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The crystal structures and the phase transformation of Zn–Li silicates: discussion

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Yu *et al.* (1978) reported on the preparation, polymorphism, and structure determination of a phase of composition $Zn(Zn_{0.1}Li_{0.6}Si_{0.3})SiO_4$. The purpose of this note is to point out that a considerable literature on lithium zinc silicates exists (West, 1975; West and Glasser, 1970, 1972; Villafuerte-Castrejon and West, 1979) of which the authors are apparently unaware, and to suggest, in light of this literature, some possible errors in the results of Yu *et al.*

Phase studies of the system Li_2O–ZnO–SiO_2 have shown that wide ranges of polymorphic orthosilicate solid solutions are the only equilibrium ternary phases to crystallize in this system (West and Glasser, 1970). These solid solutions cover part of the join Li_4SiO_4–Zn_2SiO_4 (Fig. 1). Of most relevance to the present discussion are solid solutions and phases that occur between Li_2ZnSiO_4 and Zn_2SiO_4; their general formula may be written $Li_{2-2x}Zn_{1+x}SiO_4 (0 < x \lesssim 0.5)$. Within this range, nine different solid solution polymorphs were encountered, named γ_0, γ_I, γ_{II}, β_I, β_I', β_{II}, β_{II}', C, and C′. Unit-cell data were obtained for most of them. Structurally, they fall into two families; the γ and C polymorphs are all derived from γ_{II} Li_2ZnSiO_4 which is isostructural with high (γ_{II}) Li_3PO_4 (Zemann, 1960), whereas the β phases are derived from β_{II} Li_2ZnSiO_4 which is isostructural with low (β_{II}) Li_3PO_4 (Keffer *et al.*, 1969). β_{II} and γ_{II} both have tetrahedral structures with approximately hexagonal close-packed oxide ions, and the structures differ mainly in the manner of occupancy of the various tetrahedral sites.

Yu *et al.* grew their crystals (called hereafter Yu crystals) from a Li_2MoO_4–MoO_3 flux and claimed a composition for them corresponding to point X, Figure 1, which is just on the silica-deficient side of the metasilicate composition. I suggest, however, that the true composition of the Yu crystals lies near point Y on the orthosilicate join, with $x \simeq 0.2$, *i.e.* at $Li_{1.6}Zn_{1.2}SiO_4$. This conclusion is based on the following.

(1) Three polymorphic forms of the Yu crystals were identified, and their cell parameters correspond fairly well to those of three of the lithium zinc orthosilicate polymorphs (Table 1). Only a rough comparison can be made because the cell parameters of γ_0, γ_{II}, and C are composition-dependent, and data are available for only one composition for each phase.

(2) The powder pattern of α (Yu) corresponds fairly well to γ_0 (West and Glasser, 1970), although the latter contains more lines. This is probably because a high-resolution focusing camera was used in the latter work to record the powder patterns.

(3) The β phase of Yu appears to be isostructural with $\gamma_{II}Li_3PO_4$ (and hence with γ_{II} Li_2ZnSiO_4). Atomic coordinates are given in Table 2. One major difference is the presence of the extra four-fold set of Li(2) sites in Li_3PO_4. I suggest that these atoms are also present in the Yu crystals but, because of the small scattering power of Li^+, they escaped detection. One effect of adding extra Li^+ to the Yu crystals would be to change the coordination of oxygen from

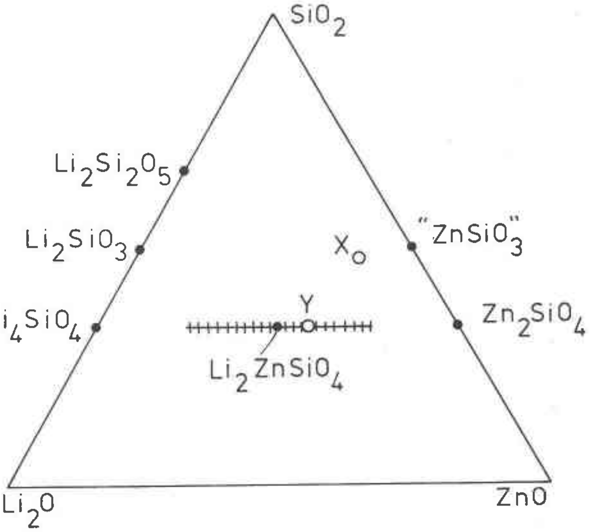

Fig. 1. Occurrence of Li_2ZnSiO_4 solid solutions (hatched) in the system Li_2O–ZnO–SiO_2. Compositions in mole percent.

Table 1. Comparison of cell parameters of the Yu crystals and LiZn orthosilicates (West and Glasser)

Cell parameter	α', Yu	C $x = 0.24$	α, Yu	γ_0 $x = 0$	β, Yu 400°C	γ_{II} $x = 0.2$ 700°C
a	13.01	13.16	6.340	∿6.32	6.406	6.45
b	10.41	10.6	10.516	∿10.72	10.520	10.64
c	10.07	5.06	5.011	∿5.06	5.043	5.12
β	∿90°	∿90°	90.50°	∿91°	-	-

Table 2. Atomic coordinates of β (Yu) and high γ_{II} Li_3PO_4 (Zemann)

		Yu		
T1, ZnSiLi	8d	0.0004	0.1607	0.1860
T2Si	4c	0.25	0.4107	0.1834
O(1)	4c	0.25	0.4021	-0.1374
O(2)	4c	0.25	0.0575	0.2201
O(3)	8d	0.04337	0.3406	0.2954
		Zemann		
Li(1)	8d	0.005	0.162	0.196
P	4c	0.25	0.411	0.192
O(3)	4c	0.25	0.41	-0.125
O(2)	4c	0.25	0.052	0.205
O(1)	8d	0.042	0.342	0.295
Li(2)	4c	0.25	0.078	0.804

three cations arranged pyramidally to four arranged tetrahedrally.

(4) The Yu crystals had a density of 3.53 g cm^{-3}; in the Li,Zn orthosilicates, D varied from 3.35 ($x = 0$) to 3.63 ($x = 0.33$). If the Yu crystals are orthosilicates, then their density corresponds to $x \simeq 0.2$.

(5) The composition of the Yu crystals was determined by electron microprobe analysis, although Li$^+$ could not be analyzed by this technique. From emission spectroscopic analysis, a value of 10 wt% Li was obtained but rejected in favor of a value of 7 wt% obtained by difference from the microprobe results. The calculated lithium content in Li,Zn orthosilicates, $x = 0.2$ is ~6 wt%, in fair agreement with both sets of data.

In conclusion, the Yu crystals appear to be nonstoichiometric orthosilicates with $x \sim 0.2$. This x value is deduced from (1) the occurrence of a (γ_0 + C) phase assemblage, (2) the density value, and (3) the magnitude of the electron density in the T1 8d sites. In spite of the compositional errors in the analysis of Yu *et al.*, this is a valuable piece of work since it is the first single-crystal study of Li,Zn orthosilicates and provides information on the structures of γ_{II} and γ_0 polymorphs.

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