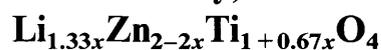


Stoichiometry, structures and polymorphism of spinel-like phases,



Virginia Santos Hernandez,^a Leticia M. Torres Martinez,^a Glenn C. Mather^b and Anthony R. West^b

^aUniversidad Autonoma de Nuevo Leon, Facultad de Quimica, San Nicolas de las Garza, NL, Mexico

^bUniversity of Aberdeen, Department of Chemistry, Meston Walk, Aberdeen, Scotland, UK AB9 2UE

A complete range of spinel-like solid solutions forms between $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Zn_2TiO_4 . Over a range of intermediate compositions, $\text{Li}_{1.33x}\text{Zn}_{2-2x}\text{Ti}_{1+0.67x}\text{O}_4$ ($0.50 \leq x \leq 0.90$), the solid solutions are primitive cubic, but for compositions to either side, they are face centred. Rietveld refinement of powder X-ray diffraction data shows that ordering of Li and Ti onto two sets of octahedral sites is responsible for the primitive structure; Li and Zn are disordered over the tetrahedral sites. A fully ordered, ideal composition occurs at $x = 0.75$, $\text{Li}_2\text{ZnTi}_3\text{O}_8$, which is isostructural with LiFe_5O_8 . The phase diagram of the spinel join shows that the ordered, primitive cubic solid solutions transform to disordered, face-centred cubic solid solutions at high temperatures, with a maximum in the transition temperature at 1150°C for $x = 0.75$. The subsolidus phase diagram $\text{Li}_2\text{TiO}_3\text{-TiO}_2\text{-ZnO}$ at 1150°C has been determined.

Conflicting reports on the occurrence of spinel-like phases in the system $\text{Li}_2\text{O-ZnO-TiO}_2$ have appeared. The two end-member phases, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Zn_2TiO_4 , are well established as spinels.^{1,2} In the system ZnO-TiO_2 , a range of spinel-like solid solutions is reported to form between Zn_2TiO_4 and ZnTiO_3 at temperatures below about 900°C ;³ it has been suggested that instead of a solid solution, a second spinel-like phase with a defective structure, $\text{Zn}_2\text{Ti}_3\text{O}_8$, forms⁴ but also that $\text{Zn}_2\text{Ti}_3\text{O}_8$ is in fact, a low-temperature polymorph of ZnTiO_3 .⁵ Spinel solid solutions are reported between Zn_2TiO_4 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$, with a change in lattice type from face-centred to primitive cubic with increasing $\text{Li}_4\text{Ti}_5\text{O}_{12}$ content.⁶ Spinel phases have been reported with the formulae $\text{Li}_2\text{ZnTi}_3\text{O}_8$ and $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$,⁷ both of which lie on the spinel join, $\text{Zn}_2\text{TiO}_4\text{-Li}_4\text{Ti}_5\text{O}_{12}$, but also with the composition $\text{Li}_2\text{ZnTi}_3\text{O}_8$, which lies to the TiO_2 -rich side of the spinel join.⁸ In addition, an area of spinel-like solid solutions between Zn_2TiO_4 , ZnTiO_3 and $\text{Li}_2\text{ZnTi}_3\text{O}_8$ has been reported.⁶ Whilst Zn_2TiO_4 was generally regarded as a cubic, inverse spinel with Ti, Zn disorder over octahedral sites, prolonged annealing at low temperatures led to a tetragonally distorted structure with octahedral site order.^{9,10} We have carried out a phase diagram study of the system $\text{Li}_2\text{O-ZnO-TiO}_2$ in order to resolve the formula(e) of the ternary spinel-like phases and to understand the nature of the face-centred to primitive transition.

Experimental

The reagents used were: Li_2CO_3 , ZnO and TiO_2 . These were all of analar grade or better and were dried at 200 , 900 and 900°C , respectively. Mixtures of $5\text{-}10\text{ g}$ total mass were ground together with an agate mortar and pestle, using acetone to form a paste, then dried and fired in Pt crucibles at 700°C , for 2 h to decarbonate. Samples were reground, pressed into pellets uniaxially and most were refired at $1050\text{-}1100^\circ\text{C}$, for 12 h . Compositions with a higher Zn content required additional firing at 1100°C for 12 h . Compositions close to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were heated at 950°C for 12 h : $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has an upper limit of stability at 1015°C .¹¹ These various conditions were established by trial and error as those necessary to achieve equilibrium. Under these conditions, loss of Li_2O by volatilisation was not a significant problem; however, if much higher firing temperatures were used, e.g. 1250°C , TiO_2 appeared in samples whose initial composition lay on the

spinel join, indicating that some Li_2O volatilisation had occurred.

Phase identification was carried out by X-ray powder diffraction, (XRD), using a Philips Hägg Guinier camera ($\text{Cu-K}\alpha_1$ radiation) for routine analysis and a Stoe STADI P diffractometer with a linear position-sensitive detector for accurate intensity measurements and for Rietveld refinement. For differential thermal analysis (DTA), a Stanton-Redcroft STA 675 was used, with alumina as an inert reference. Melting temperatures were determined approximately from the appearance of pelleted samples after each stage of a stepwise heating cycle.

Results and Discussion

The spinel join, $\text{Li}_4\text{Ti}_5\text{O}_{12}\text{-Zn}_2\text{TiO}_4$

The results of heating experiments on about 20 compositions on this join are summarised in the form of a phase diagram in Fig. 1. A complete range of spinel-like solid solutions forms and may be represented by the general formula $\text{Li}_{1.33x}\text{Zn}_{2-2x}\text{Ti}_{1+0.67x}\text{O}_4$ ($0 < x < 1$). There are three distinct regions of the phase diagram, which can be described as follows.

(a) $0 < x \leq 0.5$. In this region, the solid solutions have a similar, face-centred cubic powder XRD pattern to that of the end-member Zn_2TiO_4 . Melting temperatures decrease gradually with x .

(b) $0.5 < x < 0.9$. In this region, the solid solutions have the same basic XRD subcell lines as the compositions with $x < 0.5$, but an additional set of reflections appears, which lowers the lattice type to primitive cubic. For compositions in this region, a small, reversible DTA peak occurs, whose temperature is composition-dependent and passes through a maximum at 1150°C and $x = 0.75$ (Fig. 1). This DTA peak corresponds to the primitive to face-centred cubic transition; for most compositions in this range, the high-temperature, face-centred cubic structure cannot be preserved to room temperature by quenching, but compositions close to the limit, e.g. 0.88 , either can be preserved to room temperature as face-centred by quenching or can be prepared as primitive by cooling more slowly.

The occurrence of a DTA peak indicates that there is an enthalpy change associated with the primitive to face-centred transition and, therefore, that the transition has first order

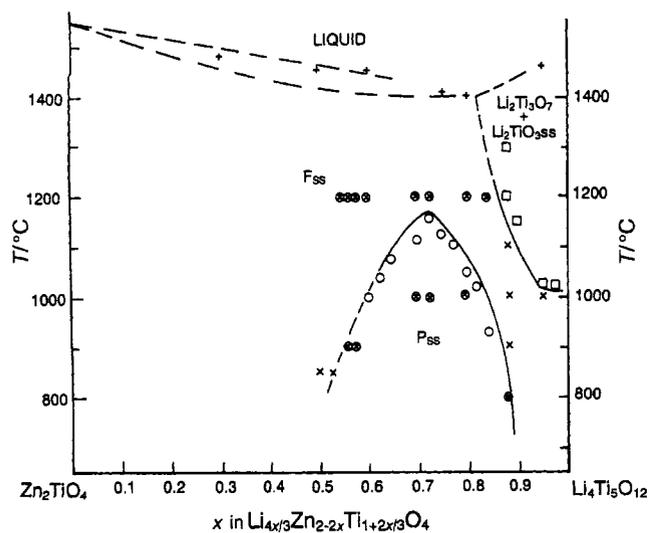


Fig. 1 Phase diagram for Zn_2TiO_4 – $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Symbols represent the phases observed at room temperature after high temperature treatment, as follows: \times , F-spinel ss; \otimes , P-spinel ss; \square , $\text{Li}_2\text{Ti}_3\text{O}_7 + \text{Li}_2\text{TiO}_3$ ss. Approximate melting temperatures are indicated as $+$. Peak temperatures on the cooling cycle of DTA are indicated by \circ ; peak temperatures on heating were generally 10 – 20 °C higher.

character. For compositions around $x=0.75$, the DTA peaks are relatively sharp, but at other compositions they become broader, indicating either a significant width to the (primitive + face-centred) two-phase region or that the transition is losing its first-order character and becoming more continuous in nature. No attempt has been made to determine accurately the thermodynamic status of the phase transition; in Fig. 1, it is simply shown as a single curve representing the temperature of the peak maximum on the DTA heating cycle; data points are peak temperatures on the cooling cycle and were 10 – 20 °C lower than on heating.

(c) $0.9 < x < 1$. In this region, the solid solutions again revert to face-centred cubic. The solid solutions decompose before melting, as does $\text{Li}_4\text{Ti}_5\text{O}_{12}$, giving $\text{Li}_2\text{Ti}_3\text{O}_7$ and Li_2TiO_3 solid solutions. The decomposition temperature rises increasingly rapidly with decreasing x , from 1015 °C at $x=1$ to ca. 1250 °C at $x=0.85$.

Crystal structures of the spinel solid solutions

The structure of one composition, $x=0.75$, was determined by Rietveld refinement of powder XRD data. The atomic coordinates of LiFe_5O_8 were used as starting coordinates¹⁰ for $\text{Li}_2\text{ZnTi}_3\text{O}_8$ ($x=0.75$) and models with various cation distributions were tested by Rietveld refinement; the final coordinates of the preferred model are given in Table 1 with the

observed diffraction pattern and difference plot in Fig. 2. The structure is a spinel derivative in which the octahedral sites are ordered into two sets with full occupancy by Ti(12d) and Li(4b), respectively, as shown in Fig. 3. The tetrahedral sites are occupied by a disordered mixture of Li and Zn. The formula may therefore be written in expanded form as $(\text{Li}_{0.5}\text{Zn}_{0.5})^{\text{tet}}[\text{Ti}_{1.5}\text{Li}_{0.5}]^{\text{oct}}\text{O}_4$. Clearly, the composition $x=0.75$ corresponds to an ideal composition for the primitive cubic spinel solid solutions, as also shown by a maximum in the phase transition temperature and therefore in its thermal stability at this composition. Somewhat unusually, this composition also coincides with an approximate minimum in the melting temperatures, although the crystalline phase prior to

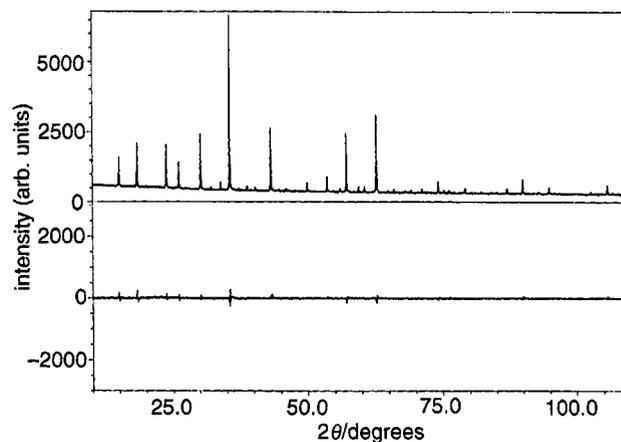


Fig. 2 Observed and difference powder XRD profiles for composition $x=0.75$

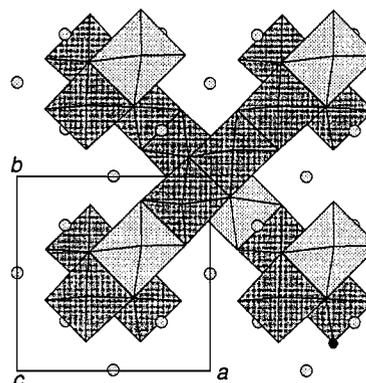


Fig. 3 Projection of part of the structure of $\text{LiZn}_{0.5}\text{Ti}_{1.5}\text{O}_4$ ($x=0.75$) showing ordering of TiO_6 octahedra (shaded) and LiO_6 octahedra (unshaded) which form edge-sharing ribbons parallel to $[110]$ and $[\bar{1}10]$ in alternate layers perpendicular to c . Spheres represent Li, Zn in tetrahedral sites.

Table 1 Structure refinement parameters and bond lengths for $\text{Li}_2\text{ZnTi}_3\text{O}_8$ [space group $P4_332$; $a=8.3710(2)$ Å]

atom	site	x/a	y/b	z/c	U_{iso}	occupancy
Li(1)/Zn(1)	8c	$-0.0016(6)$	$-0.0016(6)$	$-0.0016(6)$	$0.013(1)$	0.5/0.5
Li(2)	4b	$5/8$	$5/8$	$5/8$	$0.01(1)$	1.00
Ti(1)	12d	$0.3677(4)$	$-0.1177(4)$	$1/8$	$0.012(1)$	1.00
O(1)	24e	$0.105(2)$	$0.128(1)$	$0.392(1)$	$0.013(3)$	1.00
O(2)	8c	$0.392(2)$	$0.392(2)$	$0.392(2)$	$0.007(6)$	1.00

$R_p=2.85\%$, $R_{wp}=3.76\%$, $R_1=5.50\%$, $R_{\text{exp}}=2.5\%$

	distance to O(1)/Å	distance to O(2)/Å
Li(1)/Zn(1)	$1.99(1)(\times 3)$	$2.04(1)$
Li(2)	$2.131(9)(\times 6)$	
Ti(1)	$1.97(1)(\times 2)$	$2.02(1)(\times 2)$
	$1.877(9)(\times 2)$	

melting is the disordered, face-centred cubic structure rather than the ordered, primitive cubic one.

The structure of one other primitive cubic composition, $x=0.55$, was investigated by Rietveld refinement. The quality of the refinement was not as good as for the composition $x=0.75$, probably because of the much greater amount of disorder in the cation arrangements. Nevertheless, the broad features of the cation distribution are clear. Basically, the Ti(12d) site now contains some Li and the Zn:Li ratio in the tetrahedral sites has increased to 0.9:0.1. This means that the solid solution mechanism, on changing composition, is complex and involves site redistribution as well as site substitution. Since the overall replacement mechanism must be $3\text{Zn} = 2\text{Li} + \text{Ti}$, the structural formula for compositions $x < 0.75$ is likely to be $(\text{Li}_{0.5-3y}\text{Zn}_{0.5+3y})[\text{Ti}_{1.5-y}\text{Li}_{0.5+y}]\text{O}_4$, i.e. in order to accommodate the extra Zn in the tetrahedral sites, some Li is displaced to occupy vacancies created in the octahedral Ti sublattice.

From the phase-diagram results (Fig. 1), the primitive to face-centred phase boundary appears to occur near the composition $x=0.50$, corresponding to the formula $\text{Li}_{0.67}\text{ZnTi}_{1.33}\text{O}_4$ (i.e. $y=0.167$) and at which the tetrahedral sites are presumed to be fully occupied by Zn. The main driving force for formation of the primitive structure appears to be ordering of Li and Ti on the octahedral sites. This is increasingly difficult for compositions further from $x=0.75$, first because in the range $0.5 < x < 0.75$ there is increasing occupancy of Ti sites by Li and secondly because, for $x < 0.5$, Zn must also increasingly occupy the octahedral sites. Thus, there is little evidence for octahedral site ordering for $x \leq 0.5$.

At much lower values of x and at low temperatures, as the composition Zn_2TiO_4 is approached, there may be an increasing tendency for ordering of Ti and Zn onto two sets of octahedral sites, as shown by structural results on Zn_2TiO_4 subject to a prolonged low-temperature anneal;¹⁰ this arrangement has different symmetry (tetragonal) to that centred on $x=0.75$. This ordering is achieved only with some difficulty in stoichiometric Zn_2TiO_4 , however, and is unlikely to be facilitated by the introduction of Li into the octahedral sites since a fully ordered structure will no longer be possible. Thus, we cannot rule out the possible existence of a short range of tetragonal, ordered Zn_2TiO_4 solid solutions at low x and low temperatures but, as yet, we have no evidence for their existence.

The cubic lattice parameter of the spinel solid solutions as a function of composition x is shown in Fig. 4. Although there is some scatter in the data, there appears to be a change in slope near the ideal, ordered composition $x=0.75$. This could be consistent with a change in solid-solution mechanism at $x=0.75$, since at lower x the octahedral Ti sites will increasingly contain Li and, *vice versa*, at higher x , the octahedral Li sites will increasingly contain some Ti. An alternative interpretation of the data is that they show a general negative departure from the linearity expected for Vegard's law, which is consistent

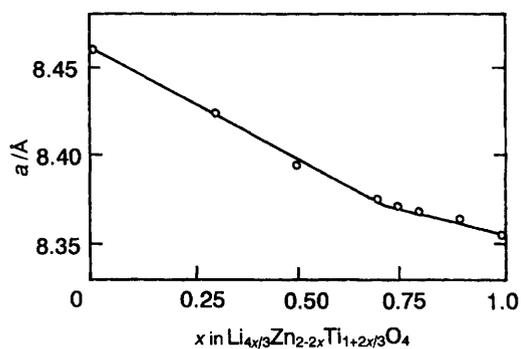


Fig. 4 Lattice parameter a vs. composition of the spinel solid solutions

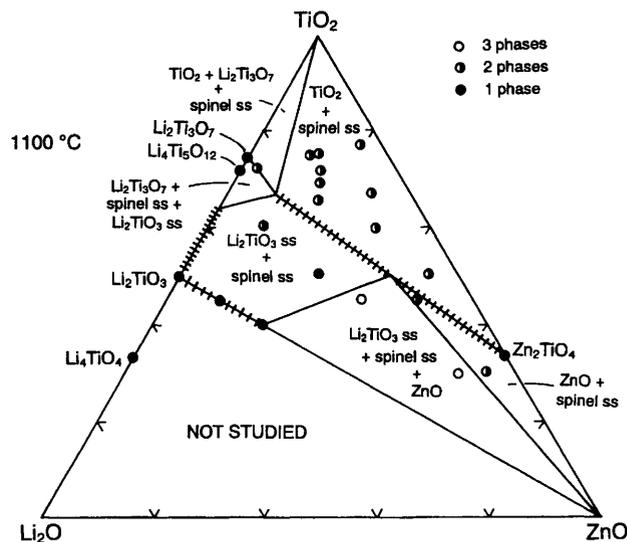


Fig. 5 Subsolidus phase diagram at 1100 °C.

with the observation that intermediate compositions show a preference for cation ordering and therefore an effective reduction in cell volume for these compositions.¹²

The subsolidus phase diagram Li_2TiO_3 - TiO_2 - ZnO

The results of a brief investigation into the phase diagram at *ca.* 1100 °C are shown in Fig. 5. No new ternary phases were encountered; Li_2TiO_3 forms a limited range of solid-solutions with ZnO .¹³ At this temperature, there was no evidence of spinel solid solutions that departed from the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - Zn_2TiO_4 join. Thus, the phase diagram can be divided into a number of two-phase and three-phase regions.

Conclusions

The spinel join, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ - Zn_2TiO_4 , forms a complete range of solid-solutions. Over a range of intermediate compositions, centred around $\text{Li}_2\text{ZnTi}_3\text{O}_8$ corresponding to $x=0.75$ in the general formula $\text{Li}_{1.33x}\text{Zn}_{2-2x}\text{Ti}_{1+0.67x}\text{O}_4$, cation ordering on the octahedral sites leads to a lowering of symmetry from face-centred cubic to primitive cubic. At $x=0.75$, ordering of Li and Ti in the octahedral sites is complete, as represented by the formula $(\text{Li}_{0.5}\text{Zn}_{0.5})[\text{Li}_{0.5}\text{Ti}_{1.5}]\text{O}_4$. This composition shows a maximum in the thermal stability of the ordered phase, as seen in the phase diagram (Fig. 1). For compositions to either side of $x=0.75$, the octahedral site order is no longer complete since the Li:Ti ratio is no longer 1:3 and, hence, the primitive to face-centred transition temperature decreases increasingly rapidly.

Octahedral site order has been reported previously in LiZnNbO_4 ($\equiv \text{Zn}[\text{Li},\text{Nb}]\text{O}_4$) and Zn_2TiO_4 ($\equiv \text{Zn}[\text{Zn},\text{Ti}]\text{O}_4$),¹⁰ although in both these cases the symmetry is lowered to tetragonal. In the present study, we saw no signs of tetragonal splitting in the powder XRD patterns of Zn_2TiO_4 and solid solutions with low x , probably because these samples were cooled rapidly from *ca.* 1100 °C, whereas prolonged annealing at low temperatures was required to develop the tetragonal, fully ordered form of Zn_2TiO_4 .¹⁰ It is possible that the phase diagram (Fig. 1) may, at lower temperatures, show both a more extended composition range for the ordered primitive cubic phase centred on $x=0.75$ and a second ordered tetragonal solid-solution based on Zn_2TiO_4 .

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References

- 1 E J W Verwey and E L Heilmann, *J Chem Phys*, 1947, **15**, 174
- 2 G H Jonker, *Trav Tercera Reun Int React Solidos Madrid*, 1957, **1**, 413
- 3 S S Cole and W K Nelson, *J Phys Chem*, 1938, **42**, 245
- 4 S F Bartram and R A Slepety's, *J Am Ceram Soc*, 1961, **44**, 493
- 5 O Yamaguchi, M Morimi, H Kawabata and K Shimizu, *J Am Ceram Soc*, 1987, **70**, C97
- 6 M-C Chaussy, H Vincent and J-C Joubert, *Bull Soc Chim Fr*, 1965, 198
- 7 N V Porotnikov, N G Chaban, K I Petrov and V G Savenko, *Russ J Inorg Chem*, 1982, **27**, 338
- 8 W A England, J B Goodenough and P J Wiseman, *J Solid State Chem*, 1983, **49**, 289
- 9 J C H Vincent and A Durif, *Bull Soc Chim Fr*, 1966, J C Joubert 246
- 10 S J Marin, M O'Keeffe and D E Partin, *J Solid State Chem*, 1994, **113**, 413
- 11 G Izquierdo and A R West, *Mater Res Bull*, 1980, **15**, 1655
- 12 M Castellanos and A R West, *J Chem Soc Faraday Trans 1*, 1980, **76**, 2159
- 13 M Castellanos, MSc Thesis, Aberdeen University, 1979

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