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Influence of oxygen annealing on the dielectric properties of $SrBi_2(V_{0.1}Nb_{0.9})_2O_9$ ceramics

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Abstract
The influences of O_2 and N_2 annealing on the dielectric properties of $SrBi_2(V_{0.1}Nb_{0.9})_2O_9$ (SBVN) ferroelectrics were studied. Ceramic samples were prepared by reaction sintering a powder mixture of constituent oxides at 950 °C for 2 h in air. Some samples were also subsequently annealed at 800 °C for 3 h in O_2 or N_2. With O_2 annealing, the Curie point of the SBVN ferroelectrics changed from ~433 to ~438 °C and the peak dielectric constant increased from ~760 to ~1010 (at 100 kHz). However, no change in the Curie point was found with N_2 annealing. Furthermore, O_2 annealing was found to reduce significantly both the dielectric constant and loss tangent of the SBVN ferroelectrics at frequencies below 1000 Hz. XRD results revealed a small reduction in the lattice constants with O_2 annealing, but no appreciable change with N_2 annealing. In addition, no detectable change in the microstructure of the SBVN samples was found with annealing. These results imply that some V^{4+} ions, which are compensated by the formation of oxygen vacancies, existed in the SBVN ferroelectrics prior to O_2 annealing. V^{4+} ions were oxidized to V^{5+} with O_2 annealing, which resulted in improved dielectric properties.

1. Introduction

Strontium bismuth niobate crystal, $SrBi_2Nb_2O_9$ (SBN), has an Aurivillius structure, which is also known as a layered perovskite structure, and exhibits ferroelectric properties at room temperature [1–3]. In comparison with isotropic perovskite ferroelectrics such as $Pb(Zr, Ti)O_3$ (PZT), SBN offers advantages including fatigue-free behaviour and ferroelectric properties independent of film thickness; however, SBN has a relatively low remanent polarization [4–6]. Much effort has been put into improving the ferroelectric properties mostly through substitution with various elements on various sites [7–12]. Partial substitution of niobium with vanadium stands out as the most effective approach to enhancing the remanent polarization of SBN ferroelectrics [10–12]. The significant enhancement of the ferroelectric properties by partial substitution with vanadium was attributed to the increased 'rattling space', defined as the possible space for spontaneous displacement of the centre ions inside the perovskite-like units, due to the smaller ionic radius of V^{5+} (0.59 Å) as compared to that of Nb^{5+} (0.68 Å) [13]. It is known that vanadium can have variable valence states V^{4+} and V^{5+} depending on the environment. Tetravalent vanadium ions are detrimental to the ferroelectric properties. V^{4+} is larger in size than V^{5+} but smaller in charge, and thus will result in a smaller spontaneous polarization when incorporated into the perovskite structure. In addition, when Nb^{5+} is substituted by V^{4+}, one oxygen vacancy will be formed for every two V^{4+} to maintain the required electroneutrality. These oxygen vacancies would contribute to the space charge, energy loss, fatigue and leakage current. In previous work on vanadium-doped SBN ferroelectrics, O_2 annealing was always applied to ensure that the vanadium ions would be V^{5+}. However, so far no experimental study has been carried out on the influences of O_2 annealing on the dielectric and ferroelectric properties of vanadium-doped SBN ceramics. This paper presents our recent study on the influences of O_2 and N_2 annealing on the dielectric constants, loss tan-

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gent and the Curie point of vanadium-doped SBN ceramics. Possible change in crystallinity and microstructure have also been examined. In addition, possible variation in the valence states of vanadium cations was studied by x-ray photoelectron spectroscopy (XPS). The relationship between O_2 and N_2 annealing, valence states and dielectric properties are discussed.

2. Experiment

Polycrystalline strontium bismuth vanadium niobate ceramic samples with a composition of $SrBi_2(V_{0.1}Nb_{0.9})_2O_9$ (SBVN) were prepared by solid state reaction sintering. SBN ceramic samples were also prepared and treated in the same manner and used as references. The preparation process was reported in our previous work [12]. All SBVN pellets were sintered in closed crucibles at 950 °C for 2 h in air, and some samples were subsequently annealed at 800 °C in O_2 or N_2 for 3 h. All sintered pellets have a relative density above 90% and a single-phase layered perovskite structure. The total weight loss in all samples was found to be less than 3 wt%, excluding the decomposition of carbonates. This weight loss was presumably due to the evaporation of Bi_2O_3, but was less than the excess Bi_2O_3 initially added (around 4.5 wt%). The effect of the remaining ~1.5 wt% Bi_2O_3 on the physical properties of SBVN ferroelectrics would be the same and, thus, is neglected in discussion hereinafter. There was no detectable weight loss during O_2 or N_2 annealing. X-ray diffraction (XRD, Philips 1830) was used to determine the formation of the desired layered perovskite phase and any possible crystallinity and microstructure changes with O_2 and N_2 annealing. The XRD spectrum of a NaCl crystal was used as a standard to calibrate the scanning angles. The step size of the scan was $0.04/°2\theta$ with a scanning speed of $0.004°2\theta\ s^{-1}$. The pseudo-tetragonal (200) and $(11\underline{10})$ peaks were chosen to calculate the lattice constant [14]. The microstructure was analysed using scanning electron microscopy (SEM, JEOL 5200) and optical microscopy; however, no appreciable change was found, and all samples showed a dense structure with a similar grain size regardless of O_2 or N_2 annealing. As comparison with vanadium-doped samples, both XRD and SEM analyses revealed that there was no detectable variation in the SBN samples with and without O_2 and N_2 annealing. The SBVN pellets were polished to have flat, parallel surfaces and an approximate 1 mm thickness. They were subsequently electroded by firing silver paste on both sides. The dielectric properties were measured by a HP 4284A Precision LCR meter (Hewlett Packard Co.) using C_p & D functions.

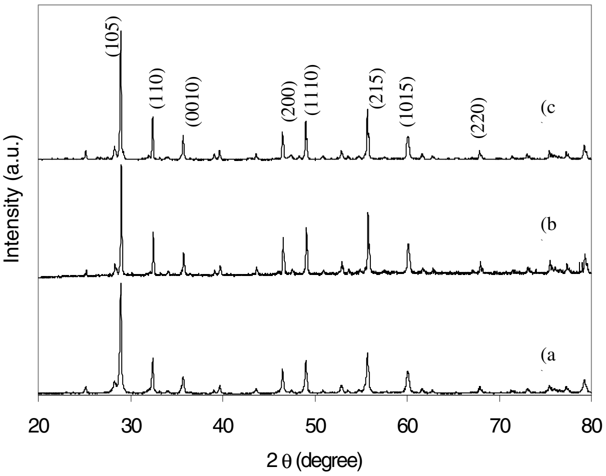


Figure 1. XRD spectra of SBVN ceramics (a) without annealing, (b) with O_2 annealing and (c) with N_2 annealing.

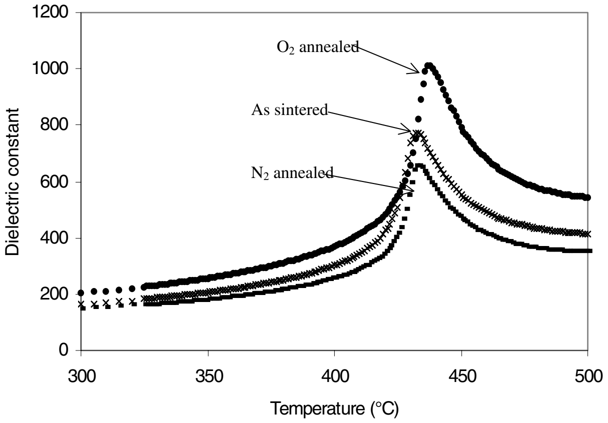


Figure 2. Temperature dependence of dielectric constants of SBVN samples with O_2 annealing (●), without annealing (×) and with N_2 annealing (■), determined using a frequency of 100 kHz and an oscillation amplitude of 50 mV.

Table 1. Properties and lattice constants of SBVN ceramics with and without annealing.

Sample	Curie points (°C)	Peak ε_r	Lattice constants (Å)[a] *a*	*c*
As-sintered	~433	~765	3.900	25.078
N_2-annealed	~433	~650	3.898	25.074
O_2-annealed	~438	~1010	3.893	25.049

[a] The accuracy of lattice parameters is 0.002 Å (pseudo-tetragonal).

3. Results and discussion

XRD analyses indicated that a single-phase layered perovskite structure was formed after sintering. Figure 1 shows the XRD spectra of the SBVN samples, as-sintered, O_2 or N_2 annealed. There are no significant differences except a slight shift of XRD peaks. Table 1 summarizes the lattice constants of the SBVN samples with and without annealing. It was found that the lattice constants, including both *a* and *c*, decreased with O_2 annealing, but were almost unchanged with N_2 annealing. The decrease in lattice constants might indicate a reduction in ionic size with O_2 annealing. Figure 2 shows the characteristic ferroelectric temperature dependence of dielectric constants of SBVN samples: as-sintered, O_2 and N_2 annealed, at a frequency of 100 kHz with an applied bias voltage of 50 mV. The Curie point of the SBVN ferroelectric increased from ~433 to ~438 °C after O_2 annealing. The dielectric constants of the O_2-annealed SBVN sample were found to increase appreciably over the entire temperature range and the enhancement was more pronounced around the Curie temperature (from ~760 to ~1010). N_2 annealing resulted in lower dielectric constants (peak value ~650), whereas the

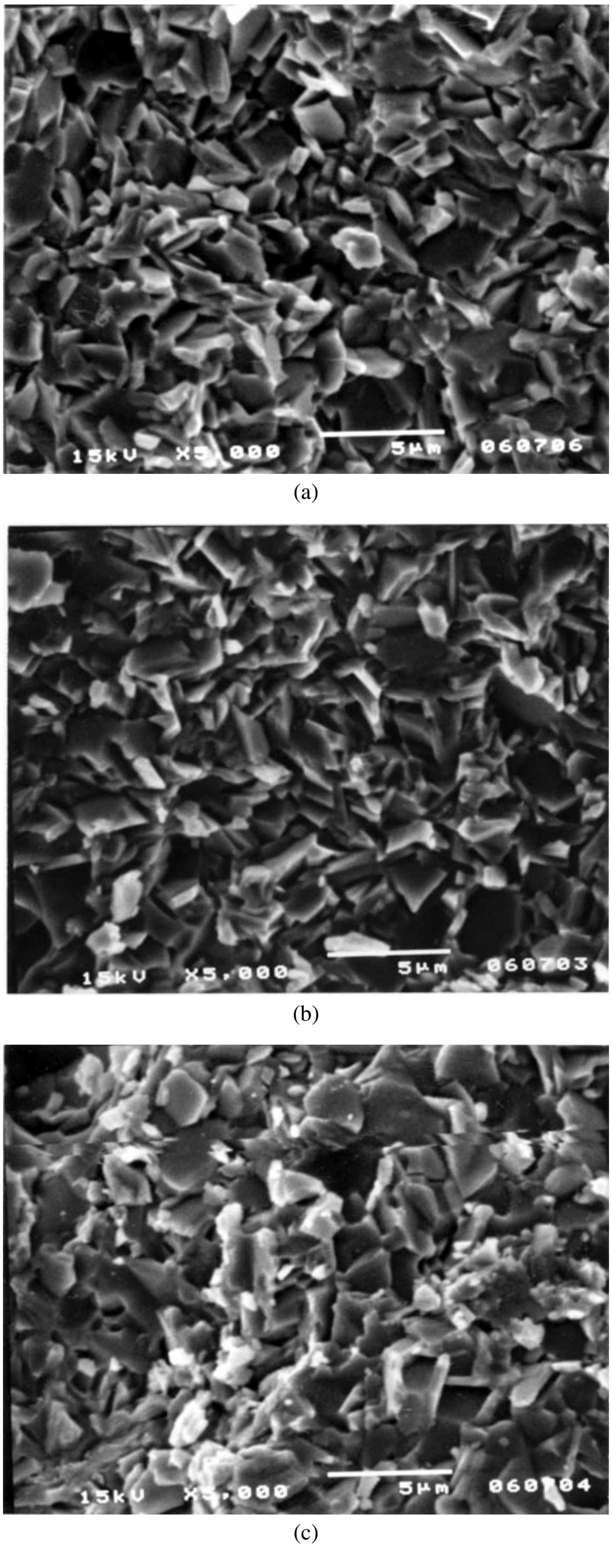
Curie point remained the same. In contrast, neither O_2 or N_2 annealing produced any detectable change in either dielectric constants or the Curie points of the SBN ferroelectrics. The possible mechanisms for the change in dielectric constants include: a reduction in residual stress; improved crystallinity and microstructure; and a change in chemical composition.

Post-sintering annealing at lower temperatures is anticipated to reduce the residual stress. A reduction in residual stress would result in an increase in dielectric constants. Such an increase in dielectric constants was indeed observed in the $SrBi_2Ta_2O_9$ and $SrBi_2(Ta_{0.9}V_{0.1})_2O_9$ ceramics with a prolonged annealing in air for 60 h [15]. Similar results were also reported in isotropic perovskite ferroelectrics [16]. However, the experimental results observed in this study are difficult to explain by reduced stress. First, it cannot explain the fact that there was no change in the dielectric constants of the SBN ceramics, although the sintering temperature for SBN is higher than that for SBVN samples. Second, a reduction in stress cannot explain the increase in the Curie temperature of SBVN when annealed in O_2, but no change with N_2 annealing. Third, a decrease in dielectric constants with N_2 annealing can not be explained by stress reduction since a relatively short annealing time of 3 h might not be sufficient for the material structure to relax. Based on the previous discussion, it is not very likely that stress reduction was the cause of the variation of dielectric properties with O_2 and N_2 annealing.

Improved crystallinity and microstructure are not likely to be the main causes for the change in dielectric constants either. Both SEM (figure 3) and XRD indicated that there was no detectable change in either crystallinity or microstructure. In addition, a change in crystallinity and microstructure cannot explain the different change in the dielectric properties of the samples annealed in O_2 and N_2. Furthermore, SBN ceramics would have a similar change in crystallinity and microstructure when subjected to the same annealing as that in SBVN.

The different dielectric properties of the SBVN ceramics annealed in O_2 and N_2 are most likely due to a change in chemical composition. A loss of some volatile constituent components would be a good possibility, although no weight loss was observed after annealing. Comparing SBVN with SBN, the only difference is the presence of vanadium in the SBVN samples. Since annealing resulted in no appreciable change in the SBN dielectric properties, vanadium is likely to be responsible for the change in the dielectric constant of SBVN ceramics. Two possible processes related to vanadium might occur during annealing. One is the evaporation of vanadium oxide, just like lead oxide in lead-containing perovskite oxides, in which loss of PbO during sintering and annealing is routine. It is anticipated that loss of vanadium oxide would be more significant in N_2 annealing than in O_2 annealing. That O_2 and N_2 annealing resulted in an opposite change in the dielectric constant suggests that loss of vanadium oxide is not a major factor.

Another possibility is related to loss of oxygen induced by a change in the valence state of vanadium ions; in other words, vanadium ions might undergo further oxidation or reduction when SBVN ceramics are subjected to annealing in an O_2 or N_2 atmosphere. As will become clear in the following discussion, a change in the valence states of the vanadium ions is likely to be the cause of appreciable change in the dielectric constants of the SBVN ceramics when subjected to O_2 and N_2 annealing.



(a)

(b)

(c)

Figure 3. SEM pictures for SBVN samples: (a) as-sintered; (b) O_2 annealed; and (c) N_2 annealed.

It is known that a shift in the Curie point to a higher temperature corresponds to an increased spontaneous polarizability. In a given material, increased spontaneous polarizability implies an increase in the possible displacement of the centre ions inside the perovskite-like units. This could

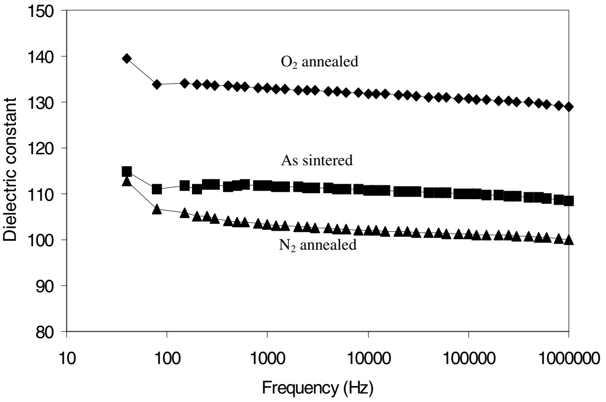


Figure 4. The dielectric constants of SBVN samples as functions of frequency at room temperature.

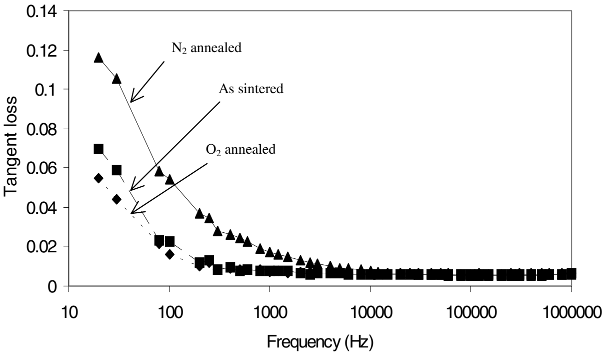


Figure 5. The tangent loss of SBVN samples as functions of frequency at room temperature.

be attributed to further oxidation of some V^{4+} in the SBVN samples prior to O_2 annealing. It is hypothesized that prior to O_2 annealing, there existed some V^{4+} ions. V^{4+} ions (0.68 Å [17][2]) are far larger than V^{5+} ions (0.58 Å [13]). As V^{4+} oxidized to V^{5+}, the ionic radius reduced significantly, which would effectively result in an increase in the 'rattling space' for spontaneous polarization. Consequently, the Curie point shifted to a higher temperature with O_2 annealing. This is in good agreement with our previous vanadium-doping work [12], which demonstrated that an increased amount of vanadium doping resulted in a linear increase in the Curie point. This increase was attributed to the increased rattling space introduced by the increasing number of V^{5+} ions, which have a smaller ionic radius in comparison with that of Nb^{5+} (0.68 Å [13]). N_2 annealing is expected to reduce some V^{5+} ions to V^{4+} ions and create more oxygen vacancies, though the change might be small. A combination of an increased amount of V^{4+} and oxygen vacancies would result in lower dielectric constants (at 100 kHz), but would exhibit no appreciable influence on the Curie point.

Figures 4 and 5 are the dielectric constant and tangent loss of SBVN ferroelectrics as functions of frequency, ranging from 20 Hz to 1 MHz at room temperature. Both the dielectric constants and tangent losses of O_2-annealed SBVN ferroelectric were almost constant over the entire frequency range. Furthermore, the O_2-annealed sample shows higher dielectric constants than the as-sintered and N_2-annealed samples through the whole frequency range. However, an appreciable reduction in the tangent losses of both as-sintered and N_2-annealed SBVN samples were found as the frequency increased from 20 to 1000 Hz. In addition, at frequencies below 1000 Hz, the tangent losses of as-sintered and N_2-annealed samples were higher than those of O_2-annealed SBVN ferroelectrics. A decrease in the loss tangent at low frequencies suggests the possible presence of space-charge polarization. The O_2-annealed SBN sample showed no appreciable change in either dielectric constant or loss tangent over the entire frequency range. A comparison of the dielectric properties of the SBN and SBVN samples implies that vanadium ions are responsible for the variation in dielectric constant and loss tangent in the SBVN samples. Such a significant decrease in space-charge polarization in the SBVN samples with O_2 annealing could be attributed to a multiple valence state of vanadium ions (V^{5+} and V^{4+}). When V^{4+} are incorporated into the SBVN layered perovskite structure by substituting Nb^{5+}, oxygen vacancies would be created. Using Kroger–Vink notation:

$$2VO_2 = 2V'_{Nb} + 4O^{x}_{O} + V^{\bullet\bullet}_{O} \qquad (1)$$

where V'_{Nb} represents V^{4+}-occupied Nb^{5+} site with one effective negative charge and $V^{\bullet\bullet}_{O}$ represents an oxygen vacancy with two effective positive charges. Both V'_{Nb} and $V^{\bullet\bullet}_{O}$ are potential charge carriers, and possible contributors to space-charge polarization. However, considering only 10 at% vanadium doping, it is unlikely that the vanadium ions will be able to form a percolated network, which is necessary for the hopping conduction mechanism. Therefore, $V^{\bullet\bullet}_{O}$ is most likely to be the contributor to the space-charge polarization. When the SBVN samples were annealed with O_2, V^{4+} ions were oxidized to V^{5+} and the amount of $V^{\bullet\bullet}_{O}$ would be reduced or eliminated from the structure. As a result, O_2 annealing resulted in a drastic reduction in space-charge polarization, which led to a reduced dielectric constant and tangent loss at frequencies below 1000 Hz. N_2 annealing is anticipated to reduce some V^{5+} to V^{4+} and simultaneously form more $V^{\bullet\bullet}_{O}$. An increased amount of $V^{\bullet\bullet}_{O}$ is expected to contribute to space-charge polarization as previously discussed, which explains the high dielectric constants and tangent loss for the N_2-annealed SBVN sample at frequencies below 1000 Hz as shown in figures 4 and 5.

XPS was used to determine the valence states of the vanadium ions in the SBVN samples. Although there was an indication of the presence of V^{4+} ions prior to O_2 annealing, no definite conclusion could be drawn from the measurements. In the SBVN samples, only 10 at% niobium ions were replaced by vanadium. It is most likely that only a very small fraction of vanadium may have a tetravalence state, and a definite measurement of valence change of vanadium ions could be very difficult to obtain using XPS. However, the change in the valence state of the vanadium ions has been reported in literature [18, 19]. XPS results from SBVN samples revealed that O_2 annealing did not result in any detectable change in other ions.

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[2] In this book, values are based on $RO^{-2} = 1.40$ Å, whereas values from [13] are based on $RO^{-2} = 1.44$ Å.

4. Conclusions

It was found that with O_2 or N_2 annealing, there was a significant change in the dielectric properties of SBVN samples, whereas both O_2 and N_2 annealing exhibited a negligible influence on the properties of the SBN samples without vanadium doping. The experimental results suggest that the changes are most likely to be due to the change in the amount of oxygen vacancies induced by the change in the valence state of the vanadium ions. O_2 annealing may result in an oxidation of possible tetravalent vanadium ions to a pentavalent state thus reducing the concentration of oxygen vacancies and improving the dielectric properties of the SBVN ferroelectrics. N_2 annealing may have the opposite influence on the dielectric properties of the SBVN samples. However, due to the low concentration of vanadium ions, XPS analyses did not produce any direct evidence supporting or refuting this possible explanation, particularly those with a tetravalent state.

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