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Synthesis and processing of spinel powders for transparent ceramics

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Abstract

Spinel powders have been synthesized by chemical coprecipitation using two different precursors, nitrates and chlorides, and by an oxides mixture route. It has been shown that depending on the precursors used and the synthesis conditions pure spinel nanopowder can be obtained at different temperatures and with different levels of agglomeration. According to TEM results, the chloride route allows obtaining pure and deagglomerated spinel powders after calcination at 800 °C with a submicrometer particle size. Sintered lyophilized powders obtained by a chloride route allow achieving materials with in-line transmittances close to 46% at 540 nm and 83% in the infrared range.

Keywords: A. Sintering; C. Optical properties; D. Spinels

1. Introduction

Magnesium aluminate spinel ($MgAl_2O_4$) has received a great deal of attention as a technological important material due to its attractive properties such as high melting point (2135 °C), high mechanical strength at elevated temperatures, high hardness (16 GPa), high chemical inertness, relatively low density (3.58 g/cm^3) and good thermal shock resistance [1,2]. Furthermore, transparent magnesium aluminate spinel ($MgAl_2O_4$) ceramics have been considered as an important optical material due to its good mechanical properties and an excellent optical transmission from 0.2 to 5.5 μm, making it useful for a wide range of optical applications, including armor window strike-faces and protective windows for sensors, windows for barcode reader, pressure vessel, high index optics for ultraviolet microlithography, etc. [3–5].

Over the last decades, a variety of techniques [6–10] have been used to prepare $MgAl_2O_4$ spinel. However, for all the synthesis routes cited above the formation of coarse agglomerates during the drying process is a common problem that reduces sinterability and homogeneity of the microstructure in the formed product. Successful sintering of spinel ceramics has been demonstrated only with fine deagglomerated powders presenting chemical and phase purity and, very importantly, a narrow particle size distribution. In this sense, Tsukuma [11] sintered to transparency high purity TSP-15 powders produced by Taimei Chemical Industry with an average grain size (d_{50}) of 0.15 μm. Goldstein et al. [12] also prepared 2 mm thick transparent spinel disks at low temperature by using $MgAl_2O_4$ powder from Nanocerox, prepared by spray flame pyrolysis with a specific surface area of 30 m^2/g. In this case, it was also shown that a post hot isostatic press step improved the degree of transparency of the disks. Also, Krell et al. [13] produced dense spinel with a high transmittance in the visible range, starting with 55 nm spinel powders by carefully designing the sintering cycle, minimizing the grain growth to 300 nm without doping additives. Alternatively, fine powders doped with sintering aids, such as B_2O_3 [6], CaO [14], and LiF [15], were prepared to enhance the sinterability. However, second phases with a refractive index different from that of the matrix induce light scattering, reducing transmittance.

In this work, spinel particles are synthesized following two different routes: oxides mixture and reverse-strike coprecipitation and three different precursors: chlorides, nitrates and

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oxides. It is shown how an adequate selection of the synthesis route and the processing conditions allows obtaining transparent spinel ceramics.

2. Experimental procedure

$MgAl_2O_4$ powders prepared by reverse-strike coprecipitation were synthesized using different precursors, magnesium and aluminum nitrates ($Mg(NO_3)_2 \cdot 9H_2O$ (ABCR) and $Al(NO_3)_3 \cdot 6H_2O$ (ABCR), respectively, and magnesium and aluminum chlorides ($MgCl_2 \cdot 6H_2O$ (Panreac) and $AlCl_3 \cdot 6H_2O$ (Fluka), respectively. Magnesium and aluminum nitrates or magnesium and aluminum chlorides were mixed with a 1:2 molar ratio, respectively. The pH value was kept constant at 10 ± 0.5 by adding ammonium hydroxide solution (Sigma-Aldrich, 28.0–30.0% in water) owing to the fact that is critical for the control of the chemical homogeneity within the particles. After 24 h of aging, a gelatinous precipitate was obtained. The amorphous gel was placed on a plate in a lyophilizer (CryoDos, Telstar) under vacuum (0.1 mbar) and held to -50 °C in order to remove the water by sublimation of the frozen gel. All powders were burnt at different temperatures in order to achieve a crystalline material. The raw materials in the oxides mixture, MgO (Merk) with an average particle size of around 1.6 µm and Al_2O_3 (Taimei, TM-DAR) with an average particle size of around 0.16 µm, were mixed in propanol with alumina balls for 1 h using an attrition mill. The powders were thermally calcined in air between 800 and 1200 °C for 2 h to obtain pure spinel. After the heating treatment the powders were ground in a ball mill and subsequently sieved through a mesh < 63 µm.

Thermogravimetric (TG) and differential temperature analysis (DTA) for the three products (TGA/DSC Star System, Mettler Toledo) were carried out under air atmosphere at a heating rate of 5 °C/min up to 1400 °C. The phase transitions of the heat-treated samples as a function of the temperature were followed by X-ray diffraction (Jobin Yvon, HORIBA) to determine the crystalline phases of the burnt powders. The particle size and the morphology of the Spinel nanopowders were investigated by TEM (2000FX, JEOL). The BET surface area of the samples was carried out under nitrogen atmosphere at 77 K (TriStar II 3020 V1.03, Micromeritics). Sintering was performed in a spark plasma sintering (SPS) apparatus (HPD 25/1, FCT) under low vacuum (10^{-1} mbar). Crystalline powders were placed into a graphite die with an inner diameter of 20 mm and sintered at the best temperature for each system for 3 min under an applied pressure of 50 MPa and a heating rate of 100 and 50 °C/min. The transmission spectrum was recorded on VIS (AvaSpec-2048, Avantes) and IR (IR-560, Nicolet Magna) equipments.

3. Results and discussion

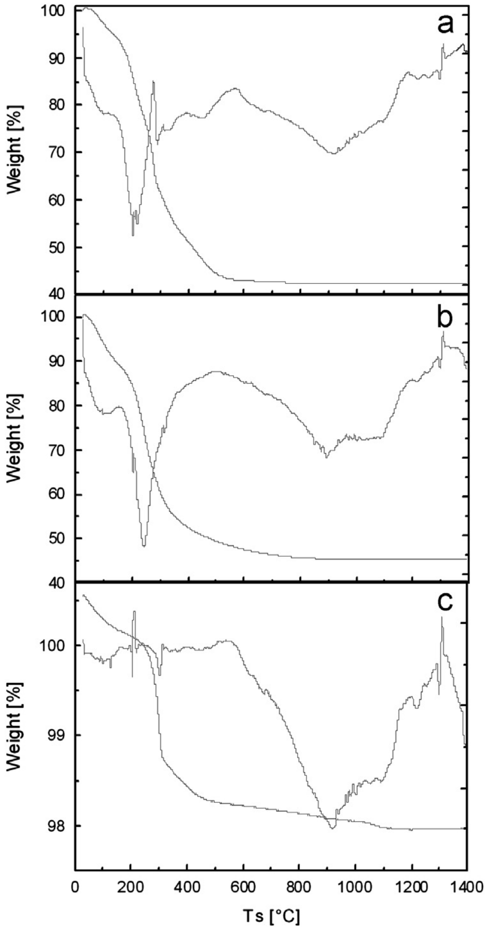

Fig. 1. TG/DTA plot of amorphous spinel powder for the nitrates (a), chlorides (b) and oxide (c) routes.

The TG–DTA curve corresponding to nitrate precursors (Fig. 1(a)) shows four clear mass losses. The first one is a broad 16% weight loss over the temperature range 30–160 °C associated to an endothermic peak corresponding to the dehydration of adsorbed water in the powders. The second mass loss of 38% takes place between 160 and 285 °C that could be related to the intermolecular water. The third mass loss, between 285 and 389 °C, corresponds to the dehydroxylation of the mixed hydroxides to oxides. Finally the fourth mass loss, associated to an exothermic peak between 388 and 515 °C, could be attributed to the evaporation of NH_4NO_3 which appears during the synthesis as a by-product. The sharp exothermic peak between 1100 and 1200 °C is due to the crystallization of spinel.

Fig. 1(b) shows the TG curve corresponding to the chlorides route with a total weight loss about 55%. In this thermogram, an endothermic peak in the 40–150 °C with a mass loss of about 11% appears which may be associated to the vaporization of physically bound absorbed water. In the temperature region 150–450 °C, an endothermic peak appears that could be associated to the dehydroxylation of the mixed hydroxides to oxides. Finally the exothermic peak between 900 and 1200 °C is attributed to powders crystallization. According to the results the synthesis of spinel by chloride route requires a lower temperature to achieve a crystalline phase.

There is no sharp peak observed in the TG curve corresponding to the oxides mixture (Fig. 1(c)); just a broad exothermic peak starting at approximately 1000 °C and having a maximum at 1400 °C. Also, a minor weight loss (3%) is observed through all the temperature range studied.