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Effects of the substitution of titanium by iron and niobium on the structure and dielectric properties in $BaTi_{1-x}(Fe_{0.5}Nb_{0.5})_xO_3$ solid solution

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Abstract

Polycrystalline samples of $BaTi_{1-x}(Fe_{0.5}Nb_{0.5})_xO_3$ with $x = 0.025$, 0.05, 0.075, 0.1, 0.125 and 0.15 have been synthesized by high-temperature solid-state reaction technique. The effects of cationic substitution of iron and niobium for titanium in the B sites for $BaTiO_3$ perovskite lattice on symmetry and dielectric properties were investigated. X-ray diffraction at room temperature and dielectric permittivity in the temperature range from 85 to 500 K with frequencies range from 10^3 to 2×10^5 Hz, respectively, were studied. The evolution from a normal ferroelectric to a relaxor ferroelectric is emphasized. T_C or T_m decreases when both iron and niobium are introduced in the lattice of $BaTiO_3$. A high dielectric constant of around 30,000 at $T_C = 280$ K was found for $BaTi_{0.925}(Fe_{0.5}Nb_{0.5})_{0.075}O_3$ ceramic. A relaxor ferroelectric with $\Delta T_m = 12$ K and ε'_r about 13,800 at 10 kHz with $T_m = 186$ K was found for $BaTi_{0.875}(Fe_{0.5}Nb_{0.5})_{0.125}O_3$ sample.

Keywords: Ferroelectrics; X-ray diffraction; Dielectric response

1. Introduction

The materials with a perovskite structure of general formula ABO_3 where A = mono or divalent ion, B = tri, tetra or pentavalent ion have been found to be very useful and interesting for different solid-state devices [1–3]. Much attention has been given to the interestes and investigation of perovskite compounds with disordered cation (complex perovskite-type). This allows us advantage to discover the materials relaxors. In addition to the usual applications of ferroelectric materials, relaxors are of great interest for dielectrics in capacitors and actuators [4]. These types of materials are characterized by their broad dielectric transition, known as the diffused phase transition with strong frequency dispersion. Such behaviours are observed at many materials, especially in lead-containing complex-compounds $Pb(Mg_{1/3}Nb_{2/3})O_3$, $Pb(Sc_{1/2}Ta_{1/2})O_3$ and $(Pb,La)(Zr,Ti)O_3$ [5–8].

On the other hand, many studies are interested in materials with a high value of the permittivity at temperatures near room temperature. PMNN-PT [9], and $Pb(Sc_{1/2}Nb_{1/2})_{0.58}Ti_{0.42}O_3$ [10] show very high values of dielectric permittivity about 35,000 and 25,000, respectively, that are inherent to the so-called a high-k materials. Another material with composition $A(Fe_{0.5}B_{0.5})O_3$ (A = Ba, Sr, Ca; B = Nb, Ta, Sb) exhibiting very high values dielectric permittivity in a very wide temperature interval [11].

Lead-free compositions could be of great interest for environmentally friendly applications. $BaTiO_3$, one of the displacive-type ferroelectric materials, is a typical ABO_3 type simple perovskite oxide. Substitution of other ions for host cations at A or B site in $BaTiO_3$ leads to remarkable changes in various characteristics [12–16]. The doped Fe in many perovskite systems changes strongly their structural and electric properties. Recently, Li et al. have shown that in $BaTiO_3$–$Ba(Fe_{1/2}Ta_{1/2})O_3$ system [17], the transition temperature T_{max} shifts towards room temperature with increasing Fe content. All these samples are classical ferroelectrics with, a dielectric constant relatively higher about 9000 at 10 kHz for $BaTi_{0.96}(Fe_{0.5}Ta_{0.5})_{0.04}O_3$ specimen.

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It is then of great importance to develop new compounds with high permittivities from the view point of practice application. From this point of view, we have prepared new series of specimens $BaTi_{1-x}(Fe_{0.5}Nb_{0.5})_xO_3$ ($x = 0.025$–0.15). Since Ti^{4+}, Nb^{5+} and Fe^{3+} have different ionic radii, masses and electronic charges, the relationship of the transition and B site substitution would be possible to elucidate as a parametric function of x in $BaTi_{1-x}(Fe_{0.5}Nb_{0.5})_xO_3$. In this paper, we report in particular the structure and dielectric properties of $BaTi_{1-x}(Fe_{0.5}Nb_{0.5})_xO_3$ system.

2. Experimental procedure

The polycrystalline ceramic samples of $BaTi_{1-x}(Fe_{0.5}Nb_{0.5})_xO_3$ were prepared by solid-state synthesis using the following chemical reaction:

$$BaCO_3 + \frac{x}{4}Fe_2O_3 + \frac{x}{4}Nb_2O_5 + (1-x)TiO_2 \rightarrow BaTi_{1-x}(Fe_{0.5}Nb_{0.5})_xO_3 + CO_2$$

The starting materials were high-purity (99.9%) powders of $BaCO_3$, Fe_2O_3, Nb_2O_5 and TiO_2. All these materials were dried at 120 °C for 15 h, weighed, mixed for 1 h and calcined at 1100 °C for 15 h. After calcination, powders were mixed for 1 h and pressed under 100 MPa into 8 mm diameter and about 1.5 mm thick. Finally, the pellets were sintered in oxygen atmosphere at 1350 °C for 3 h followed by furnace cooling. The compactness value, C (defined as the ratio between the experimental density d_{exp}, and theoretical density d_{theor}) obtained for sintered specimens were in the range 92–96%. The diameter shrinkages of ceramics disks $\Delta\Phi/\Phi$ were systematically determined as $(\Phi_{init} - \Phi_{fin})/\Phi_{init}$ (Φ_{init} and Φ_{fin} represent initial and final diameter, respectively). Their values are between 0.14 and 0.16. Microstructure studies were performed by scanning electron microscopy (SEM) (JEOL JED2300). Fig. 1 shows representative SEM micrograph of the surface of $BaTi_{0.9}(Fe_{0.5}Nb_{0.5})_{0.1}O_3$ composition as an example. Average grain size is found to vary from 2 to 10 μm as x increases from $x = 0$ to 0.15.

Room temperature powder X-ray diffraction patterns were recorded on a Philips diffractometer using Cu K_α radiation ($\lambda = 1.5406$ Å) in the angle range $5 \leq 2\theta \leq 110°$ with 10 s counting time for each step of 0.02° in order to determine the structure for all prepared ceramic compositions.

The dielectric measurements were performed on ceramic discs after deposition of gold electrodes on the circular faces by cathodic sputtering. The dielectric permittivity of the sample was measured under helium atmosphere as a function of both temperature (80–500 K) and frequency (10^2–2×10^5 Hz) using a Wayne-Kerr 6425 component analyser. All the dielectric data were collected while heating at a rate of 2 K min^{-1}.

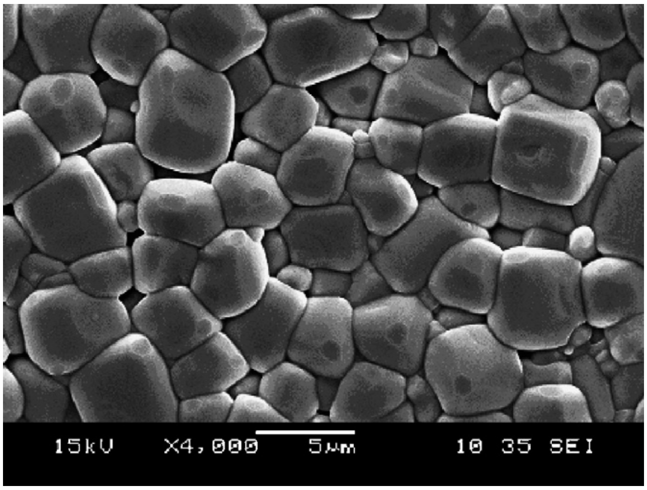

Fig. 1. SEM micrograph of the surface of $BaTi_{0.9}(Fe_{0.5}Nb_{0.5})_{0.1}O_3$ ceramic ($x = 0.1$).

3. Results and discussion

3.1. X-ray diffraction analysis

The X-ray diffraction profiles of all samples reveal that no parasite phase exists. The value of the lattice and profile parameters were determined by using a global profile-matching method with the software "fullprof" [18]. The observed, calculated and the difference of the X-ray diffraction patterns for ceramics with compositions $x = 0.025$ and 0.1 are given in Figs. 2 and 3, respectively, as examples. All the reflection peaks of the X-ray profiles were indexed. Good agreement between the observed and calculated interplaner spacing suggests that these compositions having tetragonal and cubic structure at room temperature, respectively. The insets show the results of the Rietveld refinement between 63° and 68° in 2θ. These two peaks observed for $x = 0.025$ due to the tetragonal distortion of the lattice (2 0 2) and (2 2 0) reflection emerge in one peak for $x = 0.1$ indicating that the symmetry appears to be cubic. The structure and lattice parameters for $BaTi_{1-x}(Fe_{0.5}Nb_{0.5})_xO_3$ are listed in Table 1. The structure of $BaTi_{1-x}(Fe_{0.5}Nb_{0.5})_xO_3$ is tetragonal for composition range $0 \leq x \leq 0.05$ and cubic for $0.05 < x \leq 0.15$. Fig. 4 shows the variations of the lattice parameters and cell volume versus composition. It is remarkable that as Fe/Nb doping in $BaTiO_3$ increases, the c lattice parameter decreases and the a lattice parameter increases. In addition, the c/a values are found to become smaller by the partial substitution of Ti^{4+} by Nb^{5+} and Fe^{3+}, indicating a more and more typical cubic phase that comes into being. The unit cell volume increases linearly with increasing x. This increase should be related to the values of ionic radii: both ($r_{Fe^{3+}} = 0.64$ Å) and ($r_{Nb^{5+}} = 0.7$ Å) quite higher than ($r_{Ti^{4+}} = 0.605$ Å) [19].

3.2. Dielectric studies

The evolution of real part (ε_r') of the dielectric permittivity and dielectric loss ($\tan\delta$) as a function of temperature at various frequencies (10^3–2×10^5 Hz) of $BaTi_{1-x}(Fe_{0.5}Nb_{0.5})_xO_3$ ($0.025 \leq x \leq 0.1$) samples is shown in Figs. 5 and 6. For composition relatively close to $BaTiO_3$ ($x \leq 0.075$), three dielectric peaks have been observed, which are originated from phase transitions from a cubic paraelectric to a tetragonal ferroelectric (at

Table 1
Structure and lattice parameters of different compositions in the system $BaTi_{1-x}(Fe_{0.5}Nb_{0.5})_xO_3$

Composition (x)	Structure	a (Å)	c (Å)	c/a
0.025	Tetragonal	4.0006 (8)	4.0230 (6)	1.00559
0.050	Tetragonal	4.0064 (9)	4.0138 (2)	1.00183
0.075	Cubic	4.0098 (4)		
0.100	Cubic	4.0106 (1)		
0.125	Cubic	4.0119 (5)		
0.150	Cubic	4.0129 (1)		