Synthesis, structural and dielectric properties of Ho-doped $\text{SrBi}_2\text{Nb}_2\text{O}_9$ prepared by Co-precipitation method

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ABSTRACT This paper reported the synthesis of Ho-doped SBN ($\text{SrBi}_{2-x}\text{Ho}_x\text{Nb}_2\text{O}_9$; $x = 0$ and 0.4) by a co-precipitation method and investigated the synthesized material with X-ray diffraction analyses, infrared spectroscopy, and electrical measurements. The results show that the Ho-doped SBN has low loss values at higher frequencies and the flattening of dielectric constant which are very desirable in nonvolatile ferroelectric random access memory applications.

Keywords: Co-precipitation; XRD; FTIR; Dielectric properties.

INTRODUCTION

$\text{SrBi}_2\text{Nb}_2\text{O}_9$ (SBN) is one of the oxide materials discovered with a reasonably high Curie temperature [1,2]. The most significant applications of SBN materials are in the development of ferroelectric random access memory (FeRAM) [3]. Many reports have been published on the actual processes for preparing SBN materials, which are different for obtaining special materials with given structure and properties. Solid-state reaction method is the most feasible means of fabricating SBN powders and their devices [4–6]. However, less common methods of fabricating pure and doped SBN powders are by chemical routes [7,8].

In SBN structure, three cationic sites were doped: the Bi-site in the Bi_2O_2 layer, the Sr- and Nb-site in the post-perovskite [1,9,10]. It has been reported that the substitution of lanthanide onto the sites of bismuth in bismuth layer-structured ferroelectric leads to decreased Curie temperature T_C [5,6,11]. Numerous reports focus on bismuth layer doping for SBN ceramics prepared by solid-state reaction method. As to the best of our knowledge, the prepa-

ration of doped SBN by co-precipitation is widely studied as that of samples prepared by solid-state reaction method. While no study talks about synthesis, structural and dielectric measurements of Ho-doped SBN. In this paper, we synthesized a sufficient large pure powder at low temperature by the soft chemical method and studied the electrical properties of the substituted $\text{SrBi}_2\text{Nb}_2\text{O}_9$.

EXPERIMENTAL

NbCl_5 (Sigma-Aldrich, 99.5%), $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ (Normatom), $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Fluka Chemik, 99%) and $\text{Ho}(\text{NO}_3)_3$ (Aldrich Chemistry, 99.9%) were used to prepare Ho-doped SBN powders. A stoichiometric amount of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ho}(\text{NO}_3)_3$ were dissolved in distilled water, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in dilute HNO_3 and then NbCl_5 was dissolved in ethanol. Ammonia solution was added with constant stirring to the above solution mixture until pH~9 to ensure complete precipitation. After filtration, the co-precipitate was washed several times with distilled water and dried in an oven at 80°C for 12 h. The precursor was ground and then calcined at 800°C for 24 h. The final powders Ho-doped SBN were checked by powder X-ray diffraction (XRD) and Fourier transformation infrared spectroscopy (FTIR).

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the Ho-doped SBN. Patterns were identified to match with the standard pattern of $\text{SrBi}_2\text{Nb}_2\text{O}_9$ (PDF #00-049-0607). Both of the compositions show the presence of pure single phase with an orthorhombic $A2_1am$ space group. The lattice parameters are found

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Figure 1 X-ray diffraction of Ho-doped SBN powders.

to be $a = 5.508 \text{ \AA}$, $b = 5.48 \text{ \AA}$, $c = 25.007 \text{ \AA}$ for the undoped SBN, and $a = 5.537 \text{ \AA}$, $b = 5.48 \text{ \AA}$, $c = 24.572 \text{ \AA}$ for the Ho-doped SBN. Using the Scherrer Equation (1) [12], the crystallite size of the samples is obtained as 458 and 54 nm for the undoped and Ho-doped SBN; respectively.

$$D = \frac{0.9\lambda}{\beta \cos \theta}, \quad (1)$$

where D is the crystallite size, β is the full width at half maximum (FWHM) of the peak, λ is the X-ray wavelength and θ is the diffraction angle. The difference observed in lattice parameters and crystallite size may be due to the incorporation of Ho^{3+} ($1.041 \text{ \AA}$) ions into the Bi-sites (Bi^{3+} ; $1.170 \text{ \AA}$) [13].

The FTIR spectra of the Ho-doped SBN samples are presented in Fig. 2. For both samples, the spectra comprise identical nature, suggesting that the incorporation of Ho^{3+} in SBN system does not bring significant change in the structure. The spectra reveal a superimposition of three bands centered at 430 , 615 and 805 cm^{-1} which are attributed to the characteristic vibration of $\text{SrBi}_2\text{Nb}_2\text{O}_9$ [14]. A small, weak band appears at 473 cm^{-1} for the Ho-doped SBN which is attributed to the vibration of Ho–O bond [15].

Fig. 3 shows the variation of dielectric constant (ϵ') and dielectric loss ($\tan \delta$) with frequency, at room temperature, for the pure and doped SBN. The value of ϵ' shows a sharp decrease with increasing frequencies. The strong decrease of dielectric constant towards a high frequency range may be due to the space charge polarization and interface effect [16]. However, this parameter tends to be constant for the Ho-doped SBN. The room temperature value of dielectric constant for the pure and Ho-doped SBN is observed to decrease from 245 to 143 respectively, at frequency of 10

Figure 2 IR spectra of Ho-doped SBN.

kHz. The increment in frequency provides a decrease in dielectric loss which is normal behavior of any dielectric materials. The values of dielectric loss decrease from 0.6 (SBN) to 0.02 (Ho-doped SBN) at 10 kHz.

The dielectric parameters ϵ' and $\tan \delta$ depend upon a number of factors, such as stoichiometry, doping content, structural homogeneity and composition. The introduction of Ho^{3+} leads to reduced space charge polarization effect by reduction in Bi contents. Also it shows that with Ho, the energy losses decrease at high frequencies.

The variation of dielectric constant (ϵ') at different frequencies as a function of temperature is shown in Fig. 4. Clear peaks in ϵ' are observed at 100 Hz, 1 kHz and 10 kHz where the ferroelectric to paraelectric phase transition (T_C) takes place, at 460°C and 305°C for the pure and Ho-doped SBN respectively. From Table 1, the peak value of dielectric constant is only 159 for the Ho-doped SBN, which is smaller by about two orders than that of SBN (354), which suggests that the stereochemically active Bi with its lone-

Figure 3 Frequency dependence of the dielectric constant (ϵ') and dielectric loss ($\tan\delta$) at room temperature.

Figure 4 Temperature dependence of the dielectric constant.

Table 1 Values of T_C , $\epsilon'_{\max}$ and activation energy (E_a) of Ho-doped SBN at 100 Hz

Sample	T_C (°C)	$\epsilon'_{\max}$	E_a (eV)	Bond strength (kJ mol ⁻¹)
SBN	460	354	0.83	Bi-O; 343
Ho-doped SBN	313	159	0.48	Ho-O; 606

pair electrons, enhances the dielectric polarization.

Fig. 5 shows the variation of loss tangent ($\tan\delta$) as a function of temperature at the selected frequencies. It reveals a peak anomaly in $\tan\delta$ at around T_C for all frequencies. These dielectric loss anomalies additionally confirm the phase transition from ferroelectric to paraelectric phase. The peak value of dielectric loss anomaly is 0.41 for the Ho-doped SBN which is smaller than that of SBN by 5 orders, measured at 1 kHz.

Based on literatures [17–19], the replacement of the asymmetric Bi³⁺ by symmetric lanthanide in the Aurivillius phases gives rise to T_C decreasing. Holmium plays an important role in the Ho-doped SBN ceramic. One is the reduction in the volatilization of bismuth. Different from the pure SBN, the conductivity of the Ho-doped

SBN begins to dominate, and the dielectric loss rises are associated with the loss by conduction.

Fig. 6 shows the variation of alternating current (AC) conductivity as a function of the inverse of absolute temperature. The AC conductivity was calculated using Equation (2)

$$\sigma = \omega \epsilon' \epsilon_0 \tan\delta = \sigma_0 \exp\left(\frac{-E_a}{k_B T}\right), \quad (2)$$

where ϵ_0 is the vacuum permittivity, ω is the angular frequency, k_B is Boltzmann constant and σ_0 is the pre-exponential factor.

The conductivity in the high temperature region is determined by the intrinsic defects caused by the thermally activated oxygen vacancies [20]. This thermal fluctuation

Figure 5 Temperature dependence of the dielectric loss.

Figure 6 Temperature dependence of conductivity.

can be described by Kroger-Vink notation [21].

However, in the low temperature (extrinsic) region the presence of impurity increases smoothly the conductivity. Therefore, the materials exhibit Arrhenius type conductivity behaviour in the temperature region [2.2 K⁻¹ (181°C), 1.5 K⁻¹ (393°C)]. The activation energy of the pure SBN and Ho-doped SBN is found to be 0.83 eV and 0.48 eV, respectively measured at 100 Hz. The difference in bond strength energies might lead to more improvement in the electrical properties of Ho-doped SBN. Thus, the bond dissociation energy of Ho–O is larger than that of Bi–O [22]. Hence, the substitution of Bi by the large amount of Ho controls the formation of oxygen, instead of pure SBN, which leads to Bi³⁺ deficiency accompanied with oxygen vacancies.

CONCLUSION

This paper reported the fabrication of the Ho-doped SBN powders through the co-precipitation method and investigated their structural and electrical properties. The XRD

patterns show the presence of the parent SrBi₂Nb₂O₉ phase. The FTIR results show that the effect of Ho substitution does not bring significant change in the structure. Dielectric properties depend mainly on the chemical composition. Thus, dielectric constant (ϵ) and dielectric loss ($\tan\delta$) of the pure SBN are higher than those of Ho-doped SBN. Doping Ho³⁺ could compensate for the Bi-omission caused by Bi₂O₃ volatilization, which is helpful to reduce the dielectric loss of the ceramics. The activation energy estimated from AC conductivity studies suggests that the Ho-doped SBN contains less number of charge carriers for conduction. In the light of the above, the SBN suffers from high dielectric loss. The variation of dielectric properties with frequency, at room temperature for Ho-doped SBN shows low loss values at higher frequencies and flattening of dielectric constant, which are very desirable in nonvolatile FeRAM applications.

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共沉淀法制备Ho掺杂 $\text{SrBi}_2\text{Nb}_2\text{O}_9$ 的结构及介电性能研究

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摘要 本文报道了一种共沉淀法制备Ho掺杂SBN ($\text{SrBi}_{2-x}\text{Ho}_x\text{Nb}_2\text{O}_9$: $x = 0$ 和 0.4), 并利用X射线衍射、红外光谱和电学测试对其进行表征. 结果表明, Ho掺杂SBN在较高频下具有低损耗和稳定的介电常数. 因此这种材料非常适用于非易失FeRAM存储器的应用.