Preparation, Characterization, and Ferroelectric Properties of the Alkylamine-Intercalated Layered Perovskite-Type Oxides ($C_nH_{2n+1}NH_3-Sr_2Nb_3O_{10}$, $n = 1-6$)

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A series of alkylamine-intercalated layered perovskite-type oxides, $C_nH_{2n+1}NH_3-Sr_2Nb_3O_{10}$ ($n = 1-6$), were prepared through a stepwise exchange process. X-ray powder diffraction (XRD) patterns of the samples showed a gradual increase of the interlayer spacing from 4.3 to 18.0 Å and the formation of monolayer and bilayer structures of alkyl chains between the perovskite layers. Infrared spectra (IR) and Raman spectra of the samples revealed the strong impact of the intercalated ions on the lattice of the perovskite layer. Ferroelectric hysteresis loops were observed in these oxides. In particular, the fatigue property was measured on the sample $CH_3(CH_2)_4NH_3-Sr_2Nb_3O_{10}$ (donated as ASNO5). It did not show fatigue after 10^{11} switching circles. This series of oxides may make up a new group of materials with good fatigue-free ferroelectricity. Furthermore, controllability of the interlayer height provides a useful mechanism for studying the interaction (e.g., ferroelectric coupling) between the ferroelectric layers.

Introduction

In recent years, ferroelectric oxides have been widely investigated in the manufacture of nonvolatile memories with high-speed access and unlimited endurance.[1−3] Fatigue property is one limit of these oxides and great efforts have been made to improve the performance of ferroelectric materials.[4−7] Since the fatigue-free ferroelectric property of the layered perovskite-type oxides $SrBi_2Ta_2O_9$ (denoted as SBT), $SrBi_2NbTaO_9$, and $SrBi_4Ta_4O_{15}$ was reported,[5] these kinds of oxides have attracted considerable attention.[8,9]

These oxides consist of perovskite “building blocks” of TaO_6, NbO_6, or TiO_6 octahedra, separated at intervals by bismuth oxide planes. We think that the ferroelectricity comes from the layers of perovskite-type oxides and the fatigue-free property is mainly attributed to the bismuth oxide layers. Bismuth oxide may minimize the interlayer stress upon polarization.[10] Considering the flexibility of the alkylammonium ions, it is hopeful to synthesize a new kind of layered ferroelectric oxide with good fatigue-free property if we can exchange the interlayer bismuth oxides with alkylamine. Using $KSr_2Nb_3O_{10}$ as a precursor, we once prepared a layered perovskite-type oxide intercalated with methylamine. This oxide has a structure like SBT and the cations between the perovskite layers are methylammonium ions. As we expected, it showed a clear ferroelectric hysteresis loop.[3] Here, we describe the results of the preparation, characterization, and ferroelectric properties of the alkylamine-intercalated layered perovskite-type oxides ($C_nH_{2n+1}NH_3-Sr_2Nb_3O_{10}$, $n = 1-6$) with different alkyl chain lengths.

Experimental Section

$KSr_2Nb_3O_{10}$ (denoted as KSNO) was first synthesized from K_2CO_3, $SrCO_3$, and Nb_2O_5 (molar ratio 0.65:1:1.5) at 1400 °C in air for 3 h. Then, KSNO was exchanged with 6 mol/L HNO_3 at 180 °C for 24 h, to give $HSr_2Nb_3O_{10}$ (denoted as HSNO). The alkylamine-intercalated layered perovskite-type oxides with different interlayer heights were obtained by the reaction of HSNO and the corresponding *n*-alkylamine. Here, a hydrothermal method was adopted and the details were listed in Table 1. According to the chain length of the used *n*-alkylamine, the as-prepared samples, $C_nH_{2n+1}NH_3-Sr_2Nb_3O_{10}$ ($n = 1-6$), were denoted as ASNO1, ASNO2, ASNO3, ASNO4, ASNO5, and ASNO6, respectively, from $n = 1$ to $n = 6$.

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Table 1. Synthesis Conditions of the Alkylamine-Intercalated Layered Perovskite-Type Oxides ($C_nH_{2n+1}NH_3-Sr_2Nb_3O_{10}$, $n = 1-6$)

samples	solvent	reaction temp. (°C)	reaction time (h)
ASNO1	30% CH_3NH_2 in water	60	24
ASNO2	65% $CH_3CH_2NH_2$ in water	120	48
ASNO3	50% $CH_3(CH_2)_2NH_2$ in ethanol	120	48
ASNO4	50% $CH_3(CH_2)_3NH_2$ in ethanol	120	72
ASNO5	50% $CH_3(CH_2)_4NH_2$ in ethanol	120	48
ASNO6	50% $CH_3(CH_2)_5NH_2$ in ethanol	100	48

X-ray powder diffraction patterns were taken on a Shimadzu XD-3A X-ray diffractometer operated with Cu Kα radiation and a Ni filter. The C, H, and N elemental analysis results were obtained using a Perkin−Elmer 240C elemental analyzer. IR and Raman spectra were attained at room temperature with the help of a Nicolet 510P FT-IR and a Bruker RFS-100 spectrometer, respectively.

The measurements of the electric hysteresis loops and fatigue property were carried out on a RT6000HVS (High Voltage Test System, Radiant Technolgies Inc.). The pulverous samples were first pressed into wafers with a 0.5-in. diameter die under ~200 MPa, and then silver vapor was deposited onto both sides of the wafers through the vacuum coating method. Because the samples absorbed moisture, causing the leaking current, we compensated for it using the leaking-current-compensation function of the instrument.

Results and Discussion

The structure of the layered perovskite-type oxide $KSr_2Nb_3O_{10}$ ($K^+(Sr_2Nb_3O_{10})^-$) is illustrated in Figure 1. It consists of three slabs of the perovskite-type layers ($Sr_2Nb_3O_{10}^-$), separated by one layer of K^+ ions, similar to SBT. In the perovskite layer, Sr^{2+} ions locate in the A site and Nb^{5+} ions locate in the B site. It is known that the bismuth atoms in SBT are very difficult to displace by any other atoms,[11] but the potassium ions in the KSNO are easy to be exchanged by H^+.

Figure 2 shows the XRD patterns of the as-synthesized samples. Upon intercalation, the characteristic peak of the (001) reflection shifted gradually toward a lower 2θ angle, indicating a gradually increased interlayer distance. The d values of the (001) reflection peak of the alkylamine-intercalated oxides are listed in Table 2. Using the lattice parameters of $KSr_2Nb_3O_{10}$ ($a = 0.7816$ nm, $b = 0.7764$ nm, $c = 2.9995$ nm)[12] and the diameter (≈2.4 Å) of the interlayered K^+ ions, one can calculate out that the perovskite layer thickness of $Sr_2Nb_3O_{10}^-$ is 12.4 Å. By subtracting the thickness of the perovskite layer, we can get the net interlayer height and the results are also listed in Table 2. The interlayer heights of the five alkylamine-intercalated oxides (except ASNO1) are larger than the chain lengths of the corresponding alkylamine. This phenomenon can be explained by the formation of a bilayer of alkylammonium chains,[13,14] which made the interlayer height larger than the chain length. The alkyl chains of the alkylammonium ions usually tilt or overlap.[15] A representive structure of these oxides is shown in Figure 3b. Among the six alkyamine-intercalated oxides, ASNO1 is an exceptional one. Since the methylammonium ion has the smaller chain length than the other five, and its chain length is also smaller than the unit cell of KSNO, it can lie horizontally between the two perovskite layers[13] (refer to Figure 3a).

The substitution percentages of the six alkylamine-intercalated oxides were calculated based on the el-

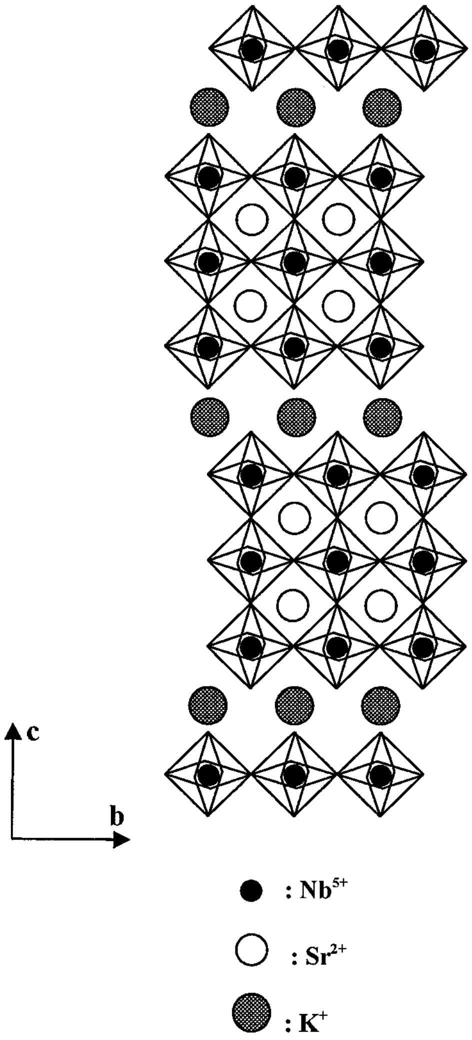

Figure 1. Schematic structure of $KSr_2Nb_3O_{10}$.

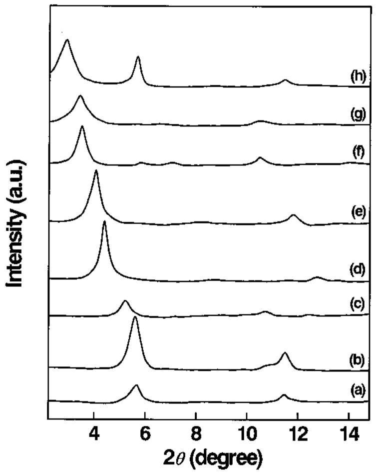

Figure 2. X-ray powder diffraction patterns of the as-synthesized samples: (a) KSNO; (b) HSNO; (c) ASNO1; (d) ASNO2; (e) ASNO3; (f) ASNO4; (g) ASNO5; (h) ASNO6.

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Table 2. Interlayer Heights and Substitution Percentages of the Alkylamine-Intercalated Layered Perovskite-Type Oxides ($C_nH_{2n+1}NH_3-Sr_2Nb_3O_{10}$, $n = 1-6$)

	ASNO1	ASNO2	ASNO3	ASNO4	ASNO5	ASNO6
d value of the (001) reflection (Å)	16.7	19.6	21.0	25.2	26.0	30.4
chain length of the intercalated alkylamine (Å)[15]	4.2	5.1	6.5	7.6	9.0	10.2
interlayer height (Å)	4.3	7.2	8.6	12.8	13.6	18.0
substitution percentage (%)	69%	52%	71%	64%	53%	49%

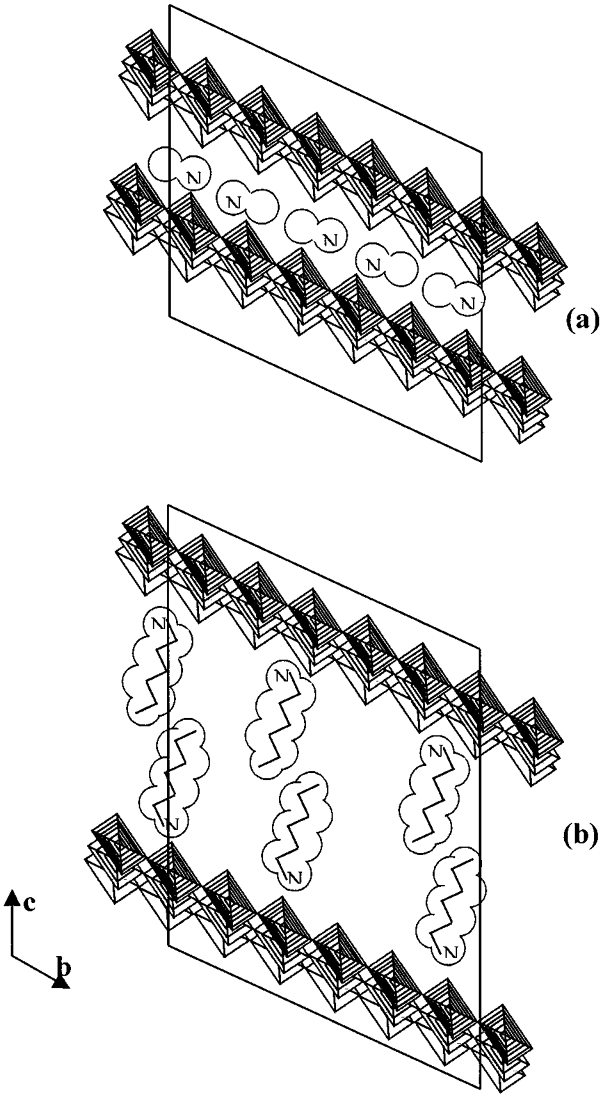

Figure 3. Two schematic representations of the structure of the interlayered alkylammonium ions: (a) monolayer configuration in ASNO1; (b) bilayer configuration in ASNO6.

emental analysis results of C, H, and N, and the results are listed in Table 2. Although the substitution percentages do not reach 100%, no precursor's peaks could be found in the XRD patterns of ASNO1, ASNO2, ASNO3, and ASNO5. This result suggested that the perovskite layers were fully propped up by alkylammonium ions in these samples. In sample ASNO4, there was a rather small remanent peak around 5.7° from the starting HSNO (Figure 2f), indicating that the intercalation was not complete. For sample ASNO6, it would be difficult to distinguish an impurity of the starting (unintercalated) material since the (002) peak for ASNO6 falls at the same position as the HSNO precursor (001) peak.

Raman spectra of KSNO, HSNO, and the six alkylamine-intercalated oxides are shown in Figure 4. The

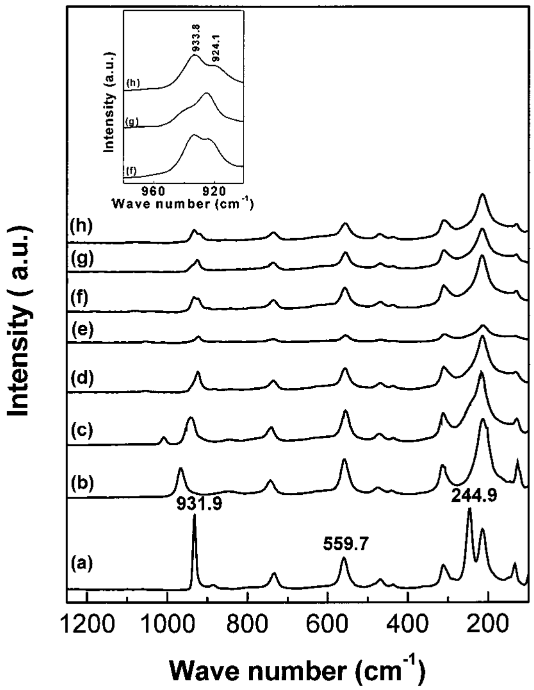

Figure 4. Raman spectra of the as-synthesized samples: (a) KSNO; (b) HSNO; (c) ASNO1; (d) ASNO2; (e) ASNO3; (f) ASNO4; (g) ASNO5; (h) ASNO6.

disappearance of the peak at 244.9 cm^{-1} in HSNO indicated the loss of K$^+$ ions after the ion exchange because the peaks in the frequency range of 100−300 cm^{-1} represent the transversal vibration of K$^+$, Nb^{5+}, and so forth.[16] The peak at 559.7 cm^{-1} showed a red shift after ion exchange. This shift could also be observed in IR spectra (see Figure 5). The peak at 931.9 cm^{-1}, which is pertaining to the lattice vibration of KSNO, underwent a 24-cm^{-1} blue shift after acid exchange. This shift revealed the strong impact of the H$^+$, which has a smaller radius and a stronger interaction with the perovskite layers than those of K$^+$.[3] In the alkylamine-intercalated samples, the layer outstretch that resulted from the alkylammonium interlayer may also lead to the blue shift. The peak at 931.9 cm^{-1} even split into two peaks, 933.8 and 924.1 cm^{-1}, in the samples ASNO4, ASNO5, and ASNO6. These splits suggested the strong impact of the interlayered alkylammonium ions on the perovskite layers. The lattice of the perovskite layers was distorted while the layers were propped up by the alkylammonium ions. When the alkylammonium ion has a long alkyl chain, as in the case of ASNO4, ASNO5, and ASNO6, the alternated two layers were separated to such a long distance that the peak split at 931.9 cm^{-1}.

This strong impact could also be observed in the IR spectra, shown in Figure 5. After intercalation, the peak

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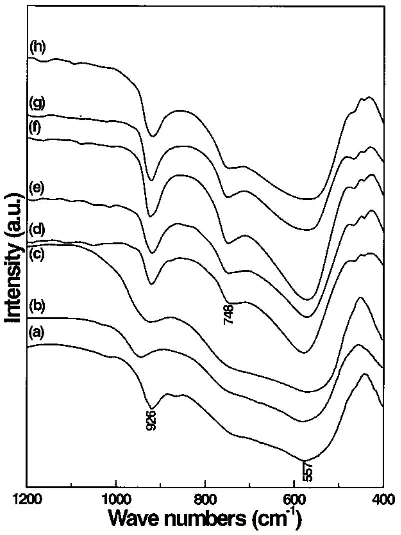

Figure 5. IR spectra of the as-synthesized samples: (a) KSNO; (b) HSNO; (c) ASNO1; (d) ASNO2; (e) ASNO3; (f) ASNO4; (g) ASNO5; (h) ASNO6.

at 926 cm^{-1} showed a blue shift and the peak at 557 cm^{-1} a red shift. Particularly, the peak at 926 cm^{-1} in KSNO underwent a 12-cm^{-1} blue shift after acid exchange. These features are similar to those of the Raman spectra. And along with the increase of the alkyl chain length, a new peak appeared at about 748 cm^{-1}. All these characters showed in Raman and IR spectra suggested the lattice distortion of the perovskite layer, which could then break up the superposition of the positive center and negative center, and finally induced the ferroelectricity.

It is also worthwhile to note that, in ASNO1, a peak appeared at around 1025 cm^{-1} (Figure 4c), and this peak was not present in the other five intercalated samples. This may be related to the special monolayer structure of the interlayered methylammonium ions in ASNO1, while the other five samples had a bilayer structure of the interlayered alkylammonium ions.

Ferroelectric switchings of the alkylamine-intercalated samples were typically measured from hysteresis loops such as those shown in Figure 6. The profiles of the hysteresis loops are rough and the charges of the samples are very low, ranging from 0.003 to 0.2 $\mu C/cm^2$. The low charges may be due to the property of the sample wafers, which were fabricated from the loose combination of nonoriented small crystals. Then, it is reasonable to expect that the thin film of such material with a much more highly ordered structure will show a higher charge. As displayed by the loops, the charges decreased after reaching the max polarization, which should be attributed to the leakage current caused by the adsorbed moisture. Upon the application of a 20-V driving voltage, saturated polarization was still not be reached. Higher driving voltage will punch through the sample wafers. In sample ASNO3, we observed the double hysteresis loops, which are shown in Figure 6c. It does not seem likely to be caused by the heterophase of the sample because there was no such symptom in the XRD pattern, FT-IR, and Raman spectra. At present, we still cannot explain this phenomenon reasonably, but whether it is caused by the ferroelectric coupling of the perovskite oxide layers is worth further research.

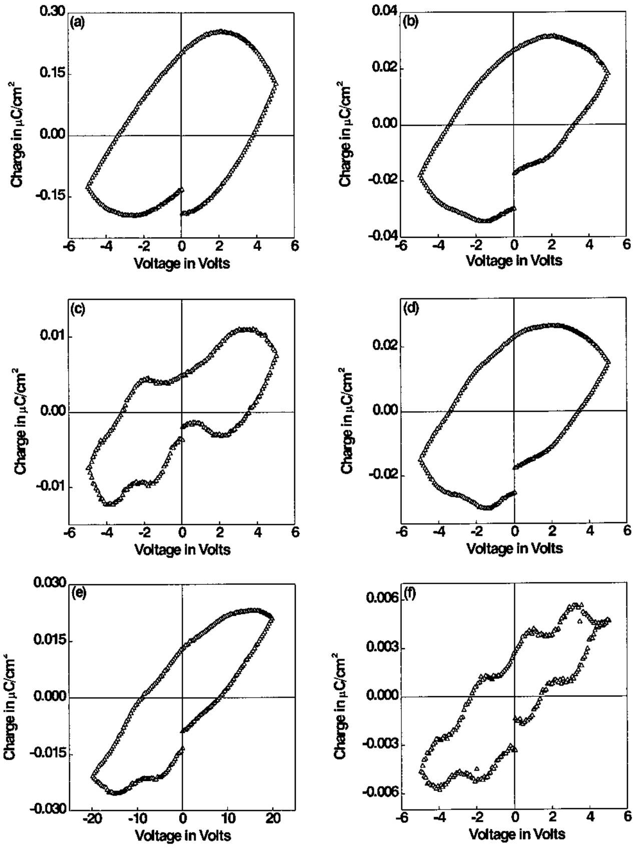

Figure 6. Ferroelectric hysteresis loops for sample wafers: (a) ASNO1, with thickness 0.93 mm, density 3.66 g/cm^3; (b) ASNO2, 0.81 mm, 3.20 g/cm^3; (c) ASNO3, 0.8 mm, 3.10 g/cm^3; (d) ASNO4, 0.84 mm, 3.01 g/cm^3; (e) ASNO5, 0.97 mm, 3.02 g/cm^3; (f) ASNO6, 0.95 mm, 2.88 g/cm^3.

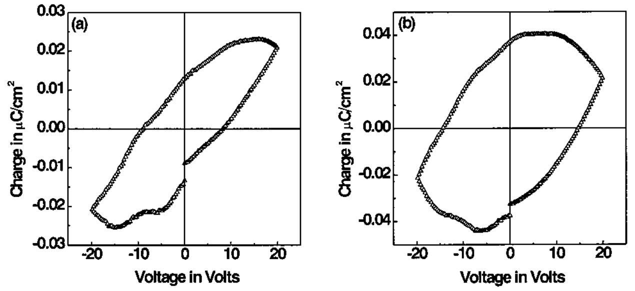

Figure 7. Ferroelectric hysteresis loops for sample ASNO5 before (a) and after (b) 10^{11} switching circles.

Fatigue property was measured on the sample ASNO5 as an example. The hysteresis curves, before and after switching, are illustrated in Figure 7, parts a and b, respectively. As we expected, our sample did not show fatigue after 10^{11} switching circles. And more, the profile of the heteresis loop became smoother after switching and the charge density showed a bit of an increase. Good fatigue-free property should come from the special structure of these alkylamine-intercalated layered oxides. It may compensate in some way for space-charge or oxygen gradients near the electrodes.[17,18] What caused the increase of the charge density is still

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unknown, but it is probably related to the absorbed moisture. Such powder samples have quite strong moisture-absorbing abilities.

Conclusions

From the studies discussed above, it is reasonable to think that the ferroelectric property of SBT comes from the perovskite layer and the fatigue-free property is related to the interlayered ions. The as-prepared layered perovskite-type oxides with the interlayered alkylammonium ions are a new kind of ferroelectric materials and have good fatigue-free property. This special fatigue-free property may be attributed to the layered structure with the flexible organic pillar. Further research on the synthesis of the thin film of these oxides is valuable and will show better results. Another striking property of this kind of alkylamine-intercalated layered perovskite-type oxides is the controllability of the interlayer height. It will be very useful in the studies of the interactions, like ferroelectric coupling, of the ferroelectric layers. Continuing research in this area is prospective and will reveal many exciting properties. Other perovskite-type oxides with a functional organic molecule interlayer can be synthesized using the same method. These materials may exhibit many attracting properties; for example, the novel optical response may be produced by the interaction between the perovskite layer with optical activity and the functional molecules.

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