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ScienceDirect

Ceramics International 42 (2016) 843–846

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Porosity of spherical $(Y_{1-x}Eu_x)_2O_3$ crystalline particles

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Received 29 March 2015; accepted 2 September 2015
Available online 9 September 2015

Abstract

The paper presents a method for estimating the porosity and the pore space structure of spherical particles $(Y_{1-x}Eu_x)_2O_3$ according to the data on their specific surface area. Using assumptions about their fractal structure, their porosity and pore space structure of particles of different diameters was estimated. It was established that the porosity of particles increases with an increase in their diameter. Based on the calculations of the fractal dimension of the mass of particles $(Y_{0,95}Eu_{0,05})_2O_3$, it was suggested that particles with a diameter of 120–200 nm and 200–300 nm have a different pore space structure. Pore space of particles with a diameter of 120–300 nm is apparently formed by an extensive system of intercrystalline spaces – pores. Pore space in particles with a diameter of 200–300 nm is probably formed by porous clusters located between the core and the outer surface of spherical particles.

Keywords: B. Porosity; Spherical particles; Structure; Fractal dimension; $(Y_{0,95}Eu_{0,05})_2O_3$

1. Introduction

One of the urgent problems in material sciences is the search for and development of new low-dimensional forms of refractory oxide materials with the ability to control their functional properties. Among them, a separate niche is occupied by powders based on monodispersed isolated nano- and submicron spherical crystalline of particles crystalline phosphor $(Y_{1-x}Eu_x)_2O_3$ obtained by low-temperature crystallization of the amorphous precursor precipitated from the solution [1–3].

Due to the features of the method for obtaining, spherical particles $(Y_{1-x}Eu_x)_2O_3$ are characterized by high (up to 50%) open porosity with a characteristic pore size in the meso-range, which allows their use as a template to create nanocomposite materials [4,5].

Spherical particles $(Y_{1-x}Eu_x)_2O_3$ are characterized by high porosity and polycrystalline (block) structure with a small size of crystallites and a large area of intercrystalline boundaries saturated with defects of different nature – the main sources of the formation of nonradiative relaxation channels for the ions of activators in the crystal matrix [6,7], which significantly reduces the functional response of materials based on such particles. Thus, the study of porosity is a relevant aim to receive materials based on spherical particles $(Y_{1-x}Eu_x)_2O_3$ with a controlled set of functional properties.

Currently, there are a limited number of publications, where the porosity of spherical particles obtained by low-temperature crystallization of the amorphous precursor was studied [6,8]. The porosity of particles was estimated from the data on the specific surface area of powder determined by Brunauer–Emmett–Teller (BET) method. Estimation of the porosity was based on the assumption that the powder consists of monodispersed isolated smooth particles, and the pores are located only inside the particles. Calculation of the porosity in these works is an estimate and does not take into account the pore space structure.

The pore space of spherical particles $(Y_{1-x}Eu_x)_2O_3$ is formed by intercrystalline spaces with the size in the range of 2–14 nm and nearly spherical shape [8]. This corresponds to the definition of irregular self-similar structure – a fractal. Assumption on the fractal nature of the porosity allows estimation of not only the magnitude of the porosity of the material, but also qualitatively assessment of the pore space structure on the basis of the data on the specific surface area. The theoretical possibility of such an approach is shown in the works [9–11].

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http://dx.doi.org/10.1016/j.ceramint.2015.09.007
0272-8842/

The aim of this work was to study the porosity and the pore space structure of spherical particles $(Y_{0,95}Eu_{0,05})_2O_3$.

2. Experimental procedures

Powders consisting of spherical crystalline particles $(Y_{0,95}Eu_{0,05})_2O_3$ were obtained by chemical coprecipitation from an aqueous solution of the amorphous precursor followed by its low-temperature crystallization. The methods for obtaining such particles are described in detail in the works [8,12].

Morphology and average diameter of spherical particles was determined by transmission electron microscopy (TEM) using a high-resolution transmission microscope JEM 2100F with an accelerating voltage of 200 kV (JEOL, Japan). The specific surface area of the samples was determined by the BET method. Absorption capacity for nitrogen at −196 °C was measured by the volumetric method in a range of nitrogen equilibrium relative pressures from 0.01 to 0.99 using a gas analyzer ASAP 2020, Micromeritics (NUMAS No. 46147. 10). The porosity and pore space structure of particles was estimated from their specific surface area.

3. Results and discussion

The paper studies a series of powders consisting of monodispersed ($d \leq 15\%$) isolated smooth particles $(Y_{0,95}Eu_{0,05})_2O_3$ with a diameter of 120–300 nm. Electron microscopic study of the internal structure of the particles showed that they are polycrystalline formations with high open porosity. Pores are intercrystalline spaces, preferably spherical in shape, with the size in a range of 2–14 nm (Fig. 1).

The porosity of the particles was estimated from their specific surface area. To determine the specific surface area of one spherical particle $(Y_{0,95}Eu_{0,05})_2O_3$, let us consider its relationship with the specific surface area of the powder on their basis determined by the BET method. Thus, we proceed from the assumption that the porosity and hence the density of particles of each typical size under study is the same.

The total surface area of the powder is:

$$S_{\Sigma} = N4\pi R^2, \tag{1}$$

where N – number of spherical particles of radius R. Thus, the mass of the powder is:

$$m_{\Sigma} = Nm_{\mathrm{i}}, \tag{2}$$

where m_{Σ} – total mass of the powder, and m_{i} – mass of a separate particle. Hence, the specific surface area of the powder is:

$$S_{\mathrm{u}} = \frac{S_{\Sigma}}{m_{\mathrm{i}}} = \frac{N4\pi R^2}{Nm_{\mathrm{i}}} = \frac{4\pi R^2}{m_{\mathrm{i}}}. \tag{3}$$

The obtained value coincides with the specific surface area of a separate spherical particle $S_{\mathrm{u}(ind)} = \frac{4\pi R^2}{m_{\mathrm{i}}}$.

Thus, the specific surface area of the ideal (non-porous) spherical particle is:

$$S_{\mathrm{u(i)}} = \frac{4\pi R^2}{m_{\mathrm{i}}} = \frac{\pi R^2}{\rho_{\mathrm{i}}\frac{4}{3}\pi R^3} = \frac{3}{4\rho_i R} \tag{4}$$

where ρ_{i} – density of the solid solution $(Y_{0,95}Eu_{0,05})_2O_3$.

Accordingly, the specific surface area S_{ur} of a real (porous) spherical particle $(Y_{0,95}Eu_{0,05})_2O_3$ is:

$$S_{\mathrm{ur}} = \frac{\pi R^2}{m} = \frac{\pi R^2}{\rho_{\mathrm{r}}\frac{4\pi}{3}R^3} = \frac{3}{4\rho_{\mathrm{r}}R}, \tag{5}$$

where ρ_{r} – real density of a spherical particle $(Y_{0,95}Eu_{0,05})_2O_3$, taking into account its porosity.

Porosity (P) is calculated by the formula:

$$P = \left(1 - \frac{\rho_{\mathrm{r}}}{\rho_{\mathrm{i}}}\right)100\% = \frac{\rho_{\mathrm{i}} - \rho_{\mathrm{r}}}{\rho_{\mathrm{i}}}100. \tag{6}$$

where, expressing densities of an ideal spherical particle (ρ_{i}) and a porous particle $(Y_{0,95}Eu_{0,05})_2O_3$ (ρ_{r}) through the mass of the material and their size ($\rho_{\mathrm{i}} = \frac{4}{3RS_{\mathrm{ui}}}$ и $\rho_{\mathrm{r}} = \frac{4}{3RS_{\mathrm{ur}}}$), we obtain a handy ratio to calculate the porosity through the specific surface area in the form of:

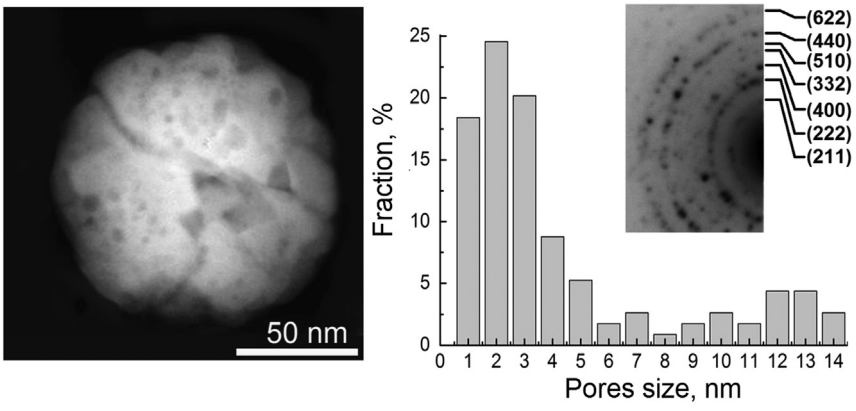

Fig. 1. HAADF STEM image of a particle $(Y_{0,95}Eu_{0,05})_2O_3$, histogram of pore distribution as of the size (inset – electronic microdiffraction).