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Short communication

A new approach to producing transparent $ZnAl_2O_4$ ceramics

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ABSTRACT

A new approach to producing of transparent bulk $ZnAl_2O_4$ ceramics based on hot pressing of powders (1600 °C, 50 MPa) in presence of sintering additive ZnF_2 is described. Using this approach in the presence of 5 wt% of ZnF_2 transparent $ZnAl_2O_4$ ceramics was prepared with transparency range from 0.2 to 7.5 μm and with band gap of about 6.05 eV. The average grain size was about 33 μm and the transmittance at the wavelength of 550 nm was about 63%.

1. Introduction

Polycrystalline zinc aluminate ($ZnAl_2O_4$) is an optical material with cubic structure (space group *Fd3m*) and has optical and mechanical characteristics comparable to aluminum-magnesium spinel ($MgAl_2O_4$) [1]. $ZnAl_2O_4$ has higher value of thermal conductivity of 25 W/(m K) [2] as compared with $MgAl_2O_4$ (15 W/(m K)) [3]. In this connection the materials on the basis of $ZnAl_2O_4$ doped with luminescent ions can be the alternative to $MgAl_2O_4$ in laser engineering [4–6] and photonics.

At the present time 3 papers describing the technique for preparation of transparent $ZnAl_2O_4$ ceramics were published [7–9]. In these papers the process of consolidation of powder was carried out in 2–3 stages using high pressures (80–250 MPa). To simplify the producing dense ceramics (reducing the pressure and temperature of hot pressing) sintering additives are used. For producing transparent $ZnAl_2O_4$ ceramics silicon oxide can be used, as described in ref. [9]. Silicon oxide can be a source of optical losses in the optical transmission, because it is not removed during the vacuum evaporation. Data on sintering additives for the $ZnAl_2O_4$ evaporating in vacuum are not found. Such sintering additives are used to obtain transparent $MgAl_2O_4$ ceramics, for example lithium fluoride [10]. LiF is used for sintering of other oxide ceramics, for example MgO [11]. Lithium fluoride can not be applied to $ZnAl_2O_4$ due to the following reactions:

$$ZnAl_2O_4(s) + 2LiF(l) \rightarrow ZnF_2(l) + 2LiAlO_2(s) \quad (1)$$

$$ZnF_2(l) \rightarrow ZnF_2(g) \quad (2)$$

where formed ZnF_2 will be removed together with LiF distorting the stoichiometry of cations Zn and Al. $LiAlO_2$ formed during reaction will be the center of intense light scattering. To activate the sintering of $ZnAl_2O_4$ it is attractive to use ZnF_2 having the melting temperature of 872 °C [12]. ZnF_2 as well as LiF can interact with zinc aluminate without changing the stoichiometry of cations Al and Zn. The liquid phase of ZnF_2 can serve as a lubricant and intermediate agent of liquid-assisted-sintering (T > 872 °C) facilitating shrinkage of sample. High vapor pressure of ZnF_2 in the temperature range of 800–1200 °C [12] makes it possible to efficiently remove the sintering additive. In this connection, the use of ZnF_2 as a sintering additive for obtaining transparent $ZnAl_2O_4$ ceramics is promising.

The aim of this study was to investigate the possibility of the fabrication of the transparent $ZnAl_2O_4$ ceramics by hot pressing of ZnF_2 doped powders, synthesized by sol-gel method. Microstructure and optical properties of obtained ceramics were studied.

2. Material and methods

Zinc aluminate powder was prepared by sol-gel method. Zinc nitrate (99.99% purity) solution (0.5 mol/l) and boehmite sol (0.12 mol/l) as a gelling agent, were mixed in a molar ratio of 1:2. Boehmite sol was obtained according to the procedure described in Ref. [13]. The stoichiometric ratio of metal cations in the sol

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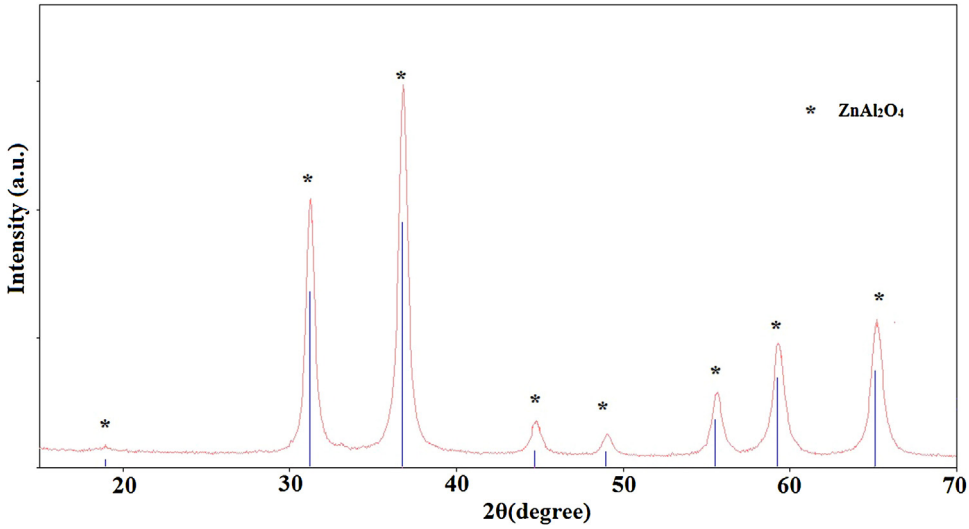

Fig. 1. XRD pattern of $ZnAl_2O_4$ powder calcined at 750 °C (3 h).

was determined by atomic emission spectroscopy with inductively coupled plasma (AES-ICP, iCAP 6300 spectrometer, Thermo Electron Corp., Great Britain). The resulting sol was dried to a xerogel at 150 °C for 3 h. Final xerogel was further milled in a planetary mill and calcined at 750 °C for 3 h, followed by sieving through sieve 56 μm. 10 mL of anhydrous isopropyl alcohol, solutions of $Zn(NO_3)_2$ and HF (45%) were sequentially added to the $ZnAl_2O_4$ powders (2.5 g), followed by stirring in a planetary mill (5 min). The resulting suspension was dried in a fluoroplastic container in air at 100 °C for 2 h, followed by calcination at 700 °C for 1 h. Thus, powders containing 0.5 and 5 wt% of zinc fluoride were obtained.

The morphology of the powders was examined by scanning electron microscopy (SEM, JEOL JSM-6390 LA, JEOL Ltd., Japan). The phase composition of the powders was identified by X-ray diffraction (XRD, diffractometer Ultima IV, Rigaku, Japan).

$ZnAl_2O_4$ powders were consolidated by hot pressing (hot press homemade) in a graphite mold. The $ZnAl_2O_4$ powders were free loaded (0.7 g) into the graphite die. Graphite paper was paved between the powder compact and dies. The residual air pressure in the system did not exceed 10 Pa. The heating rate was 10 °C/min. The soaking time at the final temperature (1600 °C) was 1 h. The main load was applied at temperatures of 800 or 1200 °C, and then increased gradually to 50 MPa (1.5 MPa/min). Before applying the main load compact was under pressure of 2.7 MPa.

Samples were ground and polished with diamond paste with a particle size of 5 μm. Optical transmission was measured by a UV/VIS spectrometer SF-2000 in the wavelength range from 200 to 1100 nm and a FT-IR spectrometer Bruker Tensor 27 in the wavelength region of 1300–10000 nm (transmission presented without correction for reflection). The microstructure of transparent samples was examined by optical microscopy (model Axioplan 2 imaging, Carl Zeiss, Germany). The average grain size was determined by intercept method (after chemical etching).

3. Results and discussion

The synthesized powder of zinc aluminate had the molar ratio n(Al)/n(Zn) = 2.027 corresponding to composition $ZnO \times 1.0135\ Al_2O_3$. A small redundancy of Al_2O_3 was allowed since it can be dissolved in spinel structure occupying the tetrahedral sites [14,15]. Fig. 1 shows the XRD pattern $ZnAl_2O_4$ powder (without ZnF_2), used in the work. The position of the peaks corresponds to the theoretical $ZnAl_2O_4$ diffractogram, the presence of other phases was not observed.

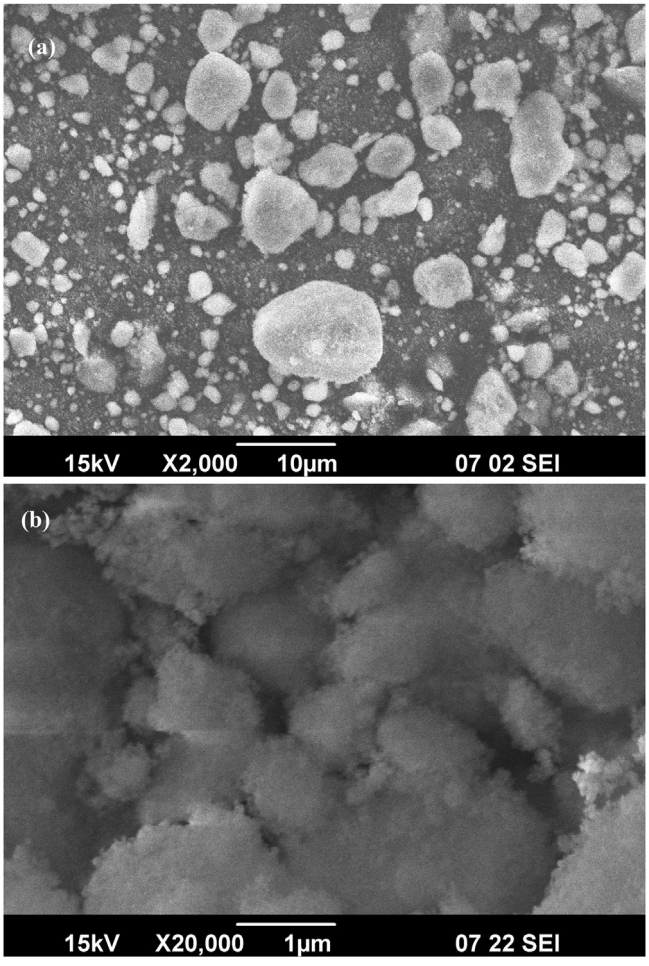

Fig. 2. SEM micrograph of the particles of $ZnAl_2O_4$ powder.

SEM micrographs of powder (without ZnF_2) show that the particles of $ZnAl_2O_4$ represent the granules with size up to 10 μm (Fig. 2a) which, in its turn, consist of finer particles (Fig. 2b). This indicates that the powder is agglomerated. Strongly agglomerated powder can contribute to formation of pores during sintering.

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