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Ferroelectricity in Silver Perovskite Oxides

Desheng Fu¹ and Mitsuru Itoh²

¹Shizuoka University,

²Tokyo Institute of Technology
Japan

1. Introduction

Many ferroelectric oxides possess the ABO_3 perovskite structure (Mitchell, 2002), in which the A-site cations are typically larger than the B-site cations and similar in size to the oxygen anion. Figure 1 shows a schematic drawing for this structure, where the A cations are surrounded by 12-anions in the cubo-octahedral coordination and the B cations are surrounded by 6-anions in the octahedral coordination. An ideal perovskite exhibits a cubic space group $Pm3m$. This structure is centrosymmetric and cannot allow the occurrence of ferroelectricity that is the presence of a switchable spontaneous electric polarization arising from the off-center atomic displacement in the crystal (Jaffe et al., 1971; Lines & Glass, 1977). The instability of ferroelectricity in the perovskite oxides is generally discussed with the Goldschmidt tolerance factor (t) (Goldschmidt, 1926 and Fig. 2),

$$t = (r_A + r_O) / \sqrt{2}(r_B + r_O),$$

where r_O , r_A , and r_B are the ionic radii of the O, A, and B ions. For a critical value $t=1$, the cubic paraelectric phase is stable. This unique case can be found in $SrTiO_3$, which has an ideal cubic perovskite structure at room temperature and doesn't show ferroelectricity down to the absolute 0 K (Müller & Burkard, 1979). However, ferroelectricity can be induced by the substitution of O^{18} in this quantum paraelectric system at $T < T_c \sim 23$ K (Itoh et al., 1999). When $t > 1$, since the B-site ion is too small for its site, it can shift off-centering, leading to the occurrence of displacive-type ferroelectricity in the crystal. Examples of such materials are $BaTiO_3$ and $KNbO_3$ (Shiozaki et al., 2001). On the other hand, for $t < 1$, the perovskite oxides are in general not ferroelectrics because of different tilts and rotations of BO_6 octahedra, which preserve the inversion symmetry. But exceptions may be found in the Bi-based materials, in which large A-site displacement is observed. This large A-site displacement is essentially attributed to the strong hybridization of Bi with oxygen (Baettig et al., 2005). Similar cases are observed in Pb-based materials, which commonly have large Pb displacement in the A-site (Egami et al., 1998) and strong covalent nature due to the unique stereochemistry of Pb (Cohen, 1992; Kuroiwa et al., 2001).

Although $BaTiO_3$ - and $PbTiO_3$ -based ceramics materials have been widely used in electronic industry (Uchino, 1997; Scott, 2000), there remain some importance issues to be solved. One of such challenges is to seek novel compounds to replace the Pb-based materials, which have a large Pb-content and raises concerns about the environmental pollution (Saito et al., 2004; Rodel et al., 2009).

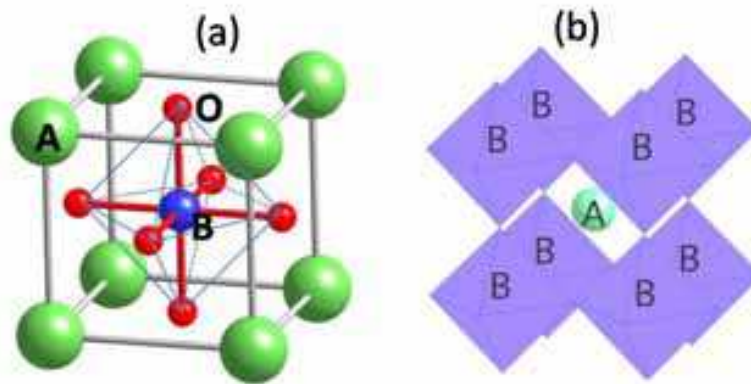


Fig. 1. The structure of an ABO_3 perovskite with the origin centered at (a) the B-site ion and (b) the A-site ion.

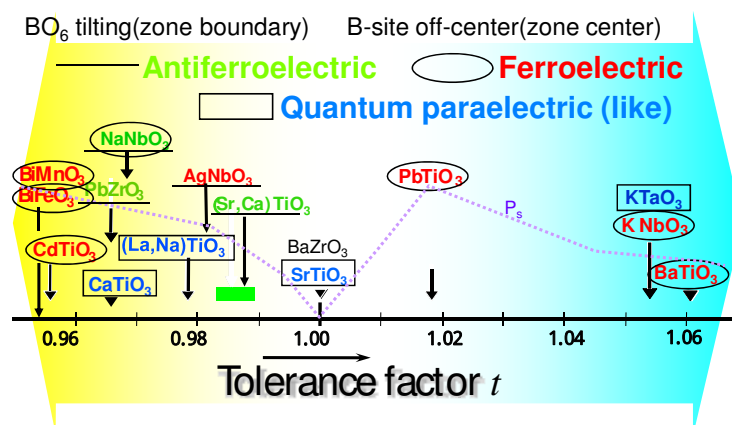


Fig. 2. Tolerance factor of typical dielectric oxides.

The discovery of extremely large polarization ($52 \mu\text{C}/\text{cm}^2$) under high electric field in the AgNbO_3 ceramics (Fu et al., 2007) indicates that Ag may be a key element in the designs of lead-free ferroelectric perovskite oxides (Fu et al., 2011a). With the advance of first-principles calculations (Cohen, 1992) and modern techniques of synchrotron radiation (Kuroiwa et al., 2001), we now know that the chemical bonding in the perovskite oxides is not purely ionic as we have thought, but also possesses covalent character that plays a crucial role in the occurrence of ferroelectricity in the perovskite oxides (Cohen, 1992; Kuroiwa et al., 2001). It is now accepted that it is the strong covalency of Pb with O that allows its large off-center in the A-site. Although Ag doesn't have lone-pair electrons like Pb, theoretical investigations suggest that there is hybridization between Ag and O in AgNbO_3 (Kato et al., 2002; Grinberg & Rappe, 2003,2004), resulting in a large off-center of Ag in the A-site of perovskite AgNbO_3 (Grinberg & Rappe, 2003,2004). This prediction is supported by the results from X-ray photoelectron spectroscopy, which suggest some covalent characters of the chemical bonds between Ag and O as well as the bonds between Nb and O (Kruczek et al., 2006). Moreover, bond-length analysis also supports such a theoretical prediction. Some of the bond-lengths ($\sim 2.43 \text{ \AA}$) in the structure (Sciau et al., 2004; Yashima et al. 2011) are significantly less than the sum of Ag^+ (1.28 \AA) and O^{2-} (1.40 \AA) ionic radii (Shannon, 1967). All these facts make us believe that AgNbO_3 may be used as a base compound to develop novel ferroelectric materials. Along such a direction, some interesting results have been obtained. It was found that ferroelectricity can be

induced through the chemical modification of the AgNbO_3 structure by substitution of Li (Fu et al., 2008, 2011a), Na (Arioka, 2009; Fu et al., 2011b), and K (Fu et al., 2009a) for Ag. Large spontaneous polarization and high temperature of para-ferroelectric phase transition were observed in these solid solutions. In the following sections, we review the synthesis, structure, and dielectric, piezoelectric and ferroelectric properties of these solid solutions together with another silver perovskite AgTaO_3 (Soon et al., 2009, 2010), whose solid solutions with AgNbO_3 are promising for the applications in microwaves devices due to high dielectric constant and low loss (Volkov et al. 1995; Fortin et al., 1996; Petzelt et al., 1999; Valant et al., 2007a).

2. AgNbO_3

2.1 Synthesis

Both single crystal and ceramics of AgNbO_3 are available. Single crystal can be grown by a molten salt method using NaCl or V_2O_5 as a flux (Łukaszewski et al., 1980; Kania, 1989). Ceramics samples can be prepared through a solid state reaction between Nb_2O_5 and silver source (Francombe & Lewis, 1958; Reisman & Holtzberg, 1958). Among the silver sources of metallic silver, Ag_2O and Ag_2CO_3 , Ag_2O is mostly proper to obtain single phase of AgNbO_3 (Valant et al., 2007b). For silver source of Ag_2O , thermogravimetric analysis indicates that phase formation can be reach at a firing temperature range of 1073-1397 K (Fig. 3). The issue frequently encountered in the synthesis of AgNbO_3 is the decomposition of metallic silver, which can be easily justified from the color of the formed compounds. Pure powder is yellowish, while grey color of the powder generally indicates the presence of some metallic silver. It has been shown that the most important parameter that influences the phase formation is oxygen diffusion (Valant et al., 2007b). In our experiments to prepare the AgNbO_3 ceramics, we first calcined the mixture of Ag_2O and Nb_2O_5 at 1253 K for 6 hours in O_2 atmosphere and then sintered the pellet samples for electric measurements at 1323 K for 6 hours in O_2 atmosphere (Fu et al., 2007). Insulation of these samples is very excellent, which allows us to apply extremely high electric field to the sample (Breakdown field >220 kV/cm. For comparison, BaTiO_3 ceramics has a value of ~50 kV/cm.)

2.2 Electric-field induced ferroelectric phase

Previous measurements on D - E hysteresis loop by Kania *et al.* (Kania et al., 1984) indicate that there is small spontaneous polarization P_s in the ceramics sample of AgNbO_3 . P_s was estimated to be $\sim 0.04 \mu\text{C}/\text{cm}^2$ for an electric field with an amplitude of $E=17 \text{ kV}/\text{cm}$ and a frequency of 60 Hz. Our results obtained at weak field have confirmed Kania's reports (Fig. 4 and Fu et al., 2007). The presence of spontaneous polarization indicates that AgNbO_3 must be ferroelectric at room temperature. The good insulation of our samples allows us to reveal a novel ferroelectric state at higher electric field. As shown in Fig.4, double hysteresis loop is distinguishable under the application of $E\sim 120 \text{ kV}/\text{cm}$, indicating the appearance of new ferroelectric phase. When $E>150 \text{ kV}/\text{cm}$, phase transformation is nearly completed and very large polarization was observed. At an electric field of $E=220 \text{ kV}/\text{cm}$, we obtained a value of $52 \mu\text{C}/\text{cm}^2$ for the ceramics sample. Associating with such structural change, there is very large electromechanical coupling in the crystal. The induced strain was estimated to be 0.16% for the ceramics sample (Fig.5). The D - E loop results unambiguously indicate that the atomic displacements are ordered in a **ferri**-electric way rather than an **anti-ferro**electric way in the crystal at room temperature.

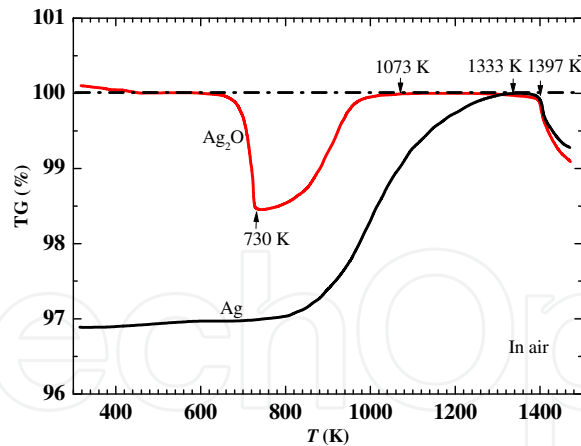


Fig. 3. Thermogravimetric curves of the AgNbO_3 formation in air using Ag_2O or metallic Ag powder as the silver source (Valant et al., 2007b). The curves are normalized to a weight of single-phase AgNbO_3 . Temperatures of phase formation completed and decomposition are also indicated. For case of Ag_2O , decomposition of Ag_2O into Ag and oxygen occurs at temperature of ~ 730 K.

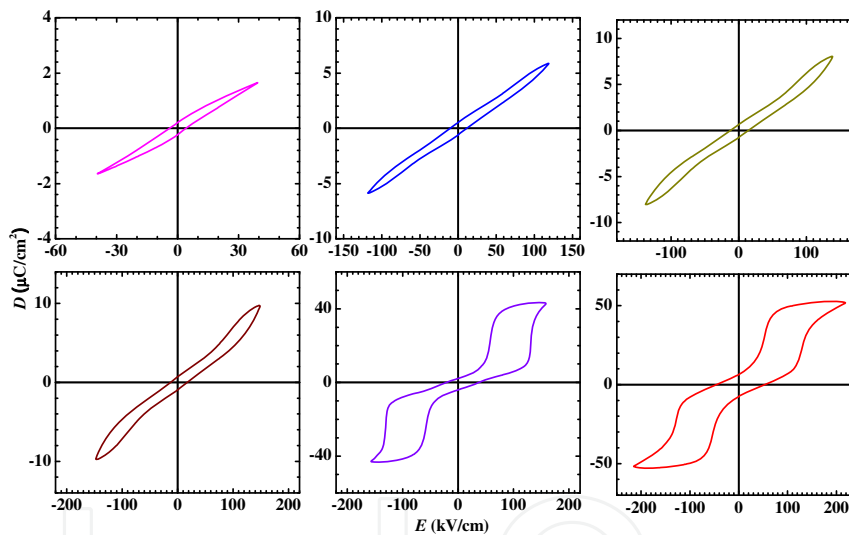


Fig. 4. D-E hysteresis loops for poly-crystalline AgNbO_3 at room temperature.

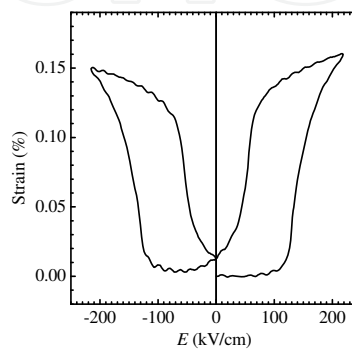


Fig. 5. Strain vs electric field for poly-crystalline AgNbO_3 at room temperature.

2.3 Room-temperature structure

There are many works attempting to determine the room-temperature structure of AgNbO_3 (Francombe & Lewis, 1958; Verwerft et al., 1989; Fabry et al., 2000; Sciau et al., 2004; Levin et al., 2009). However, none of these previous works can provide a *non-centrosymmetric* structure to reasonably explain the observed spontaneous polarization. Very recently, this longstanding issue has been addressed by R. Sano *et al.* (Sano et al., 2010). The space group of AgNbO_3 has been unambiguously determined to be $Pmc2_1$ (No. 26) by the convergent-beam electron diffraction (CBED) technique, which is *non-centrosymmetric* and allows the appearance of ferroelectricity in the crystal (Fig.6).

$Pmc2_1$ ($T=298\text{K}$)				
Site	x	y	z	U (\AA^2)
Ag1 4c	0.7499(3)	0.7468(3)	0.2601(5)	0.0114(2)
Ag2 2b	1/2	0.7466(6)	0.2379(5)	0.0114(2)
Ag3 2a	0	0.7424(4)	0.2759(6)	0.0114(2)
Nb1 4c	0.6252(2)	0.7525(5)	0.7332(2)	0.00389(18)
Nb2 4c	0.1253(2)	0.24159	0.27981	0.00389(18)
O1 4c	0.7521(9)	0.7035(12)	0.7832(24)	0.0057(5)
O2 2b	1/2	0.804(3)	0.796(3)	0.0057(5)
O3 4c	0.6057(7)	0.5191(18)	0.4943(18)	0.0057(5)
O4 4c	0.6423(7)	0.0164(18)	0.539(2)	0.0057(5)
O5 2a	0	0.191(3)	0.256(3)	0.0057(5)
O6 4c	0.1339(9)	0.0410(17)	0.980(2)	0.0057(5)
O7 4c	0.1154(8)	0.4573(17)	0.5514(19)	0.0057(5)

Table 1. Structural parameters of AgNbO_3 at $T=298\text{K}$ (Yashima et al., 2011). Number of formula units of AgNbO_3 in a unit cell: $Z=8$. Unit-cell parameters: $a = 15.64773(3) \text{\AA}$, $b = 5.55199(1) \text{\AA}$, $c = 5.60908(1) \text{\AA}$, $\alpha = \beta = \gamma = 90 \text{ deg.}$, Unit-cell volume: $V = 487.2940(17) \text{\AA}^3$. U (\AA^2)=Isotropic atomic displacement parameter.

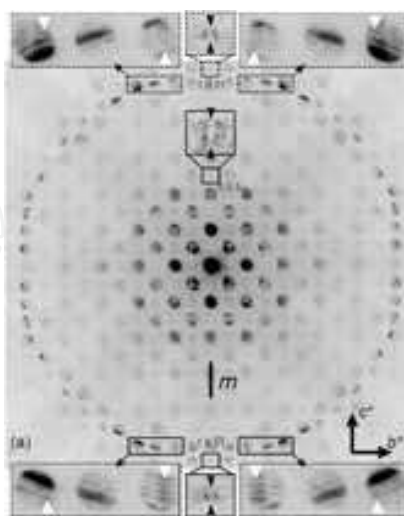


Fig. 6. Convergent-beam electron diffraction (CBED) pattern of AgNbO_3 taken at the $[100]$ incidence. In contrast to a mirror symmetry perpendicular to the b^* -axis, breaking of mirror symmetry perpendicular to the c^* -axis is seen, indicating that spontaneous polarization is along the c -direction (Taken by R. Sano & K. Tsuda (Sano et al., 2010)).

On the basis of this space group, M. Yashima (Yashima et al., 2011) exactly determined the atom positions (Table 1) in the structure using the neutron and synchrotron powder diffraction techniques. The atomic displacements are schematically shown in Fig.7. In contrast to the reported centrosymmetric *Pbcm* (Fabry et al. 2000; Sciau et al. 2004; Levin et al. 2009), in which the Ag and Nb atoms exhibit antiparallel displacements along the *b*-axis, the *Pmc2₁* structure shows a **ferri**-electric ordering of Ag and Nb displacements (Yashima et al., 2011) along the *c*-axis of *Pmc2₁* orthorhombic structure. This polar structure provides a reasonable interpretation for the observed polarization in AgNbO₃.

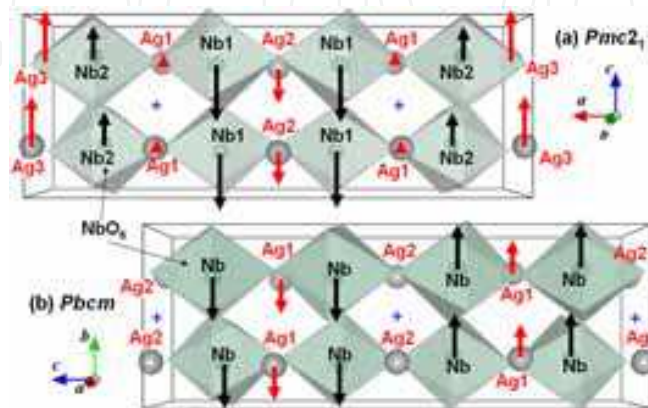


Fig. 7. (a) Ferrielectric crystal structure of AgNbO₃ (*Pmc2₁*) at room temperature. The atomic displacements along the *c*-axis lead to the spontaneous polarization in the crystal. (b) For comparison, the patterns for the previously reported *Pbcm* (Sciau et al., 2004) are also given. A cross (+) stands for the center of symmetry in the *Pbcm* structure. (by M. Yashima (Yashima et al., 2011)).

2.4 Dielectric behaviours and phase transitions

Initial works on the phase transitions of AgNbO₃ and their influence on the dielectric behaviors were reported by Francombe and Lewis (Francombe & Lewis, 1958) in the late 1950s, which trigger latter intensive interests in this system (Łukaszewski et al., 1983; Kania, 1983, 1998; Kania et al., 1984, 1986; Pisarski & Dmytrow, 1987; Paweczyk, 1987; Hafid et al., 1992; Petzelt et al., 1999; Ratuszna et al., 2003; Sciau et al., 2004). The phase transitions of AgNbO₃ were associated with two mechanisms of *displacive* phase transition: tilting of oxygen octahedra and displacements of particular ions (Sciau et al., 2004). Due to these two mechanisms, a series of structural phase transitions are observed in AgNbO₃. The results on dielectric behaviors together with the reported phase transitions are summarized in Fig.8. Briefly speaking, the structures of the room-temperature (Yashima et al., 2011) and the high temperature phases ($T > T^{O1-O2}=634$ K) (Sciau et al., 2004) are exactly determined, in contrast, those of low-temperature ($T < \text{room temperature}$) and intermediate phases ($T_C^{\text{FE}}=345$ K $< T < T^{O1-O2}$) remain to be clarified. In the dielectric curve, we can see a shoulder around 40 K. It is unknown whether this anomaly is related to a phase transition or not. It should be noticed that Shigemi *et al.* predicted a ground state of *R3c* rhombohedra phase similar to that of NaNbO₃ for AgNbO₃ (Shigemi & Wada, 2008). Upon heating, there is an anomaly at $T_C^{\text{FE}}=345$ K, above which spontaneous polarization was reported to disappear (Fig.8 (c) and Kania et al., 1984). At the same temperature, anomaly of lattice distortion was observed (Fig.8 (c) and Levin et al., 2009). The dielectric anomaly at $T_C^{\text{FE}}=345$ K was attributed to be a ferroelectric phase transition. Upon further heating, there is a small peak at $T=453$ K, which

		AgNbO ₃			
Atom		573 K	645 K	733 K	903 K
Nb	<i>x</i>	0.2460(15)	1/4	0	0
	<i>y</i>	0.2422(10)	1/4	0	0
	<i>z</i>	0.1256(6)	0	0	0
	<i>U</i> (Å ²)	1.12(6)	1.31(4)	1.38(4)	1.63(2)
Ag(1)	<i>x</i>	-0.2507(35)	0	0	1/2
	<i>y</i>	1/4	-0.001(2)	1/2	1/2
	<i>z</i>	0	1/4	1/2	1/2
	<i>U</i> (Å ²)	2.78(7)	1.98(6)	2.80(3)	3.47(4)
Ag(2)	<i>x</i>	-0.2556(26)	0		
	<i>y</i>	0.2428(18)	0.494(3)		
	<i>z</i>	1/4	1/4		
	<i>U</i> (Å ²)	1.73(6)	3.54(8)		
O(1)	<i>x</i>	0.3022	0.2827(7)	0	0
	<i>y</i>	1/4	1/4	0	0
	<i>z</i>	0	0	1/2	1/2
	<i>U</i> (Å ²)	1.31(6)	2.27(5)	3.14(5)	3.60(4)
O(2)	<i>x</i>	-0.0292(14)	0	0.2782(3)	
	<i>y</i>	0.0303(14)	0.2259(8)	0.2218	
	<i>z</i>	0.1140(6)	0.0205(8)	0.0358(4)	
	<i>U</i> (Å ²)	1.71(7)	1.94(4)	2.08(4)	
O(3)	<i>x</i>	0.5262(13)	0.2710(7)		
	<i>y</i>	0.4778(14)	0.2456(11)		
	<i>z</i>	0.1375(5)	1/4		
	<i>U</i> (Å ²)	1.17(6)	2.56(6)		
O(4)	<i>x</i>	0.2155(23)			
	<i>y</i>	0.2622(24)			
	<i>z</i>	1/4			
	<i>U</i> (Å ²)	1.67(7)			
cell	<i>a</i> (Å)	5.5579(5)	7.883(1)	5.5815(3)	3.9598(3)
	<i>b</i> (Å)	5.5917(6)	7.890(1)		
	<i>c</i> (Å)	15.771(2)	7.906(1)	3.9595(3)	

Table 2. Structural parameters for high temperature phases at 573 K (*Pbcm*), 645 K (*Cmcm*), 733 K (*P4/mbm*), and 903 K (*Pm3m*) (Sciau et al., 2004).

is not so visible. However, it can be easily ascertained in the differential curve or in the cooling curve. This anomaly is nearly unnoticed in the literatures (Łukaszewski et al., 1983; Kania, 1983, 1998; Kania et al., 1986; Pisarski & Dmytrow, 1987; Paweczyk, 1987; Hafid et al., 1992; Ratuszna et al., 2003). The detailed examination of the temperature dependence of the 220_o *d*-spacing (reflection was indexed with orthorhombic structure) determined by Levin *et al.* (Levin et al., 2009 and Fig.8(c)) reveals anomaly that can be associated with this dielectric peak. These facts suggest that a phase transition possibly occurs at this temperature. Around 540 K, there is a broad and frequency-dependent peak of dielectric constant, which is also associated with an anomaly of 220_o *d*-spacing. However, current structural investigations using x-ray and neutron diffraction do not find any symmetric changes associated with the

dielectric anomalies at 456 K and 540 K, and the structure within this intermediate temperature range was assumed to be orthorhombic $Pbcm$ (Sciau et al., 2004). At $T=T_C^{AFE}=631$ K, there is a sharp jump of dielectric constant due to an antiferroelectric phase transition (Pisarski et al., 1987; Sciau et al., 2004). The atomic displacement patterns in the antiferroelectric phase ($Pbcm$) are shown in Fig.7 (b) using the structural parameters determined by Ph Sciau *et al.* (Sciau et al., 2004). For $T>T_C^{AFE}$, there are still three phase transitions that are essentially derived by the tilting of oxygen octahedral and have only slight influence on the dielectric constant. For conveniences, the tilting of octahedral (Sciau et al., 2004) described in Glazer's notation is given in Fig.8 and the structure parameters (Sciau et al., 2004) are relisted in Table 2.

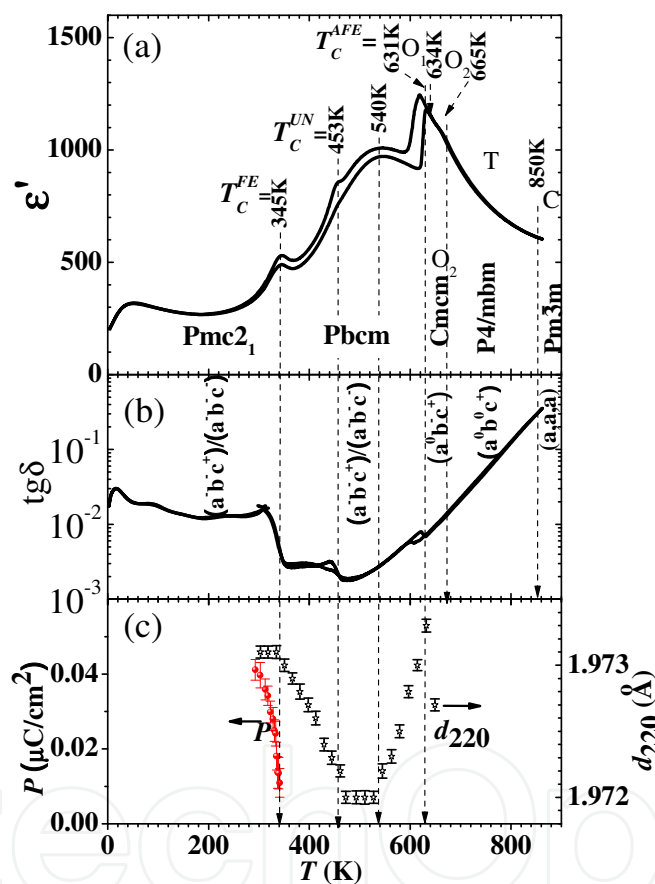


Fig. 8. Temperature dependence of (a) dielectric constant, (b) dielectric loss, and (c) polarization (Kania et al., 1984) and 220_O d -spacing of the lattice (Levin et al., 2009).

3. ($Ag_{1-x}Li_x$) NbO_3 solid solution

Li can be incorporated into the Ag-site of $AgNbO_3$. However, due to the large difference of ionic radius of Li^+ (0.92 \AA), and Ag^+ (1.28 \AA) (Shannon, 1976), the solid solution is very limited. Nalbandyan *et al.* (Nalbandyan et al., 1980), systematically studied the stable and metastable phase equilibria and showed that solid solution limit is narrow ($x \sim 0.02$) for the stable phase, but is relatively wide ($x \sim 0.12$) for the metastable phase (Sakabe et al., 2001; Takeda et al., 2003;

Fu et al., 2008, 2011a). With a small substitution of Li for Ag ($x > x_c = 0.05 \sim 0.06$), a ferroelectric rhombohedra phase is evolved in the solid solution (Nalbandyan et al., 1980; Sakabe et al., 2001; Takeda et al., 2003; Fu et al., 2008, 2011a). In this solid solution, the strong off-center of small Li (Bilc & Singh, 2006) plays an important role in triggering the ferroelectric state with large spontaneous polarization (Fu et al., 2008, 2011a).

3.1 Synthesis

Single crystals of $(\text{Ag}_{1-x}\text{Li}_x)\text{NbO}_3$ can be obtained by the melt growth process (Fu et al., 2008). Stoichiometric compositions of Ag_2O , Li_2CO_3 , and Nb_2O_5 were mixed and calcined at 1253 K for 6 h in an oxygen atmosphere. The calcined powder was milled, put into an alumina container, and melted at 1423 K for 4 h in an oxygen atmosphere. The melt was cooled to 1323 K to form the crystal at a rate of 4 K/h, followed by furnace cooling down to room temperature. Using this process, single crystals with size of 1–3 cm can be obtained for the $(100)_p$ (Hereafter, subscript p indicates pseudocubic structure) growth face. Due to the volatility of lithium at high temperature, the exact chemical composition of the crystal is generally deviated from the starting composition and is required to be determined with methods like inductively coupled plasma spectrometry.

Ceramics samples can be prepared by a solid state reaction approach. Mixtures of Ag_2O , Nb_2O_5 , and Li_2CO_3 were calcined at 1253 K for 6 h in O_2 atmosphere, followed by removal of the powder from the furnace to allow a rapid cooling to prevent phase separation. The calcined powder was milled again and pressed to form pellets that were sintered at 1323 K for 6 h in O_2 atmosphere, followed by a rapid cooling.

3.2 Structure

The structural refinements using the powder X-ray diffraction data suggest that $(\text{Ag}_{1-x}\text{Li}_x)\text{NbO}_3$ solid solution with $x > x_c$ has the space group of $R3c$ (Fu et al., 2011a). Table 3 lists the structural parameters of this model for composition $x=0.1$. Figure 9 shows a schematic drawing for this structure. In this rhombohedral $R3c$ phase, the spontaneous polarization is essentially due to the atomic displacements of the Ag/Li, Nb, and O atoms along the pseudocubic $[111]$ direction.

Ag _{0.9} Li _{0.1} NbO ₃ (R3c, No.161, T=room temperature)					
$a(\text{Å})$	5.520		α	90	
$b(\text{Å})$	5.520		β	90	
$c(\text{Å})$	13.79		γ	120	
$V(\text{Å}^3)$	364.0				
Atom	Site	x	y	z	$U(\text{Å}^2)$
Ag/Li	6a	0	0	0.2545(8)	0.5
Nb	6a	0	0	0.0097(8)	0.5
O	18b	0.5533	1	0.2599(9)	0.5

Table 3. Structural parameters for rhombohedra structure of $(\text{Ag,Li})\text{NbO}_3$ solid solution.

3.3 Ferroelectric and piezoelectric properties

Evolution of the polarization state in $\text{Ag}_{1-x}\text{Li}_x\text{NbO}_3$ solid solutions is shown in Fig.10. Basically, when $x < x_c$, the solid solutions have the *ferrielectric* state of pure AgNbO_3 with a small spontaneous polarization at zero electric field. In contrast, when $x > x_c$, a normal

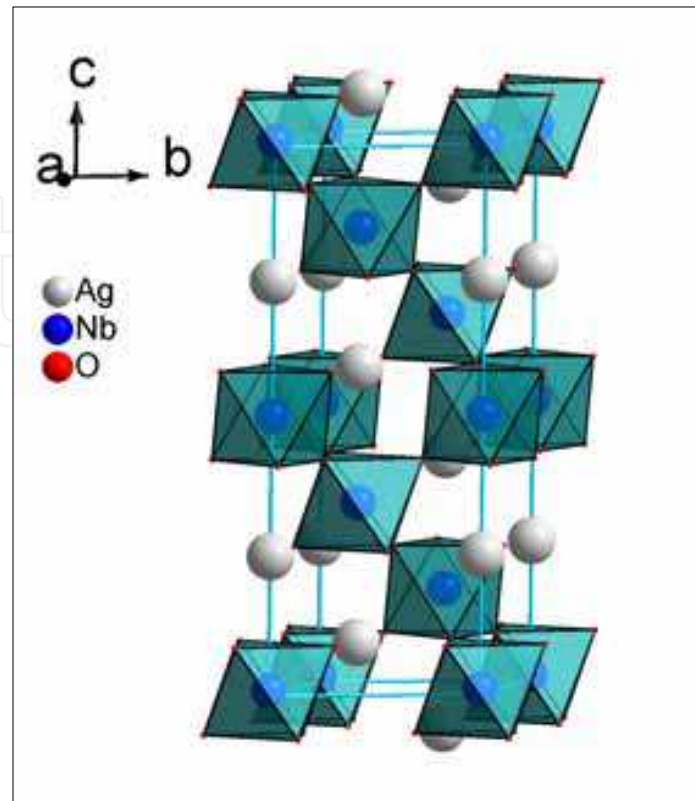


Fig. 9. Schematic structure of $\text{Ag}_{1-x}\text{Li}_x\text{NbO}_3$ ($x = 0.1$) with symmetry $R3c$ (No.161).

ferroelectric state with large value of remanent polarization (P_r) is observed. All ceramics samples show P_r value comparable to P_s of BaTiO_3 single crystal ($26 \mu\text{C}/\text{cm}^2$) (Shiozaki et al., 2001). Moreover, the polarization in $\text{Ag}_{1-x}\text{Li}_x\text{NbO}_3$ solid solution is very stable after switching. Large P_r value and ideal bistable polarization state of $\text{Ag}_{1-x}\text{Li}_x\text{NbO}_3$ ceramics may be interesting for non-volatile ferroelectric memory applications. Measurements on single crystal samples (Fig.11) indicate that saturation polarization along the $\langle 111 \rangle_p$ rhombohedra direction ($P_s^{\langle 111 \rangle} \sim 40 \mu\text{C}/\text{cm}^2$) is greatly larger than that along the $\langle 001 \rangle_p$ tetragonal direction ($P_s^{\langle 001 \rangle} \sim 24 \mu\text{C}/\text{cm}^2$) and the ratio between them is $\sqrt{3}$ (Fu et al., 2008), which is in good agreement with results of structural refinements. This suggests that the polar axis is the $\langle 111 \rangle_p$ direction of pseudo-cubic structure.

The strain- E loops indicate that there are good electromechanical coupling effects in $\text{Ag}_{1-x}\text{Li}_x\text{NbO}_3$ crystals. Although the spontaneous polarization is along the $\langle 111 \rangle_p$ axis, the $\langle 001 \rangle_p$ -cut crystal shows larger strain and less hysteresis than the $\langle 111 \rangle_p$ -cut one (Fig.11 (b) and (c)). These phenomena are very similar to those reported for the relaxor-ferroelectric crystals (Wada et al., 1998). The most significant result exhibited from $\text{Ag}_{1-x}\text{Li}_x\text{NbO}_3$ single crystal is its excellent g_{33} value that determines the voltage output of the piezoelectric device under the application of an external stress (Fu et al., 2008). The g_{33} value together the d_{33} value and dielectric constants for the $\langle 001 \rangle_p$ -cut single crystals are shown in Fig. 12. The high g_{33} value is a direct result from the large d_{33} constant and the low dielectric constant of the single crystal.

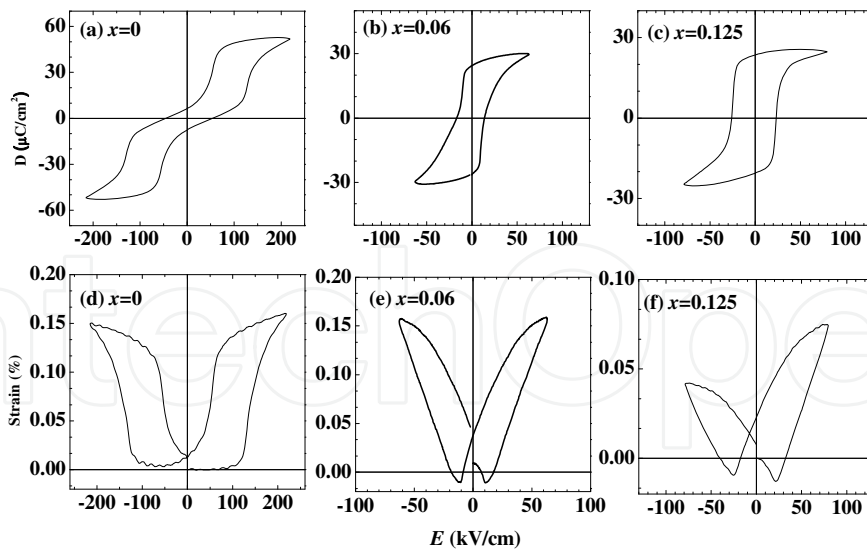


Fig. 10. Typical D - E and strain- E loops for the $\text{Ag}_{1-x}\text{Li}_x\text{NbO}_3$ ceramics samples.

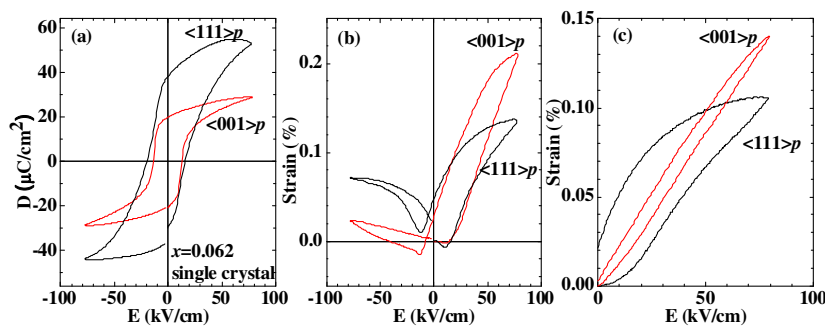


Fig. 11. (a) D - E loops, (b) strain vs E for bipolar electric field, and (c) strain vs E for unipolar field for $\text{Ag}_{1-x}\text{Li}_x\text{NbO}_3$ single crystal with $x=0.062$.

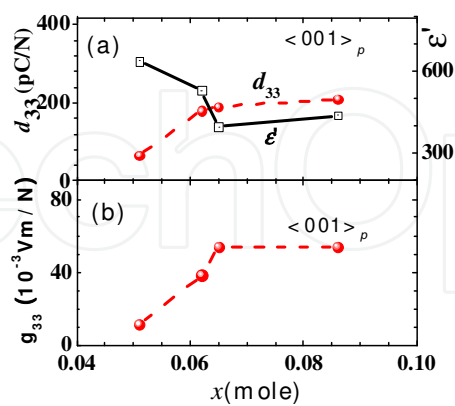


Fig. 12. Composition dependence of dielectric constant ϵ , d_{33} and g_{33} for the $\langle 001 \rangle_p$ -cut $\text{Ag}_{1-x}\text{Li}_x\text{NbO}_3$ single crystals.

3.4 Dielectric behaviours and proposed phase diagram

Figure 13 shows the dielectric behaviours of the ferroelectric $\text{Ag}_{1-x}\text{Li}_x\text{NbO}_3$ solid solutions. For comparison, the temperature dependence of dielectric constant of AgNbO_3 is also

shown. It can be seen that solid solution with $x > x_c$ shows different temperature evolutions of the dielectric constant as compared with AgNbO_3 . In sharp contrast to the complex successive phase transitions in AgNbO_3 , ferroelectric $\text{Ag}_{1-x}\text{Li}_x\text{NbO}_3$ solid solutions ($x > x_c$) show only two phase transitions in the temperature range of 0-820 K. Polarization measurements suggest that the high temperature phase ($T > T_C^{\text{FE}}$) is nonpolar, thus it seems

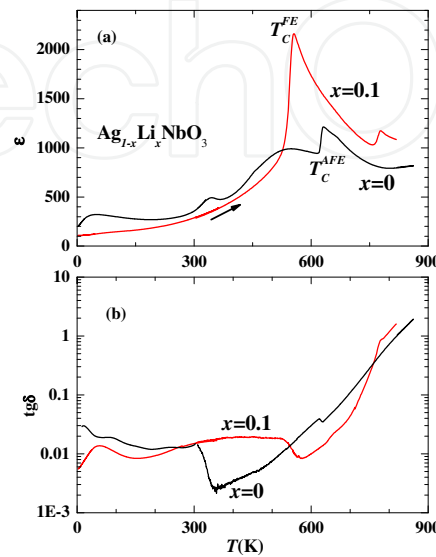


Fig. 13. Typical dielectric behaviours of $\text{Ag}_{1-x}\text{Li}_x\text{NbO}_3$ ceramics in comparison with that of pure AgNbO_3 .

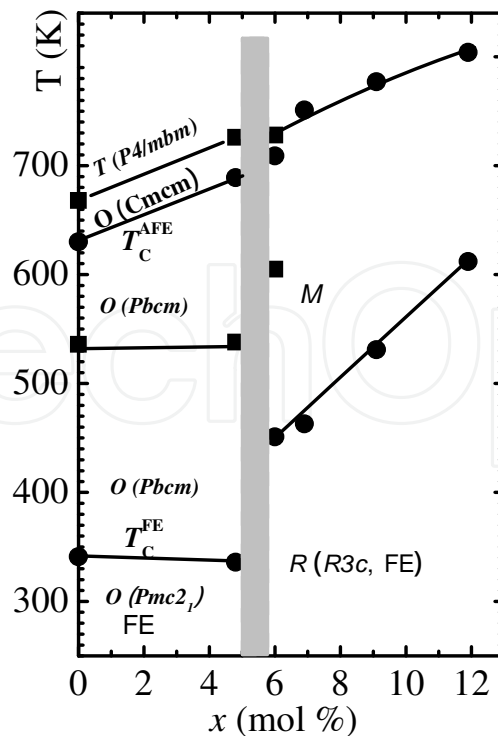


Fig. 14. Phase diagram proposed for $\text{Ag}_{1-x}\text{Li}_x\text{NbO}_3$ solid solution. The gray area indicates the phase boundary (Fu et al., 2011a).

that the higher temperature phase transition is not related to a ferroelectric phase transition. On the basis of the dielectric measurements, the phase diagram of $\text{Ag}_{1-x}\text{Li}_x\text{NbO}_3$ solution is summarized in Fig.14, where T , O , R and M represent tetragonal, orthorhombic, rhombohedra, and monoclinic symmetries, respectively. At room temperature, structure transformation from O to R phase at x_c dramatically changes the polar nature of $\text{Ag}_{1-x}\text{Li}_x\text{NbO}_3$. It is a *ferrielectric* with small spontaneous polarization in the O phase, but becomes a ferroelectric with large polarization in the R phase.

4. ($\text{Ag}_{1-x}\text{Na}_x$) NbO_3 solid solution

The ionic radius of Na^+ (1.18 Å) is comparable to that of Ag^+ (1.28 Å) (Shannon, 1976), allowing to prepare the $\text{Ag}_{1-x}\text{Na}_x\text{NbO}_3$ solid solution within the whole range of composition ($x=0-1$) (Kania & Kwapulinski, 1999). Kania *et al.* previously performed investigation on the dielectric behaviors and the differential thermal analysis for the $\text{Ag}_{1-x}\text{Na}_x\text{NbO}_3$ solid solutions, and stated that the solid solution evolves from disordered antiferroelectric AgNbO_3 to normal antiferroelectric NaNbO_3 . As described in section §2.3, we now know that AgNbO_3 is not *antiferroelectric* but rather is *ferrielectric* at room temperature (Yashima *et al.*, 2011). Moreover, recent reexamination on the polarization behaviors of stoichiometric and non-stoichiometric NaNbO_3 polycrystallines indicates that the reported clamping hysteresis loop of NaNbO_3 can be interpreted by pinning effects while stoichiometric NaNbO_3 is intrinsically *ferroelectric* (Arioka *et al.*, 2010). Therefore, reexamination on this solid solution is necessary. Evolution of the polarization with composition clearly indicates that the solid solution evolves from *ferrielectric* AgNbO_3 to *ferroelectric* NaNbO_3 (Fu *et al.*, 2011b).

4.1 Synthesis

$\text{Ag}_{1-x}\text{Na}_x\text{NbO}_3$ solid solution was prepared by a solid state reaction approach. Mixtures of Ag_2O (99%), Nb_2O_5 (99.99%), and Na_2CO_3 (99.99%) were calcined at 1173 K for 4 h in O_2 atmosphere. The calcined powder was ground, pressed into pellet with a diameter of 10 mm at thickness of 2 mm, and sintered with the conditions listed in Table 4.

Composition	Temperature	Time	atmosphere
$x=0,0.1,0.2$	1273K	5h	O_2
$x=0.4, 0.5, 0.6$	1323K	5h	O_2
$x= 0.8,0.9,1$	1373K	5h	O_2

Table 4. Sintering conditions for $\text{Ag}_{1-x}\text{Na}_x\text{NbO}_3$.

4.2 Polarization

Figure 15 shows the change in polarization with composition in the $\text{Ag}_{1-x}\text{Na}_x\text{NbO}_3$ solid solutions. For a wide range of composition $x < 0.8$, the solid solution possesses the characteristic polarization behaviours of pure AgNbO_3 : small spontaneous polarization at $E=0$ but large polarization at $E >$ a critical field. This fact suggests that the solid solution is *ferrielectric* within this composition range. This is also supported by the temperature dependence of dielectric constant (Fig.16). On the other hand, for the Na-rich composition, particularly, $x > 0.8$, we

observed large remanent polarization with value close to the saturation polarization at high field. This result indicates that a normal ferroelectric phase is stable in these compositions. Therefore, polarization measurements show that the $\text{Ag}_{1-x}\text{Na}_x\text{NbO}_3$ solid solution evolves from *ferrielectric* AgNbO_3 to *ferroelectric* NaNbO_3 (Fu et al., 2011b).

4.3 Dielectric properties

The dielectric properties of the $\text{Ag}_{1-x}\text{Na}_x\text{NbO}_3$ solid solutions are summarized in Fig.16. The change in dielectric behaviours with composition is very similar to that observed in polarization measurements (Fig.15). For $x \leq 0.8$, the solid solution shows successive phase transitions similar to pure AgNbO_3 . In contrast, it has the characteristic phase transition of pure NaNbO_3 for $x > 0.8$. The composition dependence of transition temperature derived from the dielectric measurements is shown in Fig.17. Two noticed features may be seen: (a) the thermal hysteresis is extremely large for antiferroelectric phase transition and reaches a value greater than 100 K at $x \sim 0.5$. Such large thermal hysteresis is rarely observed in normal polar phase transition. (b) It seems that there is a phase boundary at $x = x_c \sim 0.8$ (Fu et al., 2011b), around which structural transformation between *ferri*- and *ferro*-electric phases occurs.

5. ($\text{Ag}_{1-x}\text{K}_x$) NbO_3 solid solution

$(\text{Ag}_{1-x}\text{K}_x)\text{NbO}_3$ solid solutions are available only for very limited composition (Weirauch & Tennery, 1967; Łukaszewski, 1983; Kania, 2001). Weirauch *et al.* reported that solid solution of AgNbO_3 in KNbO_3 was limited to slightly less than 6 mole % and solid solution of KNbO_3 in AgNbO_3 was limited to less than 0.5 mole % (Weirauch & Tennery, 1967). However, our process indicates that KNbO_3 and AgNbO_3 can be alloyed with each other within 20 mole % (Fu et al., 2009a). Apparently, the reported solid solution limit is dependent on the process. In our samples, we found that a ferroelectric phase with large spontaneous polarization can be induced by substitution of K for Ag for $x > x_{c1} = 0.07$. This ferroelectric phase shows nearly composition-independent ferroelectric phase transition. On the other hand, the K-rich solid solution ($x > 0.8$) possesses the ferroelectric phase transition sequence of pure KNbO_3 and the transition temperature is dependent on the composition.

5.1 Synthesis

$(\text{Ag}_{1-x}\text{K}_x)\text{NbO}_3$ solid solutions were prepared by a solid state reaction method. Mixture of Ag_2O , Nb_2O_5 , and K_2CO_3 were calcined at 1173 K for 6 h in O_2 atmosphere with a slow heating rate of 1 K/min. The calcined powder was milled again, pressed in a 6-mm steel die with a pressure of 10 MPa to form the pellets, which were then preheated at 773 K for 2 h, followed by a sintering at temperature of 1253–1323 K (1323 K for $x = 0$ –0.1 and 1.00, 1273 K for $x = 0.15$ and 0.90, and 1253 K for $x = 0.17$ and 0.80, respectively) for 3 h in O_2 atmosphere. The atmosphere and heating rate are found to have significant influences on the phase stability of the solid solution.

5.2 Structural change with composition

Figure 18 shows the change in lattice parameters with composition in the $\text{Ag}_{1-x}\text{K}_x\text{NbO}_3$ solid solutions. When the amount of substitution is small, the solid solution possesses the orthorhombic structure of pure AgNbO_3 . In the phase boundary $x_{c1} = 0.07$, structural

transformation occurs and the phase changes into a new orthorhombic structure. In this new ferroelectric phase, the lattice constants show linear increase with composition. Interestingly, the orthorhombic distortion angle β is nearly independent with the composition. In the K-rich region ($x > x_{c3} = 0.8$), the solid solution has the orthorhombic structure of pure KNbO_3 at room-temperature, which is also ferroelectric. In contrast to nearly unchanged orthorhombic angle β in the Ag-rich orthorhombic phase, β shows monotonous decreases with x in the K-rich phase.

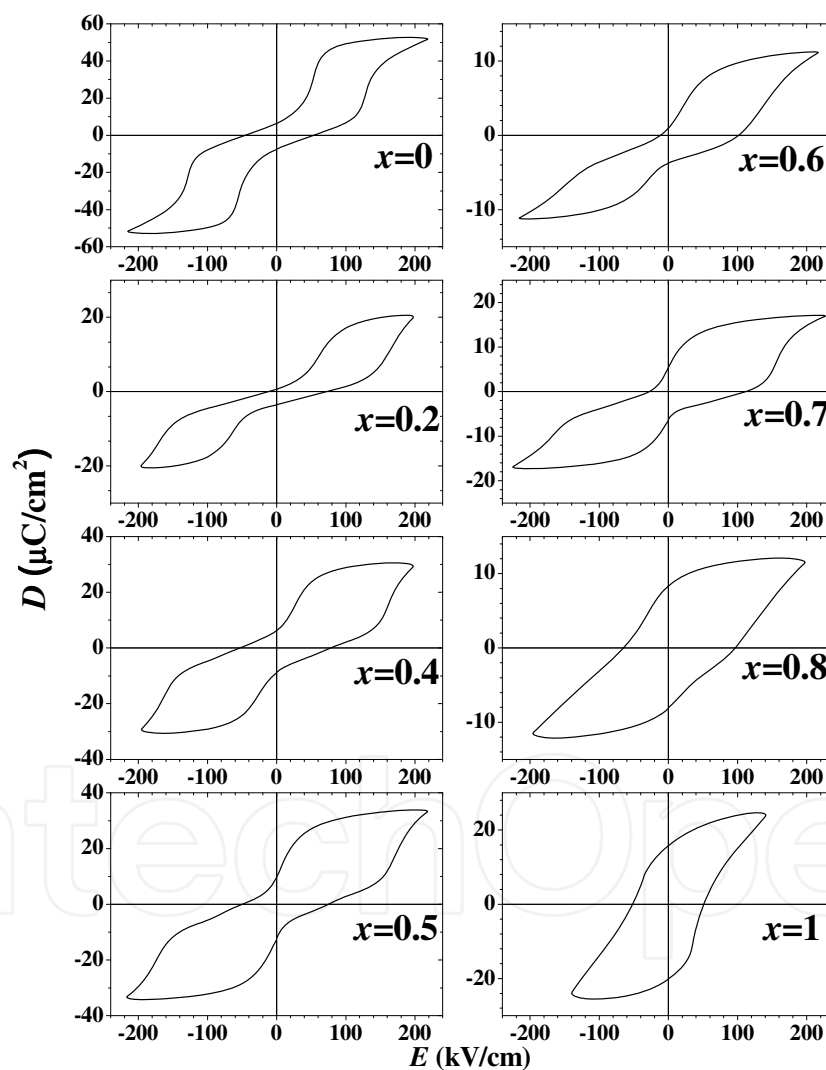


Fig. 15. Composition dependence of D - E loops obtained at room temperature for $\text{Ag}_{1-x}\text{Na}_x\text{NbO}_3$ solid solutions

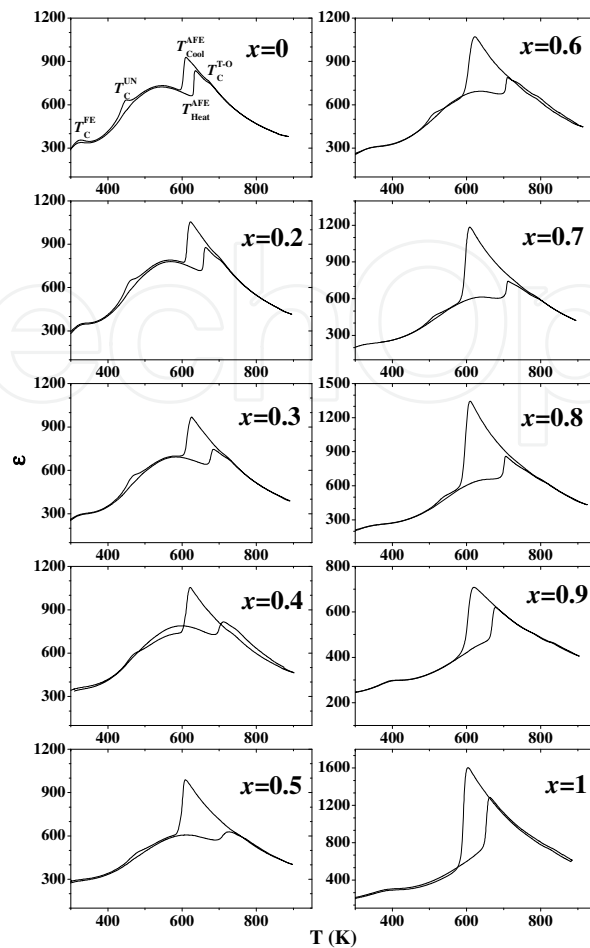


Fig. 16. Temperature dependence of dielectric constants for $\text{Ag}_{1-x}\text{Na}_x\text{NbO}_3$ solid solutions.

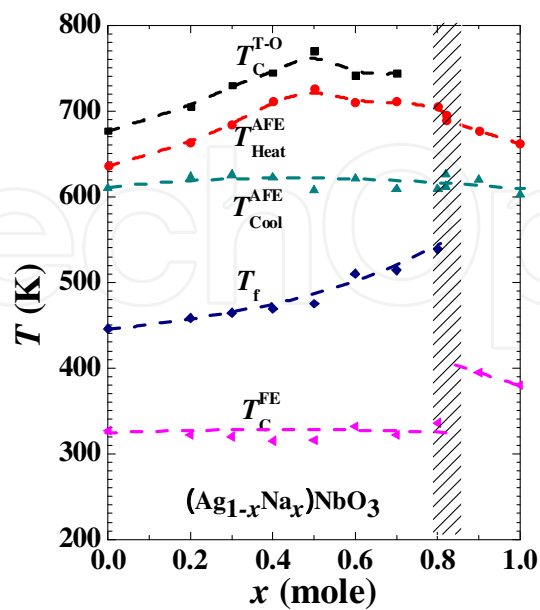


Fig. 17. Composition dependence of phase transition temperatures detected from dielectric measurements for $\text{Ag}_{1-x}\text{Na}_x\text{NbO}_3$ solid solutions.

5. 3 Ferroelectric and piezoelectric properties

Figure 19 shows typical results of polarization and strain behaviors observed at room temperature for the $\text{Ag}_{1-x}\text{K}_x\text{NbO}_3$ solid solutions. Similar to pure AgNbO_3 , merely a small spontaneous polarization was observed in samples with $x < x_{c1}$. However, when $x > x_{c1}$, a normal D - E loop with large value of remanent polarization P_r was observed. A value of $P_r = 20.5 \mu\text{C}/\text{cm}^2$ was obtained for a ceramics sample with $x = 0.10$, which is greatly larger than that observed for BaTiO_3 ceramics (Fu et al., 2010). These results show that Ag-rich orthorhombic phase ($x_{c1} < x < x_{c2}$) is really under a ferroelectric state with large polarization. For K-rich region $x > x_{c3}$, normal D - E loops were also obtained. Associating with the evolution into the ferroelectric phase, butterfly strain curve were observed. The piezoelectric constants determined from the piezo- d_{33} meter generally have values of 46–64 pC/N for these ferroelectric samples (Fu et al., 2009a).

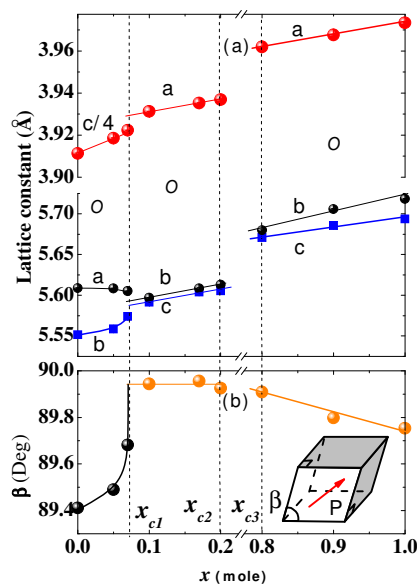


Fig. 18. Lattice parameters change with composition in $\text{Ag}_{1-x}\text{K}_x\text{NbO}_3$ solid solution. β is the orthorhombic distortion angle. The inset shows the orthorhombic distortion due to the ferroelectric displacements along the $\langle 110 \rangle_p$ direction of the pseudocubic structure.

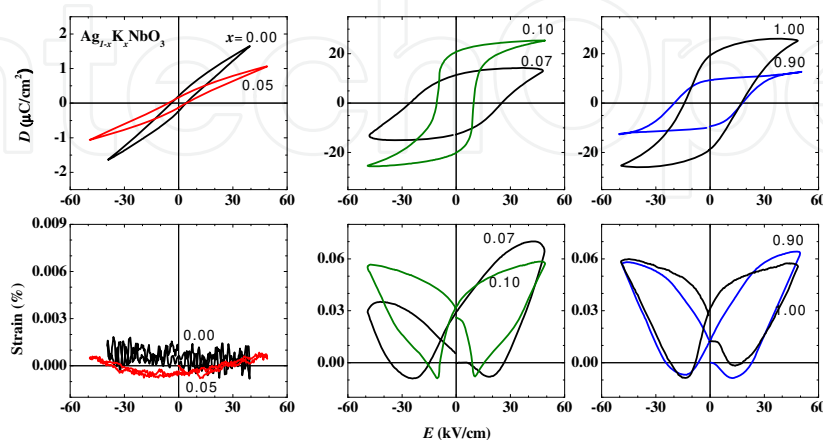


Fig. 19. Changes of polarization and strain under the application of electric field with composition at room temperature.

5.4 Dielectric behaviours and proposed phase diagram

Associating with the change in structure, dielectric behaviours of the $\text{Ag}_{1-x}\text{K}_x\text{NbO}_3$ solid solution also change with composition. As shown in Fig.20, the temperature dependence of dielectric constant can be sorted by three types: (1) AgNbO_3 -type for $x < x_{c1} = 0.07$, (2) KNbO_3 -type for K-rich region $x > x_{c3} = 0.8$, and (3) a new type for the intermediate composition $x_{c1} < x < x_{c2}$. In this intermediate composition, dielectric measurements indicate that there are two phase transitions within the temperature range of 0-750 K. One transition locates at $T_{c2} \sim 420$ K with thermal hysteresis and shows small change in dielectric constant, which seems to be due to a ferro-to-ferro-electric phase transition. Another phase transition occurs at $T_{c1} \sim 525$ K. Around this transition, the dielectric constant changes sharply and follows exactly the Curie-Weiss law. The Curie-Weiss constant was estimated to be $1.47 \cdot 10^5$ K for $x = 0.1$ sample, which is a typical value for the displacive ferroelectric transition, suggesting that this is a displacive type ferroelectric transition. A phase diagram is proposed in Fig.21, in which PE, FE, and AFE represent the paraelectric, ferroelectric, and antiferroelectric phases, respectively. When carefully comparing the phase transition temperature with the orthorhombic angle β (Fig.18) due to the ferroelectric distortion (For $x_{c1} < x < x_{c2}$ and $x > x_{c3}$. In contrast, for $x < x_{c1}$, β change is basically due to the oxygen-octahedral tilting.), one might find that there is a correlation between β and the temperature of the ferroelectric phase transition.

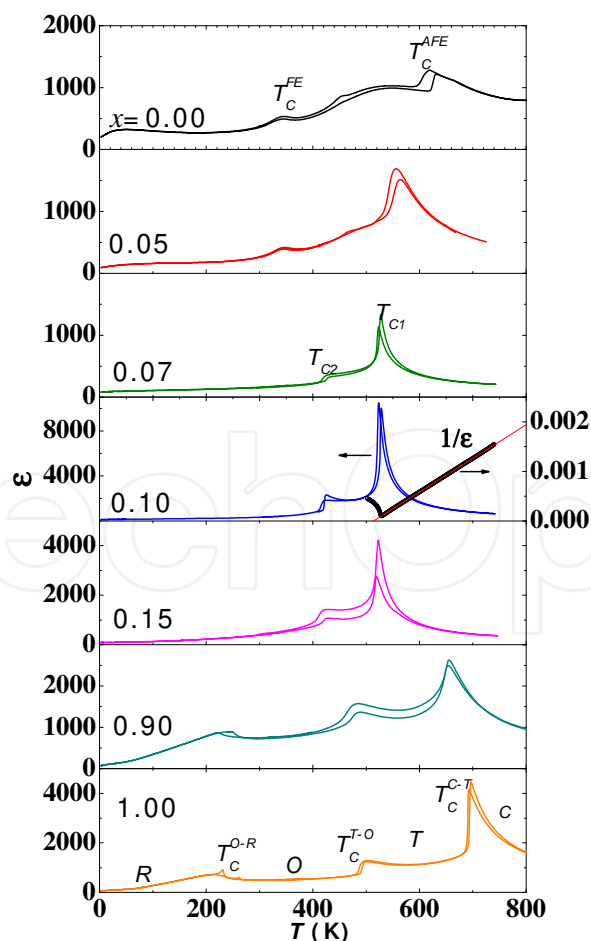


Fig. 20. Temperature dependence of dielectric constant for $\text{Ag}_{1-x}\text{K}_x\text{NbO}_3$ solid solution.

6. AgTaO₃

AgTaO₃ is another oxide of the two discovered silver perovskites (Francombe & Lewis, 1958). It is generally accepted that AgTaO₃ undergoes a series of phase transitions from rhombohedral phase ($T \leq 685$ K) to monoclinic phase ($650 \text{ K} \leq T \leq 703$ K) and then to tetragonal phase ($685 \text{ K} < T \leq 780$ K), and finally to cubic phase at $T_{T-C} = 780$ K upon heating (Francombe & Lewis, 1958; Kania, 1983; Paweczyk, 1987; Kugel et al., 1987; Hafid et al., 1992). However, due to the coexistence regions between rhombohedral and monoclinic, and monoclinic and tetragonal, the actual transition temperatures from rhombohedral to monoclinic T_{R-M} as well as that from monoclinic to tetragonal T_{M-T} still remain uncertain. Furthermore, the ground state and the origins that trigger these phase transitions still remain to be addressed (Wolczyk & Łukaszewski, 1986; Kugel et al., 1987; Soon et al., 2010).

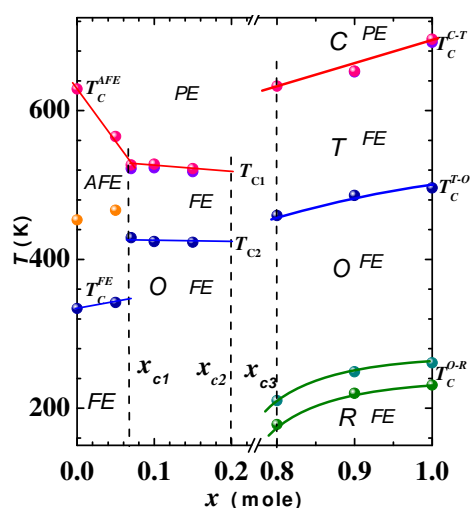


Fig. 21. Phase diagram proposed for the Ag_{1-x}K_xNbO₃ solid solution. Phase boundaries are indicated by the dashed lines. C, T, O, and R indicate the cubic, tetragonal, orthorhombic, and rhombohedral symmetries, respectively. PE, FE and AFE represent paraelectric, ferroelectric, and antiferroelectric phases, respectively.

6.1 Synthesis

Although single crystal of AgTaO₃ is available through a flux method (Łukaszewski et al., 1980; Kania, 1989), it is extremely difficult to prepare its dense ceramics sample (Francombe & Lewis, 1958; Kania, 1983) for electrical measurements. Since decomposition of AgTaO₃ occurs at 1443 ± 3 K in atmosphere (Valant et al., 2007b), sintering cannot be performed at higher temperatures to obtain dense ceramics. However, this long-standing synthesis difficulty now can be solved by a processing route involving the conventional solid-state reaction and sintering in environment with a high oxygen pressure at ~ 13 atm (Soon et al., 2010). In this synthesizing route, Ag₂O and Ta₂O₅, first underwent a grind mixing and was calcined at 1273 K for 6 hours. The calcined powder was then pressed into a pellet in 6 mm in diameter. Sintering was carried out by placing the powder compact into a sealed zirconia tube that was connected to a pressure control valve (Fig. 22). Prior to the sintering, oxygen gas at ~ 6.25 atm was filled into the sealed zirconia tube after the evacuation. Upon heating, the pressure of sealed oxygen gas increased and reached ~ 13 atm when the powder compact was sintered at 1573 K for 2 hours. This eventually led to formation of dense polycrystalline AgTaO₃.

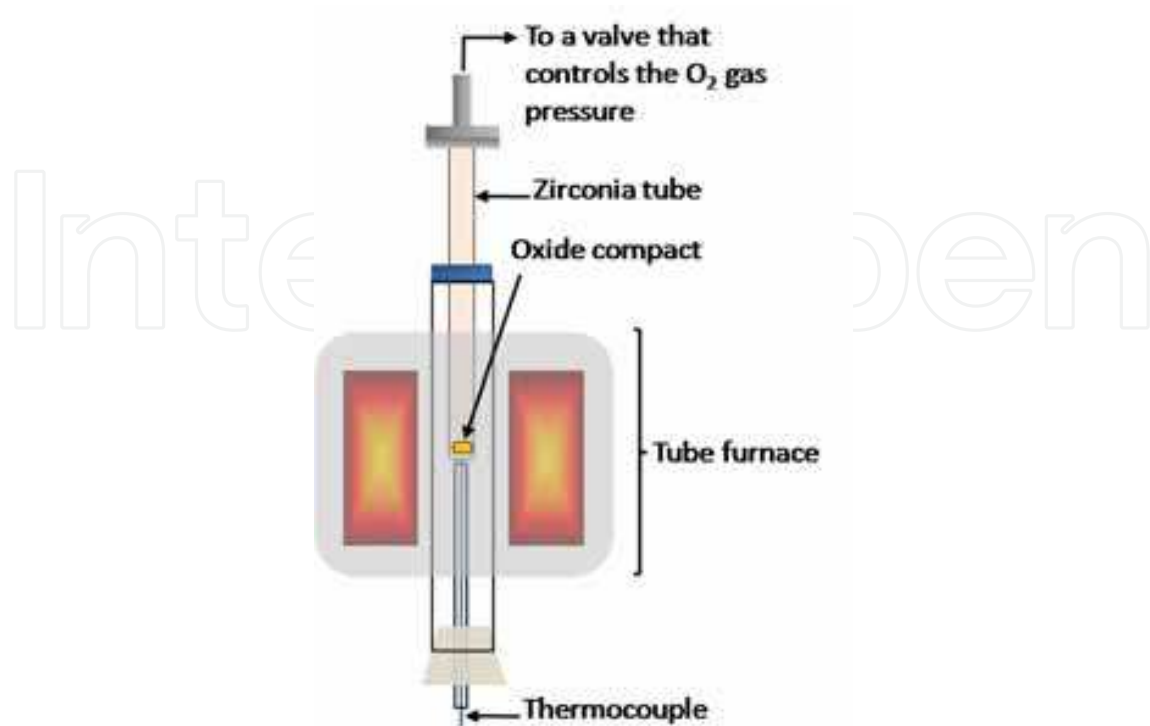


Fig. 22. Schematic diagram of the self-customized furnace employed for the sintering at high oxygen pressure.

6.2 Phase formation and dielectric behaviors

X-ray diffraction analyses (Fig.23) suggest the AgTaO_3 is rhombohedral with $R\bar{3}c$ symmetry at room temperature (Wolcyrz & Łukaszewski, 1986). Diffraction patterns obtained at 68.4 K remain unchanged, indicating that such nonpolar phase persists down to low-temperatures. This is also supported by the measurements on the dielectric constants (Fig.24) and heat capacity (Fig.25), in which no anomaly was probed in the low temperatures.

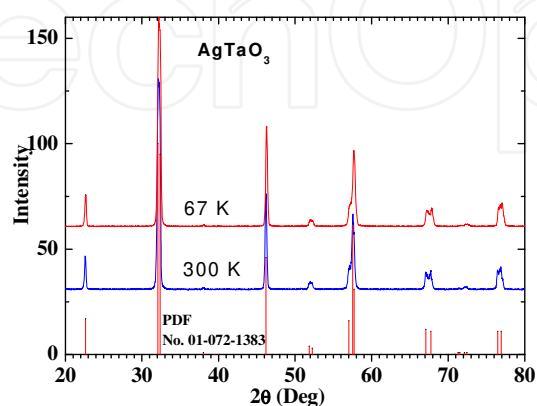


Fig. 23. XRD traces for AgTaO_3 obtained at 300 K and 68.4 K together with the standard pattern given by the powder diffraction file (PDF) No. 01-072-1383.

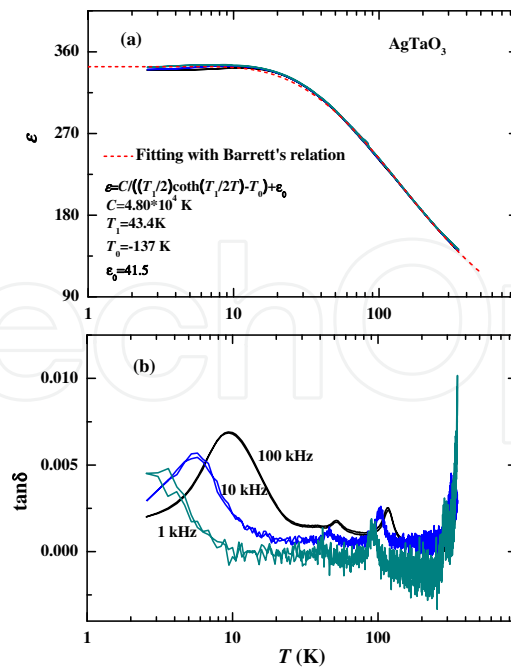


Fig. 24. Temperature dependence of (a) ϵ together with the fitting to the Barrett's relation indicated by the dashed line and (b) $\tan \delta$ for AgTaO_3 ceramics samples.

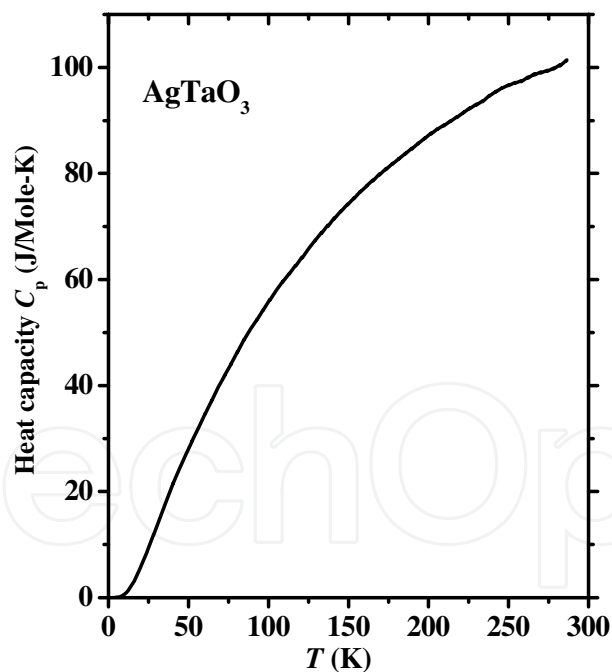


Fig. 25. Heat capacity for AgTaO_3 .

Although several frequency-dependent peaks are seen in the dielectric loss (Fig.24(b)), it can be reasonably attributed to polarization relaxations due to defects (Soon et al., 2010). Interestingly, within the low-temperature region, the dielectric behavior follows the Barrett's relation (Barrett, 1952) that is characteristic for the quantum paraelectric system (Abel, 1971; Höchli & Boatner, 1979; Itoh et al., 1999), suggesting that AgTaO_3 may be a

quantum paraelectric. On the other hand, two step-like dielectric anomalies corresponding to the phase transitions from monoclinic to tetragonal and tetragonal to cubic were observed at 694 and 780 K, respectively, upon heating the samples (Fig.26). This observation is in agreement with the previous reports (Kania,1983;Kugel et al., 1987). Furthermore, the temperature dependence of $1/\epsilon$ for AgTaO_3 shows non-linear behavior, which is similar to that of KTaO_3 , obeying the modified form of the Curie-Weiss law $\epsilon = \epsilon_L + C/(T - T_0)$ (Rupprecht & Bell, 1964).

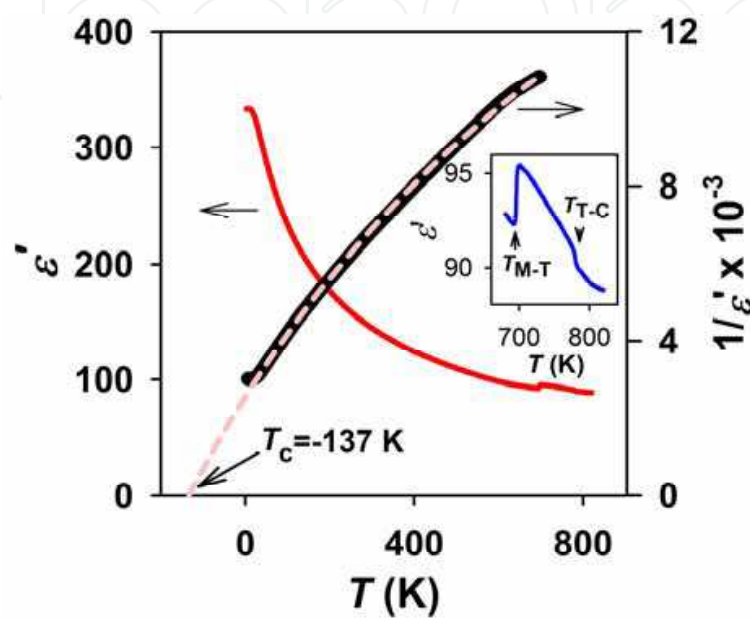


Fig. 26. Temperature dependences of ϵ' and $1/\epsilon'$ fitted to the modified Curie-Weiss law $\epsilon = \epsilon_L + C/(T - T_0)$ (dashed line, $\epsilon_L = 38.2$, $C = 4.7 \times 10^4$ K, $T_0 = -137$ K) for AgTaO_3 measured at 1 MHz upon heating. The inset further shows the step-like phase transitions from monoclinic to tetragonal and then to cubic at $T_{M-T} = 694$ K and $T_{T-C} = 780$ K, respectively.

7. $(\text{Ag}_{1-x}\text{Li}_x)\text{TaO}_3$ solid solution

Similar to the case of AgNbO_3 , ~12 mole% of Li can be incorporated into the Ag-site of AgTaO_3 to form $(\text{Ag}_{1-x}\text{Li}_x)\text{TaO}_3$ (Soon et al., 2009). Although the transition temperature is lower than room temperature, ferroelectricity can be induced in this solid solution due to the strong off-centering nature of the small Li ions.

7.1 Synthesis

$(\text{Ag}_{1-x}\text{Li}_x)\text{TaO}_3$ was prepared by the conventional solid-state reaction with Ag_2O , Ta_2O_5 and Li_2CO_3 , where the powder mixture was calcined at 1273 K for 6 hours. The calcined powder was then pressed into a pellet with 6 mm in diameter. Sintering was carried out by the same high-pressure process used for pure AgTaO_3 , which eventually led to formation of dense ceramics samples of $(\text{Ag}_{1-x}\text{Li}_x)\text{TaO}_3$

7.2 Dielectric behaviours and confirmation of ferroelectric phase

Figures 27 & 28 plot the temperature dependence of dielectric constant ϵ and loss $\tan\delta$ for $(\text{Ag}_{1-x}\text{Li}_x)\text{TaO}_3$ with $x \leq 0.12$ obtained at frequencies ranging from 1 kHz to 1 MHz,

respectively. It can be seen that a dielectric peak was gradually induced by Li^+ substitution in AgTaO_3 . In contrast to the single peak of the dielectric constant, there are two to four peaks of the dielectric loss within the same temperature window. Since the additional loss peaks do not associate with a remarkable change in the dielectric constant, it is very likely due to the defect effects dependent with sample processing. It can be seen that a well-defined peaks has occurred in the $\sim\text{MHz}$ frequency regions for the substitution at extremely low level, for example, at $x=0.02$. This indicates the existence of local polarization in the doped crystal (Vugmeister & Glinchuk, 1990; Samara, 2003). This fact again suggests that AgTaO_3 is actually under a critical state of the quantum paraelectric. Any slight modification will lead to the appearance of observable polarization in the system. For small substitution, the location of the dielectric anomaly depends on the observed frequency. Figure 29 gives an evaluation on this frequency dependence. In the figure, the temperature-axis is scaled with the peak position of 1 MHz, making it easy to see the change with composition. For $x=0.008$, the frequency dispersion is very strong, peak position of the dielectric constant shifts about 50% with respect to that of 1 MHz for $f=1$ kHz. However, for $x=0.035$, such change is less than 2%, meaning that ferroelectric phase transition temperature T_c is well defined in the sample. Thus, we can infer that a macroscopic ferroelectric phase is evolved below T_c in this composition. This was also confirmed by the results shown in Fig.30, in which ferroelectric loop was obtained for $T < T_c$ for a sample with $x=0.12$ that has the same dielectric behaviors to that of $x=0.035$.

On the basis of the above results, a phase diagram is proposed in Fig.31, in which PE and FE represents the paraelectric and ferroelectric phases, respectively. As mentioned above, since the peak of the dielectric constant is strongly dependent with frequency for $0 < x < 0.035$, the gray zone in the phase diagram may be attributed to dipole-glass phase (Vugmeister & Glinchuk, 1990; Pirc & Blinc, 1999; Samara, 2003) or a phase with nanosized ferroelectric domains (Fisch, 2003; Fu et al., 2009b), which remains to be addressed by further investigations.

8. Concluding remarks

Our recent works reveal that silver perovskites are of great interests from either the viewpoint of fundamental research or that of application research in the fields of ferroelectric or piezoelectric. Promising ferroelectric and piezoelectric properties have been demonstrated in some compounds such as $(\text{Ag,Li})\text{NbO}_3$ and $(\text{Ag,K})\text{NbO}_3$ alloys, but further works are required to improve the material performance, to understand the basic physics of the ferroelectricity/piezoelectricity of the materials, and to seek novel promising compounds among the discovered solutions or alloys with other ferroelectric systems. Moreover, integration techniques of thin films are also a direction for the future works when considering the practical applications.

9. Acknowledgment

Part of this work was supported by the Collaborative Research Project of Materials and Structures Laboratory of Tokyo Institute of Technology, and Grant-in-Aid for Scientific Research, MEXT, Japan.

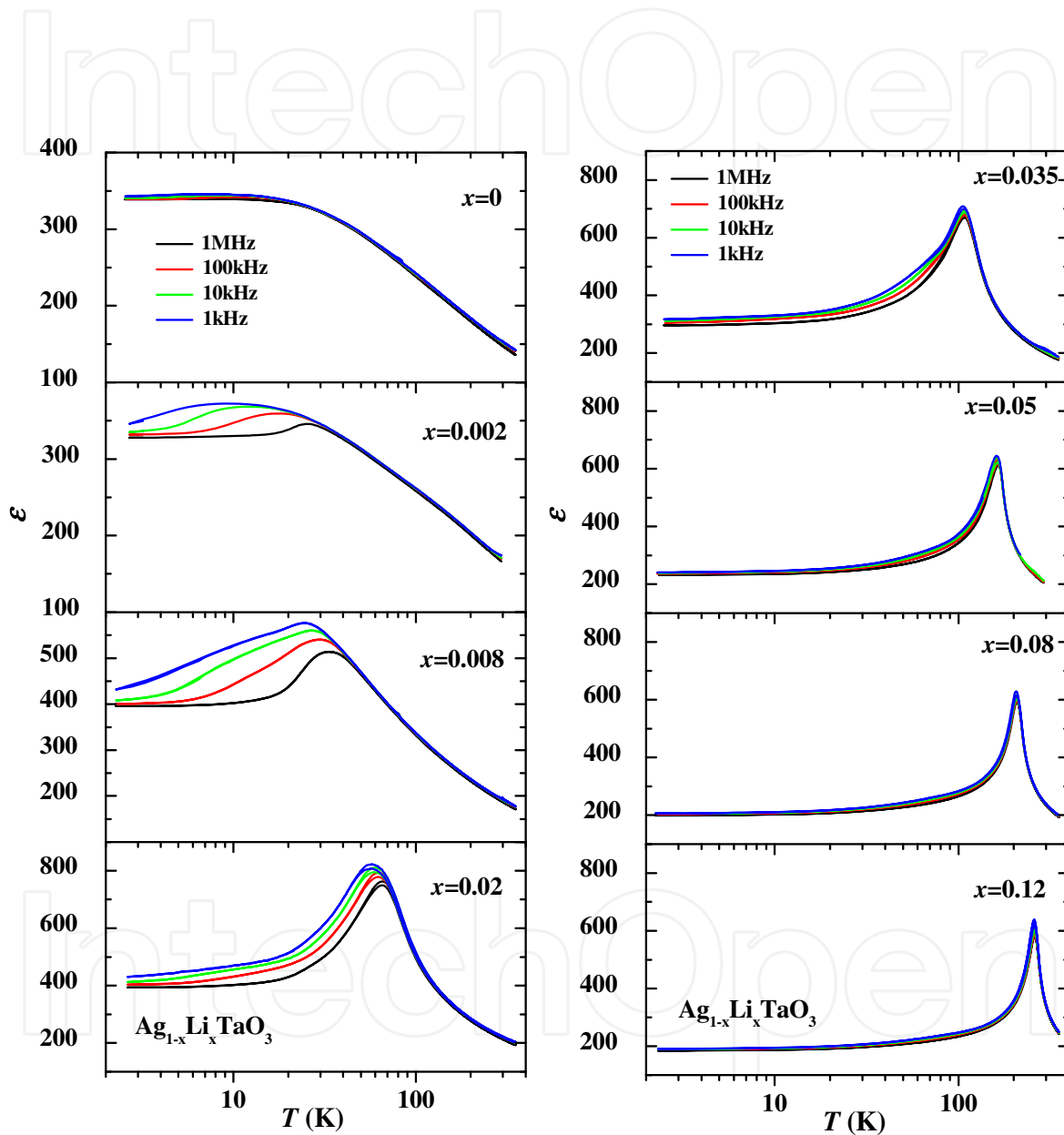


Fig. 27. Dielectric constant $\epsilon'(T)$ for $\text{Ag}_{1-x}\text{Li}_x\text{TaO}_3$ with $0 \leq x \leq 0.12$.

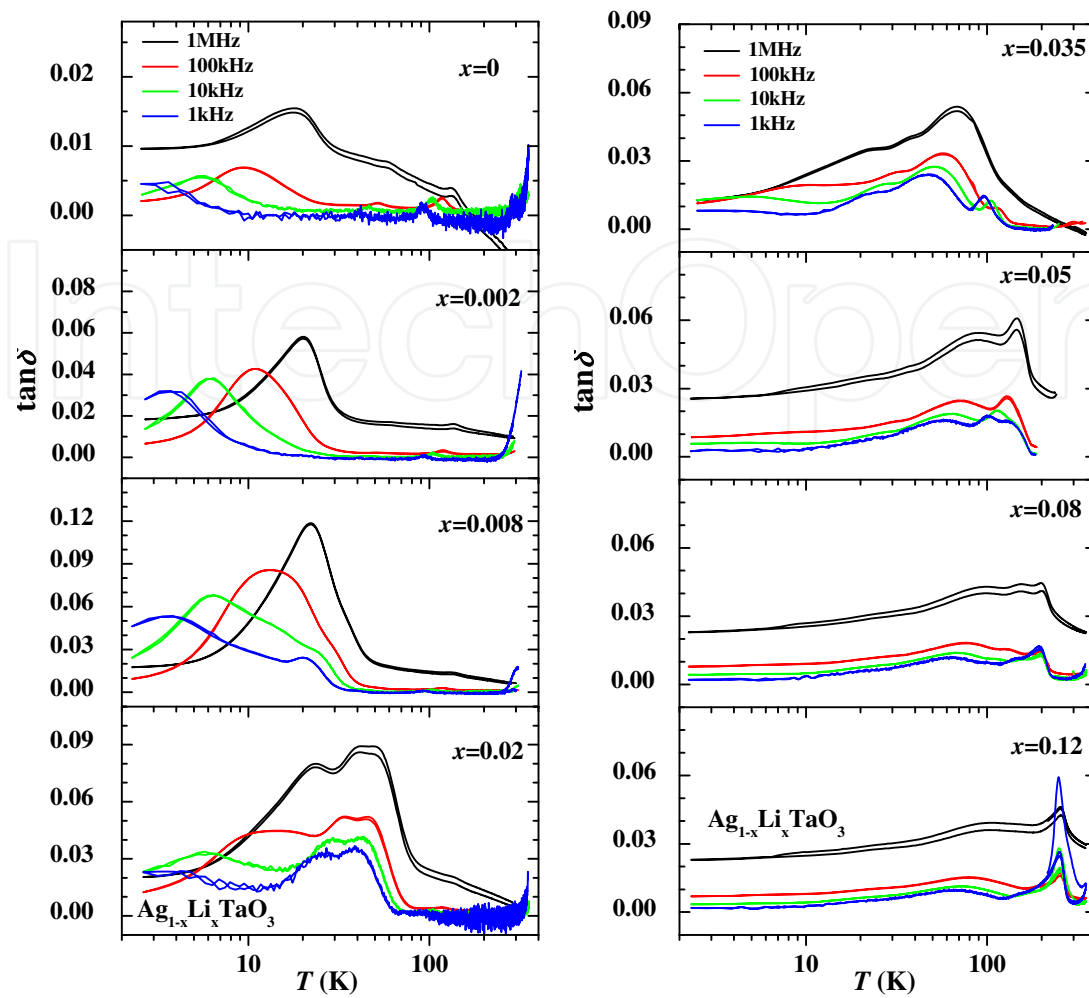


Fig. 28. Dielectric loss for $\text{Ag}_{1-x}\text{Li}_x\text{TaO}_3$ with $0 \leq x \leq 0.12$.

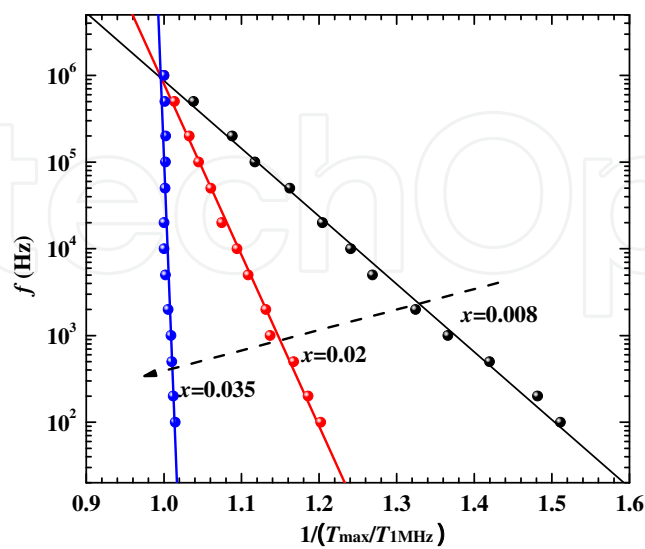


Fig. 29. Relationship between frequency and T_{max} in $\text{Ag}_{1-x}\text{Li}_x\text{TaO}_3$. T_{max} was normalized by the T_{max} of 1 MHz.

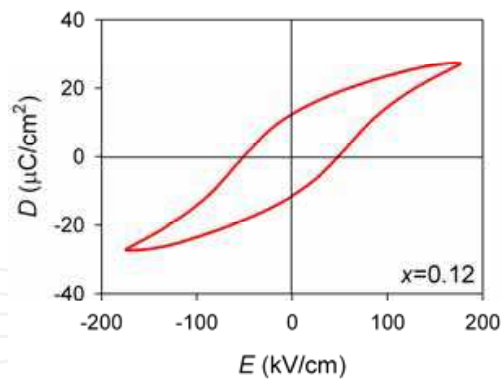


Fig. 30. Hysteretic D - E loop for $\text{Ag}_{1-x}\text{Li}_x\text{TaO}_3$ with $x=0.12$ obtained at 0.1 Hz and 77 K, indicating the ferroelectric state at $T < T_c$ ($=258$ K).

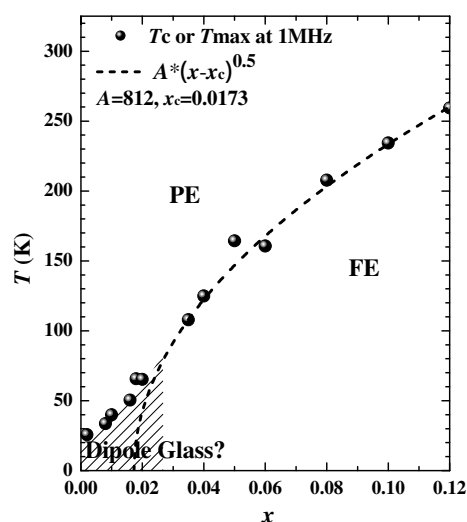


Fig. 31. Proposed phase diagram for $\text{Ag}_{1-x}\text{Li}_x\text{TaO}_3$. The dashed-dotted line shows the fitting to Morf-Schneider's relationship that is proposed for a quantum phase transition (Morf et al., 1977). PE and FE denote paraelectric and ferroelectric states, respectively. The gray zone may be a dipolar-glass state (Pirc & Blinc, 1999) or a state with nanosized ferroelectric domains (Fisch, 2003; Fu et al., 2009b).

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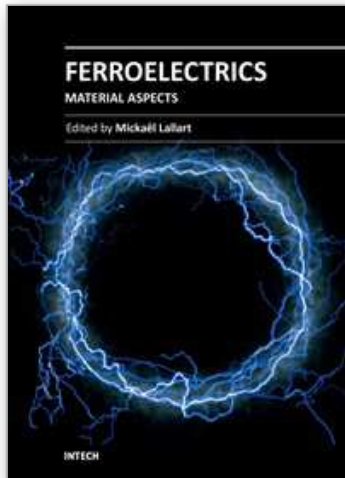
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Ferroelectrics - Material Aspects

Edited by Dr. Mickaél Lallart

ISBN 978-953-307-332-3

Hard cover, 518 pages

Publisher InTech

Published online 24, August, 2011

Published in print edition August, 2011

Ferroelectric materials have been and still are widely used in many applications, that have moved from sonar towards breakthrough technologies such as memories or optical devices. This book is a part of a four volume collection (covering material aspects, physical effects, characterization and modeling, and applications) and focuses on ways to obtain high-quality materials exhibiting large ferroelectric activity. The book covers the aspect of material synthesis and growth, doping and composites, lead-free devices, and thin film synthesis. The aim of this book is to provide an up-to-date review of recent scientific findings and recent advances in the field of ferroelectric materials, allowing a deep understanding of the material aspects of ferroelectricity.

How to reference

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Desheng Fu and Mitsuru Itoh (2011). Ferroelectricity in Silver Perovskite Oxides, *Ferroelectrics - Material Aspects*, Dr. Mickaél Lallart (Ed.), ISBN: 978-953-307-332-3, InTech, Available from:
<http://www.intechopen.com/books/ferroelectrics-material-aspects/ferroelectricity-in-silver-perovskite-oxides>

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Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
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Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

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