



Article Phase Formation in Heterovalent Equimolar Quinary Oxide Systems of ZrO₂-HfO₂-CeO₂-Nb₂O₅-RE₂O₃ Type (RE = Y, Yb, Nd, Gd)

Vasile-Adrian Surdu * D and Ecaterina Andronescu D

Department of Science and Engineering of Oxide Materials and Nanomaterials, Faculty of Applied Chemistry and Materials Science, Politehnica University of Bucharest, 060042 București, Romania; ecaterina.andronescu@upb.ro * Correspondence: adrian.surdu@upb.ro

Abstract: Tailoring electrical and mechanical properties in the fluorite oxides family is of great interest for technological applications. Other than doping and substitution, entropy-driven stabilization is an emerging technique for new solid solutions formation and enhancing or exploring new functionalities. However, there is a high number of possible combinations for higher-order diagram investigations, and the current state of the art shows limited possibilities in predicting phase formation and related properties. In this paper, we expand the compositional space of fluorite oxides in ZrO_2 -HfO₂-CeO₂-Nb₂O₅-RE₂O₃ systems. X-ray diffractometry and scanning electron microscopy measurements showed the formation of cubic fluorite-type structures when processing compositions at 1600 °C.

Keywords: ceramics; X-ray diffraction; electron microscopy; solid-state reaction



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1. Introduction

Fluorites are one of the most important family of oxides with a wide range of prominent members in the field of energy materials. Their chemical formula can be expressed as AO_2 , where A is a cation in a 4+ oxidation state. The most common representatives are ZrO_2 and CeO_2 and their solid solutions [1,2]. Compounds structured with fluorite-type cubic symmetry may be tailored to possess a wide range of properties, such as electrical properties, and to withstand high temperatures, high temperature gradients and mechanical stresses, which make them suitable for various technological applications not limited to ion conductors [3,4], thermal barrier coatings [5–7], ferroelectrics [8,9] or sensing [10].

Recently, a new strategy to enhance or discover new properties was reported and consisted of entropy-driven stabilization of fluorite-type structures [11–15]. To achieve this, a complex multi-component solid solution is designed by mixing at least five precursor oxides in an equimolar ratio.

The purpose of the present study is to further expand the compositional space in such systems and to explore the influence of pentavalent cation oxide (Nb₂O₅) and trivalent rare earth oxide's introduction. The phase formation and microstructure of four compositions are reported in ZrO_2 -HfO₂-CeO₂-Nb₂O₅-RE₂O₃ type systems (RE = Y, Yb, Nd, Gd). To the best of our knowledge, phase formation in the mentions systems has not been reported yet. However, binary and ternary systems based on ZrO_2 and CeO₂ were extensively studied. The ZrO_2 -HfO₂ system shows complete solubility over the whole composition range with three regions of solid solutions: monoclinic, tetragonal and cubic [16]. In the case of ZrO_2 -CeO₂ and HfO₂-CeO₂ systems, there is evidence of limited mutual solubility in the solid-state [17,18]. Phase equilibria in ternary ZrO_2 -HfO₂-CeO₂ were reported by Andrievskaya et al. [17,19] and showed the formation of a mixture of the three polymorphs near the equimolar region of the diagram for processing temperatures of 1250 and 1500 °C. Gild et al. [13] reported successful preparation via high energy ball milling and spark plasma sintering of eight compositions with five cations in equimolar amounts designed by

the addition of a four-principal-cation $Hf_{0.25}Zr_{0.25}Ce_{0.25}Y_{0.25}O_{2-\delta}$. The obtained materials showed low thermal conductivities, which the authors state is a result of multiple different cation species. In this context, the addition of Nb₂O₅ to $Hf_{0.25}Zr_{0.25}Ce_{0.25}Y_{0.25}O_{2-\delta}$ or other compositions with hafnium, zirconium and cerium oxide core might contribute to enhancing the properties of the materials by balancing the charge and thus avoiding oxygen vacancies formation.

2. Materials and Methods

2.1. Materials Processing

Ceramic samples belonging to equimolar region of ZrO_2 -HfO₂-CeO₂-Nb₂O₅-RE₂O₃ type (RE = Y, Yb, Nd, Gd) systems were synthetized by solid-state route. The compositions will be referred to as follows: ZHCNY for 0.2ZrO₂_0.2HfO₂-0.2CeO₂-0.2Nb₂O₃-0.2Y₂O₃, ZHCNYb for 0.2ZrO₂-0.2HfO₂-0.2CeO₂-0.2Nb₂O₃-0.2Yb₂O₃, ZHCNNd for 0.2ZrO₂-0.2HfO₂-0.2CeO₂-0.2Nb₂O₃-0.2Yb₂O₃, ZHCNNd for 0.2ZrO₂-0.2HfO₂-0.2CeO₂-0.2Nb₂O₃-0.2Yd₂O₃ and ZHCNGd for 0.2ZrO₂-0.2HfO₂-0.2CeO₂-0.2Nb₂O₃-0.2Gd₂O₃.

First, for all compositions, a 20 g mixture was prepared by hand milling for 60 min in the presence of isopropanol (Sigma-Aldrich, St. Louis, MO, USA ACS reagent \geq 99.5%) using an agate mortar and pestle, starting from high purity oxides: ZrO₂ (Sigma-Aldrich, St. Louis, MO, USA 99% trace metals basis), HfO₂ (Sigma-Aldrich, St. Louis, MO, USA 98%), CeO₂ (Sigma-Aldrich, St. Louis, MO, USA \geq 99%), Nb₂O₅ (Sigma-Aldrich, St. Louis, MO, USA 99.9% trace metals basis), Y₂O₃ (Sigma-Aldrich, St. Louis, MO, USA 99.9% trace metals basis), Yb₂O₃ (Sigma-Aldrich, St. Louis, MO, USA 99.9% trace metals basis), Nd₂O₃ (Sigma-Aldrich, St. Louis, MO, USA 99.9% trace metals basis) and Gd₂O₃ (Sigma-Aldrich, St. Louis, MO, USA 99.9% trace metals basis). The precursor composition for each mixture is summarized in Table 1.

Table 1. Precursor amount for heterovalent equimolar quinary oxide system of ZrO₂-HfO₂-CeO₂-Nb₂O₅-RE₂O₃ type (RE = Y, Yb, Nd, Gd).

Composition Precursor	0.2ZrO ₂ -0.2HfO ₂ - 0.2CeO ₂ -0.2Nb ₂ O ₃ - 0.2Y ₂ O ₃ (ZHCNY)	0.2ZrO ₂ -0.2HfO ₂ - 0.2CeO ₂ -0.2Nb ₂ O ₃ - 0.2Yb ₂ O ₃ (ZHCNYb)	0.2ZrO ₂ -0.2HfO ₂ - 0.2CeO ₂ -0.2Nb ₂ O ₃ - 0.2Nd ₂ O ₃ (ZHCNNd)	0.2ZrO ₂ -0.2HfO ₂ - 0.2CeO ₂ -0.2Nb ₂ O ₃ - 0.2Gd ₂ O ₃ (ZHCNGd)
ZrO ₂	3.2787 g	2.9486 g	3.0539 g	3.0055 g
HfO ₂	5.6009 g	5.0370 g	5.2168 g	5.1341 g
CeO ₂	4.5796 g	4.1185 g	4.2656 g	4.1979 g
Nb ₂ O ₅	3.5364 g	3.1804 g	3.2939 g	3.2417 g
Y ₂ O ₃	3.0043 g	-	-	-
Yb ₂ O ₃	-	4.7155 g	-	-
Nd ₂ O ₃	-	-	4.1697 g	-
Gd ₂ O ₃	_	-	-	4.4209 g

The powder mixtures were then pressed into 13 mm pellets using a 10-ton force 4555 Manual Bench Top Pellet Press Equipment (Carver, Inc., Wabash, IN, USA). The green bodies were then subjected to several thermal treatments performed in the range of 1300–1600 °C in an HT 18 High Temperature Furnace (Nabertherm, Lilienthal, Germany). The presintering heat treatment stage was performed at 1300 °C in air, with a heating rate of 5 °C/min, a dwell time of 6 h and a cooling rate at the normal speed of the oven. After the presintering stage, the samples were ground in an agate mortar and reshaped into 13 mm pellets under 400 MPa uniaxial pressure. The sintering stage was performed at 1400, 1500 or 1600 °C in air and with a heating rate of 5 °C/min, a dwell time of 6 h and a cooling rate at the normal speed of the other at 1400, 1500 or 1600 °C in air and with a heating rate of 5 °C/min, a dwell time of 6 h and a cooling rate at the normal speed of the other at 1400, 1500 or 1600 °C in air and with a heating rate of 5 °C/min, a dwell time of 6 h and a cooling rate at the normal speed of the other at 1400, 1500 or 1600 °C in air and with a heating rate of 5 °C/min, a dwell time of 6 h and a cooling rate at the normal speed of the other.

2.2. Materials Characterization

Room-temperature X-ray diffraction (XRD) measurements were performed on the heat-treated sample for phase composition determination. The analyses were carried out on Empyrean equipment (PANalytical, Almelo, The Netherlands), using Ni-filtered Cu-K α radiation ($\lambda = 1.5418$ Å) with a step size of 0.0263° and counting time per step of 510 s in the 2 θ range of 20–80°. Phase search and match, as well as Rietveld refinement of structures, were performed in HighScore Plus 3.0.e software (PANalytical, Almelo, The Netherlands) coupled with the ICDD PDF4+ 2021 database (Newtown Square, PA, USA).

The microstructure and elemental distribution were investigated by scanning electron microscopy—SEM—operated at 30 kV coupled with energy dispersive spectrometer—EDS (Inspect F50, FEI, Hillsboro, OR, USA). The average grain size distribution was determined using OriginPro 9.0 software (OriginLab, Northampton, MA, USA) by considering size measurements on \approx 500 grains performed by means of image processing software (ImageJ 1.50b, National Institutes of Health and the Laboratory for Optical and Computational Instrumentation, Madison, WI, USA).

3. Results and Discussion

3.1. Phase Composition

Phase composition was studied by XRD measurements and subsequent Rietveld refinement of patterns. The obtained and matched XRD patterns, as well as angular range from 27 to 31° 20, are presented in Figure 1 and the corresponding phase content for different heat treatment conditions are summarized in Table 2.

Table 2. Phase content for samples treated at 1300, 1400, 1500 and 1600 °C belonging to equimolar ZrO_2 -HfO₂-CeO₂-Nb₂O₅-RE₂O₃ systems (RE = Y, Yb, Nd, Gd).

Sample	Thermal Treatment Temperature	Monoclinic—P2/m	Tetragonal— P4/mmm	Cubic—Fm-3m	RENbO4— Monoclinic—P2/m
ZHCNY	1300 °C	$17.1\% \pm 0.5\%$	$22.3\%\pm0.5\%$	$5.9\%\pm0.5\%$	$54.6\% \pm 0.5\%$
	1400 °C	$0.8\%\pm0.5\%$	$64.9\% \pm 0.5\%$	$3.2\%\pm0.5\%$	$31.0\% \pm 0.5\%$
	1500 °C	0.0%	$68.0\% \pm 0.50\%$	0.0%	$32.0\% \pm 0.5\%$
	1600 °C	0.0%	0.0%	$76.2\%\pm0.5\%$	$23.8\%\pm0.5\%$
ZHCNYb	1300 °C	$7.0\%\pm0.5\%$	$29.6\% \pm 0.5\%$	$16.0\% \pm 0.5\%$	$47.4\% \pm 0.5\%$
	1400 °C	0.0%	$22.3\%\pm0.5\%$	$45.3\% \pm 0.5\%$	$32.4\% \pm 0.5\%$
	1500 °C	0.0%	0.0%	$68.2\% \pm 0.5\%$	$31.8\% \pm 0.5\%$
	1600 °C	0.0%	0.0%	$70.9\% \pm 0.5\%$	$29.1\%\pm0.5\%$
ZHCNNd	1300 °C	$9.5\%\pm0.5\%$	$56.1\% \pm 0.5\%$	$34.4\%\pm0.5\%$	0.0%
	1400 °C	$33.7\% \pm 0.5\%$	$6.1\%\pm0.5\%$	$41.3\% \pm 0.5\%$	$18.9\% \pm 0.5\%$
	1500 °C	$25.5\% \pm 0.5\%$	$2.4\%\pm0.5\%$	$49.6\% \pm 0.5\%$	$22.5\% \pm 0.5\%$
	1600 °C	0.0%	0.0%	$70.0\% \pm 0.5\%$	$30.0\%\pm0.5\%$
ZHCNGd	1300 °C	$18.4\%\pm0.5\%$	$30.8\% \pm 0.5\%$	$2.0\%\pm0.5\%$	$48.8\% \pm 0.5\%$
	1400 °C	0.0%	$28.5\% \pm 0.5\%$	$28.6\% \pm 0.5\%$	$42.9\% \pm 0.5\%$
	1500 °C	0.0%	0.0%	$59.5\% \pm 0.5\%$	$40.5\% \pm 0.5\%$
	1600 °C	0.0%	0.0%	$63.4\%\pm0.5\%$	$36.6\%\pm0.5\%$

After thermal treatment at 1300 °C, the composition is complex for all studied samples, and it consists of three solid solutions of cubic [20], tetragonal [21] and monoclinic [22] symmetries and RENbO₄ of monoclinic symmetry, where RE is the rare earth ion in the 3+ oxidation state. The peak profiles are broad and show a low intensity, which suggests a limited mutual solubility of the precursor oxides in this temperature condition (Figure 1). The increase of the heat treatment temperature to 1400 °C shows two kinds of effects on the studied compositions: ZHCNNd forms a higher content of lower symmetry P2/m solid solutions at this temperature approximated at 33.70%, whereas in the case of ZHCNY, ZHCNYb and ZHCNGd, an increase in the content of tetragonal P4/mmm and cubic Fm-3m solid solutions was evidenced. A further increase in the temperature to 1500 °C is beneficial in stabilizing higher-ordered solid solutions of tetragonal symmetry in the case of ZHCNYb and ZHCNGd. The ZHCNNd

composition shows a remanent P2/m solid solution at 1500 °C, but with a decreased content. XRD results after processing at 1600 °C show a binary phase composition consisting of fluorite-type cubic Fm-3m solid solution and RENbO₄ (RE = Y, Yb, Nd, Gd).



Figure 1. Cont.



Figure 1. XRD patterns corresponding to samples heat-treated at 1300, 1400, 1500 and 1600 °C belonging to equimolar ZrO_2 -HfO_2-CeO_2-Nb_2O_5-RE_2O_3 systems (RE = Y, Yb, Nd, Gd).

3.2. Microstructure

Figure 2 depicts SEM images and corresponding EDS maps for the equimolar quinary compositions after thermal treatment at 1600 $^{\circ}$ C.

The microstructure of the ZHCNY sample is heterogeneous and shows grains with an average size of $8.56 \pm 2.60 \ \mu m$ and macropores, which are placed intra- and intergranular. The corresponding EDS maps show niobium and yttrium aggregation, which is in good agreement with XRD results, where the formation of YNbO₄ was evidenced. Moreover, in these areas, a melting and recrystallization process is evidenced by plate-like grains and low-angle junctions. This effect is most probably caused by the lower melting temperature of Nb₂O₅ of 1512 °C [23]. The ZHCNYb sample also shows a heterogeneous microstructure, with grains of an average size of $6.53 \pm 4.24 \ \mu m$ and intergranular pores. In this case, the ceramic has pronounced recrystallization plate-like grains, probably caused by a lower melting temperature of Yb₂O₃ (2355 °C [24]) compared to Y₂O₃ (2425 °C [25]) and, as a result, a lower porosity.

The ZHCNNd sample shows a typical particulate composite microstructure, where NdNbO₄ is placed in a (Zr,Hf,Ce)O₂ matrix. In these processing conditions, the SEM image evidences also intragranular and intergranular cracks formation.

In the case of the ZHCNGd sample, the average grain size is the lowest in the studied series (3.72 \pm 1.65 μm). The grains are well defined and are of polyhedral shape with round edges.



Figure 2. Cont.



Figure 2. Cont.



Figure 2. Microstructure and elemental distribution of samples treated at 1600 °C belonging to ZrO_2 -HfO₂-CeO₂-Nb₂O₅-RE₂O₃ equimolar systems (RE = Y, Yb, Nd, Gd).

4. Conclusions

Four compositions in ZrO_2 -HfO_2-CeO_2-Nb_2O_5-RE_2O_3 type systems (RE = Y, Yb, Nd, Gd) were studied over the temperature range of 1300–1600 °C. XRD results showed a complex composition at lower temperatures and a binary composition at 1600 °C, consisting of cubic fluorite-type oxide and RENbO₄. Phase formation in ZrO_2 -HfO_2-CeO₂-Nb₂O₅-RE₂O₃ type systems (RE = Y, Yb, Nd, Gd) shows the obtaining of single fluorite-type polymorphs when RENbO₄ is present in the composition when compared to a mixture of three polymorphs obtained at 1250 and 1500 °C in a ZrO_2 -HfO₂-CeO₂ system. Therefore, RENbO₄ might reduce the temperature of higher symmetry cubic phase formation in the temperature range of 1400–1600 °C. The microstructure of the ceramics processed at the highest temperature is heterogeneous and shows evidence of melting and recrystallization due to the partial volatilization of Nb₂O₅. Moreover, measurements on the SEM images showed coarse-grain ceramics formation.

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