Structure – properties relationships in Ce-doped lead titanate ceramics

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The interest on the materials containing CeO_2 has increased due to the ability of CeO_2 to undergo rapid redox cycles. The oxygen partial pressure and the presence of cations with a lower oxidation state influence the reduction behaviour of CeO_2 . This work reports a comparative study on microstructure, dielectric and piezoelectric properties of Ce- and Ce, Eu doped lead titanate ceramics. The samples with a complex composition were prepared by solid-state reaction of oxide and carbonate powders. Substitutions of Ce^{4+} and Ce^{4+} , Eu^{3+} for Pb^{2+} , and Mn^{4+} for Ti^{4+} were performed. Nanostructured materials with tetragonal perovskite phase were revealed and investigated by high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) and X-ray diffraction. The local distribution of the chemical elements was revealed using the wavelength dispersive spectroscopy. The porosity of the ceramics was also investigated. Dielectric permittivity was measured in a wide temperature and frequency range. The temperature dependence of the piezoelectric properties is reported. It is found that the substitution of Eu^{3+} for Ce^{4+} improves the piezoelectric properties of the PT-type ceramics.

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1. Introduction

The ceramics containing CeO_2 have received a special attention for various applications, due to their catalytic activity, redox properties elevated oxygen transport and thermal stability [1,2]. Cerium oxide, and/or together with other rare-earth oxides, is also used for doping lead titanate compounds for SAW applications, high frequency applications like linear array transducers [3-5].

The aim of this study is the preparation of Ce- and Ce-Eu doped $PbTiO_3$ ceramics, materials with uncompensated valences, in which the following relationship exists [6]:

$$\Sigma X_A V_A + \Sigma X_B V_B > 6 \tag{1}$$

where X_A and X_B represent the number of atoms A and B and V_A and V_B their valences. The influence of the microor nanostructure on the dielectric, piezoelectric and electric properties was investigated. Such studies are of great importance for the technological point of view, and permit the obtaining of new materials with specific properties, required for various applications.

2. Experimental

Polycrystalline ceramics with the formula $Pb_{0.88}RE_xTi_{0.98}Mn_{0.02}O_3$ (RE = Ce, x = 0.08, and RE = $Ce_{0.04}Eu_{0.04}$), denoted PTCe and PTCeEu respectively, have been prepared by the conventional ceramic processing technique. The compacts were wet

mixed in methanol and calcined at 850-900 °C. Pressed pellets were embedded in PT powder and sintered at 1150 °C and 1180 °C for 2 h. Silver paste was deposited on the ceramic samples for poling and the electrical characterization. The microstructure was investigated by high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED), SEM microscopy. The elemental distribution was evidenced by the use of the electron probe microanalyser (EPMA), equipped with four wavelength dispersive spectrometers and one energy dispersive X-ray analyser. The capacitance and tan δ of ferroelectric capacitor, at different frequencies of the driving signal (0.5, 1, 10, 100, 200 kHz), while temperature was increased with 1.5 °C/min from 25 °C (RT) to 150 °C, were measured on poled samples, and the real part of the dielectric constant, ϵ ', and the conductivity, σ , were determined. The conductivity was calculated with the formula:

$$\sigma = \varepsilon_0 \varepsilon' \tan \delta 2\pi f, \tag{1}$$

where f is the driving signal frequency [7], f is the frequency, tan δ is the losses and ε_o is the vacuum permittivity.

The resonance and antiresonance planar and thickness frequencies have been measured at different temperatures from room temperature to 150 °C, and the elastic compliance s_{11}^{E} , was calculated according to IEEE standard formula. The thickness electromechanical coupling factor, k_t , has been calculated using the method indicated by Onoe [8].

3. Results and discussions

3.1. Microstructure

The prepared materials are complex substituted of the AA'BB'O₃-type. The rare earth ions (Ce and Ce+Eu) in the oxidation state 4+ and 3+ substitute Pb ions and create lead vacancies (\square_{Pb}). Manganese ions substitute Ti⁴⁺ ions, and create O⁻ ions. Using Mösbauer measurements and reflection spectra, it has been found that in perovskite compounds, ions of the same element co-exit in two oxidation states: Ti⁺⁴/ Ti⁺³, Eu³⁺/ Eu⁺², Mn⁺⁴/ Mn⁺⁵ [9,10]. It is also possible that in such a complex redox system, the cerium ions change their oxidation state from 4+ to 3+.

Selected area electron diffraction (SAED) images and HRTEM micrographs for the two materials are shown in Figs. 1 - 3. The samples of PTCe material has tetragonal structure, with lattice parameters a = 0.389 nm and c = 0.413 nm. These values were determined using CheckCell [11] software (LMPG package) from lines measured experimentally, with LispIx 4.0 [12] using Circle Tools (Fig. 1) (Table 1).

 Table 1. Measured distances and indexed for PTCE and PTCeEu materials.

	d (nm)	hkl		d (nm)	hkl
1	0.38905	100*	10	0.14211	202
2	0.28106	101	11	0.13128	221
3	0.23413	111	12	0.12648	030
4	0.22192	111	13	0.12186	130
5	0.21377	002	14	0.11623	131
6	0.20279	200	15	0.10393	004
7	0.19504	200	16	0.09654	322
8	0.17509	021	17	0.091	204
9	0.16424	112	18	0.08226	224



Fig. 1 Electron diffraction image with partial marked lines.

A HRTEM image of PTCe material is shown in Fig. 2. With the assumption that PTCe has PbTiO3 tetragonal structure, the refined structure using NCEMSS

software based on experimental data from Fig. 2, gives the new position of Ti(/Mn) atoms at $(0.434\ 0.646\ 0.537)$ of O at $(0\ 0.5\ 0.617)$, $(0.5\ 0\ 0.617)$, $(0.5\ 0\ 0.111)$ and $(0\ 0.5\ 0.111)$. Therefore, from HRTEM image in Fig. 2, we can conclude that no defects are clearly observed, so the sample has uniformly distributed doped atoms. Size of nanodomains is 0.484 nm with a plane symmetry Pm.



Fig. 2. HRTEM image of nanodomain (a), and reconstructed image (b) using EDM (electron direct methods)[12].

HRTEM pattern and reconstructed image, using the electron direct methods (EDM), for the material PTCeEu are presented in Figs. 3a and 3b. The size of nanodomain is about 0.511 nm with a plane symmetry Cm.



Fig. 3. HRTEM image of nanodomains and reconstructed image using EDM [12].

The porosity of the materials was checked. In Figs. 4 and 5, pores with size up to 1-17 μ m are evidenced in the two materials.

A complete study of the materials PTCe (sintered at 1150 °C) and PTCeEu (sintered at 1180 °C) was carried out with a new microanalysis. About 300 points /sample were examined, at a distance of 20 micrometers between two points. The distance investigated is more than 4.5 mm, on a sample with 9 mm in diameter. The results of the elemental distribution in the two materials are presented in Figs. 6 and 7. The concentration of cerium and manganese in the two materials is almost identical with that calculated.



Fig. 4. Pores in material PTCe.



Fig. 5. Pores in the material PTCeEu.



Fig. 6. Cerium and manganese distribution in PTCe material.



Fig. 7. Cerium, europium and manganese distribution in PTCeEu material.

An interesting behaviour of europium is observed in Fig. 7. About 10% of Eu^{3+} ions were transformed in Eu^{2+} in the complex redox system of the doped lead titanate. A similar result of the co-existence of Eu^{3+} and Eu^{2+} has been obtained by Mössbauer studies on a lead titanate system doped with europium [9].

4. Electrical properties

The variation of the dielectric permittivity, dielectric loss and conductivity with the driving signal frequency at room temperature, and with the temperature at a specific frequency in the range 100 Hz - 200 kHz is presented in Fig. 8 - 10.

Figs. 8 a and 8 b show the dependence of dielectric permittivity, dielectric loss and electrical conductivity on frequency, measured at room temperature. The conductivity was calculated with the formula: $\sigma = 2\pi\epsilon_0 \epsilon^2$ tan δ . The increase of complex dielectric permittivity at low frequencies is due to the contribution of ferroelectric domain walls relaxation processes. The low value of dielectric constant is typical for lead titanate type materials and it is of advantage for sensing applications. The material shows also low dielectric loss in a wide frequency range.

Figs. 9a - 9c illustrate the variation of real permittivity, dielectric loss and conductivity with temperature, up to 150 °C. The measurements have been made on poled samples. Both ε ' and tan δ increases with temperature, due to the movement of domain walls. However, the dielectric loss remains relatively low (below 3%) up to 80 °C. The marked increasing at higher temperatures of low frequencies is due to the conduction processes.



Fig. 8. The dependence on frequency of the dielectric permittivity and dielectric loss (a), and electrical conductivity (b), measured at room temperature.

Fig. 10 shows the variation with temperature of the elastic compliance, $s_{11}E$ and the thickness coupling coefficient, k_t . It can be observed that these properties are very stable with temperature up to 140 °C. This is of great advantage for the application of the material in piezoelectric resonators. Moreover, the material shows also a high anisotropy as indicated by the high value of the ratio k_t/k_p (around 8).





Fig. 9b. Temperature dependence of dielectric loss at different frequencies.



Fig. 9c. Conductivity as a function of temperature vs. frequencies of the driving signal.



Fig. 10. The variation with temperature of the elastic compliance and thickness coupling coefficient.

5. Summary

PT-type materials doped with Ce and Ce+Eu with tetragonal structure were prepared. The multiple substitutions in A and B positions lead to a change in the structural ordering. A redox system is formed in the solid solution, and the ions with multiple oxidation states: Ti^{4+}/Ti^{3+} , Eu^{3+}/Eu^{2+} , $Mn^{2+}/Mn^{5+}/Mn^{7+}$, may co-exist, together with O⁻ ions and lead vacancies. The presence of the Eu^{2+} ions and nanodomains were evidenced. These materials are suitable for various applications due to the dielectric and piezoelectric properties.

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