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Compound and Solid-Solution Formation in the System Li_2O–Nb_2O_5–TiO_2

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A systematic study of compound and solid-solution formation in the system Li_2O–Nb_2O_5–TiO_2 has been made. Several solid-solution series, based on $LiNbO_3$, $LiNb_3O_8$, $Li_2Nb_{28}O_{71}$, Li_2TiO_3, phase M, $Li_2Ti_3O_7$, and TiO_2, have been characterized. In all cases, the principal solid-solution mechanism appears to involve stoichiometric formulae with constant overall cation content. One new phase, of approximate formula $Li_{13}TiNb_5O_{21}$, has been prepared. A subsolidus phase diagram for the ternary system is presented.

Introduction

The title system contains a number of well-characterized binary compounds. Of these, $LiNbO_3$ is an important material with applications in optoelectronics (*1–3*); its properties may be modified by incorporating a certain amount of Ti^{4+} into the structure (*4, 5*). $Li_2Ti_3O_7$ has possible applications as a Li^+ ion-conducting solid electrolyte, especially at elevated temperatures (*6, 7*). TiO_2 has various applications, including use as an electrode material if its electronic characteristics can be modified suitably (*8–12*). Preliminary studies on the system Li_2O–Nb_2O_5–TiO_2 have led to the synthesis of various new materials, including extensive rutile solid solutions, $Ti_{1-4x}Li_xNb_{3x}O_2$, $0 < x < 0.17$ (*13*), $LiNb_3O_8$ solid solutions, $Li_{1-x}Nb_{3-3x}Ti_{4x}O_8$, $0 < x \lesssim 0.06$ (*13*), Li_2TiO_3 solid solutions, $Li_{2+x}Nb_{3x}Ti_{1-4x}O_3$, $0 < x \lesssim 0.22$, which exhibit an ordering–disordering transition (*14*), and a new phase, M, $Li_{1+x}Nb_{1-x}Ti_xO_3$, $0.10 < x < 0.33$, with a distorted $LiNbO_3$ structure (*15*).

The three bounding binary systems have all been well-studied and phase diagrams are available for each. In the system Li_2O–Nb_2O_5, the most recent phase diagrams (*16, 17*) show the existence of the phases Li_3NbO_4, $LiNbO_3$ with a range of stoichiometry from 50 to ~56.5 mole% Nb_2O_5, $LiNb_3O_8$, and $Li_2Nb_{28}O_{71}$. The phase diagram for the system Li_2O–TiO_2 (*18*) shows the phases Li_4TiO_4, Li_2TiO_3 with a range of stoichiometry at high temperatures extending from ~44 to 66 mole% TiO_2, $Li_4Ti_5O_{12}$, and $Li_2Ti_3O_7$ with a narrow range of stoichiometry between 74 and 76% TiO_2. The phase diagram first reported for the system Nb_2O_5–TiO_2 (*19*) shows the formation of

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Nb_2O_5 solid solutions containing up to 5 to 10% TiO_2 and the phases Nb_2TiO_7, Nb_6TiO_{17}, and TiO_2 solid solutions containing up to ~15% Nb_2O_5. In a more recent study of Nb_2O_5-rich compositions (*20*), the phase Nb_6TiO_{17} is replaced by the phase $Nb_{10}Ti_2O_{29}$, in accordance with crystallographic studies on the latter compound (*21*). The high-temperature phase, $Nb_6Ti_2O_{19}$, is also reported (*20*), with a lower limit of stability at 1425°C. Further modifications are made in the latest Nb_2O_5–TiO_2 phase diagram (*22*). These show very little solid solution of TiO_2 in Nb_2O_5 but instead formation of the phase $TiNb_{24}O_{62}$ (*23*). However, no recognition of the phase $Nb_6Ti_2O_{19}$ (*20*) is made in this phase diagram (*22*).

Systematic studies on the ternary system Li_2O–Nb_2O_5–TiO_2 have been limited to the three joins mentioned above, TiO_2–$LiNb_3O_8$ (*13*), Li_2TiO_3–Li_3NbO_4 (*14*), and Li_2TiO_3–$LiNbO_3$ (*15*), and a study of $LiNbO_3$ solid solutions on the join $LiNbO_3$–TiO_2 (*24*). In this latter study, a partial phase diagram for the join was given, together with the results on the composition dependence of the lattice parameters and ferroelectric Curie temperature of the $LiNbO_3$ solid solutions. The present paper reports the results of a comprehensive study of compound and solid-solution formation in the ternary system Li_2O–Nb_2O_5–TiO_2 for all compositions with the exception of those rich in Li_2O.

Experimental

Starting materials were Li_2CO_3 (reagent grade), Nb_2O_5 (99.9%, Aldrich), and TiO_2 (99.2%, Baker). Mixtures totalling 5 to 10 g were prepared by weighing, mixing into a paste with acetone in an agate mortar, drying, and firing in Pt crucibles or Au foil boats; Au was used for compositions containing >50% Li_2O. The mixtures were fired in electric muffle furnaces whose temperatures were controlled and measured to ±30°C. Initial firing was at 600 to 700°C for a few hours to expel CO_2 followed by ~900°C for 12–48 hr. After grinding, the samples were finally fired at temperatures in the range 900 to 1200°C for 24–72 hr, depending on composition. Careful checks were made to ensure that lithia loss by evaporation did not occur to an appreciable extent, especially for the more lithia-rich compositions.

The products of reaction were identified by X-ray powder diffraction using a Siemens D500 diffractometer, CuK_α radiation.

Results

The results of heating experiments on more than 130 compositions, given in an unpublished table,[1] were used to construct the phase diagram given in Fig. 1. This diagram pertains to subsolidus temperatures of ca. 1050 to 1150°C. The phase diagram at lower temperatures is expected to show certain differences, as discussed later. At higher temperatures, 1200 to 1300°C, most compositions are expected to show at least partial melting. The exceptions are those compositions close to the Nb_2O_5–TiO_2 join, most of which are expected to melt at considerably higher temperatures. No systematic study of the melting behavior has been made, apart from that reported previously for the binary joins Li_2TiO_3–Li_3NbO_4 (*14*) and Li_2TiO_3–$LiNbO_3$ (*15*). The various crystalline single-phase regions in the ternary system are now discussed in turn.

$LiNbO_3$ Solid Solutions

$LiNbO_3$ is an unusual material in that it exists on the join Li_2O–Nb_2O_5 as a solid-solution series over the composition range 50 to 56.5% Nb_2O_5 (*2, 25*), with a congruently melting composition at 51.4% Nb_2O_5.

[1] Available from the authors on request.

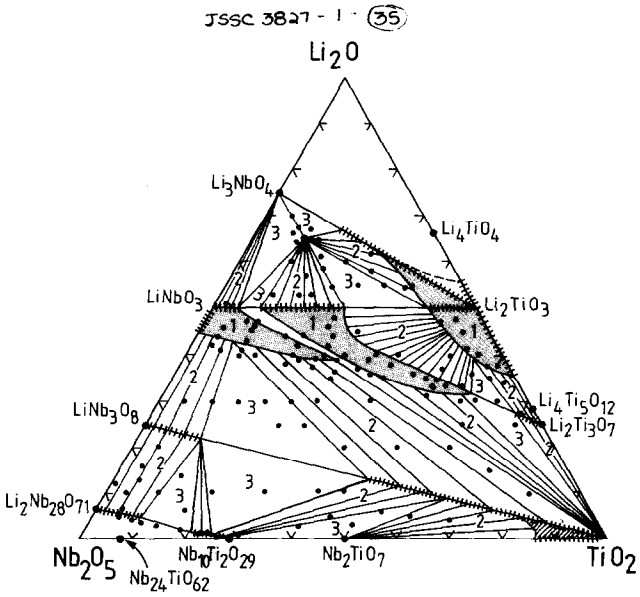

FIG. 1. Phase diagram for the system Li_2O–Nb_2O_5–TiO_2 at ca. 1100°C (in mole%). The compositions studied are marked with solid circles. Compositions to the lithia-rich side of the join Li_3NbO_4–Li_2TiO_3 were not studied. Studies in the Nb_2O_5-rich corner were inconclusive and these results have been omitted.

Limited ranges of $LiNbO_3$ solid solutions have been prepared on the joins $LiNbO_3$–Li_2TiO_3 (*15*) and $LiNbO_3$–TiO_2 (*24*). Our new results show that, in the ternary system, an extensive, wedge-shaped solid-solution area forms (Fig. 1). This solid solution is most extensive in the direction of the hypothetical compound "$Li_2Ti_4O_9$," as emphasized in Fig. 2. On the join $LiNbO_3$–"$Li_2Ti_4O_9$," the solid-solution mechanism is such that the total cation content remains constant, viz.,

$$Li + 3Nb \rightleftharpoons 4Ti.$$

This gives the solid-solution formula Li_{1-x}

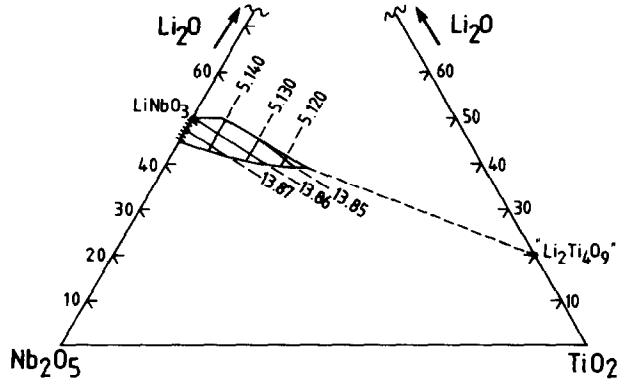

FIG. 2. The $LiNbO_3$ solid-solution field (in mole%), most extensive in the direction of the hypothetical compound "$Li_2Ti_4O_9$." Contours of constant lattice parameter are marked for *a* (5.140 to 5.120 Å) and *c* (13.85 to 13.87 Å).

$Nb_{1-3x}Ti_{4x}O_3$. The range of x is found experimentally to be $0 < x < 0.10$.

The lattice parameters of a selection of $LiNbO_3$ solid-solution compositions have been measured and used to determine the contours of constant lattice parameter content, as indicated in Fig. 2. The hexagonal a parameter shows a gradual decrease with increasing TiO_2 content. The c parameter behaves quite differently and the contours run approximately parallel to the $LiNbO_3$–TiO_2 join.

The results reported in (*24*) were for the join $LiNbO_3$–TiO_2 and are largely consistent with our studies on the complete area of $LiNbO_3$ solid solutions. From Figs. 1 and 2, the $LiNbO_3$ solid solutions on the join $LiNbO_3$–TiO_2 extend to the approximate composition 40 mole% Li_2O, 40% Nb_2O_5, 20% TiO_2. When these solid solutions are written in the form $LiNbO_3 \cdot xTiO_2$, the 40:40:20 composition corresponds to a value of x of 0.25. The limiting value of x given in (*24*) is somewhat less, i.e., 0.205.

$LiNb_3O_8$ Solid Solutions

These are described in (*13*) and have not been studied further. They are shown in Fig. 1 as a hatched line extending part way along the join $LiNb_3O_8$–TiO_2. Again, it should be noted that these solid solutions have a replacement mechanism which retains a constant total cation content.

$Li_2Nb_{28}O_{71}$ Solid Solutions

There was some evidence to suggest that $Li_2Nb_{28}O_{71}$ forms a limited range of solid solutions in the ternary system. The results are consistent with the same replacement mechanism, giving constant overall cation content, that was found for the solid-solution series involving $LiNbO_3$ and $LiNb_3O_8$ described above and for the solid solutions of TiO_2 and $Li_2Ti_3O_7$ discussed later. For the $Li_2Nb_{28}O_{71}$ solid solutions, this mechanism gives rise to the solid-solution formula $Li_{2-x}Nb_{28-3x}Ti_{4x}O_{71}$ and for which the experimental range of x values is $0 < x < 0.43$. The theoretical limit for this solid-solution series occurs when $x = 2$ and corresponds to the composition of the hypothetical phase "$11Nb_2O_5 \cdot 8TiO_2$."

Rutile Solid Solutions

Extensive rutile solid solutions on the join TiO_2–$LiNb_3O_8$ were reported in (*13*) and a more limited range on the join Nb_2O_5–TiO_2 in (*19*). These two series probably link up to form a limited area of ternary solid solutions, bounded approximately by the dashed line shown in Fig. 1, although direct experiments to confirm this have not been made.

$Li_2Ti_3O_7$ Solid Solutions

A limited range of $Li_2Ti_3O_7$ solid solutions forms with the probable replacement mechanism $4Ti^{4+} \rightleftharpoons Li^+ + 3Nb^{5+}$ and formula $Li_{2+x}Nb_{3x}Ti_{3-4x}O_7$, $0 < x \lesssim 0.08$. The hypothetical end-member of this series is the nonexistent phase "$11Li_2O \cdot 9Nb_2O_5$."

Li_2TiO_3 Solid Solutions

An extensive area of ternary Li_2TiO_3 solid solutions forms at high temperatures, in agreement with previous studies on the joins Li_2O–TiO_2 (*18*), Li_2TiO_3–Li_3NbO_4 (*14*), and Li_2TiO_3–$LiNbO_3$ (*15*). Detailed studies on the variation of the low $\rightleftharpoons$ high polymorphic transition temperature with composition have not been made for the ternary system but could be estimated by combining data for the various joins mentioned above.

Phase M Solid Solutions

Phase M is the solid-solution phase $Li_{1+x}Nb_{1-x}Ti_{1+x}O_3$, $0.10 < x < 0.33$, first prepared on the join Li_2TiO_3–$LiNbO_3$ (*15*). Studies on the ternary system show it to form a very extensive, wedge-shaped area of ternary solid solutions. These solid solutions may also, in large part, be derived by the replacement mechanism $Li^+ + 3Nb^{5+}$

$\rightleftharpoons 4Ti^{4+}$; for instance, one edge of the solid-solution field runs parallel with the $Li_2Ti_3O_7$ solid solutions described above. Structural information on these solid solutions is unfortunately lacking since, as yet, we have been unable to prepare single crystals of a size suitable for X-ray work. At the $LiNbO_3$-rich limit, the powder X-ray pattern of the solid solutions is quite similar to that of $LiNbO_3$ and hence a strong structural similarity between the M solid solutions and $LiNbO_3$ is suspected. With increasing Li_2TiO_3/TiO_2 content, major but apparently continuous changes in the X-ray powder patterns occur, as depicted for a selection of compositions in Fig. 3. Since the changes are large, it is possible that a series of structurally related phases exists, rather than a single homogeneous solid-solution series.

Phase C, "$Li_{13}TiNb_5O_{21}$"

This is a new lithia-rich phase stable only at high temperatures, $\gtrsim$900°C. Its composition has not been determined with certainty due to (i) problems of lithia volatilization on heating lithia-rich compositions for extended periods >1000°C and (ii) the slow rate of formation of this new phase. Its composition is most likely to be $65Li_2O \cdot 10TiO_2 \cdot 25Nb_2O_5$ or $Li_{13}TiNb_5O_{21}$. In order to reduce lithia loss, pelleted samples were immersed in presintered powder of the same composition and wrapped in Pt foil bags; after heat treatments the pellets were separated from the surrounding powder and analyzed by X-ray powder diffraction. The decomposition of phase C at temperatures $\lesssim$900°C takes place relatively slowly and hence phase C may be quenched readily to ambient temperatures, where it is kinetically stable. Unindexed X-ray powder data are given in Table I.

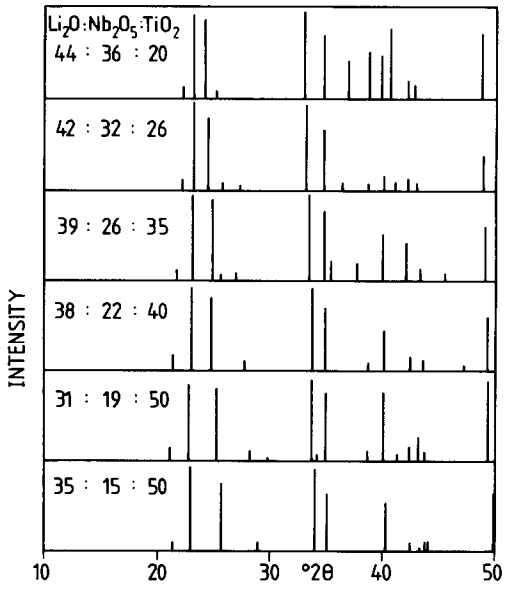

FIG. 3. A selection of X-ray line diagrams for different phase M solid-solution compositions. For each, the composition is given in terms of the oxide molar ratio.

Subsolidus Compatibility Relations at ~1100°C

Apart from the eight ternary phases/solid-solution series outlined above, all remaining compositions on the lithia-deficient side of the join Li_3NbO_4–Li_2TiO_3 give a mixture of either two or three of these eight phases, as indicated in Fig. 1. The Nb_2O_5-rich corner has not been determined in detail and is left blank.

Subsolidus Compatibility Relations at $\lesssim$950°C

Detailed studies of the phase relations at lower temperatures have not been made but some differences must inevitably be present. Thus,

—$Li_4Ti_5O_{12}$ is a thermodynamically stable phase at temperatures <1025°C and should therefore be observed in some ternary compositions.

—$Li_2Ti_3O_7$ is unstable $\lesssim$950°C and should be absent from the diagram, unless the effect of the solid-solution formation is to stabilize $Li_2Ti_3O_7$ to much lower temperatures.

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR PHASE C, "$Li_{13}TiNb_5O_{21}$"

d^a (Å)	I
6.524	23
6.159	14
4.477	4
3.761	5
3.691	31
3.487	19
3.261	20
2.882	18
2.781	5
2.632	7
2.439	17
2.381	4
2.284	2
2.238	3
2.110	100
2.047	2
1.954	5
1.880	4
1.807	3
1.773	2
1.571	6
1.487	41
1.448	4
1.273	2
1.217	5

[a] Internal standard for d measurements was NaCl.

—The Li_2TiO_3 solid solutions are considerably less extensive at lower temperatures, below the temperature of the low $\rightleftharpoons$ high transition.

—Phase C is unstable $\lesssim$950°C and should be absent from the diagram.

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