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## Ferroelectricity and electromechanical coupling in $(1 - x)\text{AgNbO}_3$ - $x\text{NaNbO}_3$ solid solutions

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We observed the evolution of polarization states and electromechanical coupling in  $(1 - x)\text{AgNbO}_3$ - $x\text{NaNbO}_3$  solid solutions using dielectric and strain hysteresis loop techniques and show that the polarization evolves from the ferrielectric ordering in  $\text{AgNbO}_3$  to the ferroelectric ordering in  $\text{NaNbO}_3$ . The crossover between these two states occurs in the solid solution with  $x \approx 0.8$ . A strain level  $\approx 0.20\%$  is available in the ceramics of these solid solutions. Such a large electromechanical effect might be interesting for the development of piezoelectric materials.

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$\text{AgNbO}_3$  is ferrielectric at room temperature with a non-centrosymmetric group of  $Pmc2_1$  (Refs. 1 and 2) in which Ag/Nb atoms shift *ferrielectrically* along the  $c$  axis of this orthorhombic structure. It has a small spontaneous polarization at zero field<sup>3</sup> but can be switched into a ferroelectric state with a very large polarization through the application of a high electric field.<sup>4</sup> Such amazing ability of polarization is of great significance for the design of lead-free ferroelectric materials. Recent investigations show that normal ferroelectric state with a large spontaneous polarization and a high  $T_c$  can be induced with small substitution of Li or K for Ag.<sup>5-7</sup> Here, we investigate the polarization evolution when Na is used as a substitution element.

Unlike  $(\text{Ag,Li})\text{NbO}_3$  and  $(\text{Ag,K})\text{NbO}_3$  systems that merely possess a limited solid solution,<sup>5-7</sup>  $(\text{Ag,Na})\text{NbO}_3$  system allows a whole solid solution between its end-members.<sup>8</sup> Kania and Kwapulinski prepared the ceramics of this system and reported its dielectric behaviors and differential thermal analysis.<sup>8</sup> On the basis of these results and the early reported structures, they suggested that  $(\text{Ag,Na})\text{NbO}_3$  system evolves from disordered antiferroelectric  $\text{AgNbO}_3$  to normal antiferroelectric  $\text{NaNbO}_3$ . As stated in the beginning of this paper,  $\text{AgNbO}_3$  is a *ferri*-electric rather than an *antiferro*-electric suggested by the previous structure analyses (for example, Sciau *et al.* proposed a room temperature structure of  $Pbcm$  (Ref. 9); however, this centrosymmetric structure does not allow the occurrence of spontaneous polarization). This long-standing issue on the crystal structure of  $\text{AgNbO}_3$  has been addressed by convergent-beam electron diffraction (CBED) technique that allows the exact determination of the space group of a single-domain area free from lattice defects. CBED observations unambiguously indicate that the space group of  $\text{AgNbO}_3$  is  $Pmc2_1$  at room temperature.<sup>1</sup> On the basis of this space group, the atomic positions in the unit cell were reliably derived from the neutron and synchrotron powder diffraction analyses.<sup>2</sup> On the other hand, the situation with  $\text{NaNbO}_3$  is still confusing in spite of the extensive studies: Ferroelectric-

ity, ferrielectricity, and antiferroelectricity have been reported. In 1949, Matthias reported that  $\text{NaNbO}_3$  is ferroelectric with a Curie point of 655 K.<sup>10</sup> Further evidence of ferroelectricity can be found from the domain movement under electric field in an optical study,<sup>11</sup> from pyroelectricity and current hysteresis loop for single crystal,<sup>12</sup> and from the ferroelectric  $D-E$  loops and piezoelectricity observed in ceramics samples.<sup>13-15</sup> Ferrielectricity in  $\text{NaNbO}_3$  was suggested by Cross and Nicholson in their report on the optical strain, dielectric constant, and hysteresis loop of  $\text{NaNbO}_3$  single crystals.<sup>16</sup> However, structure analyses generally suggest an antiferroelectric structure for  $\text{NaNbO}_3$  at room temperature.<sup>17-19</sup> More recently, Mishra *et al.* proposed that there is competing antiferroelectric and ferroelectric interactions in  $\text{NaNbO}_3$  and reported that these two phases can coexist over a wide range of temperature from 12 to 280 K.<sup>20</sup> It will be of great interest to monitor the polarization evolution in  $(\text{Ag,Na})\text{NbO}_3$  system because this will provide additional information on the ferroelectric or antiferroelectric phase stability in  $\text{NaNbO}_3$ . Here, we show that the  $(\text{Ag,Na})\text{NbO}_3$  system evolves from a *ferri*-electric state in the  $\text{AgNbO}_3$  end to a *ferro*-electric state in the  $\text{NaNbO}_3$  end from the results on the polarization/strain vs electric field. We also show that a large strain of  $\approx 0.20\%$  is available in these ceramics samples.

$\text{Ag}_{1-x}\text{Na}_x\text{NbO}_3$  solid solutions were prepared by a solid state reaction approach. Mixtures of  $\text{Ag}_2\text{O}$  (99%),  $\text{Nb}_2\text{O}_5$  (99.99%), and  $\text{Na}_2\text{CO}_3$  (99.99%) were calcined at 1173 K for 4 h in  $\text{O}_2$  atmosphere. The calcined powder was ground, pressed into pellets, and sintered at temperatures 1353–1523 K for 3 h in  $\text{O}_2$ . Pellets were polished and coated with Au electrodes for electric measurements. Dielectric measurements were performed at 1 V/mm using a Hewlett-Packard Precision LCR meter HP4284A. Dielectric hysteresis loops and electric field ( $E$ )-induced strain were measured simultaneously with a ferroelectric measurement system of an aix-ACC TF Analyzer 2000 equipped with a Canon DS-80 interferometer and a high voltage source of 10 kV.

Figure 1 summarizes our typical results of the polarization and strain ( $S$ ) responses under the application of electric

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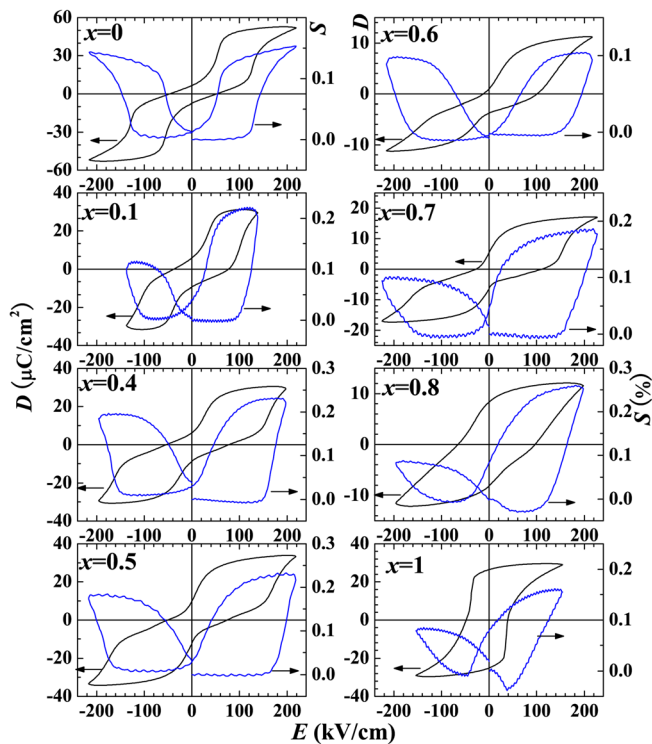


FIG. 1. (Color online) Variation of polarization and strain under the application of electric field in  $(\text{Ag}_{1-x}\text{Na}_x)\text{NbO}_3$  solid solutions.

field for the  $\text{Ag}_{1-x}\text{Na}_x\text{NbO}_3$  system. The results were obtained with a frequency of 1 Hz at room temperature. Data for pure  $\text{AgNbO}_3$  were replotted from the previous report.<sup>4</sup> We can see that, within a wide range of compositions, the solid solutions show the ferroelectric responses similar to those observed in pure  $\text{AgNbO}_3$ . When applied field is larger than a critical field, a ferroelectric state with a large polarization is induced. Associated with such a phase change,  $E$ -induced strain also increases sharply and reaches a value of  $>0.2\%$  for some cases. However, when the electric field is removed, the polarization and strain drop back down to a small value at zero field. Unlike antiferroelectric, the polarization is not zero but have a definite value at zero field, indicating that the polarization is ordered ferroelectrically in the crystal of these solid solutions.

In contrast, solid solutions with  $x > 0.8$  show different behaviors of polarization and strain. Nearly normal ferroelectric  $D$ - $E$  and  $S$ - $E$  loops were observed for these compositions. These results indicate that a ferroelectric phase exists in these Na-rich solid solutions. In the pure  $\text{NaNbO}_3$ , more perfect ferroelectric  $D$ - $E$  and  $S$ - $E$  loops were obtained. Therefore, we consider that there is a crossover from *ferr*-electric to *ferro*-electric phases in the  $\text{Ag}_{1-x}\text{Na}_x\text{NbO}_3$  solid solutions.

We also observed the dielectric behaviors of this system to examine this conclusion. The results of the temperature dependence of the dielectric constant are shown in Fig. 2, and the transition temperatures associated with dielectric anomaly are plotted in Fig. 3. Here, we can see that solid solutions with  $x < 0.8$  essentially have the temperature dependence of the dielectric constant of  $\text{AgNbO}_3$ . In contrast, solid solutions with larger Na concentrations show the dielectric behaviors similar to those of pure  $\text{NaNbO}_3$ . Again, the results on the dielectric constants suggest that there is a phase crossover in

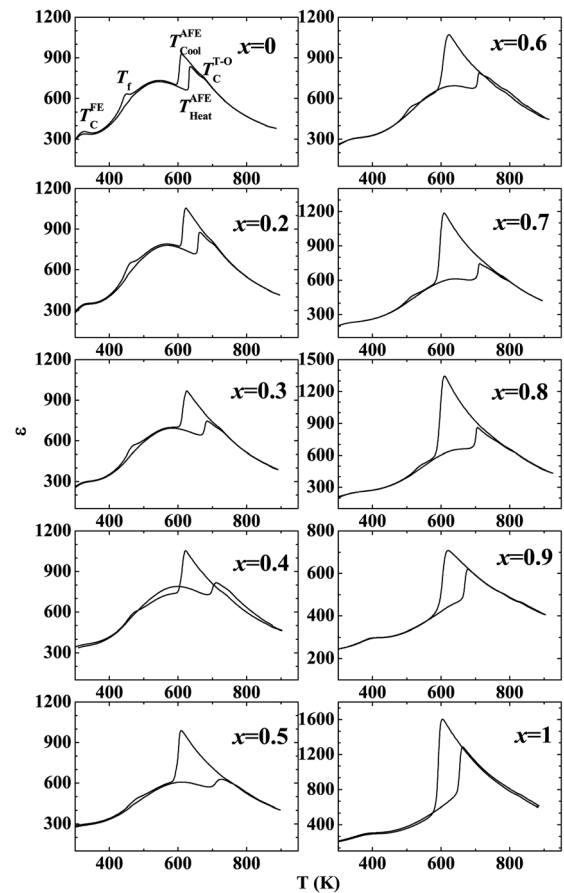


FIG. 2. Dielectric behaviors of  $(\text{Ag}_{1-x}\text{Na}_x)\text{NbO}_3$  solid solutions. Data were obtained at 100 kHz and an ac level of 1 V/mm.  $T_c^{\text{FE}}$ ,  $T_c^{\text{AFE}}$ , and  $T_c^{\text{T-O}}$  represent the ferroelectric (Ref. 3), antiferroelectric (Ref. 9), and paraelectric orthorhombic-tetragonal (Ref. 9) phase transitions, respectively.  $T_f$  was suggested to be a freezing temperature at which partial freezing of the Nb ion dynamics occurs (Refs. 24 and 25).

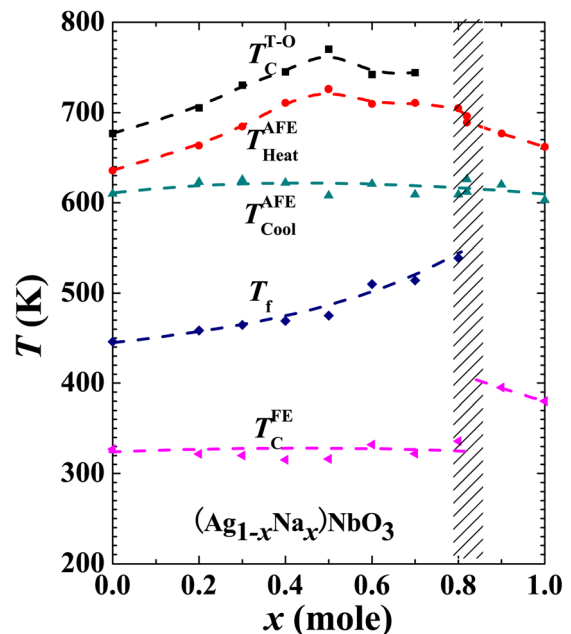


FIG. 3. (Color online) Variation of the transition temperatures detected from the dielectric measurements. It can be seen that there is a remarkable change around  $x \approx 0.8$ , which is in good agreements with polarization observations.

the  $\text{Ag}_{1-x}\text{Na}_x\text{NbO}_3$  solid solutions. It is very difficult to determine the exact phase boundary for the phase transformation because of the phase coexistence. However, combining the results of polarization and dielectric behaviors, we consider that the phase crossover occurs around the composition of  $x \approx 0.8$ .

Finally, it should be noticed that a strain of  $\approx 0.2\%$  can be obtained in both ferrielectric and ferroelectric phase of the solid solutions. This large electromechanical response indicates that this system might be used for the development of piezoelectric materials.<sup>21–23</sup>

In summary, our results of the polarization, strain, and dielectric behaviors indicate that there is a change from ferrielectric to ferroelectric phases in the  $\text{Ag}_{1-x}\text{Na}_x\text{NbO}_3$  solid solution. In the  $\text{AgNbO}_3$  end, the ferrielectric phase is stable. On the other hand, in the  $\text{NaNbO}_3$  end, the ferroelectric phase is stable. The crossover between these two phases occurs around  $x \approx 0.8$ . Large electromechanical coupling was also obtained for these solid solutions.

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