

Influence of vanadium doping on the processing temperature and dielectric properties of barium bismuth niobate ceramics

C. Karthik, K.B.R. Varma*

Materials Research Centre, Indian Institute of Science, Bangalore, Karnataka, India

Received 9 November 2005; accepted 6 February 2006

Abstract

Barium bismuth vanadium niobate, $\text{BaBi}_2(\text{Nb}_{1-x}\text{V}_x)_2\text{O}_9$ ($0 \leq x \leq 0.1$) ceramics were fabricated from the powders prepared via solid state reaction route. The single phase layered perovskite structure was preserved up to 5 at% ($x=0.05$) of vanadium. The addition of V_2O_5 substantially improved the sinterability associated with high density (96%) which was otherwise difficult in the case of pure $\text{BaBi}_2\text{Nb}_2\text{O}_9$ (BBN). The sintering temperature was significantly reduced from 1100 to 900 °C. The scanning electron microscopic (SEM) studies revealed the transformation of a porous microstructure to a well-packed platy grained with negligible inter-granular porosity. The dielectric constant of BBN ceramics at both room temperature and in the vicinity of the temperature of dielectric maximum (T_m) has increased significantly with increase in vanadium content and the loss remained almost constant. The T_m increased with increase in V_2O_5 . For instance, there was an upward shift of about 25 °C in T_m for 5 at% ($x=0.05$) vanadium-doped BBN. Interestingly, the diffuseness (γ) in the phase transition was found to decrease with increase in vanadium doping level. © 2006 Elsevier B.V. All rights reserved.

Keywords: Aurivillius oxides; Doping effects; Sintering; Vanadium; Relaxor ferroelectrics

1. Introduction

The bismuth layered structure perovskites have attained considerable importance owing to their potential ferroelectric non-volatile random access memory (NVRAM) applications apart from piezo and pyroelectric-based sensor applications. The most interesting aspect of these materials has been their high fatigue resistance against polarization switching, unlike the commercially popular ferroelectrics such as lead zirconate titanate (PZT) which loses its initial polarization after 10^6 – 10^8 switching cycles [1]. Although, significant amount of work has been devoted to the studies on Sr-based $n=2$ member of the Aurivillius family of oxides such as $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) and $\text{SrBi}_2\text{Nb}_2\text{O}_9$ (SBN) [1,2], their Ba counterparts, such as $\text{BaBi}_2\text{Ta}_2\text{O}_9$ (BBT) and $\text{BaBi}_2\text{Nb}_2\text{O}_9$ (BBN), have received much less attention perhaps owing to the difficulties in obtaining exact stoichiometric compositions as well as their decomposition nature at high temperatures. Recent studies on BBT thin films demonstrate their excellent fatigue endurance with no polarization fatigue up to 10^{12} cycles [3].

The ferroelectric studies pertaining to BBN ceramics demonstrated its relaxor nature [4]. Shimakawa et al. attributed the relaxor behavior of BBN to the presence of microscopic orthorhombic distortion in the macroscopic tetragonal symmetry [5], while Blake et al. attributed the same to the disordering of Ba and Bi cations [6]. For ferroelectric memory applications, the presence of two dimensional domain structures in these kinds of relaxor materials will improve the performance as it does not induce high internal stress and makes it suitable for switching applications. Despite having unique features, these compounds suffer from a few drawbacks such as high processing temperatures and low remnant polarization as compared to that of conventional relaxors [7,8]. One of the ways to overcome these limitations would be to go in for partial cationic substitutions which would result in low processing temperatures accompanied by high relative density. For instance, remarkable changes in the processing temperatures and dielectric properties of SBN were observed when V^{5+} ions were doped on niobium sites [9,10]. The positive changes were chiefly ascribed to the difference in ionic radii between vanadium (V^{5+}) and niobium (Nb^{5+}) cations. In order to visualize the influence of V^{5+} doping on the dielectric and ferroelectric properties of the other compounds (BBN and BBT) belonging to the Aurivillius family of oxides, to begin with BBN was doped with various concentrations of vanadium (up to

* Corresponding author. Tel.: +91 80 22932914; fax: +91 80 23600683.
E-mail address: kbrvarma@mrc.iisc.ernet.in (K.B.R. Varma).

10 at%, $x = 0.1$) and obtained enhanced dielectric and ferroelectric properties. In this paper, the details pertaining to the structural, sintering temperatures, relative density, microstructure and dielectric properties of vanadium-doped BBN ceramics are elucidated.

2. Experimental

Polycrystalline barium bismuth vanadium niobate, $\text{BaBi}_2(\text{Nb}_{1-x}\text{V}_x)_2\text{O}_9$ ceramic powders of various compositions in which x ranging from 0 to 0.1 (10 at%) were prepared via conventional solid state reaction route. Stoichiometric powders of Bi_2O_3 , BaCO_3 , Nb_2O_5 and V_2O_5 (Aldrich Chemicals) were mixed well in acetone medium using pestle and mortar. An extra (5 wt%) Bi_2O_3 was added to the starting mixture to compensate for the bismuth loss at elevated temperatures. The mixture was then calcined at 900°C for 12 h with intermediate grinding and heating stages in a closed platinum crucible. The calcined powders were ground and admixed with 2 wt% polyvinyl alcohol binder and pressed into disks at the pressure of 300 kg/cm^2 . The pressed pellets were then sintered at different temperatures ranging from 900 to 1100°C for 2 h in order to find out the optimum sintering temperatures for different compositions.

The phase formation and crystalline nature of the calcined powders and the sintered pellets were confirmed by X-ray powder diffraction (XRD, Scintag, USA). Scanning electron microscopy (SEM, Cambridge Stereoscan S360) was used for microstructural analyses. The densities of the pellets were determined by Archimede's method with xylene (density, $\rho = 0.87\text{ g/cm}^3$) as the liquid media. For electrical property measurements, the polished surfaces of the samples were sputtered with gold and thin silver leads were attached with silver paste and baked at 100°C for 15 min. The capacitance measurements were carried out in the 100 Hz to 10 MHz frequency range as a function of temperature (room temperature to 400°C) using HP4194A impedance analyzer at signal strength of $0.5\text{ V}_{\text{rms}}$. The dielectric constant was evaluated by taking the dimensions of the samples into consideration.

3. Results and discussion

3.1. X-ray structural analyses

The X-ray powder diffraction (XRD) patterns obtained for the calcined powders of various compositions in $\text{BaBi}_2(\text{Nb}_{1-x}\text{V}_x)_2\text{O}_9$ (where $x = 0, 0.02, 0.03, 0.05, 0.07$ and 0.1) are depicted in Fig. 1(a–f). The XRD patterns show the formation of monophasic vanadium-doped $\text{BaBi}_2\text{Nb}_2\text{O}_9$ up to $x = 0.05$ (5 at% of vanadium) whereas the patterns corresponding to the compositions with vanadium content higher than 5 at% ($x = 0.07$ and 0.1) show the appearance of less intense peaks corresponding to a secondary phase which is identified to be $\text{Bi}_2\text{VO}_{5.5}$, reported to be an $n = 1$ member of Aurivillius family of oxides [11]. Therefore, monophasic compounds with the vanadium content up to 5 at% were only chosen for further characterization. The studies on the influence of the formation of the

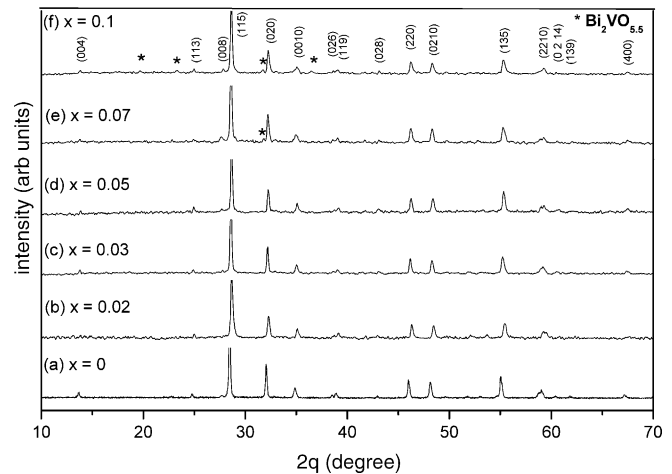


Fig. 1. X-ray powder diffraction patterns of $\text{BaBi}_2(\text{Nb}_{1-x}\text{V}_x)_2\text{O}_9$ for (a) $x = 0$, (b) $x = 0.02$, (c) $x = 0.03$, (d) $x = 0.05$, (e) $x = 0.07$ and (f) $x = 0.1$.

minor phase of ferroelectric $\text{Bi}_2\text{VO}_{5.5}$ on the dielectric properties of BBN are in progress and the details of which are out of the scope of the present paper.

The indexing and the lattice parameter refinement were carried out using an orthorhombic space group $A2_1am$. The variation of lattice parameters with vanadium doping is shown in Fig. 2. There is no significant change in lattice parameters ' a ' and ' b ', while there is a considerable decrease in the value of ' c ' with the increase in vanadium content suggesting the formation of solid solutions. The decrease in ' c ' is attributed to the smaller ionic size of V^{5+} (0.58 nm) than that of Nb^{5+} (0.69 nm) [12]. The more significant change in ' c ' as compared to that of ' a ' and ' b ' is attributed to the shrinkage of the octahedra in the direction perpendicular to a - b plane. The negligible change along a and b axes implies that the oxygen octahedra remains unaltered in the a - b plane and therefore smaller vanadium cation has more "rattling space" inside the octahedral cage, which will have prominent influence on the ferroelectric and dielectric properties of the compound.

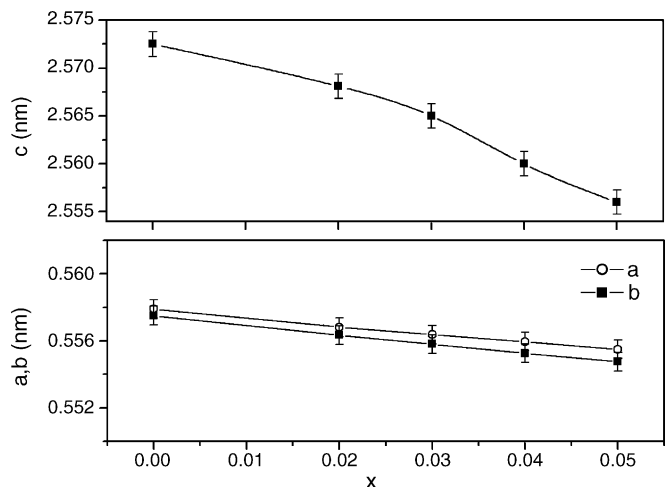


Fig. 2. Variation of lattice parameters (a , b and c) as a function of vanadium content (x).

Download English Version:

<https://daneshyari.com/en/article/1532135>

Download Persian Version:

<https://daneshyari.com/article/1532135>

[Daneshyari.com](https://daneshyari.com)