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BRIEF COMMUNICATIONS

$LiNbO_3$ with Ilmenite-Type Structure Prepared via Ion-Exchange Reaction

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Lithium niobate, $LiNbO_3$, with ilmenite-type structure was prepared by the ion-exchange reaction in the molten salts from $NaNbO_3$ which was prepared under hydrothermal conditions and also had the ilmenite structure. Its lattice constants are $a = 5.212(1)$ and $c = 14.356(5)$ Å in the hexagonal system. Above 500°C, the structure of this new compound changes from the ilmenite to the $LiNbO_3$ type.

Introduction

The perovskite- and $LiNbO_3$-type structure are general structural types for compounds of composition ABO_3, having A = Li, Na, K, or Rb, and B = Nb or Ta (*1*). We have reported the preparation of a previously unknown form of $NaNbO_3$ having the ilmenite-type structure under the hydrothermal conditions (*2*). The ion exchange of $NaNbO_3$ having the ilmenite-type structure with Li and the preparation of $LiNbO_3$ with the ilmenite-type structure will be reported here.

Experimental Procedure

The starting material for the ion-exchange reaction was $NaNbO_3$ with ilmenite-type structure, prepared by the method described elsewhere (*2*). The ion exchange was carried out in the aqueous solution of 3 *M* LiCl at temperatures up to 160°C for 1–7 days or in eutectic mixtures of LiCl and KCl at 340–380°C for 15–60 min. The chloride was dissolved with distilled water. The product was filtered and washed with distilled water and dried in air. The amount of sodium ion in the filtrate was determined by atomic absorption. The grain size of starting material was about 10 μm. $LiNbO_3$ with ilmenite-type structure was treated in molten $NaNO_3$ at 350°C for several hours. The lattice constants were determined by least-squares refinement of powder data taken by using Cu$K\alpha$ radiation. Silicon was used as an internal standard.

Result and Discussion

A single phase of $LiNbO_3$ with ilmenite-type structure was obtained by using the molten salts in the temperature range from 360 to 380°C for 30–60 min. Lower heating

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temperatures or shorter duration times led to the coexistence of $NaNbO_3$ and $LiNbO_3$ with ilmenite phase. Under conditions of higher temperature or prolonged time $LiNbO_3$ was observed in coexistence with the ilmenite phase. When a product was obtained as a single phase, Na ions were found to have been replaced almost completely with Li ions from the analysis for the filtrate. The amount of Na in $LiNbO_3$ with ilmenite-type structure thus formed was analyzed to be 0.1–0.3 wt%. The TGA for this compound showed no weight loss, and a single phase of $LiNbO_3$ was observed after heating at 1000°C. A reverse exchange, the ion exchange of $LiNbO_3$ with Na^+, at 350°C in molten $NaNO_3$, resulted in the production of two ilmenite phases which were considered to be solid solutions from the shift of X-ray powder pattern. The mixture showed a broad pattern, and the filtrate was not clear. A single phase of ilmenite phase $NaNbO_3$ was not obtained even after 5 hr, but the disruption was considerable. In the aqueous solutions, the rate of exchange was so slow that $LiNbO_3$ and $NaNbO_3$ with ilmenite-type structure coexisted after ion exchange at 160°C for a week.

The X-ray powder pattern for ilmenite-phase $LiNbO_3$ was indexed on a hexagonal unit cell with $a = 5.212(1)$ and $c = 14.356(5)$ Å. In the case of exchange of $NaNbO_3$ with Li^+, the ilmenite phases $LiNbO_3$ appeared soon; no phase with intermediate composition between $NaNbO_3$ and $LiNbO_3$ was observed. On the other hand, the reverse exchange reactions indicated the possibility of formation of solid solution for poorly crystalline materials. However, the solid solution seemed to be limited close to both terminal compositions: the shift of *d*-values for the two ilmenite phase from that of $LiNbO_3$ and $NaNbO_3$ was small and did not depend on the exchange durations. This fact corresponds to the low solubility of Li into $NaNbO_3$ with the perovskite-type structure and of Na into $LiNbO_3$ (*3*).

The transformation from the ilmenite phase of $LiNbO_3$ phase was observed at 520°C by DTA at a heating rate of 10°C/min. This transformation is exothermic, and the transition temperature was dependent on the heating rate. These facts indicate that $LiNbO_3$ with ilmenite-type structure as well as $NaNbO_3$ with the same structural type are metastable.

References

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