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Effect of Dy substitution on structural and dielectric properties in $Ba_{1-3x}Dy_{2x}Ti_{0.9}Sn_{0.1}O_3$

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Abstract

The complex perovskite oxides, $Ba_{1-3x}Dy_{2x}Ti_{0.9}Sn_{0.1}O_3$, have been synthesized by a solid state reaction technique. The effect of the replacement of Ba^{2+} by Dy^{3+} in the A site on the structural and dielectric properties were investigated. The room temperature X-ray powder diffraction (XRD) study reveals that all the compositions were a single phase cubic perovskite structure. The lattice parameters of the prepared compositions have been obtained by the Rietveld method using a computer program. A scanning electron microscopy (SEM) study revealed a decrease in the grain size with increasing Dy^{3+} concentration. It has been ~~is~~ also found that the Curie temperature decreases while the dielectric constant increases with increasing of Dy^{3+} concentration. The temperature variation of the real permittivity gives evidence of the ferroelectric phase transition and of the relaxation behavior. With increasing Dy^{3+} concentration, the degree of diffuse phase transition was enhanced, and a linear reduction in the transition temperature was obtained.

Keywords: C. Dielectric properties; D. Perovskite; X-ray diffraction; Rietveld refinements

1. Introduction

Relaxor materials have found great interest both in device applications and in the understanding of fundamentals of ferroelectric system [1–3]. Most of these materials belong to complex lead-based perovskite compounds, such as PMN-PT, PMN-PZT and PLZT [4–6], whose superior dielectric properties and relaxor behavior have considerable contributions in the development of relaxor ferroelectric materials.

The common feature of these materials is the presence of the high toxicity of lead oxide; hence the use of the lead-based materials has caused serious environmental problems. These disadvantages have motivated the search for new, efficient, and eco-friendly lead-free relaxor materials. Several lead-free materials with perovskite structure, such as $BaTiO_3$ and $SrTiO_3$ [7], have been investigated in terms of their dielectric relaxation, ferroelectric phase transition and electrical properties. In the past decades, a number of $BaTiO_3$-based materials have been developed, e.g., by the partial substitution of Sn^{4+} and Zr^{4+} for Ti^{4+} in the B sites and Sr^{2+} and Ca^{2+} for Ba^{2+} in the A-sites [8–11], for the use mainly as high dielectric materials. Furthermore, the influence of the rare-earth doping elements on the dielectric properties of various $BaTi_{1-x}Sn_xO_3$ (BTS) compositions have been recently interest of study; and it has been well documented that suitable in at both the atomic site (A-site and B-site) of ABO_3 perovskites [12,13].

The purpose of our research is to investigate the effect of the A-site cation in perovskite related materials on the dielectric properties in order to elaborate new lead-free ceramics with relaxor behavior at room temperature. However, the doping mechanisms in rare earth-doped BTS ceramics have not yet

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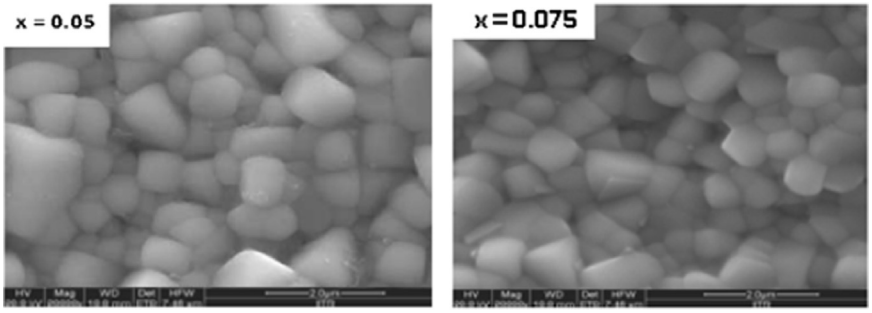

Fig. 1. SEM images of $BTSDy_x$ ($x=0.05$ and $x=0.075$) samples.

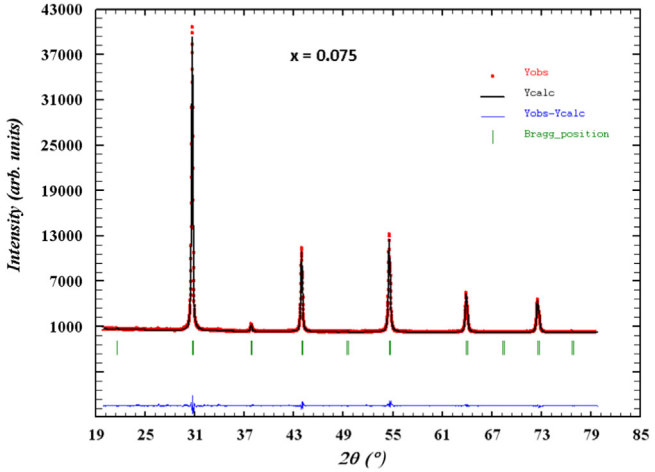

Fig. 2. The Rietveld plot of the X-ray diffraction pattern of $Ba_{1-3x}Dy_{2x}Ti_{0.9}Sn_{0.1}O_3$ ($x=0.075$).

well been understood. Therefore, the focus of our research is set to the $Ba_{1-3x}Dy_{2x}Ti_{0.9}Sn_{0.1}O_3$ system, where the effect of Dy substitution for Ba on the structural and dielectric properties is investigated. The choice of dysprosium (Dy) is justified by its various properties (dielectric, ferroelectric, photoluminescence and magnetic). The value of x was chosen to be below the threshold value for the onset of relaxor behavior in $Ba_{1-3x}Dy_{2x}Ti_{0.9}Sn_{0.1}O_3$.

2. Experimental procedure

The new polycrystalline ceramic samples of $Ba_{1-3x}Dy_{2x}Ti_{0.9}Sn_{0.1}O_3$ (x=0.05 and 0.075) were prepared by a conventional solid-state ceramic method. The powders of Dy_2O_3, $BaCO_3$, TiO_2 and SnO_2, with 99.99% purity, were used. In order to eliminate H_2O:Dy_2O_3, $BaCO_3$, TiO_2 and SnO_2, the powders were pre-heated at 603 K for 5 h. Appropriate amount of the dried powders; for such compositions were thoroughly mixed together in a crucible and heated in an electronic furnace at 1173 K, and maintained at this temperature for 24 h. The furnace temperature was gradually cooled down to room temperature and the obtained powders were grinding and pressed into pellets shaped. The pellets were finally sintered at 1673 K for 2 days in air then after, the furnace-cooled to room temperature. The process of grinding and sintering were repeated several times until the desired materials were obtained.

The structure and phase purity were checked at room temperature by X-ray powder diffraction (XRD) using CuKα radiation (λ=1.5406 Å). The patterns were recorded in the $20^\circ \leq 2\theta \leq 80^\circ$ angular range with a step of 0.017° and a counting time of 18 s per step. According to our measurements, this system is able to detect up to a minimum of 3% of impurities.

The micromorphology has been detected on a facture surface by a scanning electron microscopy (SEM) using a Philips XL30 equipped with energy dispersive X-ray detector (EDX). Agilent 4284A impedance analyzer was used to measure capacitance (C) and conductance (G) on ceramic disks as a function of frequency (40–10^7 Hz) and temperature (80–180 K).

3. Results and discussion

3.1. X-ray diffraction analysis

The phase formation of the prepared compositions was investigated at room temperature using the X-ray diffraction technique via the Full Prof Software computer program [14]. The results indicate that all the observed patterns for the investigated compositions corresponding to polycrystalline cubic phase with $Pm\bar{3}m$ space group. No additional peaks of other phases have been found, indicating that the ceramic was formed as a pure perovskite phase. Structural study as Rietveld refinement of the X-ray diffraction pattern as typical representative $BTSDy_x$ ($x=0.075$) compound is illustrated in Fig. 2. The quality of the agreement is evaluated through the goodness of the fit indicator χ^2. The initial parameters are taken from the standard Wyckoff position table are: (Ba/Dy) at 1a(0,0,0), (Ti/Sn) at 1b(0.5, 0.5, 0.5) and O at 3c(0, 0.5, 0.5). Detailed results of the refinement are listed in Table 1. One can see from this table that the lattice parameters decrease with increasing Dy content. This decrease can be directly related to the decrease of the average ionic radius $<r_{(Ba,Dy)}>$, due to the smaller ionic of Dy^{3+} (1.048 Å) compared with that of Ba^{2+} (1.43 Å)[15].

3.2. Scanning electron microscope

Scanning electron micrograph (SEM) for $x=0.05$ and $x=0.075$ is shown in Fig. 1. The SEM is capable of examinig a relatively large field of view, thus giving sufficient information on the grain growth and its uniformity. SEM micrograph is shown that our