

Preparation of $\text{Li}_{3-x}\text{H}_x\text{TaO}_4$ by means of hydrothermal synthesis and protolysis

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Protolysis of lithium orthotantalates resulted in ion exchange of Li^+ with H^+ and $\text{Li}_{3-x}\text{H}_x\text{TaO}_4$ was produced. From the disordered NaCl-type form of Li_3TaO_4 , $\text{Li}_{1.2}\text{H}_{1.8}\text{TaO}_4$ was produced by the ion exchange. The same compound was obtained directly from amorphous tantalum oxide and LiOH solution under hydrothermal conditions. Its lattice constant was calculated to be $a = 0.4270$ (2) nm (standard deviation in brackets) in the cubic system. Substitution of Li^+ with H^+ in $\beta\text{-Li}_3\text{TaO}_4$ resulted in formation of $\text{Li}_{1.1}\text{H}_{1.9}\text{TaO}_4$. Its lattice constants in the triclinic system are estimated to be $a = 0.892$ (1), $b = 0.852$ (2), $c = 0.944$ (1) nm, $\alpha = 89.1$ (1), $\beta = 117.1$ (1) and $\gamma = 87.1$ (1)°. An expansion of the a -axis on the ion exchange and the composition imply that Li^+ ions forming corrugated planes stacked along the a -axis in the ordered NaCl-type structure was replaced with H^+ .

1. Introduction

The lithium ion is known as an ion which is mobile in the crystal lattice of oxides, even though their structures are not layer or tunnel structures. Lithiation of some oxides with the ReO_3 -, spinel- or corundum-type structures [1-3] and ion exchange of LiNbO_3 and LiTaO_3 with H^+ [4, 5] are examples of topotactic reactions caused by mobile Li^+ in the fairly close packed oxide lattices.

The lithium orthotantalate, Li_3TaO_4 , has been known to have several polymorphs [6-8]. Recently, Zocchi *et al.* [9] determined the crystal structures of low- and high-temperature forms of this compound (β - and α -phase called by them). In these phases, Li^+ and Ta^{5+} ions are ordered in the rock salt-type structures. In addition to these ordered rock salt-type structures, a phase where the cations are randomly distributed have been reported [7].

On the course of preparation of alkali niobates and tantalates under low temperature hydrothermal conditions [10, 11], we found that $\text{Li}_{3-x}\text{H}_x\text{TaO}_4$ with the rock salt-type structure could be synthesized under the hydrothermal condition and the same compound was obtained by ion exchange of the disordered rock salt-type Li_3TaO_4 . We describe the preparation of $\text{Li}_{3-x}\text{H}_x\text{TaO}_4$ with the structures based on the rock salt-type structure, which is not layer or tunnel structures.

2. Experimental details

2.1. Hydrothermal synthesis

Tantalum pentoxide (99.5% Ta_2O_5) was fused with 10 times moles of potassium carbonate in a platinum crucible, cooled and dissolved in water. An equal amount of 1M HCl was added to the solution and a white amorphous substance was precipitated. The precipitate was filtrated, washed well with distilled water free from potassium and dried in air. The amorphous material (1 g) was put into an autoclave with various

amount of LiOH (0.2 to 2.0 g) and 10 ml of distilled water. The hydrothermal synthesis was carried out in the temperature and duration time ranges from 90 to 300° C and from 4 to 7 days. The product was washed with distilled water and air dried. The washing at room temperature was confirmed not to affect the chemical composition of products by their X-ray powder patterns and results of protolysis mentioned later.

2.2. Syntheses of β - and disordered Li_3TaO_4

Powders of Li_2CO_3 (99.9%) and Ta_2O_5 were mixed in molar ratios of 3:1 for the β -phase and 3.2:1 for the disordered phase. The mixtures were calcined at 1000° C for the β -phase and 750° C for the disordered phase for 20 h. X-ray powder pattern of β -phase coincided with the previously reported one [7]. That of the disordered phase was similar to those for rock salt-type compounds and the lattice constant agreed well with the value reported by Grenier *et al.* [7]. The α -phase could not be prepared even at 1500° C in contradiction to results of Zocchi *et al.* [9].

2.3. Protolysis

Ground powder of β - or disordered phase of Li_3TaO_4 (2 g) was treated with 200 ml of distilled water at 90° C for 0.5 to 72 h with stirring. The product was filtered, washed with distilled water and dried in air. At room temperature, the reaction proceeded slowly; treatment for 0.5 h resulted in undetected removal of Li^+ . Then, washing with distilled water is considered not to change much the chemical composition of products. Treatment with acids, even as weak as acetic acid, caused corruption of the tantalates to amorphous materials.

2.4. Characterization of products

X-ray diffraction powder patterns were measured on a diffractometer using $\text{CuK}\alpha$ radiation. The lattice constants were determined by least-squares refinement of powder data taken with a scanning speed of $1/4^\circ \text{ min}^{-1}$.

Silicon was used as an internal standard. The diffraction powder patterns for the products on protolysis were rather broad, especially for the products from β -phase, because of degradation of crystals and superposition of reflections. Then the resolution of reflections was not good. The reflections with 2θ from 20 to 50° were used to calculate the lattice constant for the product form β -phase and those with 2θ up to 90° for the disordered phase.

The products were treated with nitric acid, changed to amorphous materials which gave Ta_2O_5 on heating at 1000°C , and filtered. By weighing Ta_2O_5 thus formed, amount of Ta_2O_5 in the products were determined. The filtrate was analysed for lithium by the flame spectroscopy. Differential thermal analysis (DTA) and thermogravimetric analysis (TG) were carried out with a heating rate of $10^\circ\text{C min}^{-1}$ to estimate the amount of water removed and thermal stability.

3. Results and discussion

3.1. $\text{Li}_{3-x}\text{H}_x\text{TaO}_4$ with the disordered rock salt-type structure

The rock salt-type phase was prepared under the hydrothermal conditions and its formation region in the temperature–composition field is shown in Fig. 1. The optimum condition was following; the amount of LiOH was 0.25 g in the Li/Ta ratio of 2.3 and the temperature range from 90 to 250°C . The Li/Ta ratio of product was found to be 1.2 and the lattice constant was calculated to be $a = 0.4270(2)$ nm in the cubic system. Above 250°C , LiTaO_3 and (or) $\beta\text{-Li}_3\text{TaO}_4$ were produced, depending on the amount of LiOH added. The rock salt-type phase with a shorter lattice constant and containing more lithium was also obtained in the higher lithium concentration region, although it gave broad powder diffraction pattern. The maximum Li/Ta ratio and the minimum lattice constant of product obtained by the hydrothermal syntheses were 0.22 and $0.4267(3)$ nm, respectively.

By the protolysis of the disordered rock salt-type Li_3TaO_4 , Li^+ ions were replaced with protons. The

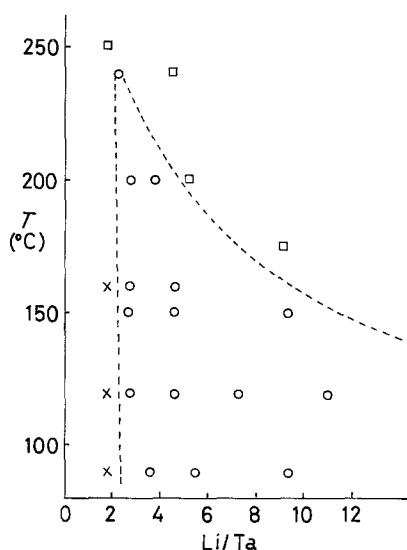


Figure 1 Formation region of $\text{Li}_{3-x}\text{H}_x\text{TaO}_4$ with NaCl-type structure. (O) NaCl-type; (□) LiTaO_3 or $\beta\text{-Li}_3\text{TaO}_4$; (x) amorphous.

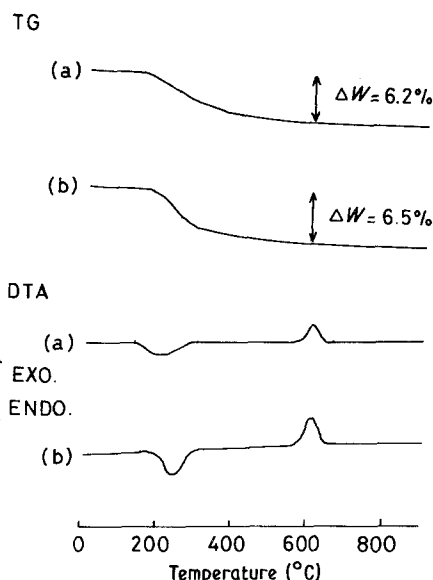


Figure 2 TG–DTA curves for $\text{Li}_{3-x}\text{H}_x\text{TaO}_4$ (a) $\text{Li}_{1.2}\text{H}_{1.8}\text{TaO}_4$ with NaCl-type structure, (b) $\beta\text{-Li}_{1.1}\text{H}_{1.9}\text{TaO}_4$.

Li/Ta ratio observed for single phase of exchanged material was 1.2; about two-thirds of Li^+ were substituted with H^+ . This phase was found to coexist with the original phase from powder diffraction patterns, until the substitution was completed. This fact indicates that no phase with intermediate composition is produced by the ion exchange in contradiction to results of the hydrothermal synthesis. The lattice constant of $a = 0.427(2)$ nm and weight loss for this compound are in good agreement with the value for the product with the same Li/Ta ratio obtained by the hydrothermal synthesis. It is noteworthy that the same compound was prepared by two different methods.

The TG–DTA curves are shown in Fig. 2. The total weight loss of the compound with Li/Ta ratio of 1.2 was 6.2%. This value agrees well to the calculated one (6.1%) on the supposition that H^+ substituted for about two-thirds of Li^+ in Li_3TaO_4 is released as water on heating. This fact indicates that water molecules are not included in the compound. Then, the chemical formula should be represented as $\text{Li}_{3-x}\text{H}_x\text{TaO}_4$; $x = 1.8$ for the product prepared via ion exchange and product with good crystallinity prepared under the hydrothermal condition.

3.2. Ion exchange of $\beta\text{-Li}_3\text{TaO}_4$

As in the case of the disordered phase, the protolysis of $\beta\text{-Li}_3\text{TaO}_4$ resulted in the formation of $\text{Li}_{3-x}\text{H}_x\text{TaO}_4$; exchange of Li^+ with H^+ . The Li/Ta ratio for the exchanged material was 1.1, $x = 1.9$, and no intermediate phase was observed. Observed weight loss of 6.5% was in good agreement with the calculated one (6.4%). The powder diffraction pattern of this compound showed a deformation to the triclinic lattice with the lattice constants of $a = 0.892(1)$, $b = 0.852(2)$, $c = 0.944(1)$ nm, $\alpha = 89.1(2)$, $\beta = 117.1(1)$ and $\gamma = 87.1(1)^\circ$ (Table I). The lattice constants of $\beta\text{-Li}_3\text{TaO}_4$ have been given by Zoochi *et al.* [9] as $a = 0.8500$, $b = 0.8500$, $c = 0.9344$ nm and $\beta = 117.05^\circ$. An expansion of the a -axis is remarkable, while other parameters remain almost unchanged on the ion exchange.

TABLE I X-ray powder data for β -Li_{1.1}H_{1.9}TaO₄

<i>hkl</i>	<i>d</i> _{calc} (nm)	<i>d</i> _{obs} (nm)	Intensity
11 $\bar{1}$	0.582	0.570	vvs
1 $\bar{1}\bar{1}$	0.569		
1 $\bar{1}0$	0.562		
111	0.428	0.422	vs
002	0.420		
200	0.396	0.395	w
20 $\bar{2}$	0.391	0.391	m
02 $\bar{1}$	0.373	0.374	s
022	0.305	0.304	w
112	0.302	0.302	m
3 $\bar{1}\bar{1}$	0.2725	0.2726	m
130	0.2725		
221	0.2577	0.2579	m
3 $\bar{1}0$	0.2477	0.2475	w
3 $\bar{1}\bar{3}$	0.2474		
223	0.2464	0.2464	w
202	0.2388	0.2388	w
02 $\bar{3}$	0.2386		
311	0.2206	0.2195	m
132	0.2174		
40 $\bar{3}$	0.2144	0.2147	vw
004	0.2099	0.2098	vw
33 $\bar{1}$	0.2098		
1 $\bar{3}2$	0.2051	0.2052	w
224	0.2049		
33 $\bar{1}$	0.1982	0.1982	w
400	0.1981		
3 $\bar{3}0$	0.1872	0.1782	m
1 $\bar{3}4$	0.1815	0.1814	vw
5 $\bar{1}3$	0.1716	0.1714	m
22 $\bar{5}$	0.1713		

a = 0.892 (1), *b* = 0.852 (2), *c* = 0.944 (1) nm. α = 89.1 (2), β = 117.1 (1), γ = 87.1 (1)°.

3.3. Thermal stabilities of the products

As seen in Fig. 2, an exothermic peak was observed at about 600°C for both Li_{1.2}H_{1.8}TaO₄ with the rock salt-type structure and Li_{1.1}H_{1.9}TaO₄ prepared from the β -phase. The exothermic peak corresponds to the decomposition of these compounds to a mixture of LiTaO₃ and β -Li₃TaO₄. The weight losses due to release of H⁺ as water for both compounds start at about 200°C and continue up to the decomposition temperature, although almost all H⁺ are removed until about 300°C. The structures of both phases were found to be kept after the removal of major part of H⁺ as water. The X-ray diffraction powder pattern for the rock salt-type phase was shifted to higher angles. That for the exchanged β -phase was very similar to that for the original compound. The monoclinic lattice was recovered by the removal of H⁺. An oxygen deficient phase, Li_{3-x}H_{x-y}TaO_{4-y/2}, is considered to exist in the temperature range between the removal of H⁺ and decomposition. Such oxygen deficient phase caused by removal of protons as water is common to tantalates [11–13].

3.4. Substitution with H⁺

In spite of the difference in the structure, the disordered rock salt-type and β -phase of Li₃TaO₄ show almost the same degrees of exchange of Li⁺ with H⁺. Volume expansion on ion exchange of Li⁺ with H⁺ is 4.0% for the disordered rock salt-type phase and 5.8% for the β -phase. These expansions are compar-

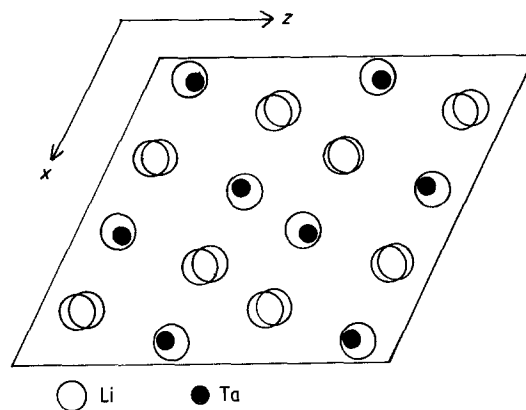


Figure 3 Cation arrangement in β -Li₃TaO₄ projected along the β -axis after Zocchi *et al.* [9]. Both cations locate at $y \sim \pm 1/8$ and $1/2 \pm 1/8$.

able to that for LiNbO₃, where the expansion of 1.3% was observed for substitution of three quarters of Li⁺ with H⁺ [5].

In the case of ordered β -phase, the elongation of the *a*-axis is particular, compared with the uniform expansion of the disordered rock salt-type phase. Fig. 3 shows the ordered arrangement of cations in the β -phase. Each set of crystallographically equivalent cations form a zigzag chain whose direction is parallel to the *a*-axis of the monoclinic cell. One of three sets of Li⁺ ions and Ta⁵⁺ ions form chains along the *c*-axis. As seen in this figure, two kinds of corrugated planes parallel to the (100) alternate along the *a*-axis, the first plane is composed of Li⁺ and Ta⁵⁺ and the second of only Li⁺. The Li⁺ ions on the last plane correspond to two-thirds of total Li⁺ ions and are comparable to the substituted amount of Li⁺ with H⁺. This fact as well as the expansion of the *a*-axis observed suggests that the second group of Li⁺ ions are replaced with H⁺ on protolysis of the β -Li₃TaO₄.

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