

Dielectric relaxation in A_2FeNbO_6 (A=Ba, Sr, and Ca) perovskite ceramics

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Abstract A_2FeNbO_6 (A=Ba, Sr, and Ca, abbreviated as AFN) ceramics were synthesized by a wolframite method with monoclinic $FeNbO_4$ precursor. X-ray diffraction studies revealed that Sr_2FeNbO_6 and Ca_2FeNbO_6 had a orthorhombic structure, while Ba_2FeNbO_6 had a cubic symmetry. Dielectric properties of the AFN ceramics were characterized in a broad frequency range (1 Hz–10 MHz) at a temperature ranged from -120 to 300 °C. Two dielectric relaxations were observed to follow the Arrhenius law at both low and high temperatures for all samples. Polaron relaxation was proposed to explain the low temperature dielectric relaxations in AFN. The high temperature dielectric relaxations in AFN were a competitive phenomenon between the dielectric relaxation and the electrical conduction of the relaxing species.

Keywords AFN · Dielectric relaxation · Polaronic relaxation

1 Introduction

Fe-containing double perovskites of the general form A_2FeNbO_6 (A=Ba, Sr, and Ca; abbreviated as AFN) have

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been actively investigated in order to understand the nature of magnetism and transport in these compounds [1, 2]. Recently, these perovskites were reported by Raevski et al. [3] to show high permittivity behavior similar to what was previously observed in $CaCu_3Ti_4O_{12}$ (CCTO) [4]. In these oxides, dielectric permittivity shows weak temperature dependence over a very wide temperature range and a steplike decrease by almost three orders of magnitude without any detectable long-range crystal structural changes. Besides the steplike dielectric relaxation, a higher temperature relaxor-like dielectric relaxation has also been reported in Ba_2FeNbO_6 ceramics by Chen et al. [5], which was attributed to an oxygen defect induced dielectric abnormality. Although it is generally accepted that the giant ϵ' in CCTO must have a non-intrinsic origin [4], the physical mechanism of the dielectric response in AFN is still not well understood.

In the present work, A_2FeNbO_6 (A=Ba, Sr, and Ca) ceramics are synthesized by a wolframite method with monoclinic $FeNbO_4$ precursor. The dielectric characteristics of AFN ceramics are evaluated in broad temperature and frequency ranges. Both the low- and high temperature dielectric relaxations were observed in all the three synthesized materials Ba_2FeNbO_6 (BFN), Sr_2FeNbO_6 (SFN) and Ca_2FeNbO_6 (CFN). The differences among the above materials were compared and discussed.

2 Experiments

$FeNbO_4$ (FN) precursor with a monoclinic phase was firstly synthesized by solid state reaction of reagent grade iron oxide, Fe_2O_3 , and niobium oxide, Nb_2O_5 . The starting powders were mixed and ball milled in ethyl alcohol for 12 h. As reported by Raymond et al. [6], the calcination

temperatures for monoclinic and orthorhombic phases were 1075 and 1200 °C, respectively. In this study, we chose 1075 °C as the calcination temperature in order to obtain monoclinic FN. Powders of FN were then mixed with BaCO₃, SrCO₃ and CaCO₃, respectively, ball milled in ethyl alcohol again for 12 h and calcined at 1200 °C for 8 h. The calcined powders were then compacted into pellets by cold isostatic pressing and were sintered in air at 1300 °C for 6 h except for SFN, which was sintered at 1400 °C due to the difficulty in densification.

Calcined powders and BFN ceramics were examined by X-ray diffraction (XRD) using a Philips X'pert diffractometer with Cu K α radiation. Silver paint was coated on both surfaces of the sintered disks and fired at 650 °C for 20 min. The sample pellets were 10 mm in diameter and about 1 mm in thickness. The dielectric properties were measured by using a frequency–response analyzer (Novocontrol Alpha-analyzer) over a broad frequency range (1 Hz–10 MHz) at various temperatures down to –120 °C. X-ray photoelectron spectroscopy (XPS, Physical Electronics, PHI-5600) was also performed on the polished BFN surfaces at room temperature. Polarization vs electric field (P–E) hysteresis loop was measured using Radiant Technology RT66 ferroelectric tester at room temperature.

3 Results and discussion

The XRD patterns of the calcined BFN, SFN and CFN powders synthesized from a wolframite method are given in Fig. 1. The BFN samples could be indexed to a cubic structure with the lattice constant $a=8.11$ Å, while SFN and CFN samples show an orthorhombic structure with the space group $Pnma(62)$. Our results agree with those

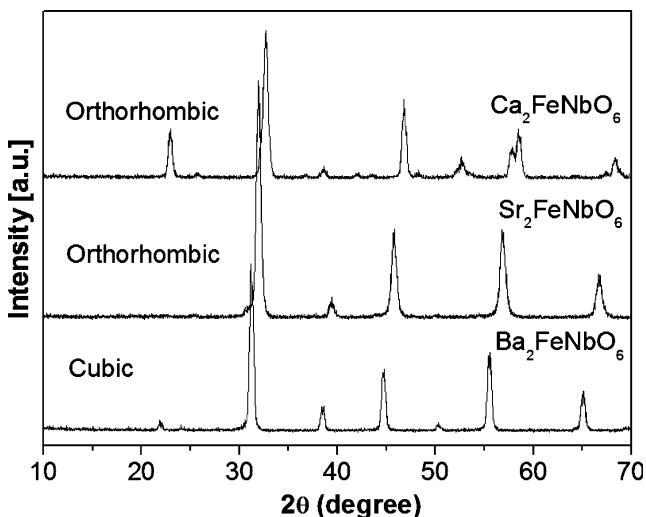


Fig. 1 XRD patterns of BFN, SFN and CFN powders calcined at 1200 °C

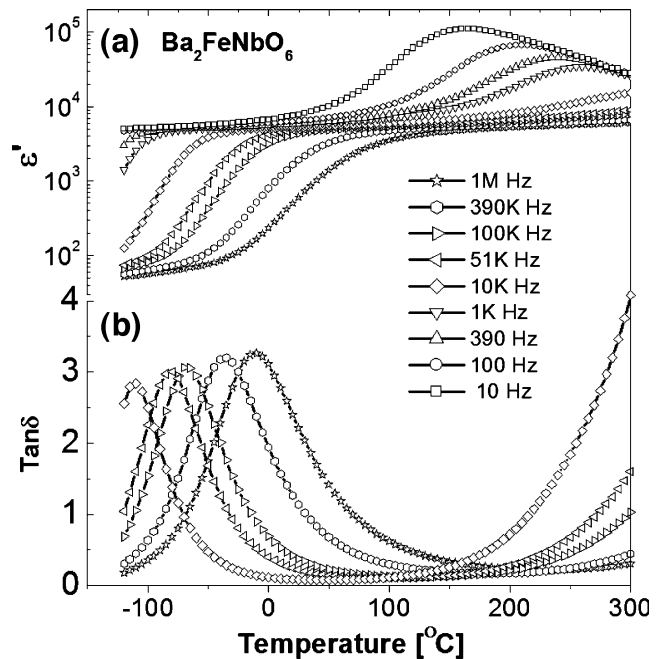


Fig. 2 Temperature dependence of the real part (a) and the imaginary part (b) of the dielectric constant of BFN ceramic under different frequencies

obtained by Rama et al. [1] and Tezuka et al. [2]. It is worthy of note that the orthorhombic space group $Pnma(62)$ does not permit the ordering of the B-site cations over the six-coordinate sites of the perovskite structure [2]. Due to similar reason, B-site ordering cannot be expected in SFN and CFN.

Figure 2 shows the temperature dependence of the real part of dielectric constant $\epsilon'(T)$, and loss tangent $\tan\delta(T)$ of BFN measured under various measuring frequencies. A low temperature (LT) relaxation and a high temperature (HT) one can be easily identified from the figure. In the LT region, $\epsilon'(T)$ exhibits a step-like increase from a lower temperature plateau value in the order of 10 towards a higher temperature plateau value in the order of 10^4 , which is very similar to CCTO [4]. The position where the dielectric step takes place shifts to higher temperatures with increasing frequencies and it is accompanied by a peak in $\tan\delta(T)$. In the HT region, a broad dielectric peak appears which also shifts to higher temperatures but decreases in amplitude with increasing frequencies. The HT relaxor-like relaxation in BFN is similar to those reported in CCTO [7].

As shown in Fig. 3, SFN and CFN ceramics have a similar dielectric response as compared to BFN. However, the magnitude of the step-like increases in dielectric constant is $\sim 2,300$ for SFN and $\sim 2,500$ for CFN, both of which is much smaller than that in BFN ($\sim 5,300$). Raevski et al. [3] attributed the LT step-like relaxation in AFN to a Maxwell–Wagner (M–W) relaxation which can be represented by an equivalent circuit consisting of the bulk contribution, connected in series to a parallel RC circuit.

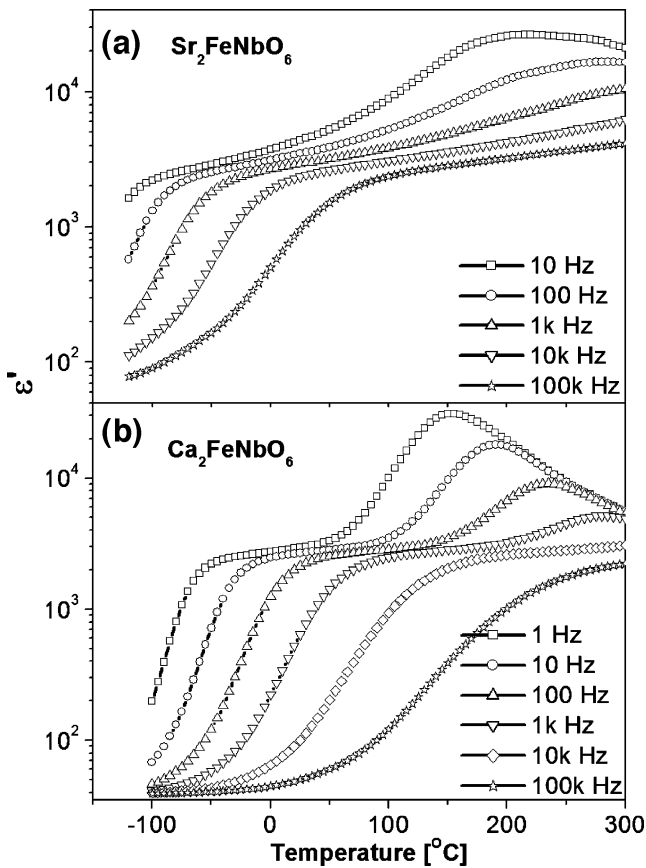


Fig. 3 Temperature dependence of the real part of dielectric constant of SFN and CFN ceramics under different frequencies

Since in the proposed M–W mechanism, the interfacial polarization and follows the Arrhenius law, it can be expected that the relaxation shifts to higher frequencies with increasing temperatures. However, the peak value of the dielectric loss was found to gradually increase with increasing frequencies (Fig. 2(b)). Ramirez et al. [8] argued that the M–W mechanism was not solely responsible for the

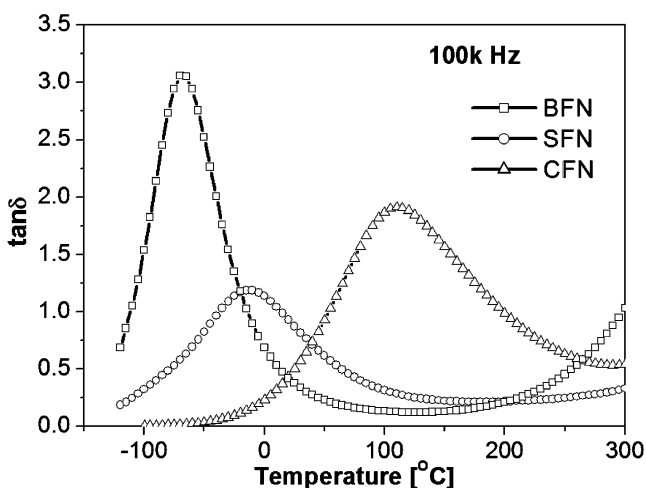


Fig. 4 Temperature dependence of the dielectric loss tangent ($\tan\delta$) of BFN, SFN and CFN measured at 100 kHz

anomaly LT relaxation in CCTO and the analog giant dielectric constant materials.

Under a fixed measuring frequency, $\tan\delta(T)$ peaked at two temperatures, one corresponding to the HT relaxation and the other corresponding to the LT relaxation. For all the three samples, the peak temperature for $\tan\delta(T)$ in the HT relaxation region was almost the same while it was significantly different in the LT relaxation region. This can be more clearly seen in Fig. 4. This phenomenon can not be clearly explained by the M–W theory. For the LT dielectric relaxation, the relaxation temperature and the corresponding frequency obeys the following Arrhenius law,

$$f = f_0 \exp(-E_a/kT), \quad (1)$$

where f_0 is a prefactor and E_a is the activation energy. Observations of the BFN, SFN and CFN ceramics are summarized in Fig. 5, where $E_a=0.18, 0.23$ and 0.34 eV for BFN, SFN and CFN, respectively. The obtained values are very close to the previously reported ones for the same materials [5, 9], and are also comparable to those reported for ErFeO_4 (0.26 eV) and LuFeO_4 (0.29 eV) [10, 11].

The step-like LT dielectric relaxation in ErFeO_4 and LuFeO_4 has been attributed to the electronic ferroelectricity which results from the fluctuation of valence electrons of the iron ions [10, 11]. Chen et al. have pointed that the LT relaxation in AFN ceramics are also originated from the electronic ferroelectricity [9]. The “electronic ferroelectricity” occurs in a strongly correlated electron system, which contains two types of electrons: itinerant d electrons and localized f electrons [12]. In an electronic ferroelectric transition, instead of a vanishing of the TO phonon frequency, the d – f exciton energy goes to zero at the critical value of the f -level energy. It is worthy of note that the ground state of this theoretical model is still not well

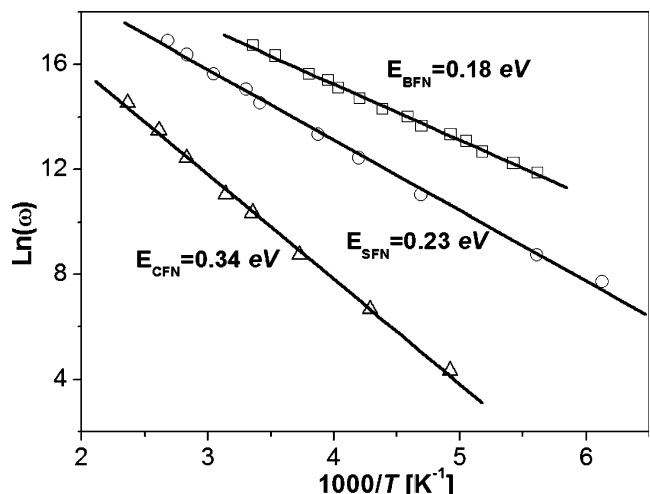


Fig. 5 Frequency dependence of the peak temperature for $\tan\delta$ for the low temperature dielectric relaxation in BFN, SFN and CFN ceramics

understood. Liu [13] pointed that the electronic ferroelectricity could be driven by the polaron effect, which leads us to deduce that the LT relaxation in AFN ceramic is a polaronic process.

In order to get a deeper insight into this strategy, X-ray photoelectron spectroscopy (XPS) of BFN ceramic were measured at room temperature. The XPS result clearly shows the coexistence of Fe²⁺ and Fe³⁺ ions as shown in Fig. 6. The Fe 2p_{3/2} peak is asymmetrical and can be divided into the contributions from Fe²⁺ and Fe³⁺ by fitting the spectrum with two Gaussian–Lorentzian curves. For BFN, the origin of Fe²⁺ ions can be caused by the formation of oxygen vacancies. In BFN, the Fe²⁺ and Fe³⁺ form Fe²⁺–O–Fe³⁺ bonds and the Fe-3d electrons in Fe²⁺ ions can hop to Fe³⁺. Under an applied field, the polaron can transport from one Fe²⁺–O–Fe³⁺ to another Fe²⁺–O–Fe³⁺. With decreasing temperature, the inertia of the Fe²⁺–O–Fe³⁺ becomes large enough that they cannot follow the field variations, resulting in a dielectric relaxation when the frequency of the polaron is equal to that of the applied field.

Further evidence for the relationship between the LT dielectric relaxation and the polaronic process arises from the Mössbauer spectroscopy of AFN. The temperature dependence of the valence fluctuation frequencies of iron ions obtained by Mössbauer spectroscopy [2] obeys the Arrhenius law, and then we could extrapolate the activation energy $E_a=0.17$ and 0.25 eV for BFN and SFN, respectively, which is very close to those (0.18 and 0.23 eV) calculated from the dielectric relaxation. This clearly leads to a conclusion that the electron hopping on the iron ion is the origin of the LT relaxation. Then, as for the large deviation in characteristic frequency among BFN, SFN, and CFN, the difference in crystal structure and ionic radius among them should be responsible for it by different electronic structure configuration. The exchange of electrons between Fe²⁺ and Fe³⁺, characteristic for hopping of

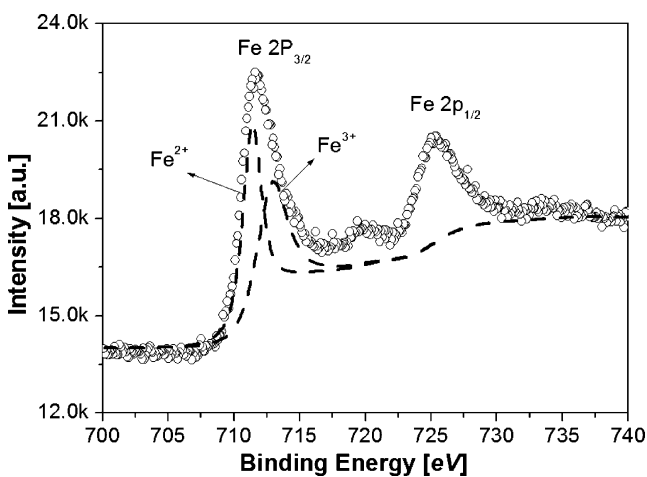


Fig. 6 XPS spectrum of the iron 2p peak of BFN ceramics

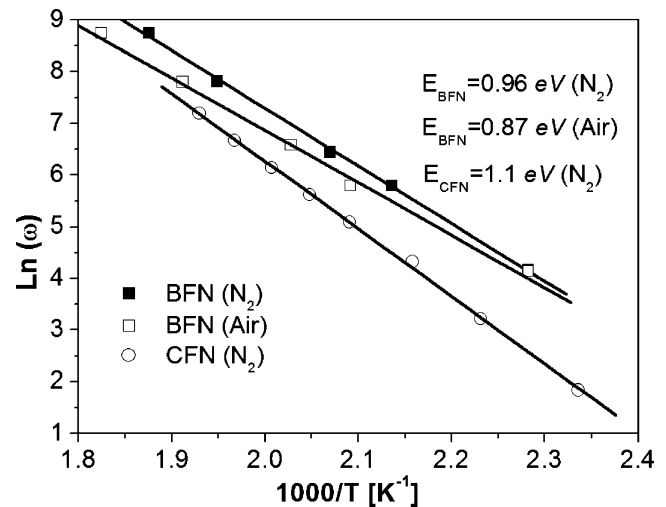


Fig. 7 Arrhenius fit of the frequency dependence of the dynamic transition temperatures T_m for high temperature dielectric relaxation in BFN and CFN

localized charge carriers, would leads a polaronic variable range hopping (VRH) conduction, which has been confirmed in CCTO [14] and BFN (Ke et al., unpublished).

As mentioned above, the HT relaxor-like dielectric relaxation is located at the same temperature region no matter what type of A-site ion is. This indicates that the HT relaxation could have a mixed effect of the intrinsic relaxation and an extrinsic one. It is worth noting that the HT dielectric peaks in AFN could be suppressed by annealing the sample in oxygen, which suggests that the relaxor-like behavior is primarily associated with oxygen vacancies [5]. To understand the physical nature of the relaxor-like relaxation, we tentatively use the Arrhenius law (Eq. 1) to describe the variation of the dielectric peak temperature with the frequency. As shown in Fig. 7, the variation relation obeys the Arrhenius law, activation energy for the HT relaxation processes were calculated to be 0.96 and 1.1 eV for BFN and CFN (it is hard to find a characteristic frequency for SFN from Fig. 3), respectively, it is very close to the activation energy (1 eV) for the motion of oxygen vacancies. It should be noted that the above results are all obtained under the N₂ measurement atmosphere. The activation energy would decrease by enhancing the external oxygen partial pressure (see Fig. 7). A detailed analysis of the conductivity of AFN shows a clearly order–disorder transition of oxygen vacancies at the same temperature range (Ke et al., unpublished).

It has been frequently reported that the similar relaxor-like dielectric relaxation behaviors are commonly observed in various perovskite oxides (such as PbTiO₃, BaTiO₃, SrTiO₃ and CaTiO₃) at the same temperature region of 400–700 °C [15–17]. According to these studies, it is clear that the relaxor-like dielectric relaxation is an oxygen vacancy-related phenomenon. Kang et al. [16, 17] have

confirmed that the relaxor-like dielectric relaxation in these ferroelectric materials is due to the competitive effects between the dielectric relaxation and the disturbance of the electrical conduction. The mutual features of the HT dielectric relaxation in mentioned oxides and AFN suggest that the HT relaxation in AFN should also be a competitive phenomenon between the intrinsic dielectric relaxation and the electrical conduction of the relaxing species. In many case of studying the dielectric relaxation behavior, the Cole–Cole equation [18] has been a powerful fitting method.

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^\beta}. \quad (2)$$

The adjustable parameters are the relaxation time, τ , and the relaxation strength, $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$. In the case that the dielectric relaxation is disturbed by the electrical conduction, the relaxation strength is modified to the exponential decay term, described with the following equation [19]

$$\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty = \Delta\varepsilon_0 \exp(E_\varepsilon/k_B T). \quad (3)$$

Then we obtained a modified Debye relaxation equation,

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon_0 \exp(E_\varepsilon/k_B T)}{1 + (i\omega\tau)^\beta}. \quad (4)$$

Indeed, the HT dielectric relaxation in AFN ceramics could be well fitted by Eq. 4. The detailed analysis will be reported in a further paper.

4 Conclusions

$A_2\text{FeNbO}_6$ (A=Ba, Sr, and Ca) ceramics were prepared by a wolframite method with monoclinic FeNbO_4 precursor. We have investigated the temperature and frequency dependence of dielectric spectra of polycrystalline AFN ceramics. Two dielectric relaxations, both following the Arrhenius law, were observed at low and high temperatures. The LT one is due to polaron relaxation through the variable range hopping of localized electrons. The HT

dielectric relaxation in AFN mainly reflects the competition between the intrinsic dielectric relaxation and the electrical conduction due to oxygen vacancies.

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