Advances in dielectric performance of atomically engineered perovskite nanosheet thin films

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Research Article

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Abstract

The search for new high-performance dielectric material receives continued research interest. Several mechanisms for high permittivity have been proposed such as BaTiO$_3$-based perovskites or CaCu$_3$Ti$_4$O$_{12}$. Nevertheless, developing thin films with such high performance remains a highly challenging task. However, reducing the BaTiO$_3$-based film thickness raises the leakage current and suppresses dielectric responses because of a low-permittivity interfacial ‘dead-layer’. Here, we propose a new materials design route to great permittivity behavior in atomically-thin films, where charge engineering of layered perovskites generates giant polarizability and results in 2-dimensional materials with colossal permittivity. Firstly, we present a concrete example Dion-Jacobson type KSr$_2-x$Bi$_x$Nb$_3$O$_{10}$ and its cation-exchanged form HSr$_{2-x}$Bi$_x$Nb$_3$O$_{10}$, which exhibit a stable colossal permittivity and a low dielectric loss. Also, Sr$_{2(1-x)}$Bi$_{2x}$Nb$_3$O$_{10}$ ($x = 0.1$) nanosheets attain by chemical exfoliation method with a high dielectric permittivity of over 500, the highest among all known dielectrics in the ultrathin films (< 20 nm). As Bi-substitution of Sr$_2$Nb$_3$O$_{10}$, the dielectric permittivity exhibits two times higher value due to higher polarizability of Bi ions and leads larger dielectric permittivity. Density functional theory calculations suggest that the substitution of high-valent Bi ions with lone pairs are responsible for the colossal permittivity. Our results provide a strategy for achieving new high-k nanodielectrics for use in nano-scaled electronics.

Introduction

As the requirements for implementable high-k ultrathin films have increased for next-generation electronics, the search for novel high-k materials has been ongoing in order to further scale down the size of such electronics including multilayer ceramic capacitors, gate dielectrics for transistors, and memory devices[1]. The discovery of such materials, however, remains limited. Conventional high-k dielectric oxides such as (Ba,Sr)TiO$_3$ require ultrathin films to achieve their capacitance because the thinner dielectric layer and higher reliability lead to higher capacitance[2]. Synthesizing spherical nanosized powders for these ultrathin films, however, remains difficult and expensive[3]. In addition, these materials are significantly affected by intrinsic size effects involving the particle and grain sizes. The size effect is often attributed to the low-k interfacial ‘dead layer’, which is caused by the degradation of the dielectric/electrode interface layer during post-annealing, the growth-induced defects, and the strain introduced from electrodes[4–6]. In addition, the film fabrication process is complicated and requires a post-annealing process which causes cracks and defects in thin films[7].

Recently, two-dimensional (2D) Dion-Jacobson (DJ) type layered perovskite nanosheets have received attention as alternative dielectric oxides, due to their high dielectric permittivity over 200 at thicknesses under 20 nm, solution-processable fabrication, great chemical stability, and thermal stability[8–10]. This type of material does not require post-annealing due to its single crystalline nature, alleviating the effects from the interfacial dead layers. The dead-layer-free nanofilms demonstrate invariant dielectric permittivity that is dependent on thickness[10, 11]. The DJ-type layered perovskites consist of negatively
charged $A_{n-1}B_nO_{3n+1}$ perovskite slabs with A cations in the interlayer space, and the weak bonding between each perovskite layer allows them to be exfoliated to extract various single crystal nanosheets. These obtained single crystal nanosheets can be assembled as thin films on various substrates by room temperature deposition processes such as Langmuir-Blodgett method, Layer-by-Layer deposition, or electrophoretic deposition. Several $A_{n-1}B_nO_{3n+1}$ perovskite (n = 3) nanosheet-based thin films such as $Ca_2Nb_3O_{10}$ ($\theta_r = 200$)[12, 13] and $Sr_2Nb_3O_{10}$ ($\theta_r = 240$)[14, 15] have been reported, yet the reported dielectric properties of these and other thin films fall far below those of their bulk counterparts.

In this study, we atomically engineer the dielectric properties of $Sr_2Nb_3O_{10}$, which shows high exfoliation yield and highest dielectric properties in DJ-type layered perovskite ($A_{n-1}B_nO_{3n+1}$, n = 3). During the substitution of more polarizable Bi ions to Sr or Nb ions, the intercalated K ions compensate for the change in the charge of the parent materials, and the niobate octahedra were tilted due to the reduced radii of the A or B-site occupant. The cation size controls factors for structural distortion and results in high remnant polarization, which enhances the dielectric properties.

Materias And Methods

Preparation of bulk ceramics

In order to investigate the effect of bismuth substitution on potassium strontium niobate ceramics, layered perovskites with the general formula $K_{1-x}Sr_xBi_2Nb_3O_{10}$ (KSBNO, x = 0, 0.1, 0.2, 0.3) were prepared by solid-state reactions. Calcination was applied at 1200°C for 10 h, and the synthesized powders (5 g) were continuously stirred in 7 M HNO$_3$ solution (200 mL) for 5 d to form $HS_{1-x}Sr_xBi_2Nb_3O_{10}$ (HSBNO, x = 0, 0.1, 0.2, 0.3). The synthesized KSBNO and HSBNO powders were compressed into compact disc-shaped pellets 12 µm in diameter, and these pellets were carefully polished to form disks 1 mm thick after sintering at 1250°C for 2 h in a furnace.

Preparation of nanosheet thin films by Langmuir-Blodgett method

SBNO nanosheets were obtained from HSBNO powders by exfoliation in tetrabutylammonium hydroxide solution for 7 d, after which the mixtures were centrifuged at 2000 rpm for 10 min. The $Sr_{2(1-x)}Bi_{2x}Nb_3O_{10}$ nanosheet solution was spread out on distilled water, with a transfer pressure of 10 mN m$^{-1}$ based on the $\pi$-$A$ isotherm graph. The 10 layer SBNO thin film was transferred by multiple transfers through the same procedure. The multilayer thin films were then irradiated with UV light for 24 h to decompose the residual organic species.

Characterization of nanosheet thin films

The local atomic structure of the delaminated SNBO nanosheets was investigated in a prove aberration-corrected STEM system (TitanTM 80–300, FEI) at the acceleration voltages of 300 kV. Cross-sectional HRTEM was carried out using a Hitachi H-9000 microscope operating at 200 kV with a point resolution of...
0.1 nm. In order to measure the electrical properties, 30 nm thickness Au top-electrodes were deposited by the E-beam evaporator. The dielectric properties and leakage properties were measured with an impedance analyzer (Agilent 4294A precision, Santa Clara, USA) and a semiconductor parameter analyzer (Keithley 4200 SCS, Ohio, USA).

**Density functional theory calculations**

DFT calculations were performed using the periodic supercell plane-wave basis approach, as implemented in Advance/PHASE. We used the generalized gradient approximation combined with Vanderbilt ultrasoft pseudopotentials. The wave-function was expanded in plane-waves up to a kinetic energy cutoff of 500 eV. The Brillouin-zone sampling was performed by using a 3 × 6 × 1 Monkhorst-Pack grid for k points in a monolayer nanosheet. Structural relaxation was performed with convergence thresholds of $10^{-8}$ eV for the energies and 0.03 eV Å$^{-1}$ for the forces. Dielectric functions were calculated using an electric-dipole approximation. The phonon frequencies and eigenvectors.

**Results And Discussion**

The dielectric nanosheet solution is synthesized by 2-step cation exchange process as shown in Fig. 1. Firstly, the layered perovskite structured KSr$_{2(1-x)}$Bi$_{2x}$Nb$_3$O$_{10}$ (KSBNO) patent materials are synthesized, and the intercalated K$^+$ ions are exchanged to H$^+$ ions in acid solution. Next, the protonated ceramics are reacted with the large organic bases such as tetrabutlyammonium hydroxide (TBA$^+$OH$^-$) solution. Then, each perovskite layer is delaminated by swelling the interlayer caused by intercalated bulky base[16].

We first explored the structural and dielectric properties of the parent compound having the formula KSBNO. The structural properties of KSBNO are presented in Fig. 2. SEM images of the KSBNO ceramics are shown in Fig. 2 (a) and there is no microstructure variation. The average grain size of all samples is over 5 µm, and all samples show dense fracturing including lamellar-structured grains without pores. According to the XRD analysis shown in Fig. 2 (b), it is clear that the peaks of KSBNO $x = 0$–0.2 were indexed as a single DJ phase layered perovskite structure, indicating that Bi$^{3+}$ ions are homogeneously substituted into the Sr$^{2+}$ lattice[17]. During the substitution of Bi$^{3+}$ for Sr$^{2+}$, we assume that intercalated K$^+$ ions acted to compensate for the change in charge[18]. However, a small amount of a secondary phase was present in the KSBNO ($x = 0.3$) sample, so the maximum substitution amount was determined as $x = 0.3$. Also, the intensities of the (002) and (004) peaks increased slightly as the Bi substitution amount increased, while the intensities of the other peaks decreased. These trends indicate that the grains of the (002) plane become larger as the Bi substitution increases[19].

Figure 3 (a) and (b) show the dielectric permittivity and loss (tan δ) of KSBNO in a sintered pellet form. As Bi ions partially substitute Sr ions up to a value of $x = 0.3$, the dielectric permittivity increases from 31 to 348 while the dielectric loss decreases from 0.111 to 0.040 at 1 MHz. The dielectric permittivity of all KSBNO samples slightly decreased as the frequency increased. The low-frequency dispersion is influenced by the space charge and interfacial polarization from free-charge motion effects in
As shown in Fig. 3 (c), the density gradually increases with increasing Bi content. The increased density might be caused by the liquid phase grain growth, due to the low melting point of Bi compounds[22]. As has been shown elsewhere, increasing the density results in reduced dielectric loss as the pore size and volume decrease[23].

To identify the origins of the enhanced dielectric constants, we employed Raman spectroscopy as shown in Fig. 4(a). The high-frequency mode spectra of KSBNO give information on niobate bonding, including the peaks from the internal-mode vibration of NbO$_6$ octahedra[24]. The high-frequency mode spectra reveal that the vibration $\nu_6(F_{2u})$ shifts to higher wavenumbers as the Bi substitution amount increases, which indicates the distortion of NbO$_6$ octahedra. We also observed a peak shift near 100 cm$^{-1}$ (low-frequency mode) indicating a reduction in the hardening soft-mode vibration. The balance between the ionic bonding and covalent bonding in the B-O$_6$ octahedra generally determines the polarizability of perovskites, and the decreased low-frequency mode peaks are connected to the increased dipole interactions of the perovskite layer. Thus, the decreased hardening soft-mode vibration indicates higher polarizability and larger dielectric permittivity, an observation that is well-known with other layered perovskites[25].

We can verify the relationship between macroscopic dielectric constants of a material and its microscopic properties such as soft-mode peaks (optical phonon frequencies) using the Lyddane-Sachs-Teller (LST) relation[26]. According to the LST relation, the static dielectric constant is proportional to the inversed square of soft-mode peaks, which agrees well with the measured dielectric permittivity of KSBNO series; the calculated inversed square values of the soft-mode peaks in KSBNO 0, 0.1, 0.2, and 0.3 ceramics are 0.23, 0.26, 0.28, and 0.33 cm$^{-2}$, respectively. Moreover, the calculated polarization values by first-principle density functional theory (DFT) calculations also agree well with the measured dielectric permittivity as shown in Fig. 4 (b). The DFT results shows that, the electronic polarization is increased as Bi substitution amount increases, leading to high dielectric permittivity.

After investigating structural properties of KSBNO, we obtain of HSr$_{2(1-x)}$Bi$_{2x}$Nb$_3$O$_{10}$ (HSBNO) ceramic, which is medium materials for cation exchange process for obtain perovskite nanosheets, through cation exchange process in acid solution. Figure 5 (a) shows the XRD patterns of HSBNO ceramics and a similar tendency is presented in the patterns. However, the all main peaks of HSBNO ceramic show lower angle shifts after cation exchange and these lower shifts ascribe the expansion of c axis by entering of hydrated proton ions (H$_3$O$^+$) instead of smaller K$^+$ ions.

The FTIR spectrum of KSBNO and HSBNO is presented in Fig. 5 (b) and (c). Both samples show the clear absorption peaks associated with the NbO$_6$ octahedron of 910 cm$^{-1}$ which is assigned to the terminal Nb-O vibrational stretching, and this indicate the niobate structure is maintained well even convert K$^+$ ions to H$^+$ ions. Also, as increasing the amount of Bi component, the peaks from terminal Nb-O vibrational stretching are gradually shifted to the lower wavelength in both samples because of smaller Bi ions as compare to Sr ions.
After investigating the structural and dielectric properties of the parent and medium materials, the negatively charged \(\text{Sr}_{2(1-x)}\text{Bi}_{2x}\text{Nb}_3\text{O}_{10}\) (SBNO) nanosheets are obtained by exfoliation of each perovskite slab of HSBNO. The single crystal SBNO nanosheets were then dispersed in solution. In particular, the \(\text{Sr}_{1.8}\text{Bi}_{0.2}\text{Nb}_3\text{O}_{10}\) (SBNO 0.1) nanosheets show great stability and better exfoliation yield, so we focused on the fabrication of SBNO 0.1 nanosheets. The exfoliated SBNO 0.1 nanosheets had three layers of a cubic perovskite unit cell with lattice parameter \(a = 0.39\) nm along \(c\)-axis.

We demonstrated the local atomic structure of the SBNO 0.1 nanosheets using HRSTEM image applied an average background subtraction filter (ABSF) to remove noise contribution in Fig. 6 (a). The intensity of atoms in HRSTEM image is proportional to the 1.64 power of atomic number (\(Z\)). The cation columns of Nb (\(Z = 41\)) and Sr (\(Z = 38\))/Bi (\(Z = 83\)) were effectively distinguishable with the columns intensity line profile in Fig. 6 (b) and (c). In fact, it is very difficult to quantify doped atoms because the volume of the specimen cannot be calculated. However, we assumed that Z-contrast image can show the Bi atom doped site because the depth of focus is sufficient for thick of the SBNO nanosheets consisted of three layers. As the results, the Bi atom doped in A-site instead of Sr atom. Also, the Bi atom was occasionally observed in B-site as shown in Fig. 6 (d).

Using these nanosheets, we fabricated SBNO 0.1 multilayer nanofilms using the Langmuir-Blodgett (LB) method at room temperature as shown in Fig. 6 (e). Surface pressure-area isotherm graphs of SBNO nanosheets and schematic diagram of each stage is presented. Firstly, fill the LB trough with DI water and drop the nanosheet solution. After stabilization, the density of the nanosheets is adjusted through the movement of the barrier on both sides. As the barrier moves inward, the nanosheets are gathering and the phase transit gas phase to liquid-condensed phase. Then, The SBNO 0.1 nanosheet film is transferred at the liquid-condensate region to obtain close-packed film.

The LB transfer process is repeated 10 times to obtain a 10-layer stacked multilayer thin film. The XRD pattern of the SBNO 0.1 nanosheet film is presented in Fig. 7 (a). The highly textured (001)-oriented SBNO 0.1 thin film is clearly seen. The cross-sectional high-resolution TEM image in Fig. 7 (b) shows a flat and well-ordered lamellar structure in the multilayer thin film, and each layer shows three parallel fringes because of the corner-sharing NbO\(_6\) octahedra. The total thickness of the 10 layer-stacked SBNO 0.1 thin film is measured to be approximately 18 nm. Figure 7 (c) shows the dielectric properties and leakage current characteristics of Au top electrode/ \(\text{Sr}_{1.8}\text{Bi}_{0.2}\text{Nb}_3\text{O}_{10}\) (18 nm)/ Nb-doped \(\text{SrTiO}_3\). The leakage current density was measured by biasing the top electrode of Au from 0 to 1.2 GV\(\cdot\)m\(^{-1}\), and it exhibited very stable insulating properties (~\(10^{-7}\) A cm\(^{-2}\)) over the entire range.

The dielectric properties of the 10-layer stacked 18 nm dielectric thin film were measured as influenced by frequency. The dielectric permittivity exhibited a constant value of 540 with low dispersion (< 10%), and the dielectric loss values were 0.01 to 0.05 in the range from 1 kHz to 1 MHz. The dielectric permittivity is 10 times larger than that of \((\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3\) films, and 2 times larger than \(\text{Sr}_2\text{Nb}_3\text{O}_{10}\) nanosheet thin films with the same thickness. The enhanced dielectric properties in the parent materials (KSBNO bulk system) were investigated by the soft-mode vibration peaks from Raman analysis (See Fig. 4 (a) and (b)). Like the
bulk materials, we consume the enhanced dielectric properties resulted from the more polarizable Bi ions in the lattice, as in the parent materials. Considering these results, the Bi-substituted \( \text{Sr}_2\text{Nb}_3\text{O}_{10} \) dielectric nanosheets can be candidates for nano-scale high-k thin film material for future electronics.

**Conclusions**

We have successfully synthesized new types of Bi-substituted \( \text{Sr}_2\text{Nb}_3\text{O}_{10} \) dielectric ceramics. The dielectric permittivity increases as Bi ions partially substitute Sr ions up, and the increased polarizability of perovskites and electronic polarizability are confirmed by Raman spectroscopy and DFT calculations. The nanosheets was deposited without a low-k interfacial layer and fabricated simply at room temperature by Langmuir-Blodgett method. The dielectric nanosheet thin films show dielectric permittivity of 540 with a low dielectric loss (< 5%). These 2D dielectrics may pave the way to realizing new and improved devices such as flexible devices that are not possible to achieve using conventional top-down process.

**Declarations**

**ACKNOWLEDGMENT**

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**CONFLICT of INTEREST**

The authors have declared no conflict of interest.

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**Figures**
Figure 1

Schematic diagram of 2-step cation exchange process.

![Diagram](image)

Figure 2

(a) SEM images of K_{Sr2(1-x)Bi2xNb3O10} powder and (b) X-ray diffraction spectra of K_{Sr2(1-x)Bi2xNb3O10} ceramics.

![Graphs](image)

Figure 3

(a) Dielectric constant and (b) dielectric loss of K_{Sr2(1-x)Bi2xNb3O10} ceramics according to frequency. Each sample was pelletized with a radius of 10 mm and thickness of 1 mm. (c) The density of K_{Sr2(1-x)Bi2xNb3O10} ceramics.

![Graphs](image)
Figure 4

Physical properties of K$_{x}$Sr$_{2(1-x)}$Bi$_{2x}$Nb$_3$O$_{10}$ bulk ceramics. (a) Raman scattering spectra were collected using a Jobin-Yvon T64000 Micro-Raman system. (b) The relation of dielectric constant to the inversed square of soft mode and calculated electronic polarization are presented in good agreement with the corresponding measured values.

Figure 5

(a) X-ray diffraction spectra of H$_{x}$Sr$_{2(1-x)}$Bi$_{2x}$Nb$_3$O$_{10}$ ceramics (b) FTIR spectra of of a, K$_{x}$Sr$_{2(1-x)}$Bi$_{2x}$Nb$_3$O$_{10}$ ceramics and (c) H$_{x}$Sr$_{2(1-x)}$Bi$_{2x}$Nb$_3$O$_{10}$ ceramics.
Figure 6

(a) Atomic structure of the SBNO perovskite unit cell using VESTA (Atomic color: yellow(Sr or Bi), green (Nb) and red (O)), (b) The ABSF filtered HRSTEM image of the delamination SNNO 0.1 nanosheets along [001] zone axis. [001] projection structure of unit cell overlaid on the image, (c) Intensity profile obtained at yellow dashed line in (b) showing that Bi atom doped in A-site, (d) ABSF filtered HRSTEM image of the SBNO perovskite showing Bi atom doped in A-site (blue circle) and B-site (yellow circle), (e) Surface pressure-area isotherm graphs of SBNO nanosheets and schematic diagram.
Figure 7

(a) XRD graph of Sr1.8Bi0.2Nb3O10 nanosheet 18 nm (10 layer) thin film, (b) Cross-sectional TEM image of the thin film on the Nb:SrTiO3 substrate, (b) Frequency dependence of the dielectric properties and leakage current density of thin film with Au top electrode.