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Influences of vanadium doping on ferroelectric properties of strontium bismuth niobates

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Layered perovskite ferroelectrics, such as $SrBi_2Nb_2O_9$ (SBN) and $SrBi_2Ta_2O_9$ (SBT), are excellent candidates for applications in information data storage in digital memory systems, since they offer several advantages like being fatigue-free and having independence of ferroelectric properties with film thickness, as compared with isotropic perovskite ferroelectrics such as $Pb(Zr,Ti)O_3$ (PZT) [1–3]. Much work has been done in the development of layered perovskite ferroelectrics for applications in information storage such as ferroelectric random access memories (FeRAM) [4–6]. Layered perovskite ferroelectrics, however, suffer from two drawbacks: a relatively low remanent polarization and a high processing temperature [7]. In addition, the d.c. conductivity of layered perovskite ferroelectrics is higher than that of PZT. Efforts have been made to enhance the properties of layered perovskite ferroelectrics by the addition or substitution of alternative cations. For example, partial substitution of Sr^{2+} by Bi^{3+} has resulted in the most noticeable improvement of ferroelectric properties [8–10]. Both the Curie points and the peak dielectric constant increased significantly with an increased Bi^{3+} substitution. The substitution of bivalent Sr^{2+} cations by trivalent Bi^{3+} introduces cation vacancies, so as to maintain electroneutrality. The incorporation of barium ions into strontium positions was also reported to produce higher remanent polarization than the intrinsic $SrBi_2Ta_2O_9$ thin films [11].

Our approach is to substitute Nb^{5+} with a much smaller cation V^{5+} to enhance the ferroelectric properties through increasing "the rattling space" and thus the polarizability in SBN. Our previous letter reported that layered perovskite ferroelectrics, SBN, with niobium substituted by vanadium up to 10 at%, by solid state reaction sintering, retained the same crystalline structure with a slight decrease in crystal lattices, in spite of the significant difference in ionic radii of vanadium (58 pm) and niobium (69 pm) cations [12]. The partial substitution of niobium by vanadium resulted in an appreciably decreased sintering temperature, partially due to the low melting point of V_2O_5. The resultant $SrBi_2(V_xNb_{1-x})_2O_9$ (SBVN, with $x \leq 0.1$) ceramics exhibit enhanced ferroelectric properties as indicated by the shift of the Curie point towards higher temperatures and increased dielectric constants at the Curie points. In addition, it was found that the incorporation of vanadium into the layered perovskite structure did not result in an increase in loss tangent. In this letter, we report the study on the P-E hysteresis loops and the d.c. conductivity of the new layered perovskite ferroelectric SBVN prepared by solid state reaction sintering. The effects of vanadium incorporation on remanent polarization, coercive field and d.c. conductivity are discussed as well.

Detailed information of sample preparation was presented in our previous letter [13] and the following is a brief summary of the preparation procedure. The polycrystalline vanadium doped strontium bismuth vanadium niobate ceramic samples with a composition of $SrBi_2(V_xNb_{1-x})_2O_9$ (SBVN) with x ranging from 0 to 0.1 (10 at%) were prepared by solid state reaction sintering. The starting materials used were $SrCO_3$, Bi_2O_3, V_2O_5, and Nb_2O_5 (Aldrich Chem. Co.), all with a purity of 99%. The powders were admixed with a desired weight ratio with approximately 4.5 wt% excess Bi_2O_3, which was to compensate for the weight loss of Bi_2O_3 due to its high vapor pressure (750 mmHg at 1570 °C). Powders were ball milled and then fired in air for 2 h at 850–1000 °C. The fired powders were ground, admixed with about 1–1.5 wt% polyvinylalcohol (PVA, Aldrich Chem. Co.) as a binder and pressed into pellets uniaxially at ~300 MPa. The pellets were sintered in closed crucibles at 950–1150 °C for 0.5–2 h in air. All sintered pellets had a relative density above 94% with less than 3 wt% weight loss. X-ray diffraction analyses indicated all samples consisted of a single layered perovskite phase without detectable secondary phase. Table I summarizes some information on the three samples studied in this letter. Prior to property measurements, all the samples were annealed at 800 °C for 3 h in oxygen. The pellets (~8.6 mm in diameter) were polished to a thickness of approximately 0.25 mm and electroded by sputtering Pt on both sides.

The P-E hysteresis loop measurement was performed using a standard Sawyer-Tower circuit with a reference resistor of 10^7 ohm and a reference capacitor of 9.43×10^{-7} mF. The parameters used for the measurement were: peak voltage, 3500 V; frequency, 10 Hz;

TABLE I Compositions, sintering condition, relative density, and the Curie points of the layered perovskite SBN samples with and without vanadium doping

Sample	Sintering condition	Relative density (%)	Curie points (°C)
SBN	1150 °C-0.5 h	94	~435
SBVN (5 at% V)	950 °C-2 h	96	~455
SBVN (10 at% V)	950 °C-2 h	97	~443

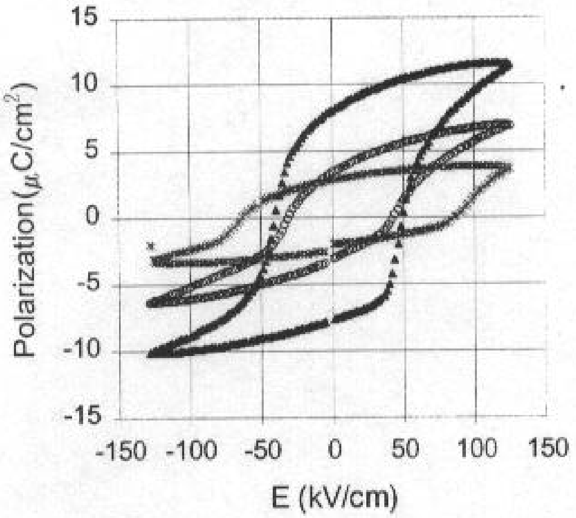

Figure 1 P-E hysteresis loops for SBVN samples without vanadium (*, at 178 °C), with 5 at% vanadium (○, at 165 °C) and with 10 at% vanadium (▲, at 165 °C).

and wave form, triangle. Fig. 1 shows the P-E hysteresis loops of the SBVN samples with $x = 0$, 0.05, and 0.1 respectively. The P-E hysteresis loop of the SBN sample was measured at 178 °C; while those of SBVN with $x = 0.05$ and 0.1 were determined at 165 °C with all other measurement parameters the same. This figure clearly demonstrated that the substitution of niobium by vanadium has a significant influence on the ferroelectric properties. The coercive field reduces from $2E_c = (E_{c+} - E_{c-}) = 125$ kV cm^{-1} for SBN without vanadium doping to 80–90 kV cm^{-1} for SBVN with 5–10 at% vanadium doping. The remanent polarization increases significantly from approximately $2P_r = (P_{r+} - P_{r-}) = 4.8$ μC cm^{-2} for SBN without vanadium doping to $2P_r = 7$ μC cm^{-2} for 5 at% doped SBVN, and to $2P_r = 16$ μC cm^{-2} for 10 at% doped SBVN. From the literature, typical $2P_r$ and $2E_c$ for SBN films were found to be around 5–20 μC cm^{-2} and 200–250 kV cm^{-1} [14–16]. Considering the difference in measuring temperature and processing conditions, and the difference between thin films and bulk ceramics, the ferroelectric properties of the SBN ceramic in this study shows very good agreement with the literature.

The exact mechanism by which the substitution of niobium by vanadium results in a significant enhancement in polarization and a decrease in coercive field is a subject for further study. One possible explanation is the increased "rattling space" inside the oxygen octahedron. The polarizability in isotropic perovskites (ABO_3) has been a subject of intensive study and it has been found that the polarizability is largely determined by the sizes of the A and B cations [17]. In general, a size decrease of B cations (located inside an oxygen octahedron) results in an increase in both polarizability and the Curie point due to "a larger rattling space" available for B cations, provided that the perovskite structure is preserved. The size change of A cations has an opposite influence compared to that of B cations, since a size increase of A cations leads to an increased size of the oxygen octahedron and thus results in an increase in both polarizability and the Curie point. The crystal structure of SBN consists of the perovskite sheet ($SrNb_2O_7^{2-}$) interleaved with bismuth oxide layers where distorted NbO_6 octahedral are the origin of ferroelectricity as a result of the shift of Nb^{5+} away from the center position below the Curie temperature. Although V^{5+} can have six-fold coordination of oxygen, it is too small to form a stable layered perovskite structure. However, partial substitution of Nb^{5+} by V^{5+} up to 10 at% results in a stable layered perovskite structure as reported in our previous work [13]. A significant size decrease from Nb^{5+} (69 pm) to V^{5+} (58 pm) would certainly result in an increase in the "rattling space" inside the oxygen octahedron and thus a significant increase in polarization.

In general, the substitution of alternative cations in isotropic perovskite ferroelectrics would have the effect of restricting domain wall motion, and would thus result in an increased coercive field [18]. A decrease in coercive fields with an increasing amount of vanadium substitution in the present study suggests a different mechanism is predominant. It is possible that vanadium cations with a much smaller ionic radius require a lower potential energy to rattle from one position to another inside the oxygen octahedron and that this leads to a lowered coercive field.

The d.c. conductivity of the new layered perovskite ferroelectrics, SBVN were studied by means of the a.c. impedance measurements using a Hewlett Packard Precision 4284A LCR Meter at temperatures ranging from 60 °C to 700 °C in a frequency range from 20 Hz to 1 MHz. Fig. 2 shows the d.c. conductivities of the SBVN ferroelectrics as a function of temperature. For all three cases, a transition temperature between 250 °C and 320 °C was observed at which the conduction mechanism changed. This figure shows that there are two predominant conduction mechanisms at different temperature ranges, regardless of vanadium doping. At temperatures below the transition point, the electrical conduction is likely to be dominated by extrinsic defects, such as unintentionally introduced impurities and the d.c. conductivities for all three samples were found

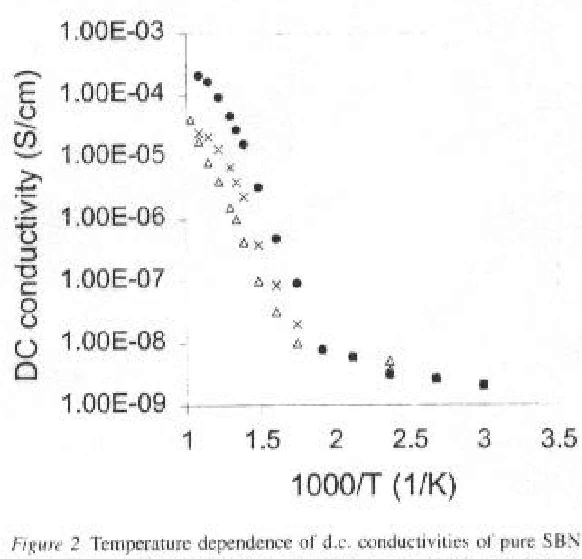

Figure 2 Temperature dependence of d.c. conductivities of pure SBN sample (●), SBN doped with 5 at% vanadium (×) and with 10 at% vanadium (△).

TABLE II Activation energies, transition temperature and d.c. conductivity at 60 °C for samples with different vanadium doping

Sample	E (eV)	Transition temperature (°C)	d.c. conductivity at 60 °C (S cm^{-1})
SBN	1.174	~250	2.12×10^{-9}
SBVN(5 at% V)	1.114	~280	2.14×10^{-9}
SBVN(10 at% V)	1.074	~320	2.09×10^{-9}

the same at approximately 2×10^{-9} S cm^{-1}. This d.c. conductivity is approximately 2 orders of magnitude lower than that reported in the literature but is still higher than the result from PZT [19, 20]. At temperatures higher than the transition point, the conduction is presumably dominated by the intrinsic defects. It is found that the d.c. conductivities of the SBVN ceramics decreased with an increased doping content at the higher temperature range, while there was an appreciable decrease from 1.174 eV to 1.074 eV as the vanadium doping increased from 0 to 10 at%. Table II summarizes the conduction transition temperature, activation energies for intrinsic conduction and d.c. conductivities at 60 °C.

Since the d.c. conductivity depends on both the concentration and mobility of charge carriers, a reduced d.c. conductivity suggests a reduced concentration and/or mobility of charge carriers. The substitution of niobium by vanadium may result in increased complexity in the crystal structure and, thus, a reduced mobility (or diffusivity) of charge carriers. A decrease in activation energy with an increasing amount of vanadium doping, however, suggests that the concentration of intrinsic charge carriers may increase due to the incorporation of vanadium cations. If the primary intrinsic charge carriers in the layered perovskite ferroelectrics, SBNV, are oxygen vacancies, a relatively lower diatomic bond strength of V-O bonds (~627 kJ mol^{-1}), as compared to that of Nb-O bonds (~703 kJ mol^{-1}) [21], could be responsible for the reduced activation energy with an increasing amount of vanadium doping. In addition, the multivalence state of vanadium cations may contribute extra electrical conduction, leading to a lower activation energy. The experimental results observed in this study suggest that the effects of vanadium doping on the d.c. conduction is complex, and further analysis is required to achieve a better understanding.

In summary, the ferroelectric properties of the layered perovskite, SBN, have been significantly enhanced with vanadium doping up to 10 at%, while the layered perovskite structure was preserved. Substitution of niobium by much smaller vanadium cations resulted in an increased "rattling space," leading to a significantly higher remanent polarization from ~2.4 μC cm^{-2} to ~8 μC cm^{-2} with 10 at% V^{5+} doping and a lower coercive field from ~63 kV cm^{-1} to ~45 kV cm^{-1}. At lower temperatures, the SBVN samples show almost the same d.c. conductivities (~10^{-9} S cm^{-1}) regardless of vanadium doping, while at the higher temperature range the vanadium doped samples have lower conductivities. Reduced d.c. conductivities at high temperatures may be attributed to the increased complexity in crystal structure with partial substitution of niobium by vanadium.

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