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Dielectric properties of layered perovskite $Sr_{1-x}A_xBi_2Nb_2O_9$ ferroelectrics ($A=La, Ca$ and $x=0,0.1$)

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In this letter, we report an experimental study on the influences of 10 at. % Ca^{2+} and La^{3+} doping on dielectric properties and dc conductivity of $SrBi_2Nb_2O_9$ ferroelectric ceramics. All the samples were made by two-step solid-state reaction sintering at temperatures up to 1150 °C for 0.5–1 h in air. X-ray diffraction analysis indicated that single-phase layered perovskite ferroelectrics were obtained and no appreciable secondary phase was found. The Curie point was found to increase from 418 °C without doping to 475 °C with Ca^{2+} doping and to 480 °C with La^{3+} doping. Dielectric constants, loss tangent, and dc conductivity of $SrBi_2Nb_2O_9$ ferroelectrics doped with Ca^{2+} and La^{3+} were studied and the relationships among doping, crystal structure, and dielectric properties were discussed. © *2000 American Institute of Physics.* [S0003-6951(00)04320-5]

Ferroelectrics have reversible spontaneous polarization making them ideally suited for use in nonvolatile random access memories (NvRAMs). Polarization is due to dipoles that can switch directions spontaneously under the influence of an electric field and the dipoles are a result of the noncentrosymmetric crystal structure.[1,2] Previous research has focused on $Pb(Ti, Zr)O_3$ (PZT), but one of the current problems with PZT is the fatigue resistance of the material. PZT thin films tend to degrade most of the initial amount of switching charge (‘‘fatigue’’) after 10^6-10^8 cycles of full polarization switching.[3] Bismuth layered perovskite materials have high fatigue resistance and are able to withstand 10^{12} erase/rewrite operations[4] and therefore have attracted an increasing attention for NvRAM application.[5] The crystal structure and chemical composition of these layered perovskites were systematically studied by Aurivillius[6] in the 1950’s. Among the layered perovskites, $SrBi_2Nb_2O_9$ (SBN), $SrBi_2Ta_2O_9$ (SBT), and their solid solutions (SBNT) are the most promising candidates, because they possess a reasonable spontaneous polarization which is one of the key parameters for the information storage applications. However, they suffer from relatively high processing temperature, relatively low spontaneous polarization, and relatively high dielectric loss.[7,8] Much research has been reported in the open literature aimed at improving the dielectric and ferroelectric properties of the SBNT materials [e.g., Refs. 9 and 10]. In particular, doping with various metal oxides has been demonstrated one of the effective approaches to improve the properties.[11,12] For example, Bi^{3+} doping has resulted in an appreciable enhancement of dielectric properties.[11] Wu and Cao[13,14] have substituted Nb^{5+} with vanadium and found a significant enhancement in dielectric and ferroelectric properties. In addition, it was found that the sintering temperature was significantly reduced by approximately 200 °C.

In this letter, we report our recent study on the influences of Ca^{2+} and La^{3+} doping on the electrical properties of SBN ceramics. One of the objectives of this research is to enhance the dielectric and ferroelectric properties of SBN by substituting Sr^{2+} (1.44 Å) with smaller ions, Ca^{2+} (1.34 Å) and La^{3+} (1.36 Å) (all with coordination number = 12).[15] It is anticipated that the incorporation of smaller Ca^{2+} or La^{3+} could lead to a reduced lattice constant of perovskite unit cells; however, in layered perovskites, the Bi_2O_2 interlayer would impose a structural constraint so that the perovskite unit cell would not be free to shrink. Consequently, a combination of incorporation of small cations and unchanged unit cells would lead to both large spontaneous and ionic polarization. Another objective is to study the possibility of reducing the dc conductivity and loss tangent of SBN ferroelectrics, a similar approach as that widely used in isotropic perovskite ferroelectrics.

The chemicals used were $CaCO_3$, $La_2(CO_3)_3 \cdot 8H_2O$, $SrCO_3$, Bi_2O_3, and Nb_2O_5 (all from Aldrich Chem. Co., with a purity of 99%). Three compositions were studied in the current research: SBN, $Ca_{0.1}Sr_{0.9}Bi_2Nb_2O_9$ (hereafter referred to as CSBN), and $La_{0.1}Sr_{0.9}Bi_2Nb_2O_9$ (LSBN). Details of the sample preparation and characterization were the same as reported previously.[10] Table I summarizes the sintering conditions and the relative density (percentage of the theoretical density calculated from lattice constants) of the final products. This table shows that the incorporation of calcium oxide and lanthanide has improved the sinterability. This result is similar to that with the addition of vanadium oxide,[13] albeit the improvement is less significant. The weight loss of all three samples is comparable and is less than the amount of extra bismuth oxide added. Figure 1 shows the X-ray diffraction spectra of the three samples studied and indicates that a single phase layered perovskite in all samples was

TABLE I. Sintering conditions and relative density of SBN, CSBN, and LSBN.

Samples	First sintering conditions	Final sintering conditions	Relative density
SBN	900 °C; 2 h	1150 °C; 0.5 h	94%
CSBN	900 °C; 2 h	1150 °C; 1 h	95%
LSBN	900 °C; 2 h	1150 °C; 1 h	96%

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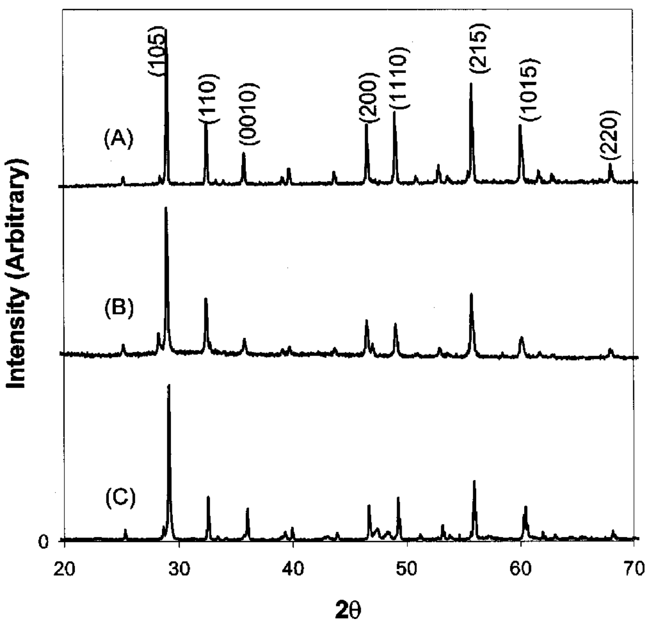

FIG. 1. XRD spectra of (A) SBN, (B) LSBN, and (C) CSBN.

formed after prefiring and no secondary phase detectable. The above XRD results indicate that both Ca^{2+} and La^{3+} were incorporated into the layered perovskite structure and presumably occupied Sr^{2+} sites. Although it is not experimentally shown whether Ca^{2+} and La^{3+} replaced Sr^{2+} or Bi^{3+}, comparison of the ionic radii reveals that Bi^{3+} [0.96 Å (Ref. 15)] is more than 30% smaller than the other ions and the substitutions in the Bi^{3+} sites are not very likely.

Figure 2 shows the dielectric constants of samples SBN, LSBN, and CSBN as a function of temperature, determined at a frequency of 100 kHz and an alternating voltage of 50 mV. It is seen that with 10 at % lanthanum and calcium doping, the Curie points increased from 418 °C for SBN, to 475 °C and to 480 °C for CSBN and LSBN, respectively. However, the dielectric constants at both room temperature and the Curie point were found to decrease with Ca^{2+} and La^{3+} doping. The decrease in dielectric constants can be explained by a decrease in atomic polarization. Dielectric constant is determined by four polarizations: atomic, ionic, dipolar, and space charge polarization. Under the experimental conditions used in the current study, i.e., a high frequency of 100 kHz and a low electric field (~0.4 V/cm), only atomic and ionic polarization would contribute to the dielectric constants. The incorporation of smaller cations (7% smaller in ionic radius) would result in a reduced atomic polarization.

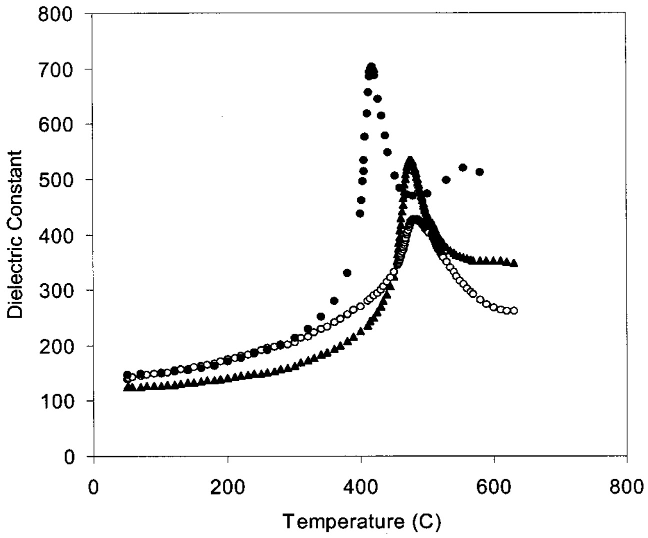

FIG. 2. Dielectric constant of SBN (●), CSBN (▲), and LSBN (○) as a function of temperature, measured at a frequency of 100 kHz.

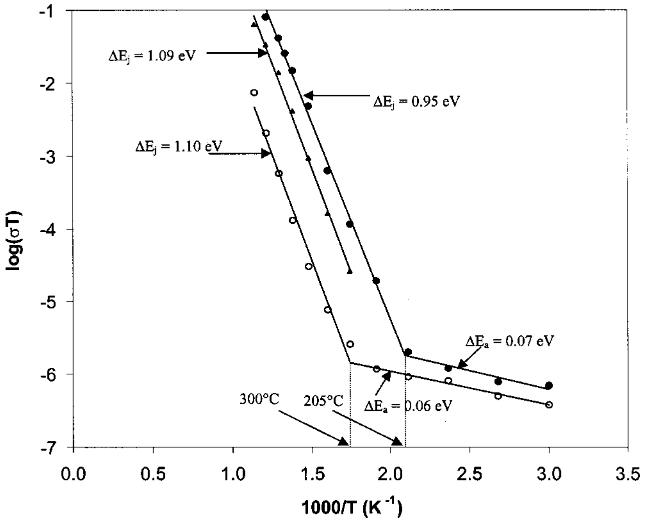

FIG. 3. dc conductivity of SBN (●), CSBN (▲), and LSBN (○) as a function of temperature.

Figure 3 is the dc conductivity of samples SBN, CSBN, and LSBN, as a function of temperature. This dc conductivity was estimated from the bulk resistance, R_g, which was derived from the equivalent circuit model in complex impedance planes of a resistor and a capacitor in parallel.[16] It was found that throughout the temperature range studied in the current research, the dc conductivity of both LSBN and CSBN samples are appreciably lower than that of SBN. There are two regions predominant with different conduction mechanisms. At the low temperature region, the conduction is presumably predominant by the extrinsic impurity conduction with a very similar activation energy, whereas the conduction at the high temperature range is likely predominant by intrinsic defects. The activation energy, ΔE_j, of LSBN and CSBN, at the high temperature range was found higher than that of SBN and ΔE_j is assumed to be the energy necessary to create and move vacancies. The transition temperature between the intrinsic and extrinsic conduction increased from 205 °C for SBN to 300 °C for LSBN. Higher transition temperature and higher activation energy for LSBN could be explained by the fact that the substitution of La^{3+} into the Sr^{2+} sites resulted in an enhanced stability of the perovskite structure due to the larger chemical bond strength of La–O bonds (799 ± 4 kJ/mol at RT),[17] as compared with that of Sr–O bonds (425.5 ± 16.7 kJ/mol at RT).[17] In addition, stronger chemical bonds would certainly suppress the formation of intrinsic defects and, thus, result in an increased transition temperature. At the low temperature range, a reduced dc conduction may also be attributed to the substitution of trivalent La^{3+} into the crystal structure. The simplified defect chemical reaction could be written as follows:

$$\mathrm{La_2O_3} \rightarrow 2\mathrm{La}^{\bullet}_{\mathrm{Sr}} + 3\mathrm{O}^{x}_{\mathrm{O}} + V''_{\mathrm{Sr}},$$

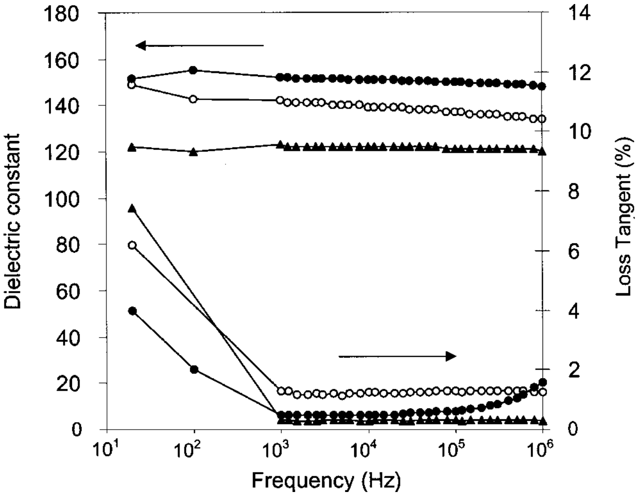

FIG. 4. Loss tangent and dielectric constant of SBN (●), CSBN (▲), and LSBN (○) as a function of frequency at room temperature.

where $La^{\bullet}_{\mathrm{Sr}}$ represents a lanthanum ion in the strontium site with one effective positive charge, O^{x}_{O} represents an oxygen ion in the oxygen site without effective charge, and V''_{Sr} represents strontium vacancies with two effective negative charges. For ionic conduction in oxide systems, oxygen vacancies are commonly charge carriers for both intrinsic and extrinsic conduction. The partial substitution of divalent Sr^{2+} by trivalent La^{3+} would introduce one extra oxygen anion which would occupy possible oxygen vacancies available or create Sr^{2+} vacancies. Consequently the amount of charge carriers, i.e., oxygen vacancies would be decreased and thus the dc conductivity reduced. However, the bond strength could not explain the high activation energy observed in CSBN and no other explanation is found at the moment.

Figure 4 shows the room temperature dielectric constant and loss tangent of samples SBN, CSBN, and LSBN, as a function of frequency, which ranged from 20 Hz to 1 MHz. Doping of Ca^{2+} and La^{3+} resulted in reduced dielectric constants throughout the frequency range. This reduction could be attributed to the reduced atomic polarization due to the smaller ionic radii of both Ca^{2+} and La^{3+}. However, the loss tangent of the LSBN sample was found to be higher than that of SBN ferroelectrics; whereas the Ca^{2+} doped sample exhibited a reduced loss tangent except at low frequencies. It is known that the loss tangent in ferroelectrics is due to a combination of the space charge polarization and domain wall relaxation. The exact mechanism for the variation in loss tangent with La^{3+} or Ca^{2+} doping is not clear; however, it is possible that the La^{3+} or Ca^{2+} doping may change the mobility of domain walls. This phenomenon was widely observed in isotropic perovskite ferroelectrics.[18] More study is required to achieve a better understanding of the relationship between the compositions, microstructure, and physical properties of layered perovskite ferroelectrics.

In summary, a single phase layered perovskite SBN ferroelectric doped with 10 at % of La^{3+} or Ca^{2+} has been synthesized through solid state reaction sintering. It was found that the incorporation of both Ca^{2+} and La^{3+} resulted in a somewhat reduced dielectric constant, which could be attributed to the reduced ionic radii of Ca^{2+} and La^{3+} and the slightly reduced lattice constants. The incorporation of La^{3+} has led to an appreciable reduction in dc conductivity throughout the temperature range studied in the current research. The reduced dc conductivity is explained by the reduction in the concentration of oxygen vacancies, and by enhanced structure stability due to the stronger chemical bond strength of La–O bonds. The study of ferroelectric properties, such as $P-E$ hysteresis, is in progress.

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