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A NEW COMPOUND IN THE TERNARY SYSTEM, Li₂O-TiO₂-Nb₂O₅

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Abstract - A new compound was confirmed to be formed at around the composition Li:Ti:Nb=19:10:12 in the system Li₂O-TiO₂-Nb₂O₅ by reaction at 1100 °C for 2 - 120 hrs in air between Li₂CO₃, TiO₂ and Nb₂O₅. This compound was also produced by reaction of LiNbO₃-0.5 TiO₂ on Li₂TiO₃. Single crystals of the compound were grown using a Li₂MoO₄ flux method. The crystals were shown to possess a hexagonal symmetry with the lattice parameters of a₀=8.89 Å and c₀=55.10 Å by a Weissenberg film.

I INTRODUCTION

The ternary system of Li₂O-TiO₂-Nb₂O₅ has not been so studied as has the binary system of Li₂O-Nb₂O₅ or Li₂O-TiO₂, although a few studies on the phases involving the three components have been reported in relation to solid solution on the join Li₂TiO₃-Li₂NbO₄ (1) or phase equilibrium close to LiNbO₃ in the LiNbO₃-TiO₂ system. (2) The ternary system of Li₂O-TiO₂-Ta₂O₅ has been investigated only on the phases appearing close to LiTaO₃. (3,4) By these ways, the investigations on the ternary system Li₂O-TiO₂-Me₂O₅(Me= Nb, Ta) are almost confined to the phases with the composition close to LiNbO₃ or LiTaO₃. These situations prompted an extensive search for a new phase in the system Li₂O-TiO₂-Nb₂O₅, leading to find out a new compound in this system. Thus, this paper reports determination of the conditions under which a new compound occurs in the ternary system and also reports crystal growth of this compound by flux method.

II EXPERIMENTAL

The starting materials were Li₂CO₃, TiO₂(anatase), and Nb₂O₅, all of reagent grade. These powders with appropriate proportions were mixed, and 250 mg charge of the mixture was heated in air in a Pt boat.
at desired temperatures of 700 - 1100 °C for 2 - 120 hrs. Phases present in a product after heating were identified by X-Ray powder diffraction (XRD) using CuKα radiation, and, on the basis of the XRD results, the formation range of the new compound was determined. The new compound was also produced by solid state reaction of LiNbO₃·0.5TiO₂ with Li₂TiO₃ at 1100 °C. The LiNbO₃ and Li₂TiO₃ used were produced by heating an equimolecular mixture of Li₂CO₃ and Nb₂O₅ at 900 °C for 2 hrs and of Li₂CO₃ and TiO₂ at 800 °C for 2 hrs, respectively.

Single crystals of the new compound were grown using a Li₂MoO₄ by flux method. Either a mixture of Li₂CO₃, TiO₂ and Nb₂O₅ with the composition of the compound or a powder of the compound itself was used as the starting material for the growth. The mixture of this starting material with a flux was placed in a Pt crucible, soaked at 1100 °C, and then cooled down to 750 °C at a rate of 5 °C/hr. The mixing ratio of the starting material to a flux varied in the range of 5 - 20 wt%. The crystals were identified by a Gandolfi camera. A Weissenberg camera was used to determine the crystallographic symmetry and the cell parameters of the compound. The dielectric constant (ε) and the loss tangent (tan δ) of the sintered compact of the compound with the 19Li:10Ti:12Nb composition were determined in the range of frequency 50K - 20MHz at room temperature using Q-meter.

![Fig. 1 Phase relation in the system of Li₂O-TiO₂-Nb₂O₅ at 1100 °C.](image-url)

III-1 Formation of a new compound

Figure 1 shows the ternary phase diagram of Li$_2$O-TiO$_2$-Nb$_2$O$_5$ in which the phases are represented in a product after the reaction of Li$_2$CO$_3$, TiO$_2$ and Nb$_2$O$_5$ with the various compositions at 1100 °C for 2 hrs. First, the reactions with the representative compositions of Li,Ti,Nb=3:2:1 (the point r denoted in Fig. 1), 2:2:1 (s), and 1:1:1 (t) were carried out, giving the mixed phases of a new compound(N) + Li,Ti$_2$, the N + TiO$_2$, and LiNbO$_3$ + TiO$_2$, respectively. So, starting from these points, the compositions were successively changed along the lines of Li:Nb=5:3, Li:Ti=2:1, and Ti:Nb=5:6 in such a way that the phase of Li,Ti$_3$, LiNbO$_3$ or TiO$_2$ in a product is eliminated to give a single phase of N. As a consequence, the region A producing the single phase of the N was found to exist. It is also seen that phase identification around the region A produces the mixed phases of LiNbO$_3$ + TiO$_2$ in the region X, the N + TiO$_2$ in Y, the N + Li,Ti$_2$ in Z, LiNbO$_3$ in W, the N + LiNbO$_3$ in the point a.

The phases appearing on heating at 700 - 1100 °C a mixture of Li$_2$CO$_3$, TiO$_2$, and Nb$_2$O$_5$ with the composition of Li:Ti:Nb=10:5:6 in the region A were examined. TG measurements indicated that the Li$_2$CO$_3$ in the mixture was completely decomposed at above 600 °C. It was found that the several small peaks corresponding to the N appear at 700 °C in addition to the major phase of LiNbO$_3$, followed by a rapid increase of the N with a rapid decrease of LiNbO$_3$ at 800 °C. At 900 - 1100 °C, only the single phase of the N appears. The reactions extended to 120 hrs at 1100 °C gave almost the same result as for 2 hrs.

From the phase diagram in Fig. 1, it can be realized that there is another approach to reach the region A giving the single phase of N: it starts from the LiNbO$_3$, goes on the Li:Nb=1:1 line up to the LiNbO$_3$-0.5TiO$_2$ (point u) (step I), and then turns toward the Li$_3$Ti$_2$O$_5$ on the Li:Ti=2:1 line, finally enters the A (step II). The XRD results of the products obtained by reaction of LiNbO$_3$ with xTiO$_2$ (0<x<0.5) at step I showed that the LiNbO$_3$ is present up to x=0.2, and the two phases of LiNbO$_3$ + TiO$_2$ at 0.3<x<0.5. Determination of the lattice parameters of LiNbO$_3$ (Fig. 2) indicates that the parameter $a_0$ greatly decreases linearly with increasing x up to x<0.25, then gradually decreasing at 0.25<x<0.5, in contrast with a slight decrease of the $c_0$ at 0<x<0.5. Since the ionic radius of Ti$^{4+}$ (r=0.0605 nm) is smaller than that of Nb$^{5+}$ (r=0.064 nm), the dissolution of Ti$^{4+}$ ions into LiNbO$_3$ must occur to produce the solid solution of LiNbO$_3$-xTiO$_2$ (0<x<0.25). At 0.25<x<0.5, the solubility of TiO$_2$ in LiNbO$_3$ must be beyond its limit. This agrees with the above XRD result that TiO$_2$ begins to appear from the x=0.3. The process involved in step II, representing the reaction of the two phases of the solid solution LiNbO$_3$-yLi$_2$TiO$_3$+0.25TiO$_2$ with yLi$_2$TiO$_3$ at successive proportion of y=0.07, 0.17, 0.21, and 0.33, was followed by X-Ray analysis (Fig. 3). It is seen that, as the Li,Ti$_2$O$_3$ is added to the two phases, the TiO$_2$ decreases and disappears at y=0.17, while the LiNbO$_3$ phase still remains, and that the single phase of the N results at y=0.33 belonging to the region A. The measurement of the lattice parameters of LiNbO$_3$ (Fig. 2) shows that both of the $a_0$ and $c_0$ again begin to decrease rapidly with increasing Li$_2$TiO$_3$ added. These results imply that the addition of Li$_2$TiO$_3$ promotes the further dissolution of TiO$_2$ into the LiNbO$_3$-0.25TiO$_2$ phase. The apparent absence of Li$_2$TiO$_3$ phase in spite of its increasing amount to y=0.21 suggests that the Li$_2$TiO$_3$ itself could be dissolved in the LiNbO$_3$ phase. The single phase of N could eventually occur beyond the solubility limit of TiO$_2$ and Li$_2$TiO$_3$ in the LiNbO$_3$ phase.
Fig. 2 Variations of the lattice parameters of LiNbO₃ with the composition of LiNbO₃ₓTiO₂ (0<x<0.5) and with LiNbO₃₀.₅TiO₂ + yLi₂TiO₃ (0<y<0.21).

Fig. 3 X-Ray diffraction pattern of products obtained by reaction at 1100 °C between LiNbO₃₀.₅TiO₂ and yLi₂TiO₃.
A) y=0, B) y=0.07, C) y=0.17, D) y=0.21, E) y=0.33
O: the phase of N, Δ: TiO₂, unmarked peaks correspond to LiNbO₃
The value of the dielectric constant for sintered compacts of the N compound with the relative density of 90% was determined to be $\varepsilon \approx 33$ in the range of 50kHz - 20 MHz and that of $\tan \delta$ decreased from 0.14 to 0.02 with increasing the frequency.

III-2 Crystal growth of the new compound

In the previous section it was noted that a new compound designated as the N can be prepared by reaction between Li$_2$CO$_3$, TiO$_2$ and Nb$_2$O$_5$, or by reaction of LiNbO$_3$.0.5TiO$_2$ with Li$_2$TiO$_3$. However, there has not been a strong evidence that the new compound is a single phase. For this reason, attempts were made to grow single crystals of the new compound by flux method. When a mixture of Li$_2$CO$_3$, TiO$_2$, and Nb$_2$O$_5$ was used as the starting material for the crystal growth, the growth results were the same as if a powder of the new compound itself had been used: the growth using the composition of Li:Ti:Nb=19:10:12 gave the crystals suitable for X-Ray analysis or microscopic observation. The mixing ratio of the starting material to a Li$_2$MoO$_4$ flux was determined to be 10 wt%, since 5 wt% ratio produced opaque and block-shaped crystals, while the ratios more than 15 wt% very fine crystals. Figure 4 shows the single crystals of the new compound obtained at the composition of Li:Ti:Nb=19:10:12. As-grown crystals have almost clear, thin, plate-like hexagonal morphology, and show an appearance of the layered structure, as the crystals become larger. A Gandolfi camera of its one crystal showed a virtually identical X-Ray diffraction pattern to that of the new compound obtained by powder reaction, demonstrating that the new compound is composed of a single phase. Observation of a hexagonal plate crystal under polarization microscope showed an extinction and also a conoscopic figure, indicating that the direction normal to the hexagonal plate is the c-axis. A Weissenberg film of the axis-rotation normal to this crystal face showed a 6-fold symmetry. Thus, it is understood that this new compound possesses a hexagonal symmetry. The lattice parameters of the new compound were determined to be $a_s=8.89$ Å and $c_s=55.10$ Å on the basis of which the X-Ray diffraction pattern of the new compound could be indexed.

![Fig. 4 Single crystals of the new compound grown with the composition of Li:Ti:Nb=19:10:12.](image)
A) optical microscopic photograph, B) SEM photograph
REFERENCES