JOURNAL OF SOLID STATE CHEMISTRY **96**, 446–450 (1992)

Preparation of $LiTi_2O_4$ Single Crystals with the Spinel Structure

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Received July 1, 1991; in revised form September 13, 1991

Single crystals of the spinel-type $LiTi_2O_4$ (Cubic, *Fd*3*m*, a = 8.4095(12) Å) have been prepared by the reaction of lithium metal and TiO_2 at 1373 K in a sealed iron vessel. The structure refinement by a single crystal X-ray diffraction study confirmed a normal spinel cation distribution; the lithium cations are located at the tetrahedral 8*a* sites, the titanium cations occupy the octahedral 16*d* sites, and the oxygen parameter u = 0.2622(4) with the final R = 3.8% (R_w = 2.7%) for 60 independent observed reflections. The octahedral Ti–O distance is 2.005(3) Å, and the tetrahedral Li–O distance is 1.999(3) Å. The superconductivity for the crystals was observed by the magnetization measurements. © 1992 Academic Press, Inc.

Introduction

The spinel-type $LiTi_2O_4$ is known to be a superconductor with a transition temperature T_c = 11 K (*1*). This compound was originally synthesized and structurally characterized by Deschanvres *et al.* (*2*) as an end-member in the solid solution system $Li_{1+x}Ti_{2-x}O_4$ ($0 \leqq x \leqq \frac{1}{3}$). The solid solution system $LiM_xTi_{2-x}O_4$ (M = Li^+, Mn^{2+}, Mg^{2+}, Cr^{3+}, Al^{3+}) was also investigated with regard to the compositional dependence of the lattice parameters and physical properties such as the normal superconducting or metallic–semiconducting transition (*3–6*). In all the experimental studies reported to date, sintered powder samples were used, although single crystals were needed in order to investigate the more precise structural and electronic properties.

Recently, single crystals of the reduced alkaline titanates (e.g., $NaTi_2O_4$ (*7*), $NaTi_8O_{13}$ (*8*), $Na_{0.25}TiO_2$ (*9*), and hollandite-type K_xTiO_2 (*10*) and Cs_xTiO_2 (*11*)) were prepared by the reactions of alkaline metals (Na, K, Cs) and titanium oxides using sealed Fe or Ni vessels at high temperatures. We have applied this preparation method to the Li–Ti–O system and have succeeded in the preparation of the stoichiometric $LiTi_2O_4$ single crystals. In this paper, we report the preparation and crystal structure of $LiTi_2O_4$ single crystals.

Experimental and Results

Preparation of the Crystal

Starting materials were TiO_2 powder (99.9%), which was composed of rutile and anatase and was dried at 673 K, and lithium metal blocks with 99% purity. They were placed in a sealed iron vessel with an atomic ratio of Li/Ti = 1/2, heated in a resistance furnace at 1373 K in an argon gas flow for 10 hr, and slowly cooled to room tempera-

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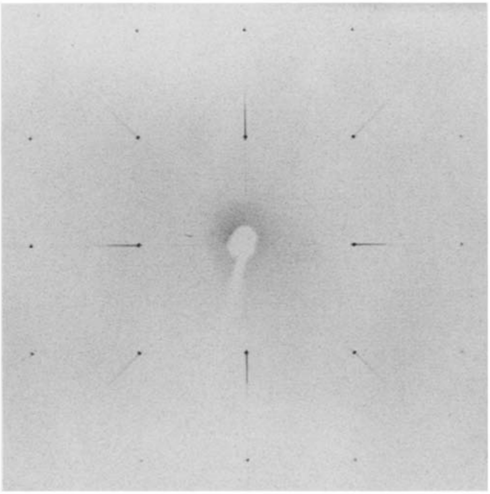

FIG. 1. $\{hk0\}^*$ precession photograph of the spinel-type $LiTi_2O_4$ crystal. Mo$K\alpha$ radiation filtered by Zr foil was used.

ture. No apparent leakage of lithium vapor from the vessel was observed.

The main products were blue-black powder, which could not be identified to the reported compounds in the Li–Ti–O system, and the aggregated NaCl-type $LiTiO_2$ (JCPDS No. 16-223) grains and the crystals. Some dark blue, droplet-like crystals with a maximum diameter of about 1 mm were found on the surface of the $LiTiO_2$ crystals. Electron microprobe analysis showed that the dark blue crystals were free from iron contamination from the vessel. It has not yet been possible to determine the chemical composition of the crystals by wet chemical analysis, as the prepared crystals are too small.

Precession photographs indicate that the crystals belong to the cubic spinel structure with the space group $Fd3m$ and lattice parameter a = 8.41 Å, as shown in Fig. 1. The lattice parameter, determined by least-squares refinement (*12*) using Mo$K\alpha$ radiation (λ = 0.71069 Å) and 20 well-centered reflections in the range $19° \leqq 2\theta \leqq 28°$ measured on an automated Rigaku AFC-5 four-circle diffractometer, is 8.4095(12) Å. These data suggest that the crystals belong to the solid solution system $Li_{1+x}Ti_{2-x}O_4$ (*2*). In the $Li_{1+x}Ti_{2-x}O_4$ system, the lattice parameter decreases linearly with increasing x in the range $0 \leqq x \leqq \frac{1}{3}$; the compositional dependence obeys Vegard's law (*3*, *4*). The lattice parameter (a = 8.4095(12) Å) for the present crystals agrees with those for the stoichiometric $LiTi_2O_4$ (x = 0) samples: 8.408 Å by Ueda *et al.* (*4*) and 8.410(1) Å by Murphy *et al.* (*13*). These facts lead us to the stoichiometric chemical composition $LiTi_2O_4$ for the present crystals. The chemical formula $LiTi_2O_4$ was also confirmed by the present structure refinement.

Superconductivity of these $LiTi_2O_4$ crystals was confirmed by the magnetization measurements with a SQUID magnetometer. Figure 2 shows a typical result of the diamagnetic susceptibility cooled in an external magnetic field of 10 Oe. The onset temperature of superconducting transition is roughly 12 K, and the transition width ΔT_c is about 1.5 K.

Attempts to perform single crystal resistivity measurements on $LiTi_2O_4$ have not succeeded yet, so far due to the high contact resistivity of Ag/epoxy contacts on the crystal surface and the small size of the crystals.

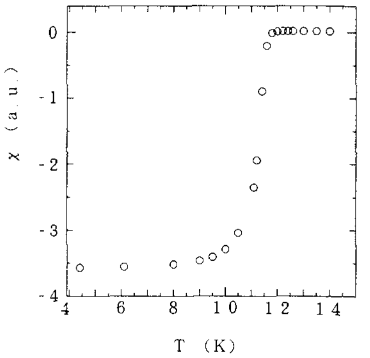

FIG. 2. Temperature dependence of the susceptibility for $LiTi_2O_4$ crystals in a cooling field of 10 Oe.

Structure Determination

The single crystal data were obtained on the four-circle diffractometer (operating conditions: 40 kV, 40 mA) with graphite monochromatized Mo$K\alpha$ radiation (λ = 0.71069 Å) in the $2\theta - \omega$ scan mode at room temperature and reduced to structure factors after due correction for Lorentz and polarization effects. Fluctuations of the intensities, monitored by examining a set of the three standard reflections taken after every 50 observations, were within 2.5%. A total of 85 independent reflections were measured within the limit of $2\theta \leqq 70°$, out of which 60 reflections with $|F_{\mathrm{obs}}| > 3\sigma(|F_{\mathrm{obs}}|)$ were regarded as observed. No absorption and extinction corrections were performed.

The structure refinement was initiated with the atomic coordinates specified by Harrison *et al.* (*3*), origin at center $3m$ and the oxygen parameter u = 0.261. Cation site-distribution and site-occupancy refinements in the 8*a* and 16*d* positions, applied at the final stage, confirmed the stoichiometric chemical formula $LiTi_2O_4$ and a normal spinel cation distribution; the lithium cations were located at the tetrahedral 8*a* sites and the titanium cations occupied the octahedral 16*d* sites. A full-matrix least-squares refinement using the computer program RFINE-II (*14*) with anisotropic temperature factors converged to a final R of 0.038 and R_w [$w = 1/\sigma^2(F_{\mathrm{obs}})$] of 0.027 for 60 observations, and R of 0.063 and R_w of 0.027 for all reflections, with shift/error for all parameters less than 0.01. The final difference Fourier map using the GSFFR program (*15*) showed no significant residual electron density.

The scattering factors for neutral atoms tabulated by Cromer and Mann (*16*) were used in the calculations. The anomalous dispersion correction factors were taken from "International Tables for X-ray Crystallography" (*17*). The crystallographic and experimental data are summarized in Table I. The final atomic coordinates and temperature factors are given in Table II.

TABLE I

CRYSTALLOGRAPHIC AND EXPERIMENTAL DATA OF $LiTi_2O_4$

Space group	$Fd3m$
Crystal size (mm)	0.05 × 0.04 × 0.03
a (Å)	8.4095(12)
V (Å^3)	594.7(3)
Z	8
D_x (g/cm^3)	3.726
Scan type	$2\theta - \omega$
Scan speed (°/min)	2.0
Maximum 2θ (°)	70
Independent reflections	85
Observed reflections	60 (>3σ)
Final R	0.038
Final R_w [$w = 1/\sigma^2(F_{\mathrm{obs}})$]	0.027

Discussions

The interatomic distances and bond angles were calculated using a program UMBADTEA (*18*). The Ti–Ti distance in the present $LiTi_2O_4$ is 2.9732(3) Å, and the refined oxygen parameter u (*3*) is 0.2622(4), which is in good agreement with the results by the line intensity analysis of the powder diffractometer tracings: 0.2645(20) by Johnston (*1*) and 0.261(1) by Harrison *et al.* (*3*). Accordingly, the TiO_6 octahedron is slightly distorted and has two O–Ti–O angles 83.97(14)° and 96.03(14)°, while the LiO_4 tetrahedron is not distorted (O–Li–O angle: 109.47(19)°). The tetrahedral Li–O distance in $LiTi_2O_4$ is 1.999(3) Å, which is well consistent with the average four-fold distance of 1.98 Å reported in the literature (*19*).

The Ti–O distances are linearly related to the titanium valence states in the reduced titanates (*20*). In $LiTi_2O_4$, the average charge of Ti ions is +3.5, and the octahedral Ti–O distance is 2.005(3) Å. This value is quite consistent with the average Ti–O distances in the compounds having the formal

TABLE II

ATOMIC POSITIONAL PARAMETERS AND TEMPERATURE FACTORS

Atom	Position	x	y	z	B_{eq}	β_{11}	β_{12}
Li	8*a*	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	1.63	0.006(3)	0
Ti	16*d*	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.66	0.0023(1)	−0.0003(2)
O	32*e*	0.2622(4)	0.2622	0.2622	0.46	0.0016(3)	−0.0004(4)

titanium valence of +3.5: 2.014 Å in $NaTi_2O_4$ (*7*) and 2.009 Å in Ti_4O_7 (*21*). The previously reported Ti–O distance (1.981(16) Å) for $LiTi_2O_4$ (a = 8.405(1) Å) (*1*) is slightly shorter than the present value (2.005(3) Å) and is apparently against the above-mentioned linear relation between the octahedral Ti–O distances and titanium valence states (*20*).

The present preparation method will be a modification of the flux method as follows: the lithium metal is kept in liquid state even at high temperature in the presence of a high lithium vapor pressure, and dissolves TiO_2 powder. Then the high temperature Li–Ti–O solution is formed at 1373 K in various parts of the sealed vessel, and by the subsequent slow cooling, single crystals of $LiTi_2O_4$ and $LiTiO_2$ are precipitated. As a result, the excess TiO_2 powder which does not take part in this reaction is reduced by the lithium metal vapor in the vessel, and the above-mentioned unknown blue-black phase is formed.

It was reported that the spinel-type $LiTi_2O_4$ transformed to the ramsdellite-type phase above 1223 K (*1*). However, in the present preparation experiments at 1373 K, the ramsdellite phase could not be obtained. If truly the phase transformation occurs at about 1223 K, it is very interesting that the soaking temperature to produce the spinel-type crystals in this study is beyond the transformation temperature. The high lithium vapor pressure in the present preparation method may play an important role in the preparation of the spinel-type $LiTi_2O_4$ crystals at high temperature above the transformation temperature of about 1223 K. Namely, it is possible to say that a lithium vapor pressure is necessary to produce the spinel-type $LiTi_2O_4$ crystals, as in the case of the reduced sodium titanates (*20*).

In our additional preparation experiments, the ramsdellite-type black crystals have been grown together with the spinel-type crystals at 1473 K using a similar Fe vessel. Precession photographs indicate that the black crystals belong to the orthorhombic system with the space group $Pbn2_1$ or *Pbnm*. The lattice parameters, determined on the four-circle diffractometer, are a = 4.979(1), b = 9.561(1), c = 2.955(1) Å, and V = 140.69(7) Å^3, which are consistent with the values reported by Johnston (*1*). Details of the chemical composition and crystal structure of the ramsdellite-type crystals will be presented in a separate paper (*22*).

Acknowledgments

The authors express their gratitude to Professor H. Takei, Institute for Solid State Physics, University of Tokyo, for his valuable advice and help in the production of the reaction vessels.

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