

Manufacture of luminescent ceramics by vacuum sintering of nanopowder oxides



V. Kortov*, A. Kiryakov, S. Nikiforov, D. Ananchenko, S. Zvonarev

Ural Federal University, Mira Str. 19, 620002 Ekaterinburg, Russia

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ABSTRACT

A method of nanopowder sintering in vacuum with the presence of carbon was used to manufacture oxygen-deficient Al_2O_3 and MgO luminescent ceramics. They were sintered at varying temperatures and annealing time. It was shown that during sintering in vacuum, the phase composition, microstructure and luminescent properties of the ceramics change. In the obtained ceramics, the spectra of pulse cathodoluminescence and photoluminescence as well as thermoluminescence glow curve are registered. The luminescence intensity grows with increasing temperature and sintering time. The photoluminescence spectrum significantly changes in the ceramics doped with chromium during sintering. The oxygen-deficient ceramics synthesized in vacuum are promising for applications in optical electronics and solid state dosimetry of ionizing radiations.

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1. Introduction

Wide-gap oxides (Al_2O_3 , MgO , ZrO_2 , etc.) are widely used in modern technologies due to high melting temperature, mechanical strength and stability of their physical and chemical properties. Development of techniques for creating oxygen deficiency in the anion sublattice of oxides has extended their applications as functional materials. Formation of oxygen vacancies with relatively high concentration ($\sim 10^{17} \text{ cm}^{-3}$) in oxygen-deficient oxides is accompanied by changes in their electric, optical and luminescent characteristics. The methods of obtaining oxygen-deficient oxides are based on the processes of their partial reduction under thermal treatment in reducing medium, e.g. with the presence of carbon. When the pressure of the residual gases is low and the temperature is high, gaseous carbon monoxide (CO) is formed. It is good reducing agent. In particular, the method of carbothermal reduction is used in growing alumina single crystals from the melt with the presence of carbon [1] as well as in the production of high-grade titania slag [2]. Highly sensitive luminescent detectors of ionizing radiations were developed on the base of oxygen-deficient alumina single crystals; these detectors are used for personal dosimetry and environmental radiation monitoring [3].

Oxygen-deficient luminescent oxides can be obtained by using

other methods, among which high-temperature heating in vacuum. During this, the oxide is partially reduced and oxygen vacancies are formed mainly in near-surface layer of the samples. Experiments were described where alumina crystals of stoichiometric composition were heated for several hours at $T = 1500^\circ\text{C}$ in vacuum 10^{-4} Pa with the presence of carbon. In the spectra of optical absorption of such crystals after the reported thermal treatment in vacuum, bands of F-centers created by oxygen vacancies were registered. The crystals were suitable for dosimetric measurements [4].

In recent years, an interest in luminescent properties of nano-sized materials has increased [5–8], including nanopowders and ultrafine ceramics. First of all, nanostructured analogs of well-known phosphors were studied. It was found that nanostructured phosphors were more radiation-resistant in comparison with their macrocrystalline analogs. It allows increasing excitation density and growing luminescence yield. Moreover, such phosphors are suitable for detecting high-dose radiation as luminescence centers remain stable under high-dose irradiation. Nanopowders are promising materials for obtaining ultrafine luminescent ceramics by using high-temperature sintering in vacuum. These ceramics remain highly radiation-resistant, and they can be used as materials for detectors of ionizing radiations with different forms and sizes. However, the studies of vacuum sintering of oxide nanopowders to obtain luminescent ceramics are still in its early stage [9].

The purpose of the paper is a brief analysis of new and recently obtained by us experimental data to consider the features of

* Corresponding author.

E-mail address: vskortov@mail.ru (V. Kortov).

manufacture of luminescent ceramics by vacuum sintering of nanopowder oxides.

2. Experimental

The experimental ceramic samples were synthesized from the commercial high-purity Al_2O_3 and MgO nanopowders with the particle size of 45–75 nm. The powder was pressed into pellets 5 mm in diameter and 1.3 mm thick under 1000 kg/cm^2 . To make ceramics doped with chromium, nanopowders of $\alpha\text{-Al}_2\text{O}_3$ and Cr_2O_3 were mixed and, after the addition of ethanol, the suspension was formed. Further mixing took place in an ultrasound bath. The mixture was dried at 70°C for 8 h. After that the powder which consisted of oxides mixture was subject to uniaxial pressing with the unit-area pressure reported above.

The ceramics were sintering in the vacuum ($\sim 10^{-2}$ Pa) electric furnace SNVE 9/18 (Russia) at the temperature range from 1000°C to 1700°C and at a heating rate of $30^\circ/\text{min}$ and the annealing time varying from 30 min to 3 h.

The samples were sintering with the presence of carbon. For this purpose a highly pure graphite (99.99%) rod with the mass of 20 g was placed 5 mm from the samples in the vacuum chamber of the furnace. It was done to create a strong reducing medium which is needed to synthesize oxygen-deficient samples of oxide ceramics.

The XRD analysis of the initial powders and the pressed samples before sintering was carried out using a D8 DISCOVER X-ray diffractometer with Cu (K_α) radiation and a graphite monochromator. Structural properties have been studied by the Rietveld method. The surface structure of the obtained ceramics was studied with a SIGMAVP scanning electron microscope (Carl Zeiss, Germany) and a secondary electron detector (In-lens) in high vacuum with 5 kV accelerating voltage. The samples had been preliminary coated with a 10 nm - thick gold layer using Quorum Q150T ES high vacuum system.

PCL spectra were registered at room temperature using KLAVI spectrometer (Russia). The spectra were excited with an electron gun. The duration of electron beam pulse was 2 ns, the electron energy and current density were 130 keV and 60 A/cm^2 , respectively. The PL spectra were obtained using a luminescent LS-55 spectrometer (Perkin Elmer, USA) in the range of (200–800) nm. The measurements were made under excitation with a pulse xenon lamp of 150 W power, 10 Hz frequency and 20 ms delay of PL registration after the pulse. The duration of excitation pulse was 20 ms, PL spectrum was recorded in the time window between excitation pulses to exclude the influence of excitation pulse on the measurement of the spectrum. The spectrometer was equipped with a built-in filter with the bandpass more than 290 nm. The experimental setup with FEU-142 photomultiplier with the maximum spectral sensitivity of 350 nm was used in registering TL. The setup provided linear heating of the irradiated ceramics in the range of 300–820 K at a rate of 2 K/s. A filter BGG 9 («Optics-M» Ltd., Russia) with the bandwidth of 300–700 nm was applied for protection from the thermal background of the heater.

To find the dependence of the TL peak intensity on the absorbed dose, the ceramic samples were preliminarily exposed from the $^{90}\text{Y}/^{90}\text{Sr}$ β -source with the dose rate of 32 mGy/min .

3. Results and discussion

While nanopowders are sintered in vacuum, the processes defining the phase composition, structure and luminescent characteristics of ceramics can occur. Below there are the results which show formation of the reported properties during the synthesis of oxygen-deficient oxide ceramics in vacuum.

3.1. X-ray diffraction analysis

XRD patterns of the initial pellet of Al_2O_3 and sample sintered at 1550°C is given in Fig. 1. According to the data from XRD analysis, the initial compact consists of the mixture of metastable phases of Al_2O_3 (θ and δ -phases). After sintering at $T = 1550^\circ\text{C}$ for 1 h, the sample contains only $\alpha\text{-Al}_2\text{O}_3$. Transition of metastable θ and δ -phases into a stable α -phase occurs in Al_2O_3 at $T = 1200\text{--}1300^\circ\text{C}$. Sintering at $T = 1550^\circ\text{C}$ provides a complete (100%) phase transition and obtaining ceramics with homogeneous phase composition. It is also known that luminescence in $\alpha\text{-Al}_2\text{O}_3$ is more intensive than that in its metastable phases [9].

XRD analysis of the samples from MgO nanopowder shows that the precursor pellets and the ceramics sintered at $T = 1100\text{--}1500^\circ\text{C}$ features only cubic phase, i.e. the phase composition of the samples does not change at high-temperature treatment.

3.2. SEM analysis

Fig. 2 shows SEM images of the ceramics sintered under various heating conditions. It is seen that the sintering in vacuum at 1500°C (3 h) gives rise to agglomerates with the mean size of about 600 nm (Fig. 2a). The sample contains at large number of pores and the pore size is commensurate with the agglomerate size. With an increasing synthesis temperature up to 1600°C , the particles grow further, and a number of pores decrease (Fig. 2b). The particles below 100 nm in size emerge when the temperature growth above 1500°C . Further increase of the sintering temperature up to 1700°C increases the fraction of the small particles (Fig. 2c). Some of these particles are just 10–40 nm in size, i.e., they are smaller than the particles in the original nanopowder. Moreover the ceramics synthesized at 1700°C have an average particle size about 3.5 μm . Thus, the end-products of sintering under the above-reported condition are the samples of ultrafine alumina ceramics.

It is noteworthy that the effect of formation of nanoparticles of small size (10–40 nm) is observed only when alumina nanopowder is sintered in vacuum with the presence of carbon, i.e. under highly-reducing condition. In this case, due to partial reduction of Al_2O_3 , lower oxides (Al_2O , AlO) are formed [10]. The given process proceeds more intensively at $T = 1700^\circ\text{C}$ and higher. One can hypothesize that the particles which appear in this process consist of lower oxides.

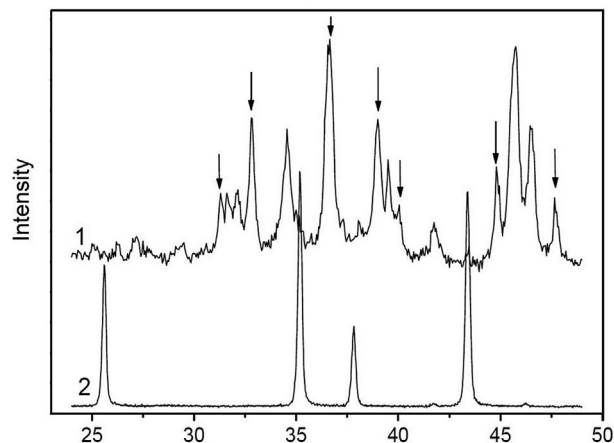


Fig. 1. Diffraction patterns of the Al_2O_3 samples: initial pellet – (1) and sample sintered at 1550°C – (2). Arrows indicate the main lines corresponding to the θ -phase, the remaining lines correspond to the δ -phase. The diffraction pattern (2) corresponds to the α -phase.

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