The ferroelectricity of perovskite-type oxides with alkylamine interlayer

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The ferroelectricity of layer perovskite-type oxides intermittent with alkylamine, synthesized by hydrothermal method, has been reported. Ferroelectric hysteresis loops were observed in these newly synthesized powder crystals, which were pressed into wafers with platinum electrodes deposited by a pulsed laser. Element analysis shows 69% cations between two layers were exchanged into alkyl ammonium. X-ray powder diffraction pattern, infrared spectra, Raman spectra, and electron microscopy were used to characterize the samples. The results show that perovskite layer contributes to the ferroelectric property. So-synthesized samples may make up a new group of materials with potential use especially in the field of fatigue-free ferroelectricity. © 1999 American Institute of Physics.

In recent years, the studies of ferroelectric materials have attracted considerable attention worldwide in the manufacture of nonvolatile memories with high-speed access and unlimited endurance. But the use of these materials is limited by the fatigue property, and great efforts have been made to improve the performance of ferroelectric materials. Since the fatigue-free property of SrBi_2Ta_2O_9 (denoted as SBT), SrBi_2NbTaO_9 and SrBi_4Ta_4O_15, which exemplify a large family of layered perovskite oxides, was reported, this kind of oxide has become more and more important in new material field. The three oxides mentioned above have the structure that TaO_6 and NbO_6 octahedrons build up the perovskite layer with Sr_2^+ in the dodecahedral cavities and bismuth oxide plane is between the two layers. And it is not known about the bismuth atom to be displaced by any other atoms. We think that the ferroelectric property comes from the layers of perovskite-type oxides. The layer of bismuth oxide plays an important role in these compounds: e.g., bismuth oxide may minimize the interlayer stress upon polarization. Then, it is reasonable to think that the fatigue-free property of these materials has something to do with the structural flexibility of these compounds. Considering the exchangeability of the interlayer cations of many layer perovskites, we can prepare alkylamine sandwiched layer perovskite in a structure like SBT. Here we describe the results of the preparation and characterization of CH_3NH_3Sr_2Nb_3O_10 layer perovskite.

Since SBT can also be written as (Bi_2O_2)^{2+} (SrTa_2O_6)^{2-}, our scheme is to synthesize KSr_2Nb_3O_10 [K^+ (Sr_2Nb_3O_10)^-] with perovskite layer constructed by three NbO_6 octahedrons using a ceramic method, then exchange K^+ by H^+, and be followed by reaction with CH_3NH_3 to give CH_3NH_3Sr_2Nb_3O_10. KSr_2Nb_3O_10 (denoted as CR2) is first synthesized from K_2CO_3, SrCO_3 and Nb_2O_5 at 1400 °C for 3 h. HSr_2Nb_3O_10 (denoted as HR2) was obtained by reaction of CR2 with 6 mol l^{-1} HNO_3 at 180 °C for 24 h. Sample HMA2 (CH_3NH_3Sr_2Nb_3O_10) comes from the reaction between HR2 and methylamine at 60 °C for 24 h. Here, a hydrothermal synthesis method was adopted.

X-ray diffraction (XRD) measurements are carried out. The indexed patterns were shown in Fig. 1. In Fig. 1(a), the (001) peak of CR2, with d-value 15.5 Å, implies that CR2 should have a three-layered NbO_6 octahedron structure. It is coincident with the assumed chemical formula. After ion exchange, the d-value of HMA2’s (001) peak is increased to

![FIG. 1. X-ray powder diffraction patterns of the samples CR2 (a), HR2 (b), and HMA2 (c). The peaks have been indexed.](attachment:image.png)
16.7 Å. The result of x-ray fluorescence analysis indicates the content of K is sharply decreased upon hydrothermal exchange reaction. The exchangeability of potassium ion confirms, to some extent, the layered structure of the samples.

The transmission electron microscopy (TEM) photographs of CR2, HR2, and HMA2 were given in Figs. 2(a)–2(c). We can clearly observe the flake-like structure of these crystals, in agreement with the result of XRD. The HMA2 SEM photo, given in Fig. 2(d), shows the morphology of the sample wafers, which are composed of disordered small crystals and interspace. It is interesting to note that HMA2 exhibits a larger crystal size than CR2 and HR2, maybe the hydrothermal process is beneficial to crystal growth.

Element analysis of C, H, and N content in HMA2 shows that 69% interlayer protons of HR2 are combined with methylamine.

Raman and IR spectra of CR2, HR2, and HMA2 are shown in Figures 3 and 4, respectively. Because the peaks between frequency of 100 to 300 cm$^{-1}$ represent the transversal vibration of K$^+$, Nb$^{5+}$, etc., the disappearance of 244.9 cm$^{-1}$ peak in HR2 and HMA2 compared to CR2 indicates the loss of K$^+$ after ion exchange. In Raman spectra, the 931.9 cm$^{-1}$ peak pertaining to CR2 lattice vibration has a 24 cm$^{-1}$ blueshift after acid exchange, as also observed in IR spectra which shows the 12 cm$^{-1}$ blueshift of 926 cm$^{-1}$ peak from CR2 to HR2. This shift is attributed to the H$^+$, which has a smaller radius and a stronger interaction with perovskite-layers than K$^+$. In HMA2, the layer-outstretch resulted from the methylamine interlayer also leads to the blueshift. Both of these two effects can change the lattice electropositive center and electronegative center. If these changes distort the lattice and break up the superposition of positive center and negative center, ferroelectricity will be observed.

The pulverous samples were pressed into wafers under ~200 MPa to measure the ferroelectric properties. In order to increase the hardness of the wafers, a small amount of the poly(vinyl alcohol) was blended into the samples. Platinum
was deposited on two sides of the wafers by a pulsed laser as electrodes, and the measurements of electric hysteresis loops were carried out with RT6000HVS (High Voltage Test System, Radiant Technologies Inc.).

Ferroelectric switching is typically measured from hysteresis loops such as those shown in Fig. 5. These loops were obtained on samples HR2 and HMA2, albeit the profiles of the hysteresis loops are rough and the charges of both samples are very low. As displayed by the loops, the charges decrease after reaching the max polarization, which should be attributed to leakage current due to adsorbed damp and blended poly(vinyl alcohol). Upon the application of a 20 V drive voltage, saturated polarization was still not reached. Unfortunately, the composite wafers could not survive under higher electric-field strength (40 V), which broke down the samples. As to the low charges observed on the samples, it may be understood by taking into consideration that the sample wafers are 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.

It is noteworthy that ferroelectric hysteresis loop was not observed in the sample CR2. The fact also precludes the poly(vinyl alcohol)’s contribution to the ferroelectric switching.

From the abovementioned studies, we think that ferroelectricity property of SBTO comes from the perovskite layer and so-produced perovskite-type oxide intermittent with alkylamine is a kind of ferroelectric material. Further researches, like fatigue-free property and synthesis of thin film, to these kind oxides are valuable. Other perovskite-type oxides with functional organic molecule interlayer can be synthesized through the same method and will make up a large group of materials. These materials may exhibit many attracting properties: e.g., the interaction between the perovskite layer with optical activity and the functional molecules may produce novel optical response.

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