Molten salt synthesis of spinel-type LiTi_2O_4

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Spinel-type LiTi_2O_4 was prepared directly by the reaction of lepidocrocite-type potassium titanate and molten LiCl at 750–850°C in a stream of H_2 gas. The Li/Ti ratio in the spinel-type phase prepared at 850°C was 0.54, and the lattice parameter and superconductive critical temperature T_c were $a = 8.3935(2) \text{ \AA}$ and 12.3 K, respectively. The product at 750°C exhibited no superconductive diamagnetism down to 2.5 K, and the product at 800°C showed weak superconductive diamagnetism at 10.5 K. The morphology of the particles prepared at 850°C showed an irregular shape with a particle size of 1–10 μm .

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Key-words : Spinel-type LiTi_2O_4 , Molten salt synthesis, Superconductivity

[Received December 2, 2013; Accepted February 11, 2014]

1. Introduction

Lithium titanate LiTi_2O_4 with a spinel-type structure is a superconductor with $T_c = 13 \text{ K}$ which was discovered by Johnston et al. in 1973.¹⁾ This spinel-type lithium titanate has a wide composition range, $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ ($0 \leq x \leq 1/3$), and T_c depends on the chemical composition.²⁾ It was difficult to reproducibly prepare a powder sample of LiTi_2O_4 with identical superconducting properties because of the volatility of lithium and the phase change at high temperature.²⁾ Various synthesis methods have been proposed. Johnston et al. attempted the preparation of the Li–Ti–O system by two methods: arc melting using Li_2CO_3 , TiO_2 and Ti, and sintering mixtures of $\text{Li}_2\text{Ti}_2\text{O}_5$ and Ti_2O_3 at 800–1480°C under He or Ar atmosphere.¹⁾ Single crystals of LiTi_2O_4 were prepared by the electrolysis of molten salts or a flux method.^{3)–5)} Murphy et al. reported a unique method of obtaining a powder sample of LiTi_2O_4 via the soft-chemical route.⁶⁾ Electrochemical insertion of Li^+ ions into anatase-type TiO_2 in molten salt LiCl could produce LiTiO_2 and LiTi_2O_4 .⁷⁾ A thin film of LiTi_2O_4 could be formed by r. f. magnetron sputtering, or pulse laser deposition.^{8),9)} Feng et al. succeeded in the preparation of a powder sample of LiTi_2O_4 by solid-state reaction from LiOH , TiO_2 and Ti_2O_3 in Ar atmosphere at 890°C.¹⁰⁾

We reported that perovskite-type titanates ATiO_3 (A: Ca, Sr, Ba) could be prepared from the lepidocrocite-type potassium titanate at a temperature lower than that of the conventional solid-state reaction,^{11),12)} and this preparation method was useful for loading a catalytic metal atom in the perovskite-type structure.¹³⁾ In the course of this investigation, LiTi_2O_4 could be obtained by the reaction of lepidocrocite-type potassium titanate and molten LiCl at 750–850°C in a stream of H_2 gas. In this paper, we will describe the synthesis of spinel-type LiTi_2O_4 using molten salt and its properties.

2. Experimental

A lepidocrocite-type potassium titanate was used in a commercial chemical (Terasas Lss) obtained from Otsuka Chemical Co., Ltd. The mixture of potassium titanate and LiCl with the molar ratio of 1:4 was put into an alumina boat and heated at 600–

1000°C for 3 h in a stream of H_2 gas. The product was washed with distilled water to dissolve the potassium and lithium salts, and separated by filtration, washed with distilled water and dried at 50°C. The products were identified by X-ray powder diffraction patterns using monochromated $\text{Cu K}\alpha$ radiation. The lattice constants were determined from the X-ray powder diffraction patterns measured in the 2θ range from 10 to 120°. The morphology of the particle was observed by scanning electron microscopy (SEM). The chemical composition was analyzed as follows. The prepared LiTi_2O_4 was converted to hydrated titanium oxide in concentrated $\text{HNO}_3 + \text{HCl}$ solution (HNO_3 5 mL + HCl 15 mL + H_2O 10 mL) under hydrothermal condition at 200°C for 12 h. The product was separated by filtration and the amounts of lithium and potassium ions in the solution were determined by an atomic absorption spectroscopy. The solid was heated at 1000°C for 1 h and the product (rutile-type TiO_2) was weighed. The oxygen content was determined on the basis of mass gain by TG analysis. The temperature dependence of the DC magnetic susceptibility was measured with zero-field cooling modes in the temperature range from 2.5 to 20 K in an external field of 10 Oe using a superconducting quantum interference device magnetometer (MPMS-5S, Quantum Design).

3. Results and discussion

Figure 1 shows the X-ray powder diffraction patterns of products prepared from potassium titanate and molten LiCl at 650–1000°C. The spinel-type phase was observed in the products at 650–900°C. An approximate single phase of spinel-type LiTi_2O_4 was obtained at 850°C, and its X-ray powder diffraction pattern indicated a small amount of TiO as well as the spinel-type compound. The X-ray powder pattern of the product prepared at 800°C showed unidentified weak diffraction peaks at approximately 10 and 20° in 2θ degree. Those of the products prepared at 650–750°C showed the coexistence of a small amount of rutile-type TiO_2 . At above 900°C, ramsdellite-type $\text{Li}_2\text{Ti}_3\text{O}_7$ appeared, and at 1000°C, it was obtained as a single phase. This phase change from spinel to ramsdellite-types was confirmed with the previous work by Gover et al.,¹⁴⁾ in which a phase transition from the spinel to ramsdellite occurred between 875 and 925°C.

Figure 2 shows the temperature dependence of magnetic susceptibility of the products prepared at 800, 850 and 900°C.

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Fig. 1. X-ray powder diffraction patterns of starting compound and products prepared at 650–1000°C. The star denotes an unidentified peak.

Fig. 2. Temperature dependence of magnetic susceptibility of products prepared at 800, 850 and 900°C.

This broad superconductive transition is a typical example for polycrystalline samples. The product at 750°C exhibited no superconductive diamagnetism down to 2.5 K. The superconductive critical temperature T_c of the products at 850 and 900°C was 12.3 K, and the volume fraction of superconductivity for the product at 850°C was calculated to be 23%. According to Harrison et al.¹⁵⁾ and Ueda et al.,¹⁶⁾ the volume fraction of superconductivity for the $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ powder sample depended on the value of x in $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$, and the volume fraction for $x = 0.05$ was 50–60%. When compared with these previous data, our sample was inferior to the samples prepared by solid-state reaction. T_c of the product at 800°C decreased to 10.5 K, and its volume fraction of superconductivity was also decreased to 5.8%. Although a small amount of TiO was observed in the samples prepared above 800°C, a stoichiometric TiO was reported to have $T_c = 2.3$ K.¹⁷⁾

The Li/Ti ratios of the products at 750, 800 and 850°C were 0.53, 0.53 and 0.54, respectively, and no potassium atom was detected in these samples by chemical analysis. In the TG curve of the sample prepared at 850°C, the mass gain (2.17 mass %) was observed and from this value, the oxygen content was calculated to be 4.2. Since this oxygen content was overestimated because of

Fig. 3. Lattice parameter vs reaction temperature for spinel-type LiTi_2O_4 obtained by molten salt synthesis. The standard deviation of the lattice parameter is within the size of the marker.

Fig. 4. Superconducting transition temperature vs value of x in $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ and the lattice parameter. The filled circles, filled square and open triangles denote the powder samples obtained by Johnston, the sample prepared in this work and single crystal samples,^{3)–5)} respectively. The data obtained in this work and from single-crystal samples are plotted against the lattice parameter. The arrows indicate that no superconductivity was observed above the temperature indicated by the tip of the arrow. The vertical error bar for superconducting samples marks the temperature at which 10 and 90% of the samples become superconducting. The vertical error bar for single-crystal samples is omitted.

a small amount of impurity phase TiO, the exact oxygen content in the spinel-type phase was estimated to be 4.0–4.1. Although the Li/Ti ratio was almost constant, regardless of the reaction temperature, the lattice parameters increased with the reaction temperature as shown in Fig. 3. The chemical composition of the product at 850°C, which is the sample with the lowest amount of impurity phase and the highest T_c , can be represented as $\text{Li}_{1.05}\text{Ti}_{1.95}\text{O}_4$, and its lattice parameter is $a = 8.3935(2)$ Å. According to investigations^{3)–5)} of single crystals of LiTi_2O_4 , their lattice parameter and critical temperature T_c were varied from 8.3914 to 8.4095(12) Å and 11.3 to 12.7 K, respectively, and every transition width was very small (~ 1.5 K). Johnston¹⁸⁾ reported a diagram of the relationship among the lattice parameter, chemical composition and T_c , and the data obtained in this work and from single-crystal samples^{3)–5)} were plotted in Johnston's diagram,

Fig. 5. SEM images of (a) starting compound and (b) product prepared at 850°C.

as shown in **Fig. 4**. Most of the superconducting samples with $T_c > 10$ K exist in the region of $a > 8.39$ in the lattice parameter, and samples with shorter lattice parameters, which have a higher lithium content, did not exhibit superconductivity or have lower T_c (~ 1.5 K).²⁾ The relationship between site distributions of Li and Ti atoms in the spinel-type structure of $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ and superconductive property has been discussed, and the large variation of T_c was explained by not only nonstoichiometry owing to the preparation method but also lithium deficiency and the associated Ti network disorder.^{2),18)–20)} Nonetheless the trend for the powder sample of $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ prepared using molten salt is consistent with the previous data in Johnston's diagram.

This preparation method with molten salt can easily crystallize the spinel-type LiTi_2O_4 ; however, a small amount of the second phase, TiO coexisted and excess Li in the molten salt cannot control the chemical composition.

Figure 5 shows SEM images of the starting compound and the product prepared at 850°C. The starting compound has flake like particles with 2–5 μm size and the morphology of the particles prepared at 850°C showed an irregular shape with a particle size of 1–10 μm . This morphological change comes from crystal growth in molten salt.

4. Conclusion

The molten salt synthesis with lepidocrocite-type potassium titanate could easily produce the superconductive spinel-type LiTi_2O_4 with $T_c = 12.3$ K. The optimum synthetic condition was a reaction temperature of 850°C for 3 h in a stream of H_2 gas. The chemical composition and lattice parameter were $\text{Li}_{1.05}\text{Ti}_{1.95}\text{O}_4$ and $a = 8.3935(2)$ Å, respectively. This method was available

for the preparation of spinel-type titanate as well as perovskite-type ones.

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