

Structure characteristics and valence state study for $\text{La}_{1-x}\text{K}_x\text{TiO}_3$ synthesized under high-pressure and high-temperature

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Abstract

By using a high-pressure and high-temperature method, perovskite oxides of the type $\text{La}_{1-x}\text{K}_x\text{TiO}_3$ ($x = 0.30, 0.35, 0.40, 0.45, 0.50$) with mixed valence state were synthesized. This new synthesis route has several advantages. XRD analysis shows a cubic cell for the samples. XPS of the surface and EPR measurements indicate that the Ti ions have a mixed valence of 3+ and 4+ and that A-cation vacancies exist in the samples. As x increases, the amount of Ti^{3+} ions and A-cation vacancies decreases. The valence state of the Ti ions can be altered by changing both pressure and temperature.

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1. Introduction

Due to their many interesting properties, perovskite oxides, RTiO_3 compounds ($R = \text{rare earth}$), have attracted many researchers recently [1,2]. RTiO_3 compounds can be viewed as distorted perovskites with orthorhombic structure (GdFeO_3 -type). Stoichiometric LaTiO_3 is a typical Mott insulator at room temperature. Substitution of La^{3+} by divalent ions (Ba^{2+} , Sr^{2+}) results in rich structural characteristics, transport and magnetic properties [3–6], whereas substitution by Na^+ , i.e., $\text{La}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ produces paraelectricity [7]. Polycrystalline materials of $\text{La}_{1-x}\text{K}_x\text{TiO}_3$ ($0 \leq x \leq 0.4$) were prepared by solid-state reaction in an Ar atmosphere by mixing $\text{La}_{0.5}\text{K}_{0.5}\text{TiO}_3$ and LaTiO_3 , both previously obtained by heating a mixture of La_2O_3 , K_2CO_3 , TiO , Ti_2O_3 , and TiO_2 in an Ar atmosphere. Semiconductor to metal transitions had been found in $\text{La}_{1-x}\text{K}_x\text{TiO}_3$ ($x \geq 0.1$) as the temperature decreased [8]. Because Ti^{4+} ions are considerably stable under

ambient condition, the synthesis of $\text{R}_{1-x}\text{M}_x\text{TiO}_3$ compounds ($R = \text{La, Nd, and Y}$; $M = \text{Ba}^{2+}, \text{Sr}^{2+}, \text{Ca}^{2+}, \text{K}^+, \text{and Na}^+$) required a reducing H_2 atmosphere when using TiO_2 as starting material or an inert Ar atmosphere when using Ti , TiO , Ti_2O_3 , and TiO_2 . It has been reported that the valence states can be altered under high-pressure and high-temperature [9,10]. In this paper, we use a new synthesis route. By using a high-pressure and high-temperature method, perovskite oxides of $\text{La}_{1-x}\text{K}_x\text{TiO}_3$ were synthesized under 4.0 GPa and at 980 °C by using TiO_2 as starting material. The structure and mixed valence characteristics of the samples were investigated by XRD, XPS, and EPR.

2. Experimental

The samples were prepared by mixing TiO_2 , La_2O_3 , and KHCO_3 according to the nominal ratio of $\text{La}_{1-x}\text{K}_x\text{TiO}_3$. The mixtures were thoroughly ground and placed into a high-pressure chamber (see Fig. 1). High-pressure and high-

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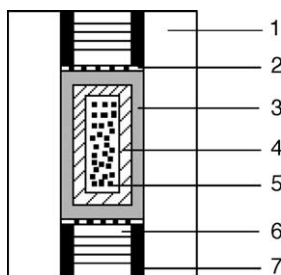


Fig. 1. High-pressure chamber: (1) pyrophyllite; (2) molybdenum metal pellet; (3) graphite heater; (4) sample; (5) hexagonal borazon (h-BN) tube; (6) pyrophyllite; (7) steel cylinder.

temperature synthesis was carried out using a belt-type high-pressure apparatus. The magnitude of the pressure generated inside the cell was calibrated by the electrical resistance change related to the phase transformation of Bi, Tl, and Ba (2.55, 2.69, and 7.7 GPa). The samples were heated electrically through a graphite heater, and the temperature was measured by inserting a Pt30% Rh–Pt6% Rh thermocouple into the cell. The high-pressure and high-temperature synthesis procedure is aimed to increase the pressure to 4.0 GPa, then increase the temperature to 980 °C. After being kept under high-pressure and high-temperature for 30 min, the samples were quenched to room temperature under high-pressure, and finally the pressure was released.

Powder X-ray diffraction (XRD) data were collected at room temperature on a Rigaku 12 kW copper rotating anode X-ray diffractometer. The XRD data for index and cell parameter calculations were collected by a scanning mode with a step interval of 0.02° and a preset time of 4 s per step with silicon used as an internal standard. X-ray photoelectron spectroscopy (XPS) for the powder samples were measured on an ESCALAB MKII X-ray photoelectron spectrometer with Mg K α radiation and the base pressure was 10⁻⁷ Pa. C1s = 284.6 eV was used to correct the charge effect. Electron Paramagnetic Resonance (EPR) for the powder samples were measured on a BRUKER ER200D EPR spectrometer at room temperature with 9.79 GHz microwave frequency, 6.5 mW microwave power, 100 kHz modulator frequency, 0.32 mT field modulation intensity, 0.348 T middle range and 0.6 T scan range. During the measurements, both the amount (10⁻³ mol) and measurement conditions were kept the same for all the samples.

3. Results and discussion

Fig. 2 shows the X-ray diffraction patterns of La_{1-x}K_xTiO₃. The $x = 0.50$ sample is single phase and belongs to the cubic perovskite structure, however, for other samples, trace of La₂O₃ exist as impurity, though the main phase still keep the cubic symmetry. A structural study on double perovskite oxide (AA')(BB')O₃ [11] showed that an ordered distribution of A and A' or B and B' cations produced a relatively strong superstructure peak (1/2 1/2 1/2) around

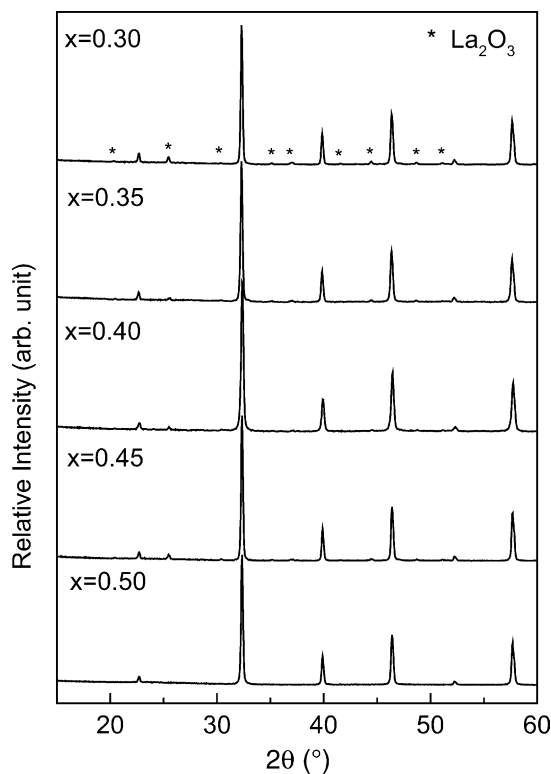


Fig. 2. XRD patterns of La_{1-x}K_xTiO₃ samples ($x = 0.30$ – 0.50).

19°. In our samples, the absence of this peak suggests that La³⁺ and K⁺ ions are disorderly distributed at the A-site. In Ref. [8], the $x = 0.30$ sample belongs to the pseudo-cubic perovskite structure and an impurity phase (La₂Ti₂O_{7- δ}) was detected. It is clear that the different preparation routes by using different starting materials may produce materials with different microstructure characteristics. In Ref. [8], the loss of K was due to the volatilization during the reactions. In this paper, it is reasonable that the loss of K is lower under much higher pressure and lower temperature. The loss of K and the observed excess of La₂O₃ lead to A-cation vacancies. In La_{0.5}K_{0.5}Ti(IV)O₃, La³⁺ and K⁺ ions have their respective 50% occupancy at A-site. The average charge of the A-site in La_{1-x}K_xTiO₃ increases as x decreases. In order to maintain electrical neutrality, reduction of Ti(IV) to Ti(III) is necessary or A-cation vacancies must be produced. These two factors have an important influence on the cell volume. The following analysis of XPS and EPR shows that both Ti(III) ions and A-cation vacancies exist in all samples. As x increases, the cell volume was almost the same for all samples, which is different from Ref. [8]. Four factors should be considered. As x increases, A-site substitution of La³⁺ (0.136 nm) by K⁺ (0.164 nm) increases the cell volume, B-site substitution of Ti³⁺ (0.067 nm) by Ti⁴⁺ (0.0605 nm) decreases the cell volume. A-cation vacancies increase the cell volume. As x increases, the decreasing number of A-cation vacancies increases the cell volume. High-pressure also affects the cell volume.

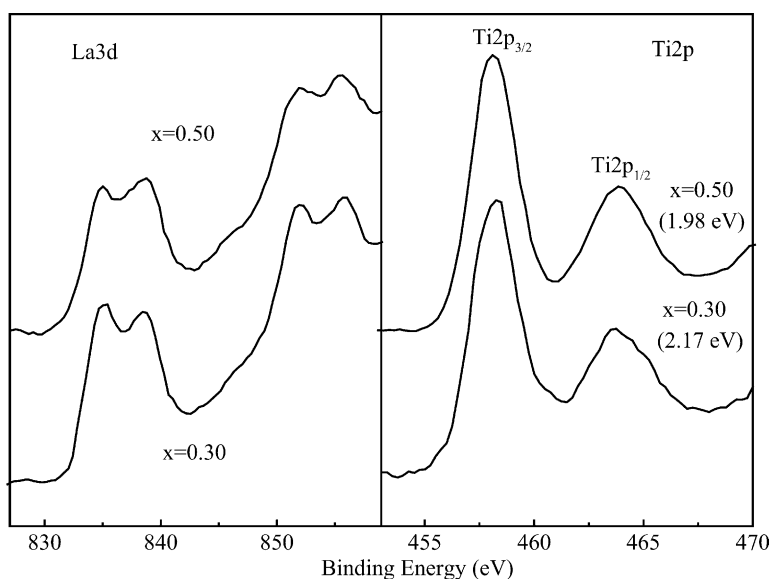


Fig. 3. Core level spectra of La3d and Ti2p. The data in brackets are half height width of Ti2p_{3/2}.

The surface characteristics of the samples were studied by XPS. XPS spectra recorded at room temperature are shown in Fig. 3. The binding energies of core levels are listed in Table 1. It can be seen that the binding energies of La3d_{5/2} are between 835.0 and 835.5 eV, suggesting the appearance of La³⁺. The satellite peak appearing at the higher binding energy side of the La3d_{5/2} level is approximately 3.9 eV away from the main peak. The electronic structures of LaBO₃ (B = Ti, Cr, Mn, Fe, and Co) had been investigated using XPS [12]. In the La3d spectra of LaBO₃, the satellite peaks observed on the high binding energy side of the main peak higher by about 4 eV were interpreted in terms of the excitation of an electron from the anion valence band into the La4f band. From these results, it is considered that the presence of satellite of the La3d peak in our samples is due to the monopole excitation arising from a sudden change in the screening of the valence electrons upon the removal of a core electron.

The half height widths of Ti2p_{3/2} of the samples are given in Table 1 and Fig. 3. Rao and Sarma [13] studied the Ti2p spectra for Ti₄O₇ and Ti₃O₅. It was found that there was a small shoulder at the low binding energy side apart from the main peak about 1 eV lower, which is thought to be Ti³⁺2p_{3/2}. As the Ti³⁺ ions are easily oxidized to Ti⁴⁺ ions in air and the effective electron escape depth is not more than 5 nm in

the process of X-ray photoelectron emission, i.e., only the surface of the samples is detected, the Ti³⁺2p_{3/2} peaks for our samples are not easily detected. However, because the positions of Ti³⁺ and Ti⁴⁺ ions are different, if Ti ions are in a mixed valence state, the half height width of the Ti ions in the mixed valence state is wider than that of single Ti⁴⁺ ions. The measurements for the core level of Ti2p show that the half height widths of Ti2p_{3/2} for the samples with 0.30 ≤ x ≤ 0.45 are larger than that of TiO₂ (1.94 eV). Furthermore, the half height widths of Ti2p_{3/2} for the samples decreases with increasing of x. This suggests that Ti ions on the surface of the samples with 0.30 ≤ x ≤ 0.45 are in a mixed valence.

The electronic configurations of Ti⁴⁺ and Ti³⁺ ions in the ground state are 3d⁰ and 3d¹, respectively. There is no EPR signal for Ti⁴⁺ ions. If Ti³⁺ ions are in an absolutely symmetric cubic crystal field, there is no EPR signal. If Ti³⁺ ions are in a slightly asymmetric cubic crystal field, there should be an EPR signal. From the results of XRD, though the samples belong to cubic structures, La³⁺ and K⁺ ions are disorderly distributed at the A-site forming the positive electronic center around La³⁺ and the negative electronic center around K⁺, which lead to a distortion of lattice at a very small scale. Hence, the Ti³⁺ ions are in slightly asymmetric cubic crystal field and EPR signal should be observed. So Ti(III) having one unpaired electron can be distinguished from Ti(IV) by EPR. The EPR spectra of the samples with 0.30 ≤ x ≤ 0.50 detected at room temperature are shown in Fig. 4. Two strong signals are observed in the range 0.048–0.648 T. The g-factors of the narrow and broad signals are 2.001 and 1.941, respectively. Both signals are symmetric. Studies on BaTiO₃ and donor BaTiO₃ showed two EPR signals with g = 2.00 and 1.96, respectively [14]. The signal with g = 2.00 resulted from barium vacancies and the signal with g = 1.96 was due to the Ti(III) ions. For our samples, the signal with g = 2.001

Table 1
Binding energies of core level for La_{1-x}K_xTiO₃ (eV)

x	O1s	La3d _{5/2}	K2p _{3/2}	Ti2p _{3/2} ^a
0.30	531.0	835.0	293.1	458.4 (2.17)
0.35	531.1	835.1	293.3	458.2 (2.16)
0.40	531.4	835.3	293.2	458.2 (2.14)
0.45	531.6	835.3	293.5	458.2 (2.12)
0.50	531.9	835.5	293.4	458.4 (1.98)

^a The data in parenthesis are half height width of Ti2p_{3/2}.

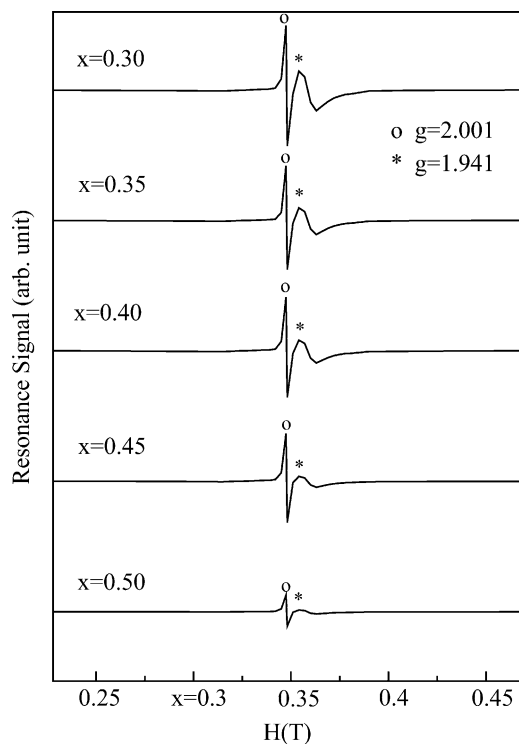


Fig. 4. EPR spectra of $\text{La}_{1-x}\text{K}_x\text{TiO}_3$ samples ($x = 0.30\text{--}0.50$).

is ascribed to A-cation vacancies, whereas the signal with $g = 1.941$ to the Ti(III) ions. A-cation vacancies are due to the loss of K^+ and La^{3+} ions. The existence of Ti^{3+} ions shows that the valence state of Ti^{4+} ions can be altered by changing both pressure and temperature.

The relationship between the relative EPR signal intensity and x is shown in Fig. 5a and b. The relative signal intensity of $g = 1.941$ decreases with the increasing of x , indicating that the number of Ti(III) ions in $\text{La}_{1-x}\text{K}_x\text{TiO}_3$ decreases with the decreasing of the average effective charge of A-site cations. The same change of the $g = 2.001$ signal intensity with increasing of x indicates that the amount of A-cations vacancies decreases with increasing of x .

The high-pressure and high-temperature synthesis method has several advantages: (1) owing to the effect of airtight sealing, high-pressure and high-temperature can provide a reducing condition, which is equivalent to the use of a reducing agent and inert gas. This causes the reduction of Ti^{4+} to Ti^{3+} ions. (2) High-pressure can densify the starting materials, increase the cross-section of the reaction, accelerate the diffusion between the reaction materials powders and decrease the reaction activation energy. It means that it can accelerate the reaction rate, shorten the synthesis time and decrease the synthesis temperature. In comparison with the other preparation method in Ref. [8], temperature is lower and time is shorter in the present case. (3) The $\text{La}_{1-x}\text{K}_x\text{TiO}_3$ perovskite oxides ($x = 0.30\text{--}0.45$) can be synthesized under high-pressure and high-temperature. However, they cannot be synthesized by a solid state reaction method in air

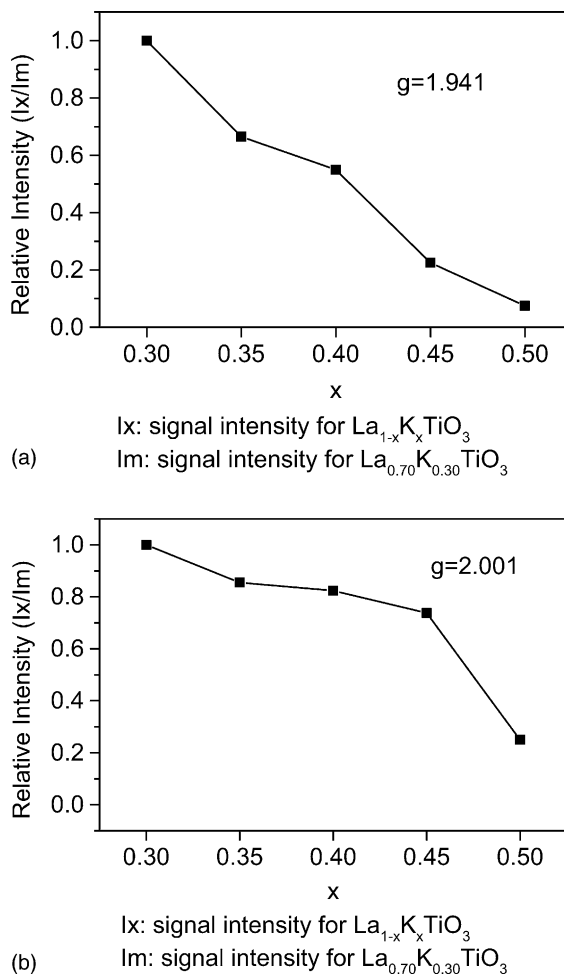


Fig. 5. (a) Relative intensity of $g = 1.941$ EPR signal vs. dopant x . (b) Relative intensity of $g = 2.001$ EPR signal vs. dopant x .

at temperature below $1300\text{ }^\circ\text{C}$ (no higher temperatures were investigated).

4. Conclusions

From the above discussion, it can be concluded that high-pressure and high-temperature has an important influence on crystal symmetry and valence state of Ti ions. Therefore, the high-pressure and high-temperature synthesis method is very effective in synthesizing perovskite oxides of mixed valence, especially those containing Ti^{3+} ions. It is expected that the $\text{La}_{1-x}\text{K}_x\text{TiO}_3$ perovskite oxides with mixed valence state induced by high-pressure and high-temperature might have some interesting properties, which are to be studied.

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