in scintillation detectors and laser gain media. Lu_2O_3:Yb^{3+} crystals exhibit a potential to replace Yb^{3+}: YAG for 976 nm diode pumped high-power laser applications. But these types of crystals are difficult to be grown due to the high temperature growth issues, which limit size and quality. Further ZnO is a material with unique combination of semiconductor material with a significant fraction of ionic bonding. ZnO powder and thin films are commonly employed in scintillators, where large volume and high transparency in the spectral range of emission is required. It has to be noted that to obtain ZnO single crystal is a long and expensive technological process. Thus optical ceramics, in the form of polycrystalline material could be an attractive choice to single crystals to be implemented for scintillators. Recently Taira et al. [8,9] have reported about a new means for anisotropic ceramics. Though transparent ceramics of ZnO [10–15] are fabricated by other techniques, SPS technique was preferred by us due to its rapid heating rate and time-effectiveness. This article focuses on the various parameters catered to yield good quality transparent ceramic of YLO and ZnO, with shorter processing time and lower sintering temperature than obtained with other conventional ceramic processing techniques and crystal growth methods.

2. Experimental procedure

Due to commercial non availability of 10% Yb^{3+} doped Lu_2O_3 (YLO) powder, YLO nanopowders were synthesized by the co-precipitation method. The detailed procedure is reported elsewhere [16]. Commercially available ZnO was procured from Alfa Aesar, which was sieved to obtain grain size ≈ 50 µm. For each experiment 2 g of YLO and ZnO powder was filled into graphite die having an inner diameter of 8 mm. The graphite die was covered with a thermal insulator carbon fiber to avoid contamination from the graphite die to the starting powder. An optical pyrometer was used to measure temperature on the graphite die surface. The graphite mold was placed in SPS operating chamber (DR. SINTER LAB Spark Plasma Sintering system, Model SPS-511S/SPS-515S) under Vacuum of 10^{-6} Torr. The pulse sequence for SPS applied voltage for all the samples was 12:2 (i.e. 12 ON/2 OFF). The shrinkage of the densifying powder was continuously monitored by the displacement of the punch rod. The temperature was first increased to 600 °C within 3 min and then increased to a range of temperatures from 1400 °C to 1800 °C for YLO and 900 °C to 1100 °C for ZnO with different heating rates (R_H) ranging from 5 °C/min to 200 °C/min and dwell time. Uniaxial pressures ranging from 40 MPa to 100 MPa were applied at room temperature (T_R) and sintering temperatures (T_S) and their significances have been analyzed. The cooling rate (R_C) and R_H were maintained equal in all the experiments. The higher value of R_H and higher value of R_C lead to opacity and cracking in ceramics. The SPS densified ceramics of YLO and ZnO obtained were black in color, due to the reducing nature of SPS experimental process and porosity. The thermal insulator layer on the ceramics was removed and the ceramics were annealed at 900 °C for YLO ceramics and 700 °C for ZnO ceramics during 1 h in air to compensate the lost oxygen in SPS chamber. Then the ceramics were mirror polished on both sides using diamond slurry. The thickness of the ceramics after polishing was approximately 2 mm. The obtained transparent ceramics of ZnO and YLO are shown in Fig. 1. The density and porosity were measured by in distilled water by Archimede's method. The microstructure was observed by a scanning electron microscope (Jeol 840 SEM). The optical transmittance spectrum was measured by using a double beam spectrophotometer (Varian Cary 5000) at a range of between 200 and 3000 nm.

3. Results and discussion

In order to obtain transparent ceramics, the various vital parameters such as grain size, grain-boundary phase and pores has to be dealt with. It has been reported that higher transmittance

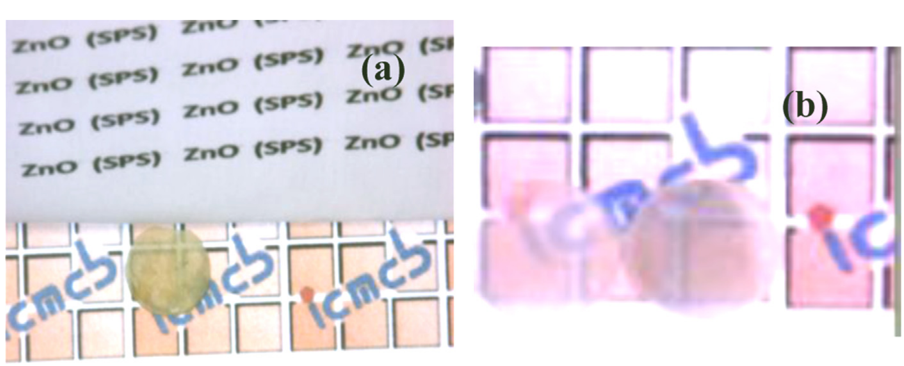

Fig. 1. Transparent ceramics of (a) ZnO and (b) YLO fabricated by spark plasma sintering.