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Ferroelectricity in Pulsed Laser Deposited $Ba(Fe_{1/2}Nb_{1/2})O_3$ Thin Films *

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Complex perovskite $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin films are grown on $Pt/TiO_2/SiO_2/Si$ substrates by pulsed laser deposition. Non-linear polarization–electric-field (P–E) loops are observed at low temperatures under different electric fields and frequencies. The broad peak in the corresponding current density–electric field (J–E) loop confirms the existence of domain switching. The remnant polarization decreases slightly when the temperature decreases from 153 to 123 K, which differentiates $Ba(Fe_{1/2}Nb_{1/2})O_3$ from normal ferroelectrics. The Raman spectra of $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin films show two-mode-like behavior in the high-wavenumber region, which can be caused by the local chemically heterogeneous zones of NbO_6 and FeO_6. The weak ferroelectricity observed in the $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin films might originate from the composition fluctuation and subsequent symmetry breaking in the material. The present results might provide a new aspect to the understanding of the intrinsic dielectric nature in $Ba(Fe_{1/2}Nb_{1/2})O_3$.

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Perovskite-based materials have long been key issues in material science because of their abundant physical properties and wide applications in electronic devices. Chemical substitutions of the B site with two different ions, B′ and B″, considerably extend the ABO_3 perovskite family and result in complex perovskites, the physical properties of which greatly depend on the electron configurations and ordering degree of multiple B site ions.[1−4]

Complex perovskite $Ba(Fe_{1/2}Nb_{1/2})O_3$ has a very similar tolerance factor to the prototypical ferroelectrics $BaTiO_3$. However, distinctively different dielectric behaviors have been determined. The dielectric characteristic of $Ba(Fe_{1/2}Nb_{1/2})O_3$ ceramics features a very high frequency-dependent dielectric constant plateau of the order of 10^4 over a wide temperature range, and the dielectric constant drops rapidly to less than 100 as the material is cooled through a critical temperature, where no phase transition has ever been detected.[5] Similar dielectric behavior has also been reported in other Fe-containing complex perovskites, $A(Fe_{1/2}B_{1/2})O_3$ (A = Ba, Sr, Ca, and B=Nb, Ta).[6−8] These so-called giant dielectric constant materials have drawn much scientific attention because of their potential impact on the minimization of electronic devices, and have been pursued to understand the relaxation mechanisms.[9−12] The low temperature dielectric relaxation with strong frequency dispersion in $Ba(Fe_{1/2}Nb_{1/2})O_3$ ceramics shares some similarity with that of ferroelectric relaxors, and $Ba(Fe_{1/2}Nb_{1/2})O_3$ was regarded as one when Saha and Sinha first reported on this in 2002.[13,14] However, later investigations argued against this initial opinion because of the absence of evident ferroelectric characteristics in $Ba(Fe_{1/2}Nb_{1/2})O_3$ ceramics.[6,15−20] Rivera *et al.* suggested the Maxwell-Magner effect for the giant dielectric constant in their early research.[6,15] Recently, they argued that the space charge due to the flipping of Fe^{4+}, Fe^{3+} and Fe^{2+} ions creates pseudo dipoles and produces dielectric relaxation in $Ba(Fe_{1/2}Ta_{1/2})O_3$.[18] Wang *et al.* evaluated the dielectric behaviors of $Ba(Fe_{1/2}Nb_{1/2})O_3$ and $Ba(Fe_{1/2}Ta_{1/2})O_3$ ceramics over a broad temperature frequency range, and discussed the mix-valent structure of Fe^{2+}/Fe^{3+}, which may contribute to the low-temperature dielectric relaxation.[5,19]

On the other hand, our previous work[21] on the $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin films deposited on the $Pt/TiO_2/SiO_2/Si$ substrates by pulsed laser deposition (PLD) suggested possible ferroelectricity in the thin films as a non-linear capacitance-voltage (C–V) curve was observed. However, the dielectric loss of the $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin films at room temperature may contribute to the non-linear C–V curve, due to the variable valence of Fe ions. It is of great significance to evaluate the ferroelectric properties at low temperature. To confirm the ferroelectricity of the material and further investigate the possible mechanism for the dielectric behaviors, low temperature hysteresis loops are measured for the $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin films in the present work. Weak ferroelectricity is suggested at low temperatures, which may provide a new aspect to understand the dielectric nature of $Ba(Fe_{1/2}Nb_{1/2})O_3$. In addition, the possible structure origin of ferroelectricity in the thin films is also discussed based on the Raman spectra of $Ba(Fe_{1/2}Nb_{1/2})O_3$. The Raman spectrum of $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin films deposited in different oxygen pressure is also discussed.

$Ba(Fe_{1/2}Nb_{1/2})O_3$ thin films are deposited with a fixed energy density of 1.5 J/cm^2 and a repetition rate of 3 Hz at 550℃ by a KrF excimer PLD system (COMPex 201, Coherent, Göttingen, Germany) at a wavelength of 248 nm. After deposition, the thin films

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are annealed at growth temperature for 15 min in an oxygen atmosphere and cooled down to room temperature at 3℃/min. The surface morphology is obtained by atomic force microscopy (AFM, Veeco diInnova, Santa Barbara, CA). Au top electrodes of 0.3 mm in diameter are deposited through a mask by ion sputtering for characterization of the electrical properties. A precision materials analyzer (RT66A, Radiant Technology, Albuguerque, NM) connected to a temperature controller (HFSE91-P, Linkam, Surrey, UK) is employed to measure the P–E loops at different temperatures. The dielectric characteristics of the thin film are measured by a precision LCR meter (4284 A, Hewlett-Packard Co., Palo Alto, CA) with a temperature range of 10–400 K. The Raman spectra of the different samples are collected at room temperature by a HR-800 LabRaman (Jobin Yvon, France) using excitation of Ar^+ laser light at a wavelength of 514.532 nm. The spectral resolution is about 1–2 cm^{-1}.

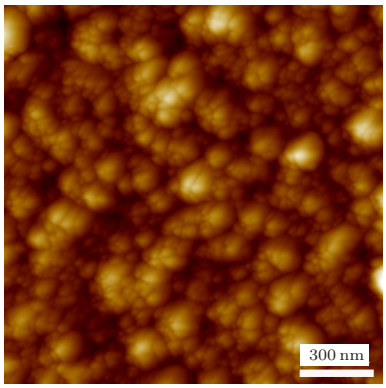

Fig. 1. The surface morphology of the $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin film grown by PLD. The scanning area is 1500 × 1500 nm^2.

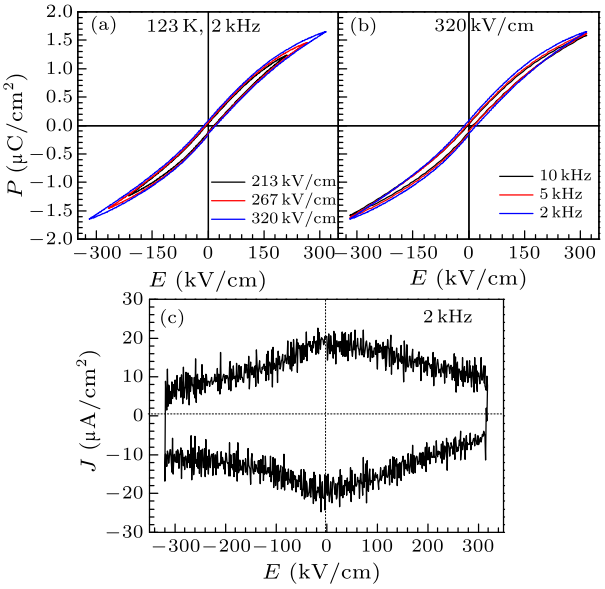

Fig. 2. The P–E loops of the $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin film with various (a) electric fields, and (b) frequencies at 123 K. (c) The corresponding J–E loop with an electric field of 320 kV/cm under 2 kHz.

The crystal structure of $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin films has been reported previously.[21,22] The single phase of the perovskite structure is determined by XRD data. Figure 1 is an AFM image of the $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin film. A dense surface morphology with a typical grain size of 50–60 nm is suggested.

Figures 2(a) and 2(b) show the P–E loops of the $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin film with varied electric fields and frequencies at 123 K. Non-linear characteristics are observed for all the loops, though the remnant polarization P_r is quiet small, with values of $2P_r = 0.26\,\mu C/cm^2$ under an electric field of 320 kV/cm at 10 kHz. The frequency dependence of the P–E loops is quite weak, which suggests little contribution from the electrodes.[23] The corresponding J–E curve at 2 kHz is shown in Fig. 2(c). The broad peak near $E = 0$ is consistent with the small coercive field and remnant polarization suggested by Fig. 2(a), which confirms the weak ferroelectricity of $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin films at 123 K.

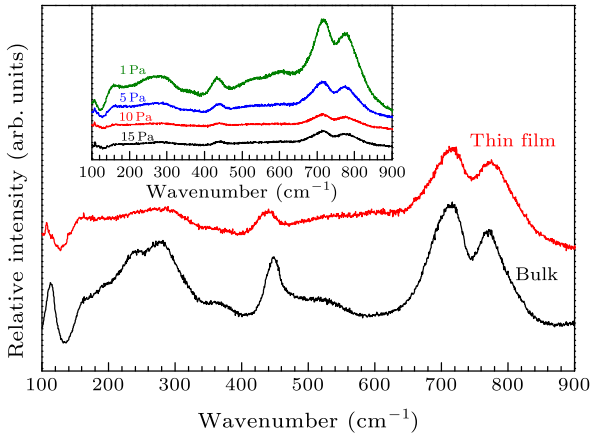

Fig. 3. The Raman spectra of both the bulk ceramic and thin film of $Ba(Fe_{1/2}Nb_{1/2})O_3$ at room temperature. The inset is the Raman spectra of thin films deposited in different oxygen pressures.

Previous studies[16,19,24] on $Ba(Fe_{1/2}Nb_{1/2})O_3$ ceramics have suggested both a cubic and monoclinic crystal structure for the material, which is probably due to the different experimental procedures. Our result for the ceramic target supports cubic symmetry with a space group of $Pm\bar{3}m$. While the XRD data for $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin films indicate an obvious peak shift and possible derivation from cubic symmetry.[22] To better investigate the local crystal structure of $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin films and to look for the microstructure origin of the weak ferroelectricity, Raman scattering is employed to investigate the local symmetry because it has a superior capacity for detecting subtle crystal structure distortions in very small crystal regions.[25,26] For comparison, the Raman spectrum of a $Ba(Fe_{1/2}Nb_{1/2})O_3$ ceramic is also analyzed. The broader Raman bands of the thin film are caused by its small thickness, which is about 150 nm.

As shown in Fig. 3, first-order Raman bands are observed in both the bulk ceramic and thin films,

which indicate local symmetry breaking in the materials, as first-order Raman lines are forbidden in centrosymmetric structures. The Raman spectra of $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin films deposited in different oxygen pressures is shown in the inset. A higher intensity of the Raman bands is observed in the thin films deposited in lower oxygen pressure, which indicates a more severe local structure distortion. The same behavior was reported recently in similar complex perovskite $Pb(Fe_{1/2}Ta_{1/2})O_3$ at room temperature,[27] when the system also showed the space group of $Pm\bar{3}m$ by XRD data. The presence of the polar nanoregions caused by the heterogeneous distribution of different B-site ions is regarded as the possible reason for symmetry breaking in the system. The similar inhomogeneity in the local structure could also be expected in the $Ba(Fe_{1/2}Nb_{1/2})O_3$ system. In our previous work,[21] non-linear capacitance-voltage curves of $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin films have been suggested. Larger remnant polarization is observed in thin films deposited with lower oxygen pressure, which is consistent with the Raman spectra.

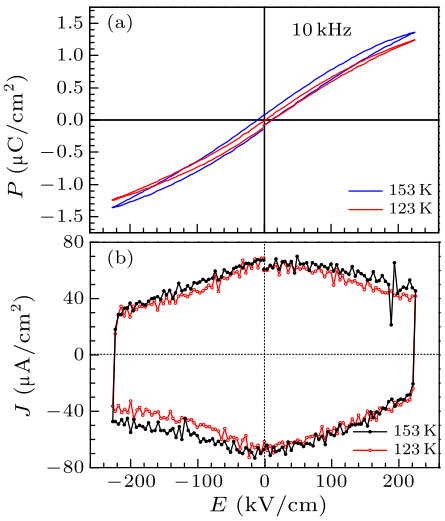

Fig. 4. (a) The P–E loops, and (b) the corresponding J–E curves of the $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin film at different temperatures under 1 kHz.

The most obvious features of the Raman spectra of $Ba(Fe_{1/2}Nb_{1/2})O_3$ are the strong bands in the high-wavenumber region around 700 cm^{-1}, which are regarded as the characteristic bands for most complex perovskites. This highest-wavenumber band is related to the symmetric breathing modes of the oxygen octahedron. Most interestingly, the highest-wavenumber band splits into two Raman bands in both the bulk ceramic and thin film samples. Similar Raman band splitting has been reported in ferroelectric relaxor-based $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$ systems under high-pressure[28] and $Pb(Fe_{1/2}Nb_{1/2})O_3$ thin films.[29] This two-mode-like behavior was described in detail in our recent work on the local crystal structure evolution of $Ba[(Fe_{1/2}Nb_{1/2})_{1-x}Ti_x]O_3$ solid solutions by Raman scattering.[30] The decoupling of several modes could be regarded as a result of the local composition fluctuation that exists in very local Nb-rich regions, as well as Fe-rich regions, in the material. Recently, a similar composition fluctuation has been directly observed in $Pb(Fe_{1/2}Nb_{1/2})O_3$[31] by ^{93}Nb NMR spectra, where different local environments of Nb ions are created in Fe-poor and Fe-rich regions. Meanwhile, the actual local symmetry at the Nb site is not cubic due to the chemical disorder for B-site ions when the system is in average cubic phase, which is consistent with the result indicated by the Raman spectra of $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin films.

Second-order Jahn–Teller (SOJT) distortion of the octahedral site cations plays a significant role in producing ion displacement in the perovskite materials.[32] In $Ba(Fe_{1/2}Nb_{1/2})O_3$, only the Nb^{5+} ions have the proper electron configuration (d_0) needed to favor an SOJT distortion, while none of the Fe^{3+} or Fe^{2+} ions are prone to displacement. As a consequence, if the Nb^{5+} ion is displaced to form a short Nb-O bond, then the overbonding at oxygen can only be relieved by another neighboring Nb^{5+} ion to form a long Nb-O bond, which is needed to achieve an appropriate bonding interaction at oxygen. Thus, the cooperative displacement of the Nb^{5+} ions cannot be expected in $Ba(Fe_{1/2}Nb_{1/2})O_3$, regardless of the ordering or disordering distributions of the Fe^{3+} and Nb^{5+} cations. However, as with the existence of the Nb-rich regions, displacive distortion could be expected due to the SOJT effect of the Nb^{5+} ions, which could produce very local polar regions and result in the weak ferroelectricity observed in $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin films.

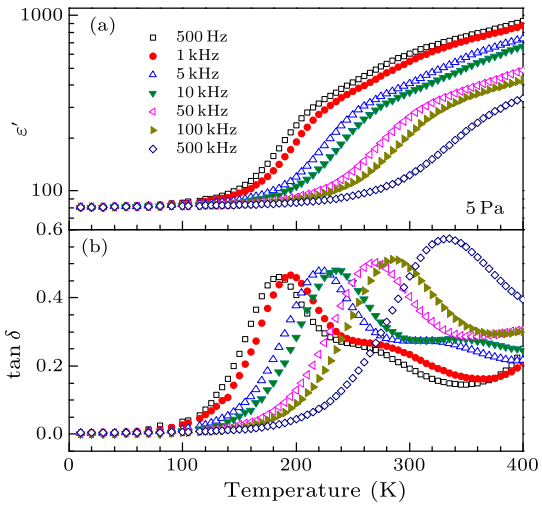

Fig. 5. (a) Dielectric constant, and (b) dielectric loss of the $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin film in the temperature range 10–400 K at various frequencies.

The temperature dependence of the hysteresis loops and corresponding J–E curves are shown in Figs. 4(a) and 4(b). Very similar J–E curves are observed at 153 and 123 K. However, a slight increase in both the remnant and maximum polarizations is suggested at increased temperature. The uncommon increase is taken cautiously as the measurement of P–

E loops includes the contribution from electric conductivity and dielectric displacement, except for the actual ferroelectric domain switching.[33] As a material with high dielectric loss, the inaccuracies in the P–E loops are easily induced. However, the dielectric loss decreases to a very low value at low temperatures, which is believed to have little impact on the ferroelectric hysteresis loops. The dielectric loss for the $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin film under a frequency of 10 kHz at 120 K is about 1%, while the value increases to 5% at 150 K. It may already have an impact on the hysteresis loops. Further increasing the temperature will greatly increase the electric conductivity of the thin film, which makes the accurate measurement of polarization much more difficult. Further investigation is still needed to understand the temperature dependence of the ferroelectric characteristics of the $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin film.

On the other hand, the weak ferroelectricity indicated by the non-linear P–E loops and corresponding J–E curves at low temperatures is somehow sustained until room temperature, as a butterfly-shaped C–V curve of the $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin film is observed at room temperature and was reported earlier.[19] The Raman spectra of $Ba(Fe_{1/2}Nb_{1/2})O_3$ at room temperature also support this idea. Moreover, the symmetry breaking caused by composition fluctuation in the $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin films seems to depend on the oxygen vacancies. The Raman spectra of $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin films deposited with different oxygen pressures indicate a decreasing full width at half maximum (FWHM) of the highest-wavenumber Raman bands around 700 cm^{-1}, with decreasing deposited oxygen pressure (not shown here), which implies a stronger composition fluctuation in more oxygen-deficient thin films.

The dielectric characteristics of the $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin film under a varied frequency in the temperature range 10–400 K is shown in Fig. 5. A similar dielectric relaxation to the bulk ceramic is exhibited with much smaller dielectric constant and loss, which indicates the large contribution of the defects in the dielectric behavior of the material. The starting temperature for the dielectric relaxation is around 100 K, which is consistent with the temperatures where weak ferroelectricity is observed. The existence of the local polar regions may contribute frequency dispersion in the dielectric response, which shares similarities with the typical behavior of relaxor ferroelectrics. However, the interactions between the dilute polar regions in $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin films are probably very weak, due to the slim P–E loops at low temperatures. In addition, the dipoles produced by the flipping of Fe^{3+} and Fe^{2+} ions overpower the effect of polar regions as the temperature increases.

Meanwhile, even though similar Raman spectra are observed for the thin film and bulk ceramic, no solid ferroelectric-related characteristics have ever been reported in $Ba(Fe_{1/2}Nb_{1/2})O_3$ ceramics. This should be because of the much larger dielectric loss in the bulk ceramic, which makes it very difficult to evaluate the ferroelectric characteristics.

The weak ferroelectricity is indicated by non-linear P–E loops, and the broad peak in the corresponding J–E curves confirms the contribution from domain switching, which supports the weak ferroelectricity in $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin films. Raman scattering indicates composition fluctuation in $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin films, in which local Nb-rich regions as well as Fe-rich regions may exist in the material, and the composition fluctuation and subsequent symmetry breaking just provide the structural origin for the weak ferroelectricity in $Ba(Fe_{1/2}Nb_{1/2})O_3$ thin films. The present results might provide a new aspect to the understanding of the intrinsic dielectric nature in $Ba(Fe_{1/2}Nb_{1/2})O_3$.

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