JOURNAL OF MATERIALS SCIENCE LETTERS **21**, 2002, 947–949

Influence of tungsten doping on dielectric properties of strontium bismuth niobate ferroelectric ceramics

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The effect of doping on various physical and chemical properties of solid materials is commonly known, and this effect has been extensively exploited in piezoelectrics and ferroelectrics to improve their performance. For example, there have been numerous reports on the effect of doping in the $Pb(Zr, Ti)O_3$ (PZT) system [1, 2]. Various doping ions, such as La^{3+}, Nd^{3+} and Nb^{5+}, in PZT result in enhanced remanent polarization and a decreased coercive field. Such ions are commonly known as "soft doping" ions [3, 4]. Similar doping effects were also found in bismuth layer-structured ferroelectrics (BLSFs), such as $SrBi_2Nb_2O_9$ (SBN) and $SrBi_2Ta_2O_9$ (SBT) [5, 6]. Millan *et al.* [7–9] studied the substitution of Bi^{3+} in SBN by Pb^{2+}, Sb^{3+}, and Te^{4+}, and found that the SBN structure could be preserved by such a substitution, whereas dielectric properties varied with the type of doping cations. There are also several reports on the substitution of Sr^{2+} in $SrBi_2(Nb,Ta)_2O_9$ (SBTN) by Bi^{3+}, $Ba^{2+}$and Ca^{2+} [10–12]. Although a lot of research effort has been made in the study of SBTN ferroelectrics [13–15], there is very limited work on improvement of dielectric and ferroelectric properties of the SBTN through substitution of the B site ions, i.e. Nb^{5+} or Ta^{5+}.

Recently we reported on the significant enhancement of dielectric and ferroelectric properties of SBN ferroelectrics through partial substitution of niobium by pentavalent vanadium cations [16, 17]. With 10 at.% vanadium substitution, the remanent polarization increased from $\sim 2.4\ \mu C/cm^2$ to $\sim 8\ \mu C/cm^2$, whereas the coercive field reduced from ~63 kV/cm to ~45 kV/cm. The enhanced ferroelectric properties of the layered perovskite ferroelectric properties were explained by an enlarged "rattling space" via doping smaller vanadium ions. Similar to vanadium ions, doping with tungsten ions could be another approach for improving the dielectric and ferroelectric properties of SBTN ferroelectrics. Tungsten ions do form perovskite-like units as a center ion, or in B site, e.g. in Bi_2WO_6 [18]. In addition to the relatively smaller ionic radius (W^{6+}: ~64 pm with a coordination number (CN) of 6) as compared to that of Nb^{5+} (~69 pm with CN = 6), tungsten ions have a higher valence state, which might exert additional influence on the dielectric and ferroelectric properties. In this paper, we present the study of the influence of tungsten doping on the dielectric properties of SBN ferroelectric ceramics.

Polycrystalline SBWN ceramic samples doped with tungsten oxide with a composition of $Sr_{1+x}Bi_{2-2/3x}$-$(W_xNb_{1-x})_2O_9$ with x ranging from 0 to 0.2 (20 at.%) were prepared by solid state reaction sintering. The starting materials used were $SrCO_3$, Bi_2O_3, WO_3, and Nb_2O_5(Aldrich Chem. Co.), all with a purity of 99%. The chemicals were admixed with desired ratios with an excess of 3 wt% of Bi_2O_3 to compensate for possible loss during sintering. For all samples, a two-step firing process was applied in this study. The first step, calcining at relatively low temperatures (950–1000 °C), was to promote chemical reactions among the constituent compounds to form a single-phase layered perovskite. The second step, sintering at relatively high temperatures (1150–1200 °C), was to achieve high densification. Because of the high melting temperature of WO_3, ceramic samples with tungsten are sintered at 1200 °C. After sintering, all of the ceramic samples have a relative density of 90–95%.

X-ray diffraction (XRD, Philips 1830) was used to determine the formation of layered perovskite phase after both first-step and second-step firing. For the electrical property measurements, the sintered pellets were polished to have flat and parallel surfaces at both sides with a thickness of ~1 mm. Pt wires were connected to the sample surfaces which were electroded with silver paste and heat-treated on hot plate around 500 °C for 10 min. The dielectric constant and loss tangent as functions of temperature up to 600 °C and frequency ranging from 20 Hz to 1 MHz were measured by a HP Precision LCR Meter 4284A.

Fig. 1 shows the XRD spectra of SBN ceramics doped with various amounts of tungsten oxide. It is clear that single phase layered perovskites were formed when the doping content was below 2.5 at.% with no detectable secondary phase. However, XRD spectra of samples

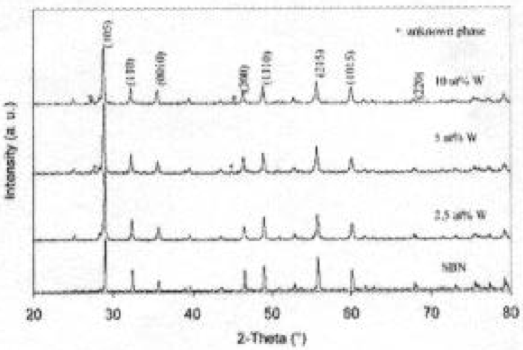

Figure 1 XRD spectra of the $Sr_{1+x}Bi_{2-2/3x}(W_xNb_{1-x})_2O_9$ ferroelectric ceramics.

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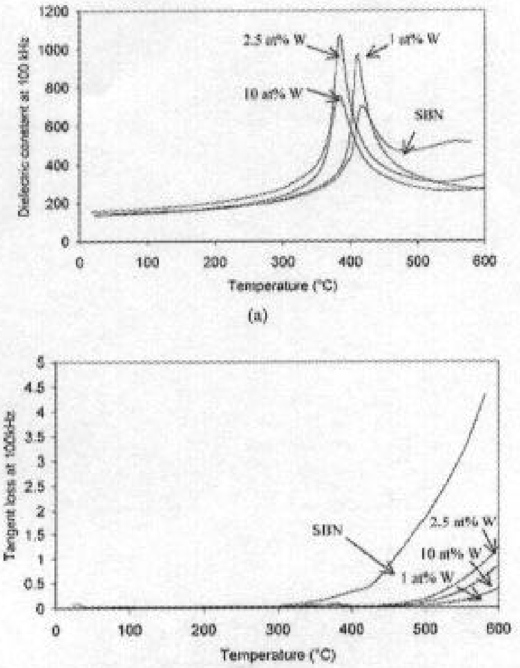

(a)

(b)

Figure 2 Dielectric constants (a) and tangent losses (b) as a function of tungsten content measured at 100 kHz.

consisting more than 5 at.% tungsten showed some unidentifiable peaks, suggesting formation of possible unknown secondary phase. The intensity of these unidentified peaks are also seen to increase as the tungsten content increased, indicating the increased amount of the unknown secondary phase. Compared to the vanadium doping (single phase being kept at least up to ~30 at.% [19]), tungsten has a much lower solubility in SBN, though the ionic radius of tungsten ions is closer to that of pentavalent niobium ions than that of pentavalent vanadium ions. It is not known why tungsten has such a lower solubility, but it is possible that the higher valence state (6+) of tungsten may influence the stability of the crystal structure of SBN ferroelectrics.

Fig. 2 shows the dielectric constants (Fig. 2a) and tangent loss (Fig. 2b) as a function of temperature for SBWN ceramics consisting of 0, 1, 2.5 and 10 at.% tungsten, determined at a frequency of 100 kHz with a oscillating amplitude (50 mV). For all the samples, there is a sharp transition in dielectric constant at their respective Curie points. It is very clear that tungsten doping resulted in increased peak dielectric constants and lowered Curie points. Under the measurement conditions (100 kHz and 50 mV) used in the current study, the dielectric constant consists of contributions of ionic and atomic polarization only. Since the ionic radius of W^{6+} is smaller than that of Nb^{5+}, an increasing amount of W^{6+} would likely lead to a reduced contribution of overall atomic polarization. Therefore, an increased peak dielectric constant may likely be attributable to increased ionic polarization. XRD results (Fig. 1) indicated that there was no noticeable shift of XRD peaks with tungsten doping, suggesting no appreciable change in the lattice constant of SBN perovskite crystal. The XRD spectra further indicated that only a small amount of tungsten ions (less than 5 at.%) could be incorporated into the perovskite structure. Considering such a low doping level and the structural constraint imposed by the $Bi_2O_2^{2+}$ interlayers, it is very likely that the change of crystal lattice constants is very small. As a result, almost unchanged crystal unit cells accommodating smaller ions with higher a valence state would likely lead to an increased ionic polarization and, thus, an increased dielectric constant. In addition, the incorporation of tungsten ions into the SBN structure would likely introduce some cationic vacancies, so as to maintain the electroneutrality. Two possible defect chemical reactions could be simplified as the following:

$$\text{Null} = \text{W}^{\bullet}_{\text{Nb}} + \frac{1}{2}\text{V}''_{\text{Sr}} \tag{1}$$

or

$$\text{Null} = \text{W}^{\bullet}_{\text{Nb}} + \frac{1}{3}\text{V}'''_{\text{Bi}} \tag{2}$$

These cationic vacancies may also have an appreciable contribution to the dielectric constants. Further, an increased amount of tungsten doping also resulted in a reduced Curie temperature, which implied decreased stability of perovskite structure. The relationship between the Curie temperature and tungsten doping will be discussed further later in this paper.

Fig. 2b shows that the loss tangent at a frequency of 100 kHz were greatly decreased with a small amount of tungsten doping, this influence becomes more pronounced at elevated temperatures. It is not clear what exactly is the mechanism of the reduction of loss tangent with tungsten doping; however, the possible formation of cationic vacancies may result in a reduced tangent loss. Similar to La^{3+} doping in PZT ferroelectrics [3], the formation of cationic vacancies would effectively suppress the formation of oxygen vacancies and, thus, decrease the electrical conductivity through a reduced amount of charge carriers. Besides, a reduced tangent loss was also found in the SBN ceramics with vanadium doping [16]. It is interesting to notice that both V–O (~627 kJ/mol) and W–O (~672 kJ/mol) chemical bonds have weaker bond strength as compared with that of Nb–O bond (~703 kJ/mol) [20].

Fig. 3 shows the tangent loss of SBN doped with various amounts of tungsten as a function of frequency

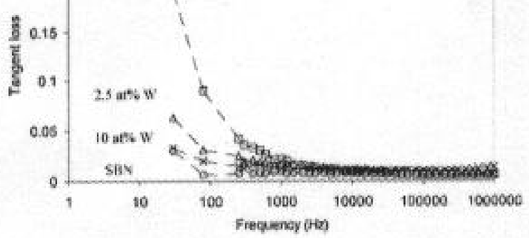

Figure 3 Tangent loss of the four typical samples in the SBWN system over frequency at room temperature.

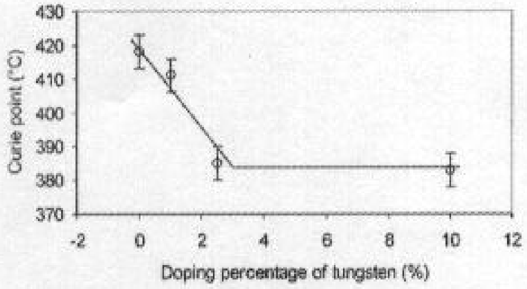

Figure 4 Curie temperature vs. tungsten doping in SBN.

ranging from 20 Hz to 1 MHz at room temperature. The results of four samples consisting of 0, 1, 2.5 and 10 at.% tungsten were included in the figure. It is seen that tangent loss for SBN without tungsten doping remained almost constant throughout the frequency range studied, whereas other three samples consisting of 1 to 10 at.% tungsten showed an appreciable reduction in tangent loss as the frequency increased from 20 Hz to 1 kHz. Under the current experimental conditions (50 mV and 20 Hz–1 MHz), there are three possible contributions to dielectric constant: atomic, ionic, and space charge polarization, since the electric field (~0.5 V/cm) is too small to alter spontaneous polarization (dipolar polarization). Response frequencies for atomic and ionic polarization are 10^{15} and 10^{13} Hz, respectively, whereas space charge has a response frequency of approximately 1 kHz. The tangent loss is likely due to space charge polarization and domain wall relaxation. It is reasonable to assume that the space charge is the main reason that caused an appreciable decrease in tangent loss as the frequency increases from 20 to 1 kHz. Doping with tungsten is seen to result in increased tangent loss at room temperature particularly at frequencies below 1 kHz. The increased tangent loss of SBN doped with tungsten may also be attributed to the possible introduction of cationic vacancies as discussed before as one possible mechanism, which will need further verification.

Fig. 4 shows the Curie temperature T_c of SBWN as a function of the amount of tungsten doping. It was found that the Curie temperature decreased sharply with an increasing amount of tungsten doping at low concentrations, however, remained constant at higher doping levels. With 1 at.% doping, T_c dropped from ~418 °C to ~411 °C. With higher doping content (>2.5 at.%), T_c decreased to ~385 °C at 2.5 at.% and decreased much slower to ~383 °C at 10 at.%. The results implied that the incorporation of tungsten into the SBN crystal structure reached a saturation point of approximately 2.5 at.%. XRD spectra in Fig. 1 indicated the formation of unidentified secondary phase in the samples with tungsten doping levels at and above 5 at.%. Both Figs 1 and 4 suggested a low solubility of tungsten, as substituting ions, in SBN crystal structure is of approximately 3 at.%. A higher doping content of tungsten would either go to the grain boundary phase or form a secondary phase.

In summary, although the ionic radius of W^{6+} was only a little smaller than that of Nb^{5+}, the single phase layered structure could be kept within a very small doping range (~2.5 at.%). The Curie points decreased from ~418 °C for SBN to ~383 °C for SBWN with 10 at.% tungsten. Dielectric constant was found to gradually increase with an increasing concentration of tungsten, reach a maximum at approximately 2.5 at.%, and then reduce with a further increase in tungsten concentration. This phenomenon was explained mainly by the formation of an unknown secondary phase as the tungsten concentration increases. In addition, it was found that a low concentration of tungsten was likely to introduce space charge polarization into the system, resulting in an appreciable decrease in both dielectric constant and tangent loss as frequencies reduced from 20 Hz to 1 kHz.

Acknowledgments

Y.W. would like to acknowledge nanotechnology fellowship and S.L. would like to acknowledge NSF IGERT Fellowship for financial support from the Center of Nanotechnology at University of Washington.

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Received 9 November 2001
and accepted 27 February 2002