High-Pressure and -Temperature Synthesis and its XPS Study of $\text{La}_{1-x}\text{Na}_x\text{TiO}_3$

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Perovskite oxides of $\text{La}_{1-x}\text{Na}_x\text{TiO}_3$ ($x=0.05, 0.1-0.5$) were synthesized under high-pressure and -temperature. XRD analysis showed that sample is cubic for $x=0.05$ and pseudo-cubic for $0.1 \leq x \leq 0.5$. Cell volumes of samples with $0.1 \leq x \leq 0.5$ decrease as x increase, and the cell volume for $x=0.05$ is less than that for $x=0.1$. This implies that the deficiency of cation may exist in the samples. XPS and EPR measurements indicated that Ti ions were mixed valence of +3 and +4 and vacancy of A-site ions existed in samples. The valence state of Ti ions can be altered by high-pressure and -temperature.
[high-pressure and -temperature synthesis, phase transition, XPS, EPR, mixed valence]

1. Introduction

Perovskite oxide of RTiO_3 ($R=\text{rare earth}$) has been one of the subjects of recent studies[1-5]. The RTiO_3 compounds can be viewed as an distorted perovskite with orthorhombic structure (GdFeO_3 -type) where TiO_6 octahedron tilts alternatingly. A fairly stoichiometric compound of LaTiO_3 system is a Mott insulator and shows an insulating behavior accompanying the antiferro-magnetically spin-ordered phase below 140K[4,6,7]. Many studies about substitution by divalent ions (Ba^{2+} , Sr^{2+} and Ca^{2+}) for La^{3+} have been reported[8-13]. But the reports about substitution by monovalent alkali metal ions are less frequent than by divalent alkali-earth metal ions. Some studies about the paraelectricity, thermostability and ion conductivity of $\text{La}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ system have been carried out[14-17]. In Ref.[18], polycrystalline materials of $\text{La}_{1-x}\text{Na}_x\text{TiO}_3$ ($0 \leq x \leq 0.4$) were prepared by solid-state reaction under an Ar atmosphere by mixing stoichiometric amounts of LaTiO_3 and $\text{La}_{0.5}\text{Na}_{0.5}\text{TiO}_3$. LaTiO_3 was prepared by heating a stoichiometric mixture of La_2O_3 , Ti_2O_3 and TiO in an Ar atmosphere. $\text{La}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ was prepared by heating a mixture of La_2O_3 , TiO_2 and Na_2CO_3 . The products with $x \geq 0.1$ showed semiconductor to metal transitions as temperature decreased, and striking decreases of resistivity around 25K were observed. Because Ti^{4+} ions are stable, at ambient pressure the compounds $\text{La}_{1-x}\text{M}_x\text{TiO}_3$ ($M = \text{Ba}^{2+}, \text{Sr}^{2+}, \text{Ca}^{2+}, \text{K}^+$ and Na^+) using in previous work were synthesized under Ar atmosphere using TiO_2 , Ti_2O_3 and TiO as starting materials or under reducing atmosphere using TiO_2 . Different preparing methods by using different starting materials may give different results. From our experience, the valence state of ions may be altered by high-pressure and -temperature. So we synthesized the samples $\text{La}_{1-x}\text{Na}_x\text{TiO}_3$ under 2.8~4.0 GPa and at 930~1090°C by using La_2O_3 , NaHCO_3 and TiO_2 as starting materials. The structure of samples and valence states of cations were determined by XRD, XPS and EPR respectively.

2. Experimental

$\text{La}_{1-x}\text{Na}_x\text{TiO}_3$ oxides were prepared by mixing stoichiometric amounts of La_2O_3 , NaHCO_3 and TiO_2 . These starting compounds were thoroughly ground and then put into high pressure chamber (see Fig.1). The pressure was increased to

the expected value (2.8~4.0GPa). The temperature was then increased gradually to the expected value (930~1090°C). After being kept at high-pressure and -temperature for the expected value (30~50 min), the specimens were quenched to room temperature under high pressure, and finally the pressure was released.

Fig.1. Pressuring chamber.

1. Pyrophyllite 2. Molybdenum metal pellet 3. Graphite heater 4. h-BN tube 5. Sample 6. Pyrophyllite 7. steel cylinder

Powder X-ray diffraction data were collected at 25°C on a Rigaku 12kW copper rotating anode X-ray diffractometer with a graphite monochromator attachment. The XPS for powder sample were measured on an ESCALAB MKII X-ray photoelectron spectrometer with MgK_α radiation and the base pressure was 10^{-7}Pa . $\text{C1s}=284.6$ was used to correct the charge effect. The EPR for powder sample were measured on a BLUKER ER200D EPR spectrometer at room temperature with Microwave Frequency=9.77GHz, Microwave Power=6.5mW, Modulator Frequency=100KHz and Field Modulation intensity=0.32mT.

3. Results and discussion

The XRD patterns of the samples are shown in Fig. 2. The samples with $x = 0.05$ and 0.1 are single phase. The analysis

indicated that the sample with $x=0.05$ is identified to cubic structure and that with $0.1 \leq x \leq 0.5$ to pseudo-cubic, although small amount of an impurity phase (TiO_2) were detected. According to the nominal ratio of $\text{La}_{1-x}\text{Na}_x\text{TiO}_3$, the ratio of cation number is $(\text{La,Na})/\text{Ti} = 1$. When the amount of Na ions deflect the ratio, the amount of B-cation (Ti ion) may decrease in order to maintain the perovskite structure. The appearance of TiO_2 may be related with the loss of Na ions during synthesis. Thus, as the value of x increased, their crystal structures varied from cubic to pseudo-cubic. This variation is attributed to different ratio of La/Na and $\text{Ti}^{4+}/\text{Ti}^{3+}$. In Ref.[18], the sample is pseudo-cubic for $x=0.1$ and cubic for $0.2 \leq x \leq 0.4$. Different preparing methods and starting materials give different results. Some studies about sample with $x=0.5$ were reported, but gave different lattice structures. The sample is cubic in Ref.[14], tetragonal in Ref.[15] and pseudo-cubic in Ref.[16,17], but our results is the same as Ref.[16,17]. In our sample with $x=0.5$, weak diffraction peak such as $(1/3, 1/3, 1/3)$ (at about 38°) arising from the superlattice with double period of the primitive cell was observed. The distribution of La^{3+} and Na^+ is disordered. The superlattice diffraction peaks may be due to the tilt of oxygen octahedron. The lattice parameters were calculated for samples with $x \leq 0.5$. The relationship between cell volume and x is shown in Fig.3. The cell volume of pseudo-cubic phase decreased as x increases, but that for $x=0.05$ sample is smaller than that for $x=0.1$. From the formula of $\text{La}_{0.5}\text{Na}_{0.5}\text{TiO}_3$, La^{3+} and Na^+ in A-site are both 50% respectively, so the valence of Ti ions is +4. In order to maintain the electrical neutrality, there must be Ti^{3+} ions or vacancy of A-site ions for samples with $0.05 \leq x \leq 0.4$. From the results of XPS and EPR, both Ti^{3+} ions and vacancy of A-site ions exist in samples with $0.1 \leq x \leq 0.5$. The decrease of cell volume with x suggests that the effect of B-site substitution ($\text{Ti}^{3+}(0.067\text{nm})$ to $\text{Ti}^{4+}(0.0605\text{nm})$) is dominant over that of A-site substitution ($\text{La}^{3+}(0.136\text{nm})$ to $\text{Na}^+(0.139\text{nm})$). As only Ti^{3+} ions exist in sample with $x=0.05$ and no vacancy of A-site ions exist, as detected by EPR, its cell volume shows smaller value.

Fig.3. The change of cell volumes vers dopant x .

The binding energies of core levels are given in Table 1. It can be seen that the binding energies of $\text{La}3d_{5/2}$ are between 835.0eV and 835.6eV, which infers that La ions are in trivalent state.

Fig.2. XRD patterns of $\text{La}_{1-x}\text{Na}_x\text{TiO}_3$ samples.

Table 1. Binding energies of core level for $\text{La}_{1-x}\text{Na}_x\text{TiO}_3$

x	O1s	La3d _{5/2}	Na1s	Ti2p _{3/2}
0.05	530.3	835.6	1071.2	458.7
0.1	530.5	835.0	1071.5	458.1
0.2	530.9	835.1	1071.6	458.5
0.3	531.3	835.0	1071.6	458.4
0.4	531.8	835.3	1071.5	458.2
0.5	532.0	835.6	1072.2	458.4

The half height widths of $\text{Ti}2p_{3/2}$ of samples are given in Fig.4. The $\text{Ti}2p$ spectra for Ti_4O_7 and Ti_2O_3 were reported[19]. It is found that there is a shoulder at low binding energy (BE) apart from main peak about 1eV, which is thought $\text{Ti}^{3+}2p_{3/2}$. As the Ti^{3+} ions are easily oxidized to Ti^{4+} ions in air, the $\text{Ti}^{3+}2p_{3/2}$ peaks for our samples are not easily detected. However, the half height width of $2p_{3/2}$ photoelectron peak of Ti ions in mixed valence is wider than that of single Ti^{4+} ions owing to the different binding energy (BE) of $\text{Ti}^{3+}2p_{3/2}$ and $\text{Ti}^{4+}2p_{3/2}$. The measurements for core level of $\text{Ti}2p$ show that the half height widths of $\text{Ti}2p_{3/2}$ for the samples with $0.05 \leq x \leq 0.4$ are larger than that of TiO_2 (1.94eV) and for $x=0.5$ is almost same. This suggests that Ti ions may be in mixed valence for $x \neq 0.5$.

In order to investigate the valence state of Ti ions exactly, the EPR of samples was detected, as shown in Fig.5. Two strong signals for samples with $0.1 \leq x \leq 0.4$ at room temperature are observed. One is narrow, and the other is broad. Their g-values are 2.003 and 1.943 respectively. But only one broad signal with $g=1.943$ is observed for sample with $x=0.05$. The studies about BaTiO_3 and donored BaTiO_3 showed two EPR signals with $g=2.00$ and 1.96 respectively[20, 21]. The signal with $g=2.00$ is resulted from

Fig.4. Core level spectra of Ti2p.
(the data in parenthesis are half height width of Ti2p_{3/2})

vacancy of barium, and the signal with $g=1.96$ is related with Ti^{3+} ions. So for our samples, the signal with $g=2.003$ is related with the vacancy of A-cation and the signal with $g=1.943$ is related with Ti^{3+} ions. The existence of Ti^{3+} ions shows that the valence state of Ti^{4+} ions can be altered by high-pressure and -temperature.

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Fig.5. EPR patterns of $La_{1-x}Na_xTiO_3$ samples.

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