

Preparation and Crystal Chemistry of Some Tetrahedral Li_3PO_4 -Type Compounds

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The crystal chemistry of Li_3PO_4 , Li_3VO_4 and Li_3AsO_4 are compared. All three have an isostructural low phase, designated β_{II} , and an isostructural high phase, γ_{II} , but in Li_3VO_4 and Li_3AsO_4 the high-low transformation proceeds reversibly through one or more transitional phases some of which can be quenched to ambient. The crystal chemistry of derivative Li_3PO_4 phases, including $\text{Li}_2\text{MgSiO}_4$, $\text{Li}_2\text{ZnSiO}_4$, $\text{Li}_2\text{CoSiO}_4$, $\text{Li}_2\text{MgGeO}_4$ and $\text{Li}_2\text{ZnGeO}_4$ is compared and the occurrence of high, low, and of distorted high and low phases is correlated with the temperature of preparation and rate of cooling. The derivative Li_3PO_4 phases show extensive or complete mutual solubility not only with each other, but with Li_3PO_4 , with M_2XO_4 compounds ($\text{M} = \text{Zn}^{2+}$, Mg^{2+} ; $\text{X} = \text{Ge}^{4+}$, Si^{4+}) and also with Li_4XO_4 compounds ($\text{X} = \text{Ge}^{4+}$, Si^{4+}). The sequence of phase transformations encountered on heating or cooling is quite sensitive to the stoichiometry of the derivative phases.

Introduction

The crystal structures of both the high and low temperature forms of Li_3PO_4 have been determined (1, 2). The low form occurs in nature as the mineral lithiophosphate (3): it can also be precipitated from aqueous solution (4). The Li_3PO_4 structures are derived from that of wurtzite (ZnS) and are built up of oxygens in approximately hexagonal close packing; the cations occupy ordered tetrahedral sites. Other isostructural oxide phases (Li_3AsO_4 , high and low forms; Li_3VO_4 , low form) have been found (1, 5, 6): however, Li_3VO_4 is also reported as having a total of five polymorphs (7, 8).

Recently, independent investigations have disclosed that Li_3PO_4 -derivative structures can be prepared; for example, $\text{Li}_2\text{ZnSiO}_4$ and $\text{Li}_2\text{MgSiO}_4$ (9-12). In the more detailed of these studies, the range of stoichiometry and polymorphism of the $\text{Li}_2\text{ZnSiO}_4$ and $\text{Li}_2\text{MgSiO}_4$ phases in the Li_4SiO_4 - Zn_2SiO_4 and Li_4SiO_4 - Mg_2SiO_4 systems was examined (9, 10, 12). At the $\text{Li}_2\text{ZnSiO}_4$ composition, six polymorphs were prepared, four of which could be preserved to ambient. Two polymorphs are isostructural with the high and low forms of Li_3PO_4 ; the remaining four are structurally very similar to either high or low Li_3PO_4 , but are of lower symmetry. In a concurrent study, the existence of derivative Li_3PO_4 structures was also reported but the

complexities of the polymorphism of the individual compounds were not noted (11).

In the present study, new data are presented on the polymorphism and thermodynamic stability of Li_3XO_4 phases and of their derivative $\text{Li}_2\text{M}^{2+}\text{X}^{4+}\text{O}_4$ structures.

Experimental

The various compounds were prepared by heating mixtures of the appropriate oxides or carbonates. These mixtures were contained in either gold or platinum foil envelopes or crucibles and were heated in air in temperature-controlled muffle furnaces. Normally, 1-10 g samples were removed from the furnace and allowed to cool to ambient. Where rapid quenching or very accurate temperature control was desired, 20-100 mg samples were suspended in a vertical tube quenching furnace, controlled to $\pm 2^\circ\text{C}$. At the conclusion of a run, the sample was dropped into mercury. Sluggish low-temperature equilibria were investigated hydrothermally: the samples, wrapped in gold foil, were placed in externally-heated, cold-seal pressure vessels. Comparatively low water vapour pressures (300-600 bars) were used at temperatures up to ca. 600°C .

The products of reaction were identified with the aid of a Nonius Guinier camera. Powder X-ray data were obtained with this camera, or with a similar

high-temperature model. Both used quartz-mono-chromatized $\text{CuK}\alpha_{1,2}$ radiation: $\lambda_{\text{mean}} = 1.54018 \text{ \AA}$. Intensities were estimated visually from the films. In addition, phase transitions were studied directly at high temperatures using a Du Pont 900 DTA and also a continuously recording high-temperature Guinier-Lenne powder X-ray camera. Where inversion temperatures are taken from the DTA, these were obtained at a uniform heating rate which always lay in the range $15\text{--}20^\circ\text{C min}^{-1}$. Cooling usually was not programmed; the rate varied with temperature, but was generally rather less than the heating rate.

Results

Figure 1 summarizes the results which have been obtained. The nomenclature used to designate the polymorphs is that proposed for $\text{Li}_2\text{ZnSiO}_4$ (9). Low Li_3PO_4 has the β_{II} structure, high Li_3PO_4 the γ_{II} structure. The greek-letter prefix denotes the parental relationship, the suffix denotes the particular variant. In every case, where both β and γ type phases form, the β -phase or phases are stable at the lower temperatures. However, it is frequently possible to preserve a high-temperature phase metastably to ambient by rapid cooling. Once a phase has entered its region of metastable persistence, it may undergo one or more metastable phase transformations: several examples are shown in Fig. 2 which attempts to summarize schematically the relative stabilities of the polymorphs of each

compound studied. Powder X-ray data for the more important new phases are collected in Table I.

Li_3VO_4 . Li_3VO_4 was prepared by reacting Li_2CO_3 and V_2O_5 at 900°C for 14 h. It is reported to melt congruently at 1152°C ; by DTA, inversions were noted at 724° , 773° , and 1036°C (7). Another investigation showed polymorphic transitions at 662° and 730°C ; melting occurred at 1154°C (8). In the present study, heat effects were found on heating at 540° (on cooling, 440°C), 737° (on cooling, 647°C), 778° (on cooling, 694°C), and at 1058° (on cooling, 972°C). Because of the considerable hysteresis associated with the inversions, the presence of transitions at *ca.* 737° , 778° , and 1058°C on heating appears to be well established, although the true transition temperatures are not known precisely from DTA. High temperature X-ray powder photographs obtained at heating and cooling rates of $0.5\text{--}1.0^\circ\text{C min}^{-1}$ show transitions at temperatures which are comparable with those obtained by DTA.

Normal cooling of the fully reacted starting material from 900°C gave $\beta_{\text{II}} - \text{Li}_3\text{VO}_4$. By high-temperature X-ray, this transforms above *ca.* 750°C to the γ_{II} phase via an intermediate which has no counterpart among the other β - and γ -type phases. This intermediate appears reversibly upon heating and cooling, and is probably an equilibrium phase; it is designated $T_1 - \text{Li}_3\text{VO}_4$ ($T = \text{Transitional}$). The T_1 phase is closely related to both the β and γ parents but is one of the few phases encountered which cannot definitely be classified into one family or the other. A characteristic difference between β

	Li_3PO_4	Li_3VO_4	Li_3AsO_4	$\text{Li}_2\text{ZnSiO}_4$	$\text{Li}_2\text{ZrGeO}_4$	$\text{Li}_2\text{MgSiO}_4$	$\text{Li}_2\text{MgGeO}_4$	$\text{Li}_2\text{CoSiO}_4$	$\text{Li}_2\text{CoGeO}_4$	Cu_3AsS_4
β_{II}	shaded	shaded	shaded	shaded	shaded	shaded	shaded	shaded	shaded	shaded
β'_{II}				shaded	shaded		shaded		?	
β_{I}				shaded				shaded		
β'_{I}				shaded						
T-PHASES		shaded	shaded							
δ_{II}	shaded	shaded	shaded	shaded		shaded	shaded	shaded		
δ_{O}				shaded		shaded	shaded	shaded		

FIG. 1. Summary of the crystal chemistry of Li_3PO_4 and of its derivative structures. Shaded areas indicate the forms which have been obtained for each compound. A β_{II} phase, which probably exists for $\text{Li}_2\text{CoGeO}_4$, is shown by a question mark.

TABLE I
POWDER X-RAY DATA FOR SOME Li_3XO_4 AND Li_2MXO_4 PHASES RELATED TO Li_3PO_4

$\text{Li}_2\text{CoSiO}_4$ $\beta_{\text{II}}, 25^\circ\text{C}$			Li_3VO_4 $X-\beta_{\text{II}}$		Li_3VO_4 $T_{\text{I}}, 25^\circ\text{C}$		Li_3VO_4 $T_{\text{II}}, 25^\circ\text{C}$		Li_3AsO_4 $T_{\text{II}}, 25^\circ\text{C}$	
$d(\text{\AA})$	I	hkl	$d(\text{\AA})$	I	$d(\text{\AA})$	I	$d(\text{\AA})$	I	$d(\text{\AA})$	I
5.4	80	1 1 0	5.5	40	5.5	60	5.5	40	5.4	60
4.08	60	1 2 0	4.17b	100	4.33	20				
3.88	60	1 0 1	3.96	20	4.17	100	4.18	100	4.09	100
3.65	100	1 1 1, 0 2 1	3.92	80	4.14					
3.14	20	2 0 0, 1 2 1	3.71	20	3.97	80	3.97	80	3.90	100
3.10	40	1 3 0	3.69	60	3.72	60	3.72	60	3.67	80
2.71	80	2 2 0	3.20	10	3.21	20	3.21	20	3.16	60
2.68	60	0 4 0	3.18	60	3.20	20	3.19	20	3.13	80
2.47	80	0 0 2	3.10	10	3.18	60				
2.38	60	2 2 1	2.88	10	3.11	40				
2.36	20	0 4 1	2.74 _s	80	2.88	40				
			2.73	40	2.75	40	2.75	60	2.70	80
			2.52	20	2.73 _s	80			2.68 _s	40
			2.50	10	2.52	100	2.52	60	2.49	80
			2.48	60						

$\text{Li}_2\text{ZnGeO}_4$ $\beta_{\text{II}}, 25^\circ\text{C}$		$\text{Li}_2\text{MgGeO}_4$ $\beta_{\text{II}}, 25^\circ\text{C}$		$\text{Li}_2\text{CoSiO}_4$ $\beta_{\text{II}}, 25^\circ\text{C}$		$\text{Li}_2\text{ZnGeO}_4$ $\beta_{\text{II}'}, 25^\circ\text{C}$		$\text{Li}_2\text{MgGeO}_4$ $\beta_{\text{II}'}, 25^\circ\text{C}$		$\text{Li}_2\text{CoGeO}_4$ $\beta_{\text{II}'}, 25^\circ\text{C}$		
$d(\text{\AA})$	I	$d(\text{\AA})$	I	$d(\text{\AA})$	I	$d(\text{\AA})$	I	$d(\text{\AA})$	I	$d(\text{\AA})$	I	hkl
5.5	<10	5.5	20			5.5	<10	5.5	20			0 1 0
4.16	100	4.18	100	4.08	60	4.16	80	4.18	80	4.17	80	1 1 0
3.99	100	3.96	100	3.89	60	3.99	100	3.96	100	3.96	80	1 0 1
						3.98				3.95 _s		
		3.70	40	3.64	10	3.70	10	3.70	40	3.70	10	0 1 1
3.20	40	3.20	60	3.14	20	3.20	40	3.20	60	3.20	20	2 0 0, 1 1 1
2.75 _s	60	2.75 _s	80	2.71	80	2.75	60	2.75 _s	80	2.75	100	2 1 0
2.72	40	2.74	60	2.68	60	2.71 _s	40	2.74	60	2.74	60	0 2 0
2.52	60	2.50	80	2.47	100	2.52	80	2.50	80	2.50	80	0 0 2
2.50	20	2.51 _s	20			2.50	40	2.51	20			1 2 0

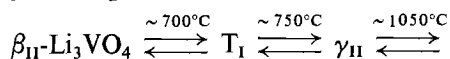
Li_3VO_4 $\gamma_{\text{II}}, 800^\circ\text{C}$		$\text{Li}_2\text{MgGeO}_4$ $\gamma_{\text{II}}, 25^\circ\text{C}$		$\text{Li}_2\text{CoSiO}_4$ $\gamma_{\text{II}}, 25^\circ\text{C}$			$\text{Li}_2\text{CoSiO}_4$ $\gamma_0, 25^\circ\text{C}$		
$d(\text{\AA})$	I	$d(\text{\AA})$	I	$d(\text{\AA})$	I	hkl	$d(\text{\AA})$	I	hkl
5.6	40	5.5	40	5.4	10	0 2 0	5.4	60	1 1 0, 0 2 0
4.7	40	4.63	20			0 1 1			
4.21	80	4.19	100	4.08	80	1 2 0	4.08	80	1 2 0
4.06	60	4.01	100	3.91	60	1 0 1	3.92	60	1 0 1
3.79	100	3.76	40	3.69	40	1 1 1, 0 2 1	3.69	20	1 1 1, 0 2 1
		3.74	40				3.67	100	
3.27	20	3.23	40	3.16	10	1 2 1	3.16	20	1 2 1
3.23	40	3.21	40	3.10	10	2 0 0	3.10	60	2 0 0, 1 3 0, 2 1 0
		2.97	10	2.90	10	0 3 1	2.90	20	0 3 1
2.79	40	2.77 _s	80	2.71	100	2 2 0	2.71	100	2 2 0
2.76	20	2.74	60	2.68	60	0 4 0	2.68	60	0 4 0
2.72	40	2.69 _s	40	2.65	20	1 3 1	2.65	20	1 3 1
							2.64	20	
2.66	40	2.64	40	2.59	20	2 1 1	2.59	20	2 1 1
2.60	100	2.55	80	2.51 _s	100	0 0 2	2.57	20	
							2.51 _s	100	0 0 2

powder patterns obtained at much slower heating and cooling rates, *ca.* $0.1^{\circ}\text{C min}^{-1}$. The T_{I} phase is again observed as an intermediate in the $\gamma_{\text{II}} \rightleftharpoons \beta_{\text{II}}$ reaction: it occurs between 650° and 750°C , approximately but over most of this range a different variant of T_{I} is encountered, the most notable difference being the apparent absence of the pseudo-orthorhombic (002) reflection. This variant has not been specially designated.

At lower temperatures, the β_{II} field must be divided; over the range of temperatures between 300° and 650°C , a β variant is obtained which is characterized by the absence of the (002) reflection. The (020) and (210) reflections either become very weak or are also absent. In addition, the (101) and (011) reflections of this phase, designated $X\text{-}\beta_{\text{II}}$, appear to split. A further variant of the β_{II} phase was produced by annealing a sample of $\beta_{\text{II}}\text{-Li}_3\text{VO}_4$ at 650°C for 21 days. Its powder pattern, obtained at ambient, is very similar to β_{II} but in addition to having the (101) and (011) reflections split, as was noted in the $X\text{-}\beta_{\text{II}}$ phase, a number of weak extra powder lines appeared (Table 1). This modification has been designated $X'\text{-}\beta_{\text{II}}$. $X'\text{-}\beta_{\text{II}}$ may be the equilibrium phase at *ca.* 650°C , or it may form metastably by inversion of $X\text{-}\beta_{\text{II}}$ during cooling. The latter view finds some support inasmuch as prolonged annealing of Li_3VO_4 at both 400° and 500°C yielded only β_{II} after cooling to ambient. In Fig. 2, $X'\text{-}\beta_{\text{II}}$ is shown as being metastable at all temperatures with respect to β_{II} .

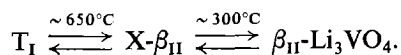
No phase changes were observed in the high-temperature powder patterns which could be used to explain the origin of the heat effect noted on the DTA at 540°C .

To summarize, the main sequence of phase transformations encountered at the heating and cooling rates typically used in DTA is:



(Unidentified high form of Li_3VO_4). Rapid quenching from *ca.* 1140°C yields T_{II} at ambient; it is probable that γ_{II} forms as an intermediate.

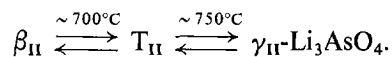
With slow cooling of $T_{\text{I}}\text{-Li}_3\text{VO}_4$,



Prolonged annealing of Li_3VO_4 (21 days) at 650°C , followed by normal cooling to ambient, yields yet another variant, $X'\text{-}\beta_{\text{II}}\text{-Li}_3\text{VO}_4$: its stability relative to the other low temperature modifications is uncertain.

Li_3AsO_4 . Two polymorphs isostructural with $\beta_{\text{II}}\text{-}$ and $\gamma_{\text{II}}\text{-Li}_3\text{PO}_4$ have been reported (6); the γ_{II}

form can be quenched to ambient. In this study, ammonium arsenate and lithium carbonate were reacted at *ca.* 850°C for 12 h. A small amount of Li_2CO_3 was the only impurity observed in the powder pattern. By DTA, reversible transitions were observed at 716° (on cooling, 642°C) and 790° (on cooling, 675°C). A small heat effect was also noted at 412°C on the heating cycle, but this is probably due to an inversion in the Li_2CO_3 impurity (13). By cooling at various rates from 850°C , three phases (β_{II} , γ_{II} and an intermediate phase) could be obtained at ambient. The intermediate phase corresponds very closely to one of the transitional phases—in this instance, the T_{II} phase—observed for Li_3VO_4 . The probable equilibrium transformation sequence is thus:



$\text{Li}_2\text{ZnGeO}_4$. The $\beta_{\text{II}} \rightleftharpoons \beta_{\text{II}'}$ inversion is rapidly reversible by DTA. The β_{II} form, stable only above 590°C , is readily preserved to ambient by rapid quenching from high temperatures.

$\text{Li}_2\text{MgGeO}_4$. Four polymorphs, γ_{II} , γ_0 , β_{II} and $\beta_{\text{II}'}$ can be obtained at ambient. The γ_{II} phase is preserved only by rapid quenching: slightly slower cooling gives a mixture of γ_0 and β_{II} -type phases. Pure γ_0 was never obtained: γ_{II} rapidly reverts to $\beta_{\text{II}'}$ on annealing at $400^{\circ}\text{--}500^{\circ}\text{C}$. The $\beta_{\text{II}'}$ \rightleftharpoons β_{II} inversion is rapidly reversible by DTA, but the β_{II} \rightleftharpoons γ_{II} inversion is reversible only with large hysteresis (*ca.* 180°C) at these heating and cooling rates. By high-temperature X-ray, a hysteresis of *ca.* 120°C was observed. The mean temperature of the β_{II} \rightleftharpoons γ_{II} inversion is 900°C .

$\text{Li}_2\text{CoSiO}_4$ and " $\text{Li}_2\text{NiSiO}_4$." Cobalt, the smallest of the divalent transition metal ions, is readily accommodated in Li_3PO_4 -type structures, whereas the corresponding nickel-containing bulk composition, reacted at 1050°C , gave only NiO and Li_2SiO_3 . Four modifications of $\text{Li}_2\text{CoSiO}_4$ were prepared, and all could be obtained at ambient by using suitable cooling rates: the γ_{II} phase by rapid quenching from above 1000°C , γ_0 by slightly slower cooling; β_{II} by static heating of any other phases at temperatures between 650 and 800°C followed by quenching, and β_{I} by slow cooling of a β_{II} -containing preparation. All the modifications had an intense deep blue colour. By DTA, the β_{II} \rightleftharpoons γ_{II} inversion occurred with considerable hysteresis—in this instance, 170°C .

$\text{Li}_2\text{CoGeO}_4$. A small, reversible heat effect was found by DTA at 485°C . The heat effect is thought to be due to a β_{II} \rightleftharpoons $\beta_{\text{II}'}$ inversion; however, no high

temperature powder data were obtained for this compound, and it is not clear from the X-ray photographs whether the modification obtained at ambient is β_{II} or β_{I} . $\text{Li}_2\text{CoGeO}_4$.

Solid Solutions Between Derivative Li_3PO_4 Phases

It has been previously shown that $\text{Li}_2\text{MgSiO}_4$ and $\text{Li}_2\text{ZnSiO}_4$ exhibit complete miscibility (12). The stability of the β - and γ -type phases was determined from hydrothermal runs and it was found that β -solid solutions extended from $\text{Li}_2\text{ZnSiO}_4$ to ca. 90% $\text{Li}_2\text{MgSiO}_4$. The upper stability limit of the β -solid solutions decreased with increasing magnesium content. A limited number of experiments have been made on various other joins to confirm the hypothesis that these structurally related Li_3PO_4 -type phases should, in general, be miscible. On the $\text{Li}_2\text{MgSiO}_4$ - $\text{Li}_2\text{MgGeO}_4$ join, a composition at $\text{Li}_2\text{MgGe}_{0.1}\text{Si}_{0.9}\text{O}_4$ was heated at 1240°C for 24 h. The product obtained at ambient was a homogeneous γ_0 solid solution. By DTA, the $\gamma_0 \rightleftharpoons \gamma_{\text{II}}$ inversion was found to occur reversibly at a temperature which was 5 - 10°C lower than for $\text{Li}_2\text{MgSiO}_4$. A hydrothermal run made at 470°C did not yield any β -phase: this result is similar to that obtained for $\text{Li}_2\text{MgSiO}_4$.

On the join $\text{Li}_2\text{ZnSiO}_4$ - $\text{Li}_2\text{ZnGeO}_4$, a composition at $\text{Li}_2\text{ZnGe}_{0.1}\text{Si}_{0.9}\text{O}_4$ was heated at 1240°C for 24 h. This also yielded a γ_0 solid solution at ambient. However, substitution of 0.1 mole fraction germanium for silicon aids in the subsequent conversion of γ -type to β -type phases. This is reflected in an increase in the upper temperature stability limit of the β -type phases to ca. 960°C compared with ca. 870°C for $\text{Li}_2\text{ZnSiO}_4$, and also in an increase in the rate of conversion of γ -type phases at much lower temperatures. By DTA, the $\gamma_0 \rightleftharpoons \gamma_{\text{II}}$ inversion temperature could not be determined accurately because the competing reaction, conversion of γ - to β -type phases, proceeded readily at ca. 600°C and only a broad indistinct endotherm was observed at the approximate temperature of the $\gamma_0 \rightarrow \gamma_{\text{II}}$ inversion. The $\beta_{\text{I}} \rightleftharpoons \beta_{\text{II}}$ inversion temperature is lowered by 5° - 10°C as compared with $\text{Li}_2\text{ZnSiO}_4$. However, the inversion now becomes more complicated as a β_{II} phase probably appears as an intermediate product. Cooling of this β_{II} phase yields β_{I} at ambient, and it becomes easier to obtain the β_{I} phase at this composition than for $\text{Li}_2\text{ZnSiO}_4$. For $\text{Li}_2\text{ZnGeO}_4$, the stability limits of the β_{II} phase expands much further, and it appears to be the equilibrium phase at temperatures below 585°C .

Solid Solution Between Li_3PO_4 and $\text{Li}_2\text{ZnSiO}_4$

Solid solution extends from $\text{Li}_2\text{ZnSiO}_4$ to at least 30 mol% Li_3PO_4 at 1400°C ; compositions richer in Li_3PO_4 were not studied. After heating for 24 h and cooling normally to ambient, γ_0 - $\text{Li}_2\text{ZnSiO}_4$ is obtained. However, with increasing Li_3PO_4 content (10, 20, and 30 mole% Li_3PO_4) the powder X-ray pattern obtained at ambient changes gradually and apparently continuously from γ_0 to γ_{I} type. The γ_{I} phase had previously been obtained at ambient from certain compositions in the Li_4SiO_4 - Zn_2SiO_4 system (9, 10); although γ_{I} was never obtained at ambient for $\text{Li}_2\text{ZnSiO}_4$ itself, it was thought to occur over a very narrow temperature range as a transitional phase in the $\gamma_{\text{II}} \rightleftharpoons \gamma_0$ inversion. The γ_{I} and γ_0 phases probably have lower crystallographic symmetry than γ_{II} , and the splitting of X-ray reflections which is characteristic of the γ_0 phase gradually becomes lessened by increasing Li_3PO_4 substitution. Thus $\gamma_0 \rightleftharpoons \gamma_{\text{II}}$ is probably a second-order transition. The γ_{I} and γ_0 distortions do not occur for Li_3PO_4 itself. On DTA, the temperature range of thermal activity characteristic of the γ -transitions broadens and gradually fades away with increasing Li_3PO_4 content of the solid solutions. β -patrial phases can also be produced by hydrothermal treatment. The solid solution containing 10 mol% Li_3PO_4 was converted completely to the β_{I} phase; by DTA, the $\beta_{\text{I}} \rightleftharpoons \beta_{\text{II}}$ inversion temperature of this solid solution was lowered by ca. 10°C compared with $\text{Li}_2\text{ZnSiO}_4$. More phosphorous-rich solid solutions were only partly converted to β_{I} solid solutions at the pressures and temperatures used.

Solid Solutions Between $\text{Li}_2\text{M}^{2+}\text{XO}_4$ and $\text{M}_2^{2+}\text{XO}_4$ Compounds

In most binary orthosilicate and germanate systems which form a derivative Li_3PO_4 -type phase, the M_2XO_4 end member has either the phenacite or olivine structure; for example, Mg_2SiO_4 (olivine) or Zn_2SiO_4 (phenacite). The $\text{Li}_2\text{M}^{2+}\text{XO}_4$ phases which form in both the Li_4SiO_4 - Mg_2SiO_4 and Li_4SiO_4 - Zn_2SiO_4 systems exhibit a considerable range of stoichiometry, extending from the ideal composition toward both the Li_4SiO_4 and $\text{M}_2^{2+}\text{SiO}_4$ end members (9, 12). It is experimentally more difficult to determine quantitatively the lithia-rich limits of these solid solutions on account of the reactivity and volatility of the high-lithia compositions, but it is rather easier to determine the $\text{M}_2^{2+}\text{SiO}_4$ -rich limits. Recognition of the existence of these solid solutions is important because the sequence of

phase transformations which occur during their cooling is controlled by two factors: the cooling rate and the stoichiometry. Thus, a range of zinc-rich γ_{II} lithium zinc orthosilicates may be cooled slowly to yield "Phase C," a new Li_3PO_4 -derivative structure containing *ca.* 62 mol% Zn_2SiO_4 . Phase C cannot be obtained at the $\text{Li}_2\text{ZnSiO}_4$ composition. As it was suspected that extensive solid solutions would be a general feature of all orthosilicate systems of this type, some experiments were undertaken in the corresponding germanium systems. In $\text{Li}_2\text{MgGeO}_4$ - Mg_2GeO_4 mixtures, only slight solid solution of Mg_2GeO_4 occurs, estimated at 1-2 mol% Mg_2GeO_4 at 1000°C. This follows closely the behaviour of the corresponding silicate system. $\text{Li}_2\text{ZnGeO}_4$ can take a considerable excess of Zn_2GeO_4 into solid solution. The solubility limits are sharply temperature dependent and are estimated at approximately 5-6 mol% Zn_2GeO_4 at 900°C, but approximately 30% Zn_2GeO_4 at 1150°C. A rapid increase in the extent of the solid solution field above *ca.* 900°C was also noted in the $\text{Li}_2\text{ZnSiO}_4$ - Zn_2SiO_4 system, although a comparison of the two systems at any one temperature shows that the extent of solid solution is greater in the silicate system. β - $\text{Li}_2\text{ZnSiO}_4$ and β - $\text{Li}_2\text{ZnGeO}_4$ cannot take more than a few mole percent Zn_2SiO_4 or Zn_2GeO_4 , respectively, into solid solution. The maximum solid solution of Zn_2GeO_4 in $\text{Li}_2\text{ZnGeO}_4$ causes a drop of *ca.* 40°, to 545°C in the temperature of the $\beta_{II} \rightleftharpoons \beta_{II}$ inversion.

A possible explanation for the large increase in the extent of the solid solutions above *ca.* 950°C in the system $\text{Li}_2\text{ZnGeO}_4$ - Zn_2GeO_4 is that a γ_{II} field appears only above 1000°C. At the $\text{Li}_2\text{ZnGeO}_4$ composition itself, no γ -type phase was found by quenching from temperatures up to its melting point, estimated to be 1450°C. High-temperature X-ray and DTA studies were limited to an upper temperature of 1200°C; so it is possible that a γ_{II} phase may appear between 1200°C and the liquidus for this composition. The more zinc-rich γ -solid solutions are, however, readily quenched to ambient, usually yielding a mixture of γ - and β -type phases. Upon slower cooling of the zinc-rich γ -solid solutions, the extra powder X-ray reflections characteristic of phase C, as it was first defined in the corresponding silicate system, appear. The phase C lithium zinc germanate is believed to be entirely metastable.

The lithia-rich limits of solid solution were not studied. However, Li_4GeO_4 appears to be isostructural with Li_4SiO_4 above *ca.* 750°C (14). By analogy with the silicate systems, extensive or complete miscibility would be expected to occur between

Li_4GeO_4 and $\text{Li}_2\text{ZnGeO}_4$ and also between Li_4GeO_4 and $\text{Li}_2\text{MgGeO}_4$.

Discussion

All members of this family including both the A_3XO_4 types and their derivative structures, exhibit polymorphism. Where more than one polymorph occurs for a compound, it is invariably found that the γ -type phase occurs as the high-temperature modification, and the β -type phase occurs as the low-temperature modification. Closer study shows that this picture, while correct in broad outline, is subject to modification in detail. These details fall into three classes. First, there are the transitional phases; they have a range of stability which is intermediate between the γ - and β -types, and are found only for A_3XO_4 compounds. Second, there are distortions of the basic β_{II} - and γ_{II} -structures which arise only in derivative Li_3PO_4 structures, i.e., those having the general formula $\text{Li}_2\text{M}^{2+}\text{XO}_4$. Third, there are the ordered phases having special compositions, such as Phase C, which arise from the annealing of solid solutions whose compositions lie between $\text{Li}_2\text{M}^{2+}\text{XO}_4$ and M_2XO_4 . X-ray powder patterns, obtained at ambient and elevated temperatures, and DTA can be used to explain the origin of each class of transitional or distortional-derivative structures, as well as to help decide their thermodynamic stability. Although the variations in powder patterns are not large, once the variations have been classified correctly, similar patterns can be recognized and often their occurrence predicted in advance for other compounds and their solid solutions. It is difficult to study these phases by single crystal methods. Twinning is very common, presumably arising during the inversions which occur on cooling. Twinning on a unit cell scale was also observed in β_{II} (low)- Li_3PO_4 crystals grown from solution (2). Thus, it is necessary to use powder X-ray data in order to classify the derivative structures.

Of the A_3XO_4 compounds, continuous high-temperature X-ray powder patterns show that only Li_3PO_4 passes through the $\beta \rightleftharpoons \gamma$ inversion without the appearance of the transitional phases which arise spontaneously in Li_3VO_4 and Li_3AsO_4 . It is suggested that the larger volume difference between the γ and β forms of Li_3VO_4 and Li_3AsO_4 , compared with Li_3PO_4 , encourages the formation of these transitional phases. It is considered likely that they arise because it is energetically easier to divide up the atomic movements which arise on passing from the high to the low phase (or vice versa) into two or

more stages. The nature and number of these transitional phases, particularly for Li_3VO_4 , needs further clarification.

The derivative $\text{Li}_2\text{M}^{2+}\text{XO}_4$ structures do not appear to give rise to any transitional structures between β and γ types. Instead, they exhibit a number of variants of the basic β and γ types which are believed to be distortional in nature. The relationship between the chemistry of the derivatives and the occurrence of one or more β - or γ -type phases can be explained as follows: substitution of Ge^{4+} for Si^{4+} tends to favour formation of β -type phases, whereas substitution of Mg^{2+} for Zn^{2+} favours γ -type phases. Thus, $\text{Li}_2\text{MgSiO}_4$ forms only γ -type phases, and $\text{Li}_2\text{ZnGeO}_4$ only β -type phases. Compounds containing ($\text{Zn}^{2+} + \text{Si}^{4+}$) or ($\text{Mg}^{2+} + \text{Ge}^{4+}$) form both β - and γ -type phases. The structural influence of Co^{2+} is similar to that of zinc. Solid solutions between the various end members show intermediate polymorphic behaviour.

It is unfortunate that the Li_3XO_4 structural variants have not been adequately described, because much infrared work has been done on these compounds (6): hopefully, these data relate only to one or the other basic structure types, rather than to one of the readily formed transitional types, but this is uncertain.

In preparing most of the compounds described, it should be noted that the rate of cooling is an important variable which affects the phase or phases obtained at ambient. Thus, while the $\gamma \rightleftharpoons \beta$ inversion tends to be relatively sluggish with falling temperature, inversions within a particular patrial, e.g., $\beta_{\text{II}} \rightleftharpoons \beta_{\text{I}}$ are apt to be much more rapid. Another important variable affecting the nature of the derivative phase or phases obtained at ambient is the exact stoichiometry. As has been shown, it is possible to make substitutions of the type $2\text{M}^+ \rightleftharpoons \text{M}^{2+}$. The quantitative extent of this substitution varies with the nature of the metal ions and also with temperature. Once formed, it is comparatively easy to preserve these solid solutions to ambient. Although they may become unstable, exsolution is comparatively slow, especially at large undercoolings. The kinetics of phase transformations amongst the solid solutions often differs markedly from that of the stoichiometric composition. Moreover, the metastable solid solutions may undergo a martensitic-type phase transformation at lower temperatures. These transformations occur in preference to an equilibrium reaction, which would involve unmixing of a homogeneous solid solution.

Other possible derivative Li_3PO_4 structures might include $\text{Na}_2\text{ZnSiO}_4$, $\text{Na}_2\text{ZnGeO}_4$, and $\text{Na}_2\text{MgGeO}_4$.

All three are reported as being isostructural and are also isotypic with NaFeO_2 (15). The cell dimensions and atomic positions are similar to those of Li_3PO_4 , so that they could be considered as derivative Li_3PO_4 structures. However, in other structure determinations of $\text{Na}_2\text{ZnSiO}_4$ (16) and $\text{Na}_2\text{ZnGeO}_4$ (17) quite different atomic coordinates are given, especially for the sodium ions, some of which are reported to be in nearly octahedral sites. From a DTA study, several polymorphs of $\text{Na}_2\text{ZnSiO}_4$ exist (18). Thus further work is needed to clarify the polymorphism and structural relationships of these phases to Li_3PO_4 and its derivatives.

It may be possible to find sulphides which have the Li_3PO_4 -type structures. Because increasing covalence favours a shift from wurtzite-type to zinblende-type structures, most sulphides which might possibly be isotypes have either the zinblende or a derivative zinblende structure. However, the crystal structure of enargite (Cu_3AsS_4) has recently been studied (19); although not explicitly recognized as such, a comparison of the atomic coordinates show that it is isostructural with β_{II} (low)- Li_3PO_4 . It is likely that as sulphides receive more study, other examples of sulphides with Li_3PO_4 -type structures will be discovered; for example, Cu_3AsS_4 may well have a nonquenchable high (γ_{II} -type) polymorph.

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References

1. J. ZEMANN, *Acta Cryst. B* **13**, 863 (1960).
2. C. KEFFER, A. MIGHELL, F. MAUER, H. SWANSON, AND S. BLOCK, *Inorg. Chem.* **6**, 119 (1967).
3. W. W. MATIAS AND A. M. BONDAREVA, *Dokl. Akad. Nauk. SSSR* **112**, 124 (1957).
4. H. E. SWANSON, M. C. MORRIS, AND E. H. EVANS, "Standard X-Ray Diffraction Powder Patterns", Sect. 4, p. 21, National Bureau of Standards, Washington, D.C., Monograph No. 25, 1966.
5. G. BLASSE, *Z. Anorg. Allgem. Chem.* **331**, 44 (1964).
6. P. TARTE, *J. Inorg. Nucl. Chem.* **29**, 915 (1967).
7. A. REISMAN AND J. MINEO, *J. Phys. Chem.* **66**, 1181 (1962).
8. R. KOHLMULLER AND J. MARTIN, *Bull. Soc. Chim. France* **4**, 748 (1961).
9. A. R. WEST AND F. P. GLASSER, *J. Mater. Sci.* **5**, 557 (1970).
10. A. R. WEST AND F. P. GLASSER, *J. Mater. Sci.* **5**, 676 (1970).

11. P. TARTE AND R. CAHAY, *C.R. Acad. Sci. Paris* **271**, 777 (1970).
12. A. R. WEST AND F. P. GLASSER, *J. Mater. Sci.*, to appear.
13. A. REISMAN, *J. Amer. Chem. Soc.*, **80**, 3558 (1958).
14. A. R. WEST AND F. P. GLASSER, Unpublished results.
15. C. A. JOUBERT-BETTAN, R. LACHENAL, E. F. BERTAUT, AND E. PARTHE, *J. Solid State Chem.* **1**, 1 (1969).
16. V. V. ILYUKHIN, A. V. NIKITIN, AND N. V. BELOV, *Sov. Phys. Dokl.* **11**, 1035 (1967).
17. E. A. KUZMIN, V. V. ILYUKHIN, AND N. V. BELOV, *Kristallografiya* **13**, 976 (1968).
18. A. E. HOLLAND AND E. R. SEGNET, *Aust. J. Chem.* **19**, 905 (1966).
19. G. ADIWIDJAJA AND J. LOHN, *Acta Crystallogr. B* **26**, 1878 (1970).