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XRD Study of Eu_2O_3–ZrO_2 Feedstock Powders and Sintered Materials

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Presented article described synthesis process of nonstoichiometric europium zirconate by solid state reaction between weight-equal mixture of ZrO_2 and Eu_2O_3 feedstock powders. To final material synthesis high temperature vacuum press was used as well as a free standing process of sintering. As a result europium zirconates were obtained. X-ray diffraction characterization revealed that relatively homogeneous materials were synthesised but scanning electron microscopy analysis showed many areas with nonhomogeneous composition. On the base of X-ray diffraction patterns, characterization of crystallite size as well as a lattice strain were calculated. The Williamson–Hall, Halder–Wagner and Cauchy–Gauss methods were used to make the calculations. Obtained data showed that there was no significant differences between crystallite size with zirconate materials obtained by solid state reaction at temperature 1350 °C in vacuum press and by free standing process. The short heating at higher temperature (1450 °C/5 h) has no influence on crystallite size as well, but 24 h of additional heating strongly increases the crystallite size.

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1. Introduction

Materials on the base of rare-earth zirconates are very promising new ceramic materials for many applications such as insulation layers of thermal barrier coatings (TBC). An essential requirement of these materials is low as possible thermal conductivity with simultaneously chemical compatibility to alumina and high thermal phases stability [1, 2]. The main factors influencing the thermal conductivity are those related with phonon scattering i.e. phonon free path, Umklapp processes, grain boundaries and crystallite size [3]. One of the most effective ways of thermal conductivity decrease is application of nanosized materials where the effect of phonon scattering is very strong [3]. In the case of nanosized ceramic materials, destined to deposition of insulation layer of thermal barrier coatings, there are many information about standard zirconia based ceramic but relatively low about new materials, for example on the base of rare earth zirconates, where their thermal properties are designed by decrease of granules size to nanoscale [4, 5].

2. Experiment

For investigation nanocrystalline powders of zirconium oxide ZrO_2, and europium oxide Eu_2O_3 were used. Feedstock powders were mixed and sintered in high temperature vacuum press and by free standing sintering at temperature 1350 and 1450 °C. Additional annealing during 24 and 5 h was applied as well respectively. On the basis of X-ray diffraction of tested powders, there were made calculations of crystallite size (D) and lattice stain (e) in initial condition and after sintering process with and without additional annealing. To those calculations three methods of approximation were used: Williamson–Hall (Cauchy/Cauchy), Halder–Wagner (Gauss/Gauss) and Cauchy/Gauss described elsewhere [6, 7]. X-ray diffraction pattern used in this investigation to analyze the phase composition was performed on JEOL JDX-7S diffractometer. Furthermore, the starting powders were subjected to the investigation the measurement of particle size, with using the method of laser light diffraction on the device Mastersizer, Malvern Inc. (UK). Morphological analysis of investigated powders were made on scanning-transmission electron microscopy STEM (Hitachi HD-2300A). This investigation was conducted using an accelerating voltage of 200 kV.

The powders were weighed in the weight ratio of 1:1, which gives the mole ratio of ZrO_2 to Eu_2O_3 as 74% to 26%, with an excess of zirconium oxide as to the stoichiometric pyrochlore structure, whose mole ratio is 67% to 33%. After weighing the powders, they were subjected to mechanical mixing in ethanol by 15 min. The next step was to make sinter, which was carried out by four methods, labeled in sequence as:

- HTSP — high temperature sintering under pressure. The sintering temperature was 1350 °C with time of process 2 h. The compaction pressure was 15 MPa and whole sintering process was made in a vacuum on level of 10^{-2} Tr.
- HTSPA — high temperature sintering under pressure with additional annealing. The sintering temperature was 1350 °C with time of process 2 h.

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The compaction pressure was 15 MPa and whole sintering process was made in a vacuum on level of 10^{-2} Tr. Then an additional heat treatment in 1450 °C was made during 5 h.

- FS1350 — freestanding sintering in temperature 1350 °C during 24 h.
- FS1450 — freestanding sintering in temperature 1450 °C during 24 h.

3. Results

In the first step, diffraction patterns of both powders were analyzed where only monoclinic zirconium was found for first analyzed powder. In the case of second powder, diffraction analysis revealed presences of dominated cubic europium with relatively small amount of monoclinic Eu_2O_3. On the base of HFWM and θ angle values calculated for zirconium (M) and europium (C) diffraction peaks, calculations of crystallite size and lattice strain were made (Table I).

TABLE I

Calculated value of crystallite size and lattice strain.

Method	Crystallite size D [nm]	Lattice strain e [%]	Pearson coeff. R
	ZrO_2		
Cauchy/Cauchy	41.6±4.1	0.135±0.023	0.842
Gauss/Gauss	32.8±1.5	0.218±0.017	0.865
Cauchy/Gauss	29.90±0.69	0.119±0.019	0.996
	Eu_2O_3		
Cauchy/Cauchy	49.7±2.8	0.080±0.012	0.956
Gauss/Gauss	40.44±0.92	0.140±0.010	0.931
Cauchy/Gauss	41.25±0.66	0.1090±0.0099	0.999

For the sake of comparison characterizations of particles size were analyzed by laser diffraction method. In the case of ZrO_2 powder a bimodal distribution of average particle size was observed. The range of ZrO_2 particle size was measured as 0.05–26.3 μm, where the fraction with the largest volume, including 22.7%, was in the range of particles diameter from 0.72 to 1.26 μm. The mode maxima were revealed for particles with a diameter range from 0.16 to 0.96 μm. The average particle size was *ca.* 1 μm. In the case of europium powder an unimodal distribution of particle size was observed. Average value of particles diameter was detected as about 4 μm. The particle size of europium oxide was in the range of 0.55–50.45 μm, but the fraction with the highest volume (maximum of the mode), including 32.72%, was detected in the range of particle diameter from 3.31 to 5.01 μm. Additional information about particles size of analyzed powders was obtained by STEM method (Fig. 1). This analysis allows to observe individual grains, their irregular shape, and heterogeneity in size. STEM observations of individual particles showed that in both cases particles are built from smaller elements which create conglomerates with higher size. For zirconium particle the size of conglomerate was *ca.* 150 nm, but the size of elementary particles was in the range of 60–120 nm. For europium particle the size of conglomerate was higher than 200 nm of the radius, but the size of the smallest elementary particles was lower than that for zirconium. It was a level of 30–80 nm.

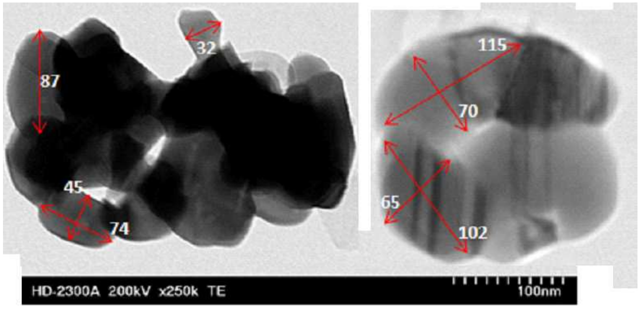

Fig. 1. The particle of ZrO_2 (left) and Eu_2O_3 (right) feedstock powders — STEM view.

TABLE II

Calculated value of crystallite size and lattice strain for sinters.

	Method	Crystallite size D [nm]	Lattice strain e [%]	Pearson coeff. R
HTSP	Cauchy/Cauchy	36.6±1.2	0.0550±0.0080	0.960
	Gauss/Gauss	30.99±0.52	0.079±0.015	0.792
	Cauchy/Gauss	31.24±0.23	0.0622±0.0079	0.999
HTSPA	Cauchy/Cauchy	37.6±2.5	0.065±0.016	0.904
	Gauss/Gauss	31.4±1.1	0.099±0.025	0.704
	Cauchy/Gauss	31.56±0.89	0.073±0.026	0.998
FS1350	Cauchy/Cauchy	44.0±3.2	0.108±0.017	0.977
	Gauss/Gauss	34.3±1.7	0.160±0.025	0.917
	Cauchy/Gauss	35.3±1.1	0.130±0.016	0.998
FS1450	Cauchy/Cauchy	81.1±8.1	0.160±0.012	0.992
	Gauss/Gauss	48.2±1.7	0.1941±0.0067	0.993
	Cauchy/Gauss	49.8±1.7	0.1555±0.0079	0.998

The same investigations were made for final materials obtained by different types of sintering processes. The assumption of presented investigation was synthesis of non-stoichiometric materials of europium zirconate type by different methods and characterization of its crystallite size in function of synthesis method and its thermal parameters. In the first step, analysis of phases constituent of synthesized materials was made. This analysis showed small but significant differences in phases constituency of sintered materials. The most homogeneous final sinter based on europium zirconate phase with overall formula $Eu_2Zr_2O_7$ was obtained after sintering by HTSPA method and FS1450 method. In the last case there can be seen the strongest reflections coming from superstructure. Comparison of synthesis process in vacuum press

(HTSP) and in free standing mode (FS1350) showed that at temperature 1350 °C much better synthesis took place during process with additional pressure. The phases constituent in this case is much uniform, without any transition phases observed for free standing process. Additionally used annealing at temperature 1450 °C by 5 h does not change significantly phases composition of HTSP sinter, but for free-standing sinter next annealing at 1450 °C during 24 h allowed for strong homogenization of phases composition with superstructure formation. The results of crystallite size and lattice strain calculated for analyzed sinters are shown in Table II and compared to data for initial powders in Fig. 2.

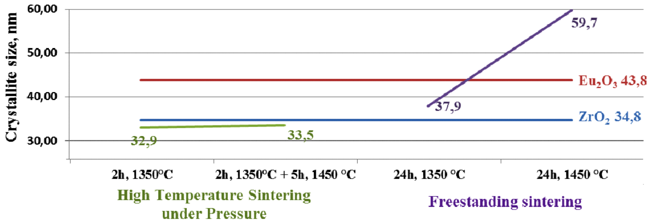

Fig. 2. Average value of crystallite size of sinters and its comparison to crystallite size of initial oxide powders.

4. Summary

The selection of sintering method has a significant impact on the synthesis process of final materials on the base of europium zirconates. This influence is related with phases constituent, degree of homogeneity and superstructure creation related with ordering/disordering phenomena. Application of sintering process in high temperature vacuum press allows to obtain final material with the best homogeneity from phases constituency point of view. Additional annealing does not give any significant changes. Free-standing sintering with long term annealing allows to obtain similar degree of homogenization but with much stronger effect of superstructure formation, as a results of zirconium dissolution in pyrochlore lattice of $Eu_2Zr_2O_7$ phase and nonstoichiometric compound formation. The strongest effect on crystallite size is related with longer time of annealing, when the activation of crystallite growth phenomena took place. Laser diffraction analysis does not allow to obtain correct results of particle size due to strong tendency to conglomerates formation of investigated initial powders of zirconium and europium. STEM analysis showed this effect precisely.

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