Journal of Alloys and Compounds 495 (2010) 524–526

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Ball milling induced solid-state reactions in the La_2O_3–HfO_2 ceramic system

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ARTICLE INFO

Article history:
Received 5 August 2008
Received in revised form 16 October 2009
Accepted 19 October 2009
Available online 25 October 2009

Keywords:
Insulators
High-energy ball milling

ABSTRACT

Ball milling of oxide blends can result in the formation of solid solutions depending on the characteristics of the oxides. In this paper the possibility of doping oxides with radioactive ^{181}Hf through the formation of these solutions is analyzed. The ^{181}Hf isotope decays to ^{181}Ta, which is an adequate probe for perturbed angular correlations (PAC) studies. Through the measurement of the hyperfine interactions of ^{181}Ta nuclei it is possible to determine the atomic distribution around the probes. We have thus studied the behavior of the La_2O_3–HfO_2 ceramic system subjected to high-energy ball milling. An oxide blend, containing few atomic percent of hafnium oxide, was milled during several hours resulting in the formation of hafnium oxide defective phases. The sample was finally annealed at high temperatures in order to facilitate the formation of solid solutions. This thermal treatment produced a solid-state reaction given place to $Hf_2La_2O_7$ pyrochlore and also the apparition of another phase or compound. The possibility of associating this last finding with a stabilized cubic phase of hafnium oxide resulting from lanthanum doping is analyzed.

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1. Introduction

Ball milling is a well-known method for generating nanostructured systems and for inducing solid-state reactions, including inorganic synthesis and mechanical alloying [1–3]. The mechanical treatment can also lead to disorder in the material, phase transformations and formation of solid solutions. The perturbed angular correlations technique (PAC) is a powerful tool to study these processes in oxide blends [4–6]. PAC gives information of the electric field gradients (EFG) at atomic sites in solids allowing the determination of the atomic configuration around them. The method requires a radioactive probe with special nuclear properties located at the site where the EFG is to be measured.

The motivation of this work is to study the formation of solid solutions in the La_2O_3–HfO_2 ceramic system. The formation of a solid solution from a binary oxides blend depends on the similarity of certain properties of the oxides such as the crystalline structure, the ionic radius and the chemical valence of the cation. In our system these conditions are not satisfied. In the case of La_2O_3, the crystalline structure is hexagonal, containing La^{3+} with 114 pm of ionic radius. HfO_2 exhibits a monoclinic crystalline structure, the cation being tetravalent with a radius of 78 pm. In spite of this, we investigate here the feasibility of doping La_2O_3 with HfO_2 by using ball milling assisted with thermal treatments. The possibility of forming solid solutions could be favored since the cations have the same coordination number in both compounds. The hafnium oxide is in few atomic percent in the blend and contains radioactive ^{181}Hf that is a suitable probe for PAC measurements.

2. Material and methods

The PAC method is based on the hyperfine interactions of nuclear moments with extra nuclear fields. A detailed description of this method can be found in the literature [7]. The γ–γ cascade at 133–482 keV, populated by the β^- decay of ^{181}Hf, was used to measure the quadrupole interaction of the 482 keV (+5/2) state of ^{181}Ta. The γ–γ PAC measurements were done using a standard setup with four conical BaF_2 detector scintillation detectors with a time resolution of 0.6 ns (FWHM). The time differential anisotropy was calculated from the coincidence spectra $N(\theta, t)$, where θ is the angle between detectors and t is the time delay between the two gamma events.

$$R(t) = 2\frac{N(180^\circ, t) - N(90^\circ, t)}{N(180^\circ, t) + 2N(90^\circ, t)} = A_{22}G_{22}(t) \quad (1)$$

$G_{22}(t)$ is the perturbation function and has the following form for a static quadrupole interaction

$$G_{22}(t) = \sum_{n=0}^{3} S_{2n} e^{-\delta\omega_n t}\cos(\omega_n t) \quad (2)$$

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doi:10.1016/j.jallcom.2009.10.130

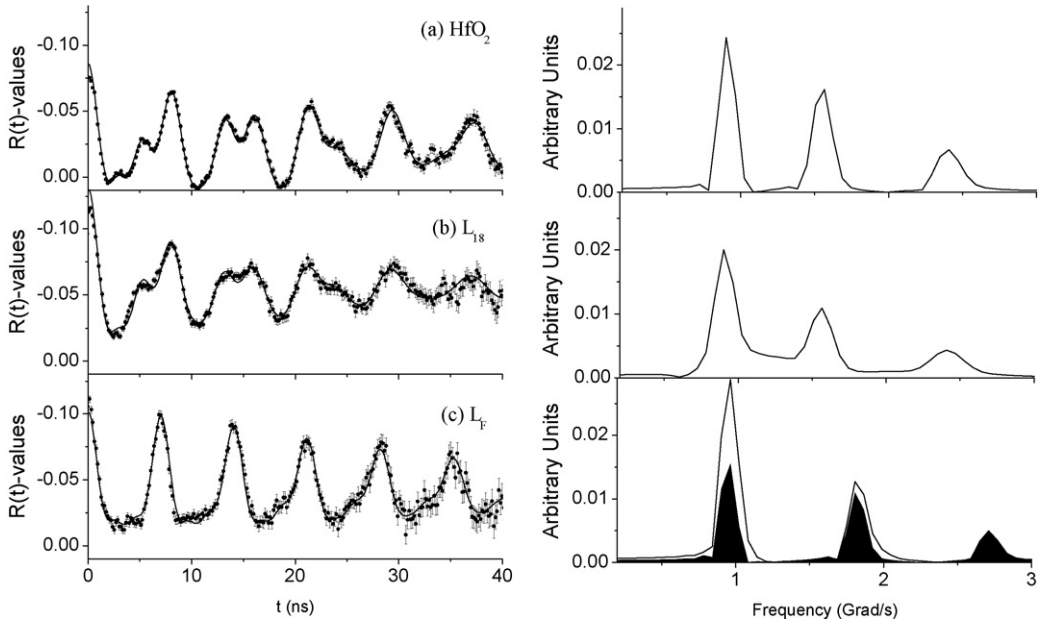

Fig. 1. PAC spectra and their Fourier transforms for (a) hafnium oxide (starting material), (b) L_{18} and (c) L_F.

The frequencies ω_n are related to the quadrupole frequency $\omega_Q = \pi eQV_{zz}/20\,\text{h}$ by $\omega_n = g_n(\eta)\omega_Q$. The coefficients $g_n(\eta)$ are known functions of the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, where V_{kk} ($k = x, y, z$) denotes the principal components of the EFG tensor. The exponential function accounts for a Lorentzian frequency distribution of width δ around ω_Q. We fitted the experimental ratio $R(t)$ by using

$$R(t) = A_{22} \sum f_i G_{22}^i(t) \tag{3}$$

where f_i is the relative fraction of nuclei that experiences a given perturbation $G_{22}^i(t)$.

Samples of La_2O_3–HfO_2 were prepared by mixing powders of radioactive hafnium oxide and La_2O_3 (ultrapure, Johnson Matthey GMBH Alfa Products) with a nominal composition of 3 at.% Hf. The radioactive hafnium oxide results from the activation of the ^{180}Hf present in natural HfO_2 (98%, Aldrich Chem. Co.) by thermal neutron capture at the CNEA (Comisión Nacional de Energía Atómica-Argentina) reactor. The milling was carried out using a horizontal-vibratory mill (Retsch MM2). The milling frequency was 30 Hz and a ball-to-powder weight ratio of 5 was chosen. The treatment was interrupted after selected times to carry out the PAC measurements, giving place to samples milled during 2 h, 6 h and 18 h (denoted hereinafter L_2, L_6 and L_{18}). Finally, L_{18} was annealed at 1000 °C during 19 h followed by an additional thermal treatment at 1200 °C during 1.5 h. The resulting product will be denoted by L_F. PAC experiments were performed at room temperature after each treatment.

3. Results and discussion

Selected PAC spectra of the starting material and the products that are resulting from the milling and annealing treatments are shown in Fig. 1. The hyperfine parameters of the starting material are $\omega_{Q1} = 127.7$ Mrad/s, $\eta_1 = 0.34$ and $\delta_1 = 3.0$, corresponding to the monoclinic phase of hafnium oxide [8]. This unique interaction gives account of the three peaks of the Fourier transform (in accordance with equation (2)).

The 18-h-milling treatment results in the apparition of a second interaction I_2 (Fig. 1(b)) and the fitted quadrupole parameters are:

$$I_1: \quad f_1 = 51.0(3.7)\%, \quad \omega_{Q1} = 128.8(0.3)\,\text{Mrad/s},$$
$$\eta_1 = 0.32(0.01), \quad \delta_1 = 3.9(0.2)\%$$
$$I_2: \quad f_2 = 49.0(2.4)\%, \quad \omega_{Q2} = 109.0(1.1)\,\text{Mrad/s},$$
$$\eta_2 = 0.58(0.02), \quad \delta_2 = 16.3(1.3)\%$$

These observations reveal that the mechanical damage results in the disappearance of part of the monoclinic hafnium oxide (I_1) in benefit of the apparition of a defective phase of the oxide (I_2). The vertical shift in the $R(t)$ values, as compared with Fig. 1(a) reveals the absorption of gamma-rays by the sample, due to the great amount of lanthanum atoms.

The fitted PAC parameters of the determined hyperfine interactions are plotted in Fig. 2. Over the 0–20 h of milling treatment, the average quadrupole frequencies and asymmetry parameters remain constant. However, it is observed an increment in the relative fraction f_2 and in the distribution width δ_2 with the milling time.

The annealing of L_{18} (19 h, 1000 °C) followed by 1.5 h, 1200 °C (sample L_F) changes dramatically the value of the quadrupole parameters of the hyperfine interaction:

$$I_1: \quad f_1 = 59.6(4.2)\%, \quad \omega_{Q1} = 148.9(0.3)\,\text{Mrad/s},$$
$$\eta_1 = 0.08(0.02), \quad \delta_1 = 1.8(0.2)\%$$
$$I_2: \quad f_2 = 40.4(2.9)\%, \quad \omega_{Q2} = 87.9(1.2)\,\text{Mrad/s},$$
$$\eta_2 = 0.94(0.06), \quad \delta_2 = 4.8(1.4)\%$$

No evidence of monoclinic hafnium oxide exists. The decrease in the distribution parameters (δ_1 and δ_2) reveals the removal of great quantity of defects. The two new interactions could correspond to new phases, to solid solutions or to new compounds. We will discuss this topic below.

At room temperature, hafnium oxide normally exists in the monoclinic form (m-HfO_2). Whereas the other phases (tetragonal t-HfO_2 and cubic c-HfO_2) are typical of high temperatures, it is well

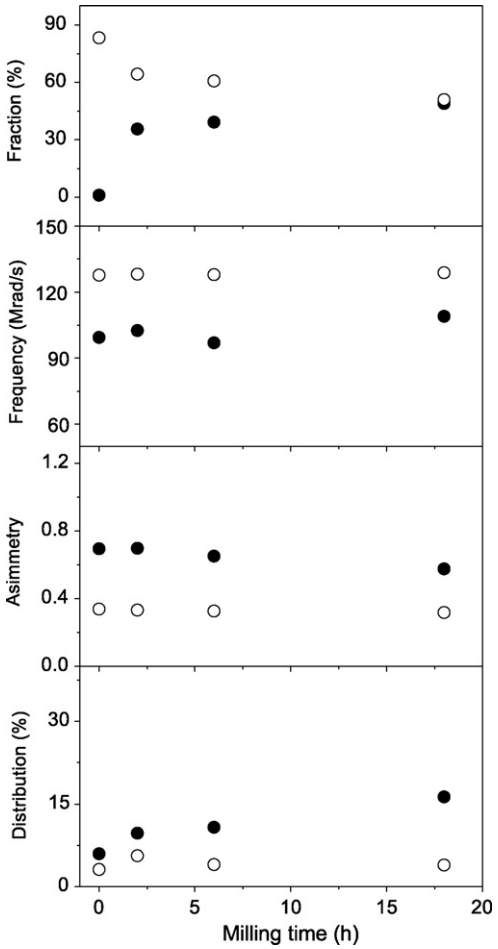

Fig. 2. Evolution of PAC parameters as a function of milling time (in hours) for the La_2O_3–HfO_2 ceramic system.

known that the addition of certain amount of appropriate oxides can stabilize them at RT. The quadrupole parameters for the stabilized phases have been reported for different aliovalent impurities (e.g. yttrium, iron and praseodymium) [5,6,9] and the typical values are:

$$\text{Cubic phase}: \quad \omega_Q = 90\text{–}100\,\text{Mrad/s}, \quad \eta = 0.75\text{–}1, \quad \delta = 5\text{–}15\%$$

$$\text{Tetragonal phase}: \quad \omega_Q = 170\text{–}178\,\text{Mrad/s}, \quad \eta = 0.42\text{–}0.62, \quad \delta = 7\text{–}16\%$$

Considering the similarity of the I_2 parameters and the stabilized cubic phase, it is possible to tentatively associate them. In our case, the stabilizing aliovalent atom would be the lanthanum forming a solid solution. Similar experiments using equimolar blends of the oxides (in order to increase the amount of HfO_2 for the X-ray diffraction studies) will be performed to elucidate this question.

The quadrupole parameters of I_1 reveal that the thermal treatment also results in a chemical reaction between the oxides to form $Hf_2La_2O_7$ pyrochlore. This compound is characterized by $\omega_Q = 147.7(0.5)$ Mrad/s and $\eta = 0.07(0.02)$ [10].

In order to analyze the role of the milling treatments in the formation of these new phases, a fresh sample was prepared. For this purpose, a blend La_2O_3–HfO_2 was manually milled during 5 min, using an agatha mortar and pestle. This new sample was pelleted and annealed at 1200 °C during 1.5 h, resulting in the PAC parameters shown below:

$$I_1: \quad f_1 = 64.5(4.4)\%, \quad \omega_{Q1} = 121.0(0.3)\,\text{Mrad/s}, \quad \eta_1 = 0.36(0.01), \quad \delta_1 = 3.0(0.2)\%$$

$$I_2: \quad f_2 = 35.5(2.4)\%, \quad \omega_{Q2} = 80.3(0.7)\,\text{Mrad/s}, \quad \eta_2 = 1.00(0.01), \quad \delta_2 = 5.1(1.0)\%$$

The manual milling does not lead to the apparition of $Hf_2La_2O_7$ pyrochlore, as I_1 depicts m-HfO_2 and I_2 with c-HfO_2. This finding suggests that the ball milling is essential for assisting the solid-state reaction but not for the diffusion of lanthanum atoms in hafnium oxide particles.

4. Conclusions

The utilization of ball milling La_2O_3 and radioactive HfO_2 together with PAC technique, allows characterizing the resulting products of mechanical treatments on binary oxides blends and the evolution of starting hafnium oxide material.

The high-energy ball milling on the La_2O_3–HfO_2 ceramic system increases the defects concentration in the components of the blend. The annealing treatment leads to a solid-state reaction producing $Hf_2La_2O_7$ pyrochlore and also to the apparition of another phase that can be tentatively associated to a stabilized c-HfO_2 at RT. Experiments to confirm this hypothesis are underway.

Acknowledgements

This work was partially supported by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CICPBA), Argentina. One of us, R.A.Q., acknowledges the fellowship of the ANPCyT, Argentina.

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