Low temperature synthesis of ATiO₃ (A: Mg, Ca, Sr, Ba) by using molten salt

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Alkaline earth metal titanates ATiO₃ (A: Mg, Ca, Sr, Ba) were prepared from two types of layered potassium titanates [K₂Ti₂O₅ and K₀.₆Ti₁.₈₅O₄ (hereafter, Lss)] by using alkaline earth metal molten salts [ACl₂ + A(NO₃)₂ (1:1)]. For A = Ca a single phase of perovskite-type compound was prepared at 600°C by using both starting compounds and the reaction temperature was lower than in 400°C that of the solid state reaction with TiO₂ (anatase) and CaCO₃. A single phase of perovskite-type SrTiO₃ was obtained at 600 and 700°C for K₂Ti₂O₅ and Lss, respectively and these temperatures were much lower than that (1200°C) of the phase of ilmenite-type MgTiO₃, it was prepared by the solid state reaction with TiO₂ (anatase) and magnesium basic carbonate at 1300°C. A single phase of perovskite-type BaTiO₃ was prepared at 600°C by using both starting compounds and also this temperature was much lower than that (above 1300°C) of the solid state reaction with TiO₂ (anatase) and BaCO₃. Although neither K₂Ti₂O₅ nor Lss could produce a single phase of ilmenite-type MgTiO₃, it was prepared by the solid state reaction with TiO₂ (anatase) and magnesium basic carbonate at 900°C. A single phase of ilmenite-type CdTiO₃ was prepared from K₂Ti₂O₅ by using cadmium molten salts [CdCl₂ + Cd(NO₃)₂ (1:1)] at 500°C. By taking account of the fact that ilmenite-type MgTiO₃ was prepared by the solid state reaction with TiO₂ (anatase) and magnesium basic carbonate at 900°C, we attempted lower temperature synthesis of alkaline earth metal titanates with molten salts preferred to crystallize perovskite-type titanates at lower temperature rather than ilmenite-type ones.

Key-words : Alkaline earth metal titanates, Molten salt, Layered potassium titanate

1. Introduction

Alkaline earth metal titanates ATiO₃ (A: Mg, Ca, Sr, Ba) are important materials for electric devices, superconductivity, photocatalysis, superoxide decomposition of peroxide precursors, chemical co-precipitation, mecanochemical complexion route, chemical vapor deposition and sol-gel method. For the perovskite-type alkaline earth metal titanates there have been a numerous papers of chemical synthesis process, and particularly preparation of BaTiO₃ fine particles which are applied to multilayer capacitors (MLCs) has been investigated extensively. Powder sample of BaTiO₃ is easily prepared by high temperature solid state reaction and hydrothermal reaction. Various synthesis routes at low temperatures for BaTiO₃ as a starting compound have been proposed; mechanochemical reaction at room temperature, hydrothermal reaction assisted with ball milling process, soft chemical reaction with titane nanosheets, solvothermal reaction for nano-sized particle and two-steps thermal decomposition of barium titanate oxide, BaTiO₃(C₂O₄)₂·4H₂O. These methods adopted high reactivity routes or more reactive starting materials in order to accomplish crystallization of BaTiO₃ at low temperature. Recently, we reported lower temperature synthesis of BaTiO₃ powder by using a reactive starting compound in molten salt. A layered K₂Ti₂O₅ was selected as a starting compound because the arrangement of Ti atoms in K₂Ti₂O₅ is similar to that of the perovskite-type structure and mixed barium salts [BaCl₂ + Ba(NO₃)₂ (1:1)] was used because of the lower melting point. In this case the use of perovskite-type structure, we attempted low temperature synthesis of alkaline earth metal titanates ATiO₃ (A: Mg, Ca, Sr, Ba) from two types of layered potassium titanates, K₂Ti₂O₅ and K₀.₆Ti₁.₈₅O₄ with the lepictoclose-type structure by using alkaline earth metal molten salts [ACl₂ + A(NO₃)₂ (1:1)]. In this paper we will describe synthesis of alkaline earth metal titanates ATiO₃ (A: Mg, Ca, Sr, Ba) by using molten salt and compared with high temperature solid state reaction with TiO₂ and alkaline earth metal carbonates.

2. Experimental

A starting compound, K₂Ti₂O₅ was prepared by heating the stoichiometric mixture of K₂CO₃ and anatase-type TiO₂ (ST-01, Ishihara Sanyo Co. ltd) at 700°C for 6 h. Another starting compound, K₀.₆Ti₁.₈₅O₄ with the lepictoclose-type structure was supplied from Ohtsuka Chemical Co. ltd and the commercial name was Terasesu Lss (hereafter, Lss). The mixture of K₂Ti₂O₅ (1g), AlCl₃·nH₂O and A(NO₃)₃·nH₂O with the molar ratio of 1:1:1 was put into an alumina crucible and heated at 400–700°C for 3 h. In the case of Lss the mixture of Lss (1g), AlCl₃·nH₂O and A(NO₃)₃·nH₂O with the molar ratio of 1:1:1 was put into an alumina crucible with H₂O (15 mL) and was treated with ultrasonic wave for 30 min. The alumina crucible was heated from 300°C to 700°C for 3 h by using a sonic wave for 30 min. The alumina crucible was heated from 300°C to 700°C for 3 h by using a sonic wave for 30 min. The alumina crucible was heated from 300°C to 700°C for 3 h by using a sonic wave for 30 min.

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The products from two types of starting compounds were washed with distilled water in order to dissolve the potassium and alkaline earth metal salts, and separated by filtration, washed with distilled water and dried at 50°C. When barium salt was used, the products was washed with a dilute acetic acid solution to dissolve barium carbonate. In order to compare with the reaction temperature conventional solid state reaction was carried out by using TiO$_2$ and alkaline earth metal carbonates at the reaction temperature from 400–1200°C for 3 h. The products were identified by X-ray powder diffraction pattern using monochromated Cu K$_\alpha$ radiation. The morphology of the particle was observed by a scanning electron microscope (SEM). The chemical composition was checked by EDX.

3. Results and discussion

3.1 Preparation from K$_2$Ti$_2$O$_5$

Figure 1 shows the X-ray powder diffraction patterns for the starting compound, K$_2$Ti$_2$O$_5$ and the products prepared at the reaction temperatures at above 400°C. The Mg products at 400–700°C were not crystallized and at 800°C the ilmenite-type phase appeared in addition to unknown phases. Even at above 900°C a single phase of ilmenite-type MgTiO$_3$ could not be obtained by this method. In the case of Ca and Sr products perovskite-type CaTiO$_3$ and SrTiO$_3$ appeared at 500°C and single phases of these compounds were obtained at 600°C. This temperature was lower than that (700°C) of perovskite-type BaTiO$_3$. SEM micrographs of K$_2$Ti$_2$O$_5$ and perovskite-type CaTiO$_3$ and SrTiO$_3$ prepared at 600°C are shown in Fig. 2. No detect of potassium and chlorine atoms in perovskite-type CaTiO$_3$ and SrTiO$_3$ was observed by EDX. Morphology of K$_2$Ti$_2$O$_5$ and both Ca and Sr products is cubic shape and the particle size is approximately 0.05, 0.5 and 0.1 μm, respectively. The particle size of the Sr product is much smaller than that of the Ca product. In Ba product the morphology of the particle was also cubic shape and the particle size of the products prepared at 700°C was ~10 μm. Surprisingly raising up of reaction temperature in only 100°C made the particle size increased though their morphology was not different among alkaline earth metals. This particle size change depending on alkaline earth metals did not observed in the case of using Lss as a starting compound as mentioned later.

Although single phase of ilmenite-type MgTiO$_3$ could not be obtained by a this method, that of ilmenite-type CdTiO$_3$ was obtained at 500°C. The X-ray powder diffraction pattern and SEM micrograph of CdTiO$_3$ were shown in Figs. 3 and 4, respectively. Morphology of CdTiO$_3$ particle is hexagonal shape which corresponds to the rhombohedral crystal system of the ilmenite-type structure. The difference between preparations of Mg and Cd products is discussed later.

3.2 Preparation from Lss

The X-ray powder diffraction patterns for the starting compound, Lss and the products prepared at the reaction temperatures at above 400°C are shown in Fig. 5. The ilmenite-type MgTiO$_3$ appeared at 300°C which was lower than that of above method, however, also by this method a single phase of the ilmenite-type MgTiO$_3$ never obtained at higher temperatures. In the case of Ca, Sr and Ba products single phases of the perovskite-type compounds could be obtained at 600, 700 and 700°C, respectively. The crystallization temperature from this starting compound was 500–600°C and this temperature region was same as that of using K$_2$Ti$_2$O$_5$ as a starting compound. SEM micrographs of Lss and perovskite-type CaTiO$_3$, SrTiO$_3$ and BaTiO$_3$ prepared at 600°C

Fig. 1. X-ray powder diffraction patterns of the starting compound, K$_2$Ti$_2$O$_5$ and the Mg (a), Ca (b) and Sr (c) products.

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are shown in Fig. 6. No detect of potassium and chlorine atoms in these perovskite-type compounds was also observed by EDX. The particle of the starting compound, Lss has flake-like shape which corresponds to the of lepidocrocite-type layered structure. The morphology of perovskite-type CaTiO$_3$ is cubic like shape with the size of $\approx 1\ \mu m$, and that of SrTiO$_3$ and BaTiO$_3$ is irregular shape with inhomogeneous size and particles with long rectangular shape are observed. Preparation of pure ilmenite-type CdTiO$_3$ was unsuccessful from Lss.

3.3 Comparison with solid state reaction

The conventional solid state reaction was carried out by using typical experimental condition in order to compare the reaction temperature to obtain a single phase of ATiO$_3$. Figure 7 shows the X-ray powder diffraction patterns of the products by the solid state reaction. The reaction temperature to obtain single phases of Mg, Ca and Sr products was 900, 1000 and 1200°C, respectively and a single phase of perovskite-type BaTiO$_3$ was not prepared even at 1200°C. Preparation of a single phase of perovskite-type BaTiO$_3$ by solid state reaction is required to raise the reaction temperature or use more reactive starting compounds such as nano-sized particles or precursors derived from sol–gel method. Table 1 summarizes temperature dependence of the phases prepared by three types of methods. For preparation of ilmenite-type MgTiO$_3$ conventional solid state reaction is superior to the molten salt method using K$_2$Ti$_2$O$_5$ or Lss as a starting compound because the later method can not produce a single phase of ilmenite-type MgTiO$_3$. On the other hand single phases of perovskite-type ATiO$_3$ were obtained successfully by the molten salt method at much lower temperature than the conventional solid state reaction. In the case of K$_2$Ti$_2$O$_5$, this lower temperature is thought to be correlated with using molten salt and the crystal structure of the starting compounds. The crystal structures of K$_2$Ti$_2$O$_5$, lepidocrocite-type Lss and perovskite-type SrTiO$_3$ are shown in Fig. 8. The way of connection of TiO$_5$ pyramids in K$_2$Ti$_2$O$_5$ is similar to that of corner-sharing of TiO$_6$ octahedra in the perovskite-type structure. The slight displacement of Ti atoms in K$_2$Ti$_2$O$_5$ can form the framework of the perovskite-type structure as shown in Fig. 9. This similarity of the crystal structures between K$_2$Ti$_2$O$_5$ and the perovskite-type may enhance to crystallize the perovskite-type compound.

Fig. 2. SEM micrographs of starting compound, K$_2$Ti$_2$O$_5$ (a) and perovskite-type CaTiO$_3$ (b) and SrTiO$_3$ (c) prepared at 600°C.

Fig. 3. X-ray powder diffraction patterns of starting compound, K$_2$Ti$_2$O$_5$ and the Cd product.

Fig. 4. SEM micrograph of the Cd product.
type ATiO₃ at low temperature, ~700°C. Also it was pointed out that the size of the cation which does not form the framework was an important factor for crystallization in molten salt. From these facts the perovskite-type CaTiO₃ and SrTiO₃ can be prepared from K₂Ti₂O₅ by molten salt method at low temperature and the ilmenite-type MgTiO₃ can not be easily crystallized from K₂Ti₂O₅. The reason why the ilmenite-type CdTiO₃ is obtained from K₂Ti₂O₅ may be correlated with the facts that the ilmenite-type CdTiO₃ is a low temperature form and transforms to the perovskite-type structure below 1000°C.37)

Fig. 5. X-ray powder diffraction patterns of the starting compound, Lss and the Mg (a), Ca (b), Sr (c) and Ba (d) products.

Fig. 6. SEM micrographs of Lss and perovskite-type CaTiO₃, SrTiO₃ and BaTiO₃ prepared at 600°C.
In the case of Lss the lepidocrocite-type layered structure cannot introduce the perovskite-type one unlike K2Ti2O5 as shown in Fig. 8, however, Lss can produce the perovskite-type compounds by using molten salt at low temperatures similar to the case of Fig. 7.

**Table 1.** Comparison with temperature dependence of the phases prepared by three types of methods

| Temp (°C) | K2Ti2O5 | Lss | Solid state reaction |
|----------|---------|-----|---------------------|
| 400      | —       | —   | —                   |
| 500      | —       | —   | —                   |
| 600      | —       | —   | —                   |
| 700      | —       | —   | —                   |
| 800      | —       | —   | —                   |
| 900      | △       | —   | —                   |
| 1000     | △       | —   | —                   |
| 1100     | △       | —   | —                   |
| 1200     | △       | —   | —                   |

—: unreacted or amorphous phase
△: almost single phase
○: single phase

**Fig. 8.** (Color online) Crystal structures of K2Ti2O5, lepidocrocite-type Lss and perovskite-type SrTiO3. Solid lines indicate the unit cell. Right parts show connections of TiO5 or TiO6 polyhedra.

**Fig. 9.** (Color online) Structural change of TiO5 layer of K2Ti2O5 to the perovskite-type polyhedral arrangement.

In the case of Lss the lepidocrocite-type layered structure cannot not introduce the perovskite-type one unlike K2Ti2O5 as shown in Fig. 8, however, Lss can produce the perovskite-type compounds by using molten salt at low temperatures similar to the case of...
K₂Ti₂O₅. This may be explained by ability of ion-exchange of Lss, K⁺ ion of which can be replaced easily with other cations. As shown in Fig. 5, the X-ray powder diffraction patterns of the products at 400°C indicated that the 00l diffraction peaks were shifted toward to higher 2θ angle for Ca, Sr and Ba products and the layered structure was collapsed for Mg product. This change suggests that K⁺ ion of Lss was replaced partially with Ca²⁺, Sr²⁺ and Ba²⁺ ions at 400°C keeping the lepidocrocite-layered structure. For Ca, Sr and Ba products the perovskite-type compounds were crystallized via the ion-exchanged phase with the lepidocrocite-type structure and the Mg product was contaminated with an unknown phase and the lepidocrocite-type compound (asterisk is indicated in Fig. 5) via an amorphous phase. This difference may come from the ionic size and electronegativity of alkaline earth metals. Mg²⁺ ion is too small to hold the lepidocrocite-type structure and Ca²⁺, Sr²⁺ and Ba²⁺ ions are suitable size to occupy in the interlayer. In these cases the size of cations which do not form the framework also plays an important role to crystallize the perovskite-type phases. Also the electronegativity of Mg²⁺ ion is higher than that of Ca²⁺, Sr²⁺ and Ba²⁺ ions and this high electronegativity may prevent from formation of a pure oxide phase in molten salt.

In K₂Ti₂O₅ the perovskite-type phases were crystallized directly by dissolution–precipitation mechanism, while in Lss those were obtained via dissolution–precipitation of ion-exchanged phase. This difference of the crystallization process is considered to influence particle sizes of the products. The solubility of K₂Ti₂O₅ into molten salt may depend on the alkaline earth metal, and then the particle size of the product was changed by the alkaline earth metal. On the other hand as the solubility of the ion-exchanged phases from Lss may be independent of the alkaline earth metal, the particle size of the products was not varied by the alkaline earth metal. Anyhow the crystallization temperatures were almost same (600–700°C) for K₂Ti₂O₅ and Lss in spite of the different process.

The catalyst, SrTiO₃·Pd with the perovskite-type structure which was prepared by this method using Lss as a starting compound exhibited good performance for oxidation of 1-phenylethanol. This low temperature method not only has advantage of energy and cost saving but also is useful for loading catalytic metal atom in the perovskite-type structure.

4. Conclusion

Pure perovskite-type ATiO₃ (A: Ca, Sr, Ba) compounds were prepared from two types of layered potassium titanates, K₂Ti₂O₅ and Lss in mixed molten salts at 600–700°C. The reaction temperatures were lower by about 400°C than conventional solid state reaction. The crystallization process was different between K₂Ti₂O₅ and Lss; perovskite-type compounds were crystallized directly from K₂Ti₂O₅ and done via ion-exchanged phases of Lss.

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