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Influence of co-dopants average valence on microstructural and electromechanical properties of lead titanate ceramics

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Abstract

Effects of Ni, Nb and Mn co-doping on microstructural, dielectric and electromechanical properties of lead titanate (PT) dense ceramics, obtained as a result of decreasing lattice anisotropy with increasing amount of co-dopants, were investigated.

Different values of the average valence (AV) of Ni–Nb co-dopants were obtained by mutual valence compensation between these acceptor–donor ions of various relative concentrations.

Significantly higher amounts of Mn^{2+} (resulted by reduction of Mn^{4+} in presence of donor co-dopants) were found in materials with Ni–Nb AV > 4+. These materials show higher coupling factors, correlated with higher mechanical quality factors, compared to the rest of materials. Hard-like piezoelectric behavior was manifested in materials with Ni–Nb AV < 4+, whereas ceramics with Ni–Nb AV > 4+, and without manganese, turned out to have a soft-like behavior.

Electromechanical properties of PT ceramics are discussed in terms of average valence of Ni–Nb co-dopants and multivalence state of manganese.

Keywords: Piezoelectric ceramics; Lead titanate; Microstructure; Electromechanical properties; Co-dopants average valence

1. Introduction

Lead titanate ceramics are traditional ferroelectric materials with many applications in non-destructive testing, micro-positioning systems, underwater detection, medical imaging and therapy. Due to their high T_C, they are of great interest in high temperature applications, as a single compound or in solid solutions with other compounds such as bismuth based double cations (in ratios that give a +3 average valence) perovskites,[1,2] bismuth ferrite (multiferroic)[3] or lead magnesium niobate (relaxor).[4] The sintering of lead titanate (PT), as a dense ceramic, is a challenging procedure due to the large crystalline anisotropy, which can mainly be reduced by doping. The most commonly reported approach is lead substitution with alkaline or rare earth elements.[5–7] In a previous work,[8] we reported about the use of Ni, Nb and Mn co-dopants for titanium substitution, as a new approach for decreasing the lattice anisotropy, in order to obtain dense PT ceramics. Their influence on the electromechanical properties of these ceramics was also investigated. At various relative concentrations of donor (Nb^{5+}) and acceptor (Ni^{2+}) co-dopants, the average valence (AV) of these ions was different from titanium valence, thus enhancing the "soft" or "hard" piezoelectric properties of PT ceramics. It was found that donor-like AV of co-dopants facilitates the reduction of Mn^{4+} to $Mn^{3+}$and Mn^{2+}, with direct influence on the domain wall mobility.

The aim of the present work is to extend our previous investigation to other new material compositions, in order to better understand the effect of these donor–acceptor co-dopants, in terms of their AV, correlated with the multiple valence of manganese, mainly on the electromechanical properties of these materials. Several investigation techniques: X-ray diffraction (XRD), scanning electron microscopy (SEM), electron paramagnetic resonance (EPR), transmission electron microscopy (TEM), impedance spectroscopy and polarization versus electric field hysteresis measurements were used to characterize the microstructural, electromechanical, ferroelectric and dielectric properties of these materials.

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2. Experimental procedure

Lead titanate ceramics co-doped with Ni, Nb and Mn, were prepared by a conventional ceramic technique. Titanium ions were substituted with the following molar ratios of co-dopants: $Ni_{0.01}$, $Nb_{0.05}$ (m 1); $Ni_{0.02}$, $Nb_{0.05}$ (m 2); $Ni_{0.04}$, $Nb_{0.05}$ (m 4); $Ni_{0.06}$, $Nb_{0.05}$ (m 6); $Ni_{0.02}$, $Nb_{0.06}$ (m 8); $Ni_{0.04}$, $Nb_{0.06}$ (m 10); $Ni_{0.01}$, $Nb_{0.07}$ (m 13); $Ni_{0.02}$, $Nb_{0.07}$ (m 14); and $Ni_{0.04}$, $Nb_{0.07}$ (m 16). All these compositions have the same amount of manganese ($Mn_{0.02}$). Another two materials, m 21 and m 23, were prepared with the same concentrations of nickel and niobium as materials m 1 and m 13, respectively, but without manganese. Lead volatilization that occurred during the high temperature processing was compensated by adding 1 mol% of lead oxide in excess to each composition. The average valence of Ni–Nb co-dopants and B-site ions in the investigated materials are given in Table 1.

The raw oxides were mixed for 3 h (at 300 rot/min), in agate vessels with methanol, in a planetary ball mill. After drying, they were calcined at 900 °C for 2 h and then milled again for 4 h at the same rotation speed. The resulting powders were pressed into disks of 22 mm diameter and 3 mm thickness, using a steel die. The pressed disks, were disposed in alumina crucibles, covered with PT powder, to prevent lead loss, and sintered in air, for 2–4 h, at temperatures ranging from 1150 °C to 1250 °C, in order to find the optimal sintering conditions for each material, then mechanically polished, to about 0.85 mm thickness and coated with silver paste electrodes, cured for 1 h at 200 °C. The samples were poled under 7 kV/mm DC field, in a silicon oil bath, for 10 min at 110 °C. Dielectric and electromechanical properties of sintered ceramic samples were measured 24 h after poling, using an AGILENT 4294A Impedance Analyzer (Agilent Technologies, Santa Clara, CA). The parallel capacitance and the dissipation factor were measured at 1 kHz and the dielectric constant was calculated using the measured capacitance and the geometry of the samples. Planar and thickness coupling factors were obtained by resonance method.[9] The mechanical quality factors of the planar/thickness modes were evaluated using the resonance/antiresonance band of the admittance/resistance spectra provided by the impedance analyzer.[10] The ferroelectric hysteresis loops were registered with a Premier II ferrotester (Radiant Technologies, Albuquerque NM, USA). The crystalline structure was investigated by X-ray diffraction using a D8 ADVANCE X-ray diffractometer (BRUKER AXS GmbH, Germany) with Ni filtered Cu radiation. The lattice parameters were determined using TOPAS (Bruker AXS). A certified corundum sample (NIST SRM 1976) was used to determine the zero-error of the diffractometer. The sample displacement parameter was refined during the fitting of the lattice constants for each sample. Anisotropic domain size and microstrain were evaluated by processing the XRD data with the MAUD program[11] in the “Popa rules” approach.[12] For this purpose, the instrumental broadening was evaluated using a heat treated CeO_2 laboratory reference sample. The experimental density was calculated by Archimedes method and the theoretical density by using the lattice constants provided by the XRD data. Ceramic morphology was revealed by using an EVO 50 scanning electron microscope (CARL ZEISS, Inc., Thornwood, NY). To characterize the local defect structure in donor–acceptor modified piezoelectric ceramics, and to determine the valence state of the Mn ion, be it 4+ or 2+, the electron paramagnetic resonance (EPR) technique was used. EPR spectra of powder materials, were recorded at room temperature (RT) on X-band CMS 8400 EPR spectrometer (9.2–9.7 GHz), with a rectangular TE_{112} resonator and 100 kHz modulation, equipped with a system for variable temperature experiments (83–480 K). The magnetic field was swept from 500 G to 6500 G and calibrated with diphenylpicrylhydrazyl (DPPH) standard marker ($g = 2.0036$). The microwave frequency was measured using a digital frequency counter analyzer CNT-90 (Pendulum Instruments AB, Bromma, Sweden). The EPR spectra of the weighed powder samples, were recorded in the same conditions of modulation amplitude, receiver gain and microwave power. Transmission Electron Microscopy (TEM) investigations, High Angle Annular Dark Field-Scanning Transmission Electron Microscopy (HAADF-STEM) and Selected Area Electron Diffraction (SAED) were performed on a probe-corrected JEM ARM 200F analytical microscope (Jeol, Japan). The specimens for TEM observations were prepared by mechanical polishing, followed by low angle ion milling in a Gatan PIPS installation.

3. Results and discussion

Table 1 shows that AV of Ni–Nb co-dopants in materials 1, 2, 8, 13, 14, 21 and 23 is higher than 4+ (the valence of substituted Ti^{4+} ions), which means these co-dopants exhibit a donor behavior, while, in materials 4, 6, 10 and 16, the co-dopants act as acceptors, with AV < 4+. The resulting valence of B-site ions (situated in the center of the oxygen octahedra of the perovskite structure) follows the same trend. Therefore, the exceeding positive charge should be compensated by lead vacancies, while the deficit of positive charge, by oxygen vacancies in order to maintain the electroneutrality. These are supposed to induce soft or hard piezoelectric properties, respectively, in the prepared materials. The AV of B-site ions was calculated assuming that all manganese ions are Mn^{4+}, as were provided by MnO_2 raw oxide. However, it was found[13] that Nb^{5+} ions facilitate the reduction of Mn^{4+} to Mn^{3+} and Mn^{2+}, resulting in a decreased AV of B-site ions, which leaves the lead vacancies, resulting from the initial stoichiometry of donor co-doped compositions, partially uncompensated. The lead deficit is likely to be compensated by oxygen vacancies, in order to restore the electroneutrality. For acceptor co-doped materials, the decrease of B-site valence should increase the number of oxygen vacancies. The effect of Nb^{5+} on the electron transfer between different valence states of manganese could be understood in terms of mutual valence compensation between donor and acceptor co-dopants. Thus, an increased amount of Nb is expected to increase the amount of Mn^{2+}, while a higher content of Ni will have the opposite effect, to preserve the electroneutrality. This is what we intend to prove in the present work, by investigating the electromechanical properties and by EPR spectroscopy, the results being shown and discussed as follows.