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Investigation of phase transition in Li_2TiO_3 by high temperature X-ray diffraction

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Abstract

Li_2TiO_3, one of the promising candidates for tritium breeding in a thermonuclear fusion reactor, has been investigated by X-ray diffraction at high temperatures. It was found that the crystal system of Li_2TiO_3 is monoclinic at 30–900 °C with a higher order structural phase transition at about 450 °C, showing agreement with dependence of thermal conductivity on temperature. This phase transition involved variation of the thermal expansion coefficient, which could also be observed by dilatometry.

1. Introduction

So far, various Li-containing oxides, such as Li_2O, $LiAlO_2$, Li_4SiO_4, Li_2ZrO_3 and Li_2TiO_3, have been proposed as candidate materials for tritium breeding in thermonuclear fusion reactors [1]. Among them, Li_2TiO_3 seems most promising because it has a good tritium release rate, low thermal expansion, and chemical stability [2]. Since the tritium breeder is used under severe conditions such as high temperatures and reducing atmospheres, information on thermal properties, at high temperatures is essential for application. One of the authors reported a higher order phase transition in Li_2TiO_3 at about 450 °C from measurement of thermal conductivity [3]. In the previous study, high temperature X-ray diffraction was used to obtain definite evidence for the phase transition; however, it could not be obtained due to lack of sufficient resolution and signal-to-noise ratio. In this work, crystal structure and thermal expansion property of Li_2TiO_3 have been investigated by using high temperature X-ray diffraction with sufficient resolution and sensitivity to clarify the existence of the phase transition. Also, thermal expansion estimated with high temperature X-ray diffraction has been compared with the result obtained by high-resolution dilatometry.

2. Experimental

Li_2TiO_3 ceramic specimens were prepared by a solid-state reaction method. Nominal compositions

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of Li_2CO_3 and TiO_2 powder were mixed in ethanol with alumina mortar, followed by pressing into pellets. The pellets were sintered at 1000 °C for 8 h in air. Obtained density of the specimen was 2.27 g/cm^3, which was equal to 66% of ideal density. Some pellets were crushed into powder to investigate the crystal structure by X-ray diffraction. The X-ray diffraction measurements at room temperature, using a RINT-2500 diffractometer (CuKα: 50 kV, 250 mA: Rigaku Co., Ltd.), revealed that the prepared specimens were single phase with monoclinic symmetry, in fair agreement with a previous report [4]. X-ray diffraction measurements from room temperature to 900 °C were carried out in air by using a RINT-2500 diffractometer with a Pt heater. For high temperature X-ray diffraction measurements, calibration of Bragg angles is necessary since they frequently deviate due to distortion and/or thermal expansion of Pt holder. In order to estimate calibration angle, Bragg angles of the peaks at 30 °C obtained by the high temperature apparatus with those obtained by room temperature X-ray diffraction apparatus using glass holder was compared. Thus estimated calibration angle was regarded to be independent on temperature, assuming that the thermal expansion of Pt holder was negligible because the sample holder we used was small enough [5].

In order to estimate thermal expansion of sintered polycrystalline specimen, some pellets were processed into a pillar shape with 4.9 mm diameter and 12.93 mm height. The processed specimens were analyzed in a dilatometer employing a Michelson's interferometer for measurement of variation of sample length (LIX-1M system: ULVAC-Riko, Inc.). The measurements were carried out *in vacuo* from room temperature to 600 °C with a heating rate of 2 °C/min.

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of Li_2TiO_3 at various temperatures between 30 and 900 °C. All the diffraction peaks at 30 °C could be indexed assuming monoclinic symmetry with $a = 5.064$ Å, $b = 8.785$ Å, $c = 9.715$ Å and $\beta = 100.07°$. Drastic change of X-ray diffraction patterns was not observed with increase of temperature, apparently suggesting no phase transition between 30 and 900 °C. However, there remained the possibility that the higher order phase transition might exist in Li_2TiO_3 in this temperature range as speculated from the measurement of thermal conductivity [3]. In order to verify the existence of higher order phase transition, information on the temperature dependence of lattice constants is necessary.

Fig. 2 shows representative diffraction peaks of Li_2TiO_3 at various temperatures. For precise observation of Bragg angles, the axis for 2θ is magnified. Every diffraction peak shifted to lower 2θ, indicating thermal expansion. Bragg angles of 0 0 6, 1 3 5, $\bar{3}$ 3 1 and 0 6 2 peaks were employed for calculation of lattice constants since they appeared at fairly high 2θ region with sufficient intensity. Because the peaks employed for the calculation of lattice constants were overlapped with other peaks, curve fitting was used for evaluation of precise Bragg angles. For the curve fitting, intensity, full width at half maximum, and Bragg angles of the peaks were parameters, optimized with the least square method. Peak shape was approximated by a Lorentz function and the intensity ratio of $CuK_{\alpha 1}$ and $CuK_{\alpha 2}$ was fixed to be 2. Fig. 3 depicts an example of the fitting. The difference between experimentally observed data and curve fitting was small enough to estimate precise Bragg angles.

Fig. 4 shows the dependence of lattice constants of Li_2TiO_3 on temperature as calculated from X-ray diffraction peaks depicted in Fig. 2. Length of a, b and c-axis increased with increasing temperature, whereas a decrease of monoclinic angle, β, with temperature was observed. At 450 °C, where existence of phase transition was suggested by thermal conductivity [3], discontinuous variation of β was detected. An apparent linear increase on temperature was observed for a, b and c; however, their behaviors can be explained in terms of the phase with smaller linear thermal expansion coefficient transforming to one with a slightly higher coefficient at 450 °C, in agreement with the result of thermal conductivity.

Fig. 5 shows the temperature dependence of molar volume of Li_2TiO_3 calculated from lattice constants depicted in Fig. 4. Molar volume increased with increasing temperature. Variation of the slope, indicating variation of thermal expansion coefficient, was clearly observed at 450 °C where existence of the phase transition was suggested. If there is the first order phase transition, discontinuous variation of volume, V, should be observed since V is the first derivative of Gibbs free energy (G) as given below:

$$(\partial G/\partial P)_T = V.$$

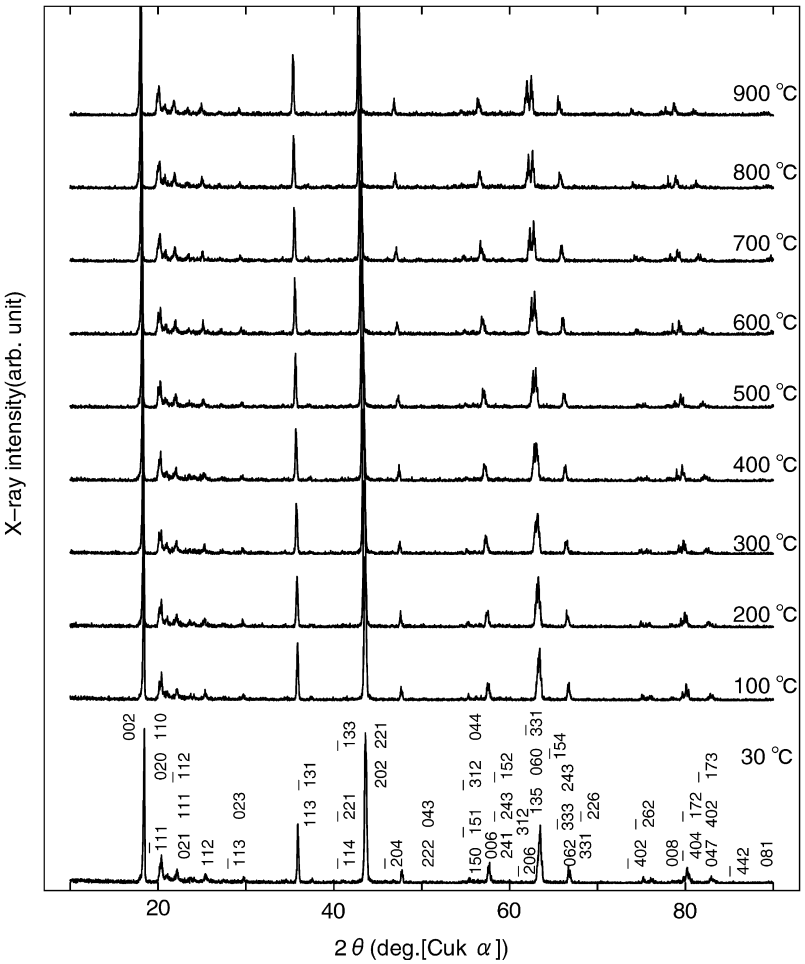

Fig. 1. X-ray diffraction patterns of Li_2TiO_3 at various temperatures. All the diffraction patterns could be indexed as monoclinic symmetry.

Here, P and T represent pressure and temperature. In Fig. 5, discontinuous variation of volume was not observed, indicating that the phase transition at 450 °C is not the first order. If the order of the phase transition is higher than 2, there is a possibility that the second derivative of Gibbs free energy should be discontinuous. One of the second derivatives of Gibbs free energy is volume thermal expansion coefficient, α, described as below:

$$\alpha = 1/V(\partial V/\partial T)_P = 1/V(\partial^2 G/\partial T \partial P).$$

Therefore, variation of slope observed in Fig. 5 at 450 °C suggests existence of higher order phase transition. Fig. 5 also shows linear thermal expansion behavior observed with the dilatometer using a Michelson's interferometer. The difference of the slope, which indicated the existence of a higher order phase transition, was observed below and above 450 °C, in agreement with the results of high temperature X-ray diffraction. Linear thermal expansion coefficients of Li_2TiO_3 measured by dilatometry below and above 450 °C were $1.8 \times 10^{-5}\,K^{-1}$ and $2.1 \times 10^{-5}\,K^{-1}$, respectively. Volume thermal expansion coefficients estimated from variation of molar volume on temperature depicted in Fig. 5 were $5.1 \times 10^{-5}\,K^{-1}$ and $6.5 \times 10^{-5}\,K^{-1}$, respectively. Considering that linear thermal expansion coefficient is one third of the volume thermal expansion coefficient for isotropic material, it was concluded that difference of thermal expansion coefficients between low and high temperature phases were observed more clearly in volume expansion behavior than in linear one and that the thermal expansion coefficients estimated by both methods showed quantitative agreement with each other.

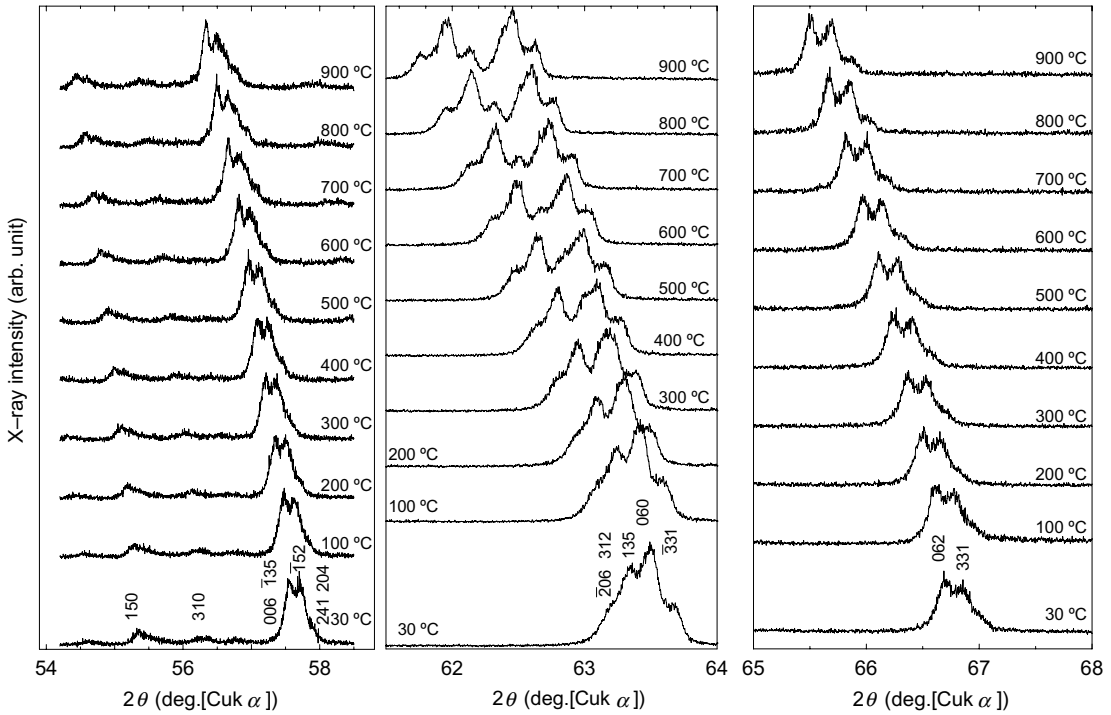

Fig. 2. Representative X-ray diffraction peaks of Li_2TiO_3 at various temperatures. Every peak shifted to lower angle with increase in temperature.

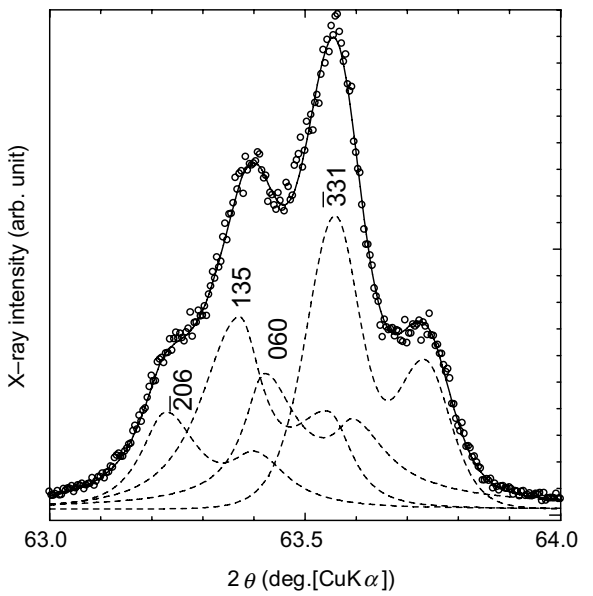

Fig. 3. Curve fitting results for representative diffraction peak of Li_2TiO_3 at room temperature. Dashed curve: calculated, solid curve: summation of calculated peaks, open circles: experimentally obtained data.

For the practical application and estimation of reliability of Li_2TiO_3 as a tritium breeding

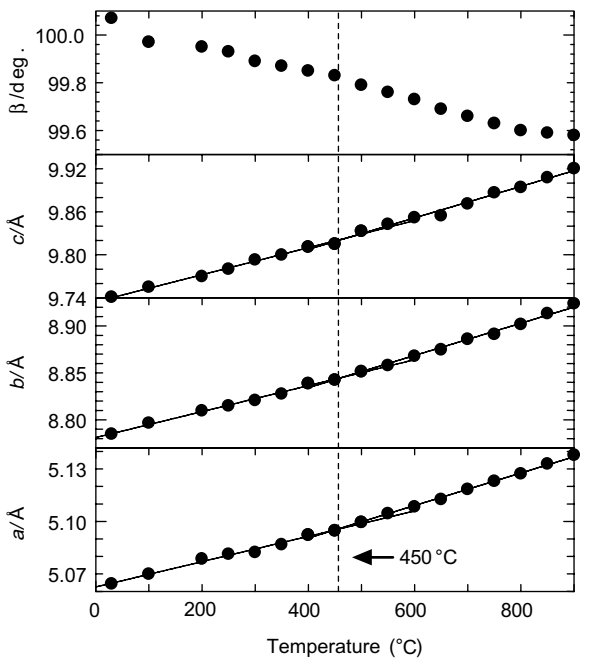

Fig. 4. Lattice constants calculated from the Bragg angles of the diffraction peaks at various temperatures. Discontinuous variation of monoclinic angle, β, and thermal expansion coefficients of a, b and c were observed at about 450 °C.

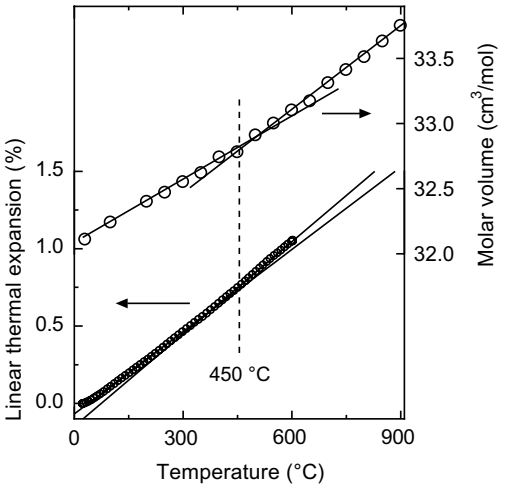

Fig. 5. Variation of molar volume of Li_2TiO_3 with temperature calculated from the results of X-ray diffraction. Linear thermal expansion obtained with dilatometry employing a Michelson's interferometer is shown for comparison. In both data, variation of thermal expansion coefficient was observed at about 450 °C.

materials, thus clarified phase transition should be considered since thermal expansion behaviors at temperatures for manufacturing and application are revealed to be different. For the practical application, information on thermal expansion behavior and crystal system at operating temperatures under H_2 and/or H_2O vapor should also be necessary. X-ray diffraction measurements at high temperatures under such atmospheres are now in progress.

4. Conclusion

By using X-ray diffraction at high temperatures, it was revealed that the monoclinic phase of Li_2TiO_3 was stable in air between room temperature and 900 °C. Also revealed was that there exists the higher order phase transition at about 450 °C, which caused the variation of volume thermal expansion coefficient. The higher order phase transition suggested by high temperature X-ray diffraction could also be detected by dilatometry.

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