

# Synthesis and properties of zektzerite, LiNaZrSi<sub>6</sub>O<sub>15</sub>, and its isotypes

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## SYNOPSIS

ZEKTZERITE and its isotypes with Zr<sup>4+</sup> replaced by Ti<sup>4+</sup> or Sn<sup>4+</sup> are readily synthesized by fusion of the constituent oxides at 1550 °C, followed by recrystallization of the melt or quenched glass at 750-850 °C and 1 bar pressure. Indexed powder X-ray data for synthetic zektzerites are presented in miniprint Table I. The powder patterns are consistent with an *A*-centred orthorhombic symmetry. Refined cell dimensions are given in Table III.

The Ti, Zr, and Sn zektzerites melt incongruently. Table IV records melting-point data. The coefficients of thermal expansion of Zr and Ti zektzerite have been determined by X-ray dilatometry. Both have moderately low coefficients of expansion: numerical values are given in miniprint Table II.

Zektzerites contain a six-repeat unit double-chain silicate anion. Although they are chemically similar to milarites, the latter contain double-ring Si<sub>12</sub>O<sub>30</sub> anions. Despite the difference in anion constitution both have structures in which many chemically similar atoms occupy similar positions. The effect of this similarity on the physical properties (e.g. X-ray powder pattern) is enhanced by

TABLE III. Cell dimensions of the Zr, Ti, and Sn zektzerite isotypes\*

	LiNaZrSi <sub>6</sub> O <sub>15</sub>	LiNaTiSi <sub>6</sub> O <sub>15</sub>	LiNaSnSi <sub>6</sub> O <sub>15</sub>
<i>a</i> (Å)	14.3319 (15)	14.2333 (29)	14.2963 (15)
<i>b</i>	17.3496 (14)	17.0645 (29)	17.1706 (20)
<i>c</i>	10.1655 (7)	9.9323 (12)	10.0443 (7)
<i>V</i> (Å <sup>3</sup> )	2527.7	2412.4	2465.6

\* Values in ( ) are e.s.d.'s.

the similar size and shape of their orthorhombic unit cells. The presence of vacant sites in zektzerite that are potentially available for cation occupancy suggests that chemically complex substitutions may occur; for example LiNa<sub>2</sub>ScSi<sub>6</sub>O<sub>15</sub> has been synthesized and is believed to be isostructural with zektzerite and emeleusite, LiNa<sub>2</sub>FeSi<sub>6</sub>O<sub>15</sub>.

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TABLE IV. Melting-points of zektzerite and its Ti and Sn isotypes

LiNaZrSi <sub>6</sub> O <sub>15</sub>			LiNaTiSi <sub>6</sub> O <sub>15</sub>			LiNaSnSi <sub>6</sub> O <sub>15</sub>		
Temp. °C	Time h	Phases present	Temp. °C	Time h	Phases present	Temp. °C	Time h	Phases present
1158	72	Zektzerite	918	6	Zektzerite†	1121	24	Zektzerite† + SnO <sub>2</sub> (tr.)
1166	24	ZrO <sub>2</sub> + ZrSiO <sub>4</sub> + Trid. + Liq.	928	72	Trid. + TiO <sub>2</sub> + Liq.			
1550	4	ZrSiO <sub>4</sub> (tr.) + Liq.	1550	4	Liquid*	1128	24	SnO <sub>2</sub> + Trid. + Liq.
						1550	4	SnO <sub>2</sub> + Liq.
m.p. (incongruent): 1162° ± 4°			m.p. (incongruent): 923° ± 5°			m.p. (incongruent): 1124° ± 4°		

Notes and abbreviations: ZrO<sub>2</sub> = monoclinic zirconia, TiO<sub>2</sub> = rutile, SnO<sub>2</sub> = cassiterite, ZrSiO<sub>4</sub> = zircon, Trid. = tridymite polymorph of SiO<sub>2</sub>, Liq. = liquid, tr. = trace present; \* = liquid quenched to a slightly opalescent glass believed to have phase separated on a submicroscopic scale. † = Ti and Sn isotypes.

## SYNTHESIS AND PROPERTIES OF ZEKTERZITE.

LiNaZrSi<sub>4</sub>O<sub>13</sub> AND ITS ISOTYPES

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ZEKTERZITE has recently been described as a new mineral species whose composition closely approaches the ideal formula LiNaZrSi<sub>4</sub>O<sub>13</sub> (Dunn, et al., 1977). A crystal structure analysis by Ghose and Man (1978) discloses that zektzerite contains an unusual six-tetrahedral repeat double chain silicate anion. Using the classification of Liebau (1969) it is a 'sechser-doppelkette'. Liebau cites zektzerite as the first and only example known at the time of a mineral in this class. Its structure was determined by Merlino (1969). Zektzerite is also isostructural with a synthetic phase, Na<sub>2</sub>Mg<sub>2</sub>Si<sub>4</sub>O<sub>13</sub>, whose synthesis, thermal stability and unit cell dimensions have been reported by Shahid and Glasser (1972) and whose crystal structure has been determined by Cradwick and Taylor (1972) and Cradwick, et al. (1972). At first sight, the isomorphous nature of Na<sub>2</sub>Mg<sub>2</sub>Si<sub>4</sub>O<sub>13</sub> and LiNaZrSi<sub>4</sub>O<sub>13</sub> seems remarkable on account of the large difference in formal charges on Mg<sup>2+</sup> and Zr<sup>4+</sup>. Consideration of the structures shows that the balance of charges is maintained by an unusual substitution: (Li + Zr) in zektzerite are replaced by (Mg + Mg) in Na<sub>2</sub>Mg<sub>2</sub>Si<sub>4</sub>O<sub>13</sub> together with concomitant introduction of alkali into otherwise vacant sites. Thus if a cation vacancy is represented by □, (□ + Li + Zr) in zektzerite are substituted by (Na + Mg + Mg). Ghose and Man (1978) predict that it ought to be possible to introduce trivalent ions such as Y, Fe and Cr into minerals of the sechser-doppelkette family. We believe that emeleusite, LiNaFe<sup>3+</sup>Si<sub>4</sub>O<sub>13</sub>, is an example of an anhydrous sechser-doppelkette mineral and that its tentative placement in the milarite family by Upton, et al. (1978) is incorrect. It was assigned to the milarite family on the basis of similarities in chemical composition and the shape and size of its unit cell.

**Experimental.** Zektzerite and its Ti and Sn isotypes were prepared by melting the constituent oxides, quenching the fused mass to a glass, and crystallizing the batch. The charges were prepared from 'Analar' alkali carbonate, reagent-grade oxides of the remaining elements and crushed quartz. The latter was supplied by Thermal Syndicate Ltd.; our analysis gave 0.08% material non-volatile with HF. Batches of 2 - 10 g were fused in Pt crucibles heated in electric resistance furnaces operated in an air atmosphere. The fusion was repeated several times, with intermediate quenching and crushing of the glass to improve its homogeneity. Its homogeneity was monitored by petrographic examination. Portions of the powdered glass were subsequently devitrified in Pt-foil envelopes, typically for 1 - 3 days at 850 - 950°C. The phases present were identified by petrographic examination and by X-ray powder diffraction using a Hägg Guinier focusing camera.

The powder pattern of synthetic Zr zektzerite was initially indexed by analogy with that of the mineral; the two patterns are very similar. The observed X-ray d-values and intensities were obtained using a microdensitometer-film reader developed especially for that purpose in our laboratories. Observed values were corrected to absolute using a film obtained from a mixture of zektzerite with 5 - 10 wt. % synthetic Mg<sub>2</sub>Si<sub>4</sub>O<sub>13</sub> spinel. The cell dimensions were refined in stages, using at first a limited number of reflections having unequivocal indices. As refinement proceeded, more reflections were included. A similar procedure was used for the Ti and Sn isotypes taking the indexed powder data for synthetic Zr zektzerite as the starting point.

Thermal expansivity was determined using a Phillips high-temperature diffractometer. Spinel was again used as an internal standard and values for  $d_0$  of spinel at higher temperatures were obtained from Henderson and Taylor (1975). After correcting the positions of the zektzerite reflections for errors, powder data at each temperature were again subjected to least squares refinement. Owing to the limited angular range imposed by the diffractometer heating stage and interferences from metal parts of the apparatus, fewer reflections could be included compared to data obtained at ambient temperature with the focusing camera. Therefore ambient temperature cell parameters determined by the least squares method and the standard deviations of the diffractometer data are somewhat larger. Nevertheless, the diffractometer data are self-consistent and can be used to calculate coefficients of thermal expansion between the stated temperatures.

**Results.** Table I gives the indexed powder data for three members of the zektzerite family: LiNaZrSi<sub>4</sub>O<sub>13</sub>, LiNaTiSi<sub>4</sub>O<sub>13</sub>, and LiNaSnSi<sub>4</sub>O<sub>13</sub>. Powder data for synthetic LiNaZrSi<sub>4</sub>O<sub>13</sub> are more complete than those reported for the natural mineral (Dunn, et al., 1977) but are otherwise consistent with the two being isostructural.

All three zektzerites can be synthesized by sintering of the constituent oxides or devitrification of a glass and it is thus concluded that each has a range of thermal stability at 1 atm. pressure. All three melt incongruently. The temperatures at which melting commences, while not especially high, are substantially greater than would be expected in the absence of a quaternary compound and suggest the existence of reasonably refractory areas in systems such as Li<sub>2</sub>O-Na<sub>2</sub>O-ZrO<sub>2</sub>-SiO<sub>2</sub>.

In the Sn and Zr preparations traces of crystalline phases persisted to 1550°C. The temperature of complete fusion is thus somewhat higher but 1550°C was the maximum that could be attained. The small quantity of crystalline phase present in the fused glasses could be readily detected optically by petrographic examination, but was insufficient to be detected by X-ray powder diffraction except in the Sn-zektzerite batch which exhibited the strongest reflections of SnO<sub>2</sub>. Zektzerites can also be prepared by sintering the constituent oxides between 900 and 950°C. However, even after prolonged sintering (10 days, with several intermediate crushings) an impure product containing several phases was obtained. Zr, Sn, and Ti zektzerites coexisted with unreacted SiO<sub>2</sub> and MgO, as well as a low-refractive index glass formed by reaction between alkali oxide and SiO<sub>2</sub>. Despite the incompleteness of the sintering reactions, zektzerite was abundant and the content of zektzerite tended to increase with prolonged annealing. This provides justification for the conclusion that zektzerites are stable at 1 atm. pressure.

The coefficients of thermal expansion of Ti, Sn and Zr zektzerites can be calculated readily from the data in Table II. Ti zektzerite has markedly lower coefficients of thermal expansion than Zr zektzerite. But in the more general view, both have moderately low coefficients of expansion which are not characterized by any pronounced anisotropy.

**Discussion.** It is interesting to note that the distinction between minerals containing double rings, Si<sub>4</sub>O<sub>13</sub>, (milarite, osumilite) and those containing double chains (zekterzite, emeleusite, etc.) may not be easy to make in practise. The limits of chemical substitution possible

TABLE I. Powder X-Ray Data for Synthetic Zektzerite and its Ti and Sn Isotopes\*

LiNaZrSi <sub>4</sub> O <sub>13</sub>			LiNaTiSi <sub>4</sub> O <sub>13</sub>			LiNaSnSi <sub>4</sub> O <sub>13</sub>		
d-values (Å)	hkt	I	d-values (Å)	hkt	I	d-values (Å)	hkt	I
8.699 (75)	020	3	7.134 (17)	200	40	8.591 (85)	020	7
7.712 (66)	200	60	4.794 (88)	227	59	7.145 (48)	200	67
6.601 (59)	021	3	4.526 (14)	112	12	6.523 (26)	021	17
5.529 (25)	220	15	4.2962 (21)	022	100	5.492 (93)	220	15
4.8540 (42)	221	100	4.2697 (61)	040	54	4.1873 (96)	221	100
4.6190 (76)	112	12	4.0746 (26)	202	62	4.5703 (76)	112	3
4.3857 (54)	022	85	3.9199 (98)	041	18	4.3355 (49)	022	67
4.3399 (74)	040	50	3.6205 (81)	132	28	4.2941 (26)	040	36
4.1454 (58)	202	96	3.5588 (83)	400	54	4.1082 (93)	202	96
3.6897 (92)	132	30	3.4334 (35)	241	56	3.6517 (499)	132	15
3.5928 (30)	400	28	3.3613 (32)	312	14	3.5741 (41)	400	17
3.4852 (57)	241	70	3.2863 (42)	420	3	3.4556 (54)	241	65
3.3114 (16)	420	11	3.1693 (86)	113	66	3.2998 (96)	420	7
3.2395 (96)	113	50	3.1472 (77)	151	58	3.2022 (27)	113	34
3.2015 (09)	151	42	3.1181 (81)	421	50	3.1675 (86)	151	24
3.1484 (87)	421	70	2.9435 (58)	242	11	3.1347 (48)	421	60
2.9974 (70)	242	20	2.8915 (25)	402	43	2.9679 (84)	242	18
2.9227 (24)	332	5	2.8207 (17)	223	15	2.9127 (20)	332	51
2.9289 (85)	402	60	2.7576 (94)	152	17	2.7802 (06)	402	51
2.8890 (885)	060	30	2.7386 (93)	422	44	2.7567 (76)	060	4
			2.6808 (13)	313	11	2.7055 (53)	313	4
2.8107 (02)	152	17	2.6669 (87)	351	10	2.6473 (94)	414	100†
2.7752 (47)	422	18	2.6345 (47)	441	48	2.5110 (11)	004	23
2.7323 (24)	332	5	2.4832 (61)	004	20	2.4865 (64)	062	26
2.7295 (94)	313	8		(80)	061	2.4766 (65)	243	9
2.7062 (62)	351	9	2.4660 (60)	531	13			
2.6807 (15)	260	11	2.3846 (42)	024	6	2.4110 (10)	024	6
2.6658 (57)	441	62	2.3320 (16)	262	5		(098)	442
2.5415 (14)	004	20	1.6	423	5		(505)	171
2.5139 (38)	082	29	2.2637 (54)	532	11	2.3491 (501)	423	20
2.5027 (22)	243	11	2.2571 (07)	224	11		(84)	262
2.4766 (67)	114	6	2.1820 (19)	314	10	2.2340 (39)	460	8
2.4274 (71)	442	5	2.1569 (74)	063	21	2.1764 (54)	063	13
2.3946 (52)	204	9	2.1074 (75)	443	8	2.1530 (27)	602	7
2.3690 (84)	423	18	2.0523 (19)	334	6	2.1420 (16)	353	9
2.2494 (502)	460	9	1.9875 (72)	372	3	2.1224 (35)	443	17
2.2249 (51)	314	8				2.0401 (39)	642	14
2.1986 (96)	063	30	1.9802 (07)	424	13	1.9980 (82)	424	3
2.1986 (70)	461	30	1.9608 (599)	082	7	1.9557 (60)	025	4
2.1611 (19)	353	15	1.9348 (47)	025	3			
	(18)	602	1.8711 (06)	064	1			
			(04)	714				
2.1503 (03)	371	8						
2.1408 (11)	443	24	1.8589 (93)	135	20	1.8897 (92)	731	15
2.0972 (67)	244	3	1.8463 (67)	191	11	1.8789 (91)	135	10
2.0915 (18)	334	5	1.8227 (19)	315	27	1.8575 (82)	463	9
			(17)	660				
2.0723 (29)	404	5	1.8199 (203)	571	1	1.8303 (11)	660	9
2.0570 (78)	462	6	1.7785 (92)	800	10		(06)	571
2.0491 (94)	641	12	1.75	534	10	1.8259 (49)	264	11
2.0334 (38)	281	5	1.7567 (72)	643	4			
2.0292 (96)	194	2						
2.0163 (61)	424	24	1.7456 (58)	245	5	1.8090 (69)	481	9
1.9941 (47)	082	3	1.7268 (67)	174	7	1.7988 (014)	661	10
1.9792 (38)	711	11	1.7149 (55)	821	15	1.7866 (70)	800	10
1.9792 (95)	025	14	1.6549 (54)	066				
1.9346 (48)	642	3						
1.9078 (80)	225	20						
1.9013 (11)	135	14	1.6435 (36)	822	7	1.7689 (98)	192	15
1.8901 (03)	514	6	1.6424 (21)	840	1	1.7281 (88)	643	12
1.8776 (77)	191	11	1.6368 (67)	210-0	2	1.7200 (18)	18	10
1.8706 (03)	444	3	1.6284 (86)	065	1	1.6698 (60)	424	18
1.8506 (10)	553	12				1.6292 (5)	5	
1.8439 (37)	571	26	1.5307 (2)	1.6210 (10)	10			
1.8253 (52)	481	9	1.5236 (6)	1.6127 (10)	10			
1.7912 (15)	800	17	1.5001 (10)	1.6028 (7)	7			
				1.5851 (2)	2			
1.7826 (30)	245	26	1.4818 (6)	1.5750 (2)	2			
1.7402 (05)	604	21	1.4709 (1)	1.5640 (1)	1			
1.7314 (14)	662	29	1.4431 (10)	1.5253 (1)	1			
1.6847 (47)	464	12	1.3734 (8)	1.5151 (10)	10			
			(35)	2.10.1	9	1.4795 (4)	4	
1.6634 (34)	374	11	1.3167 (9)	1.4552 (6)	6			
			(32)	065	6	1.4502 (6)	6	
1.6583 (84)	822	11	(28)	026				
			(84)	822				
1.6493 (88)	206	11						
1.6372 (72)	445	8						
1.6275 (73)	483	11						
			(201)	265	6			
1.6199 (98)	236	6						
1.6155 (56)	136	3						
1.6009 (05)	210-2	6						
1.5624 (25)	175	6						
1.5421 (6)	17	6						
1.5315 (6)	6	6						
1.5236 (6)	6	6						
1.5094 (6)	6	6						
1.4643 (8)	8	8						
1.4586 (12)	12	12						
1.4289 (26)	26	26						
1.4178 (9)	9	9						
1.3908 (9)	9	9						
1.3774 (20)	20	20						

Notes: \* Guinier camera, CuK<sub>α1</sub> radiation† Intensity not reliable due to interference by overlapping SnO<sub>2</sub> impurity reflection.

TABLE II. Thermal Expansion of  $\text{LiNaZrSi}_4\text{O}_{15}$  and  $\text{LiNaTiSi}_4\text{O}_{15}$ 

T = (°C)	CELL DIMENSIONS IN Å AND VOLUME IN Å <sup>3</sup> .*					
	$\text{LiNaZrSi}_4\text{O}_{15}$			$\text{LiNaTiSi}_4\text{O}_{15}$		
	a	b	c	a	b	c
12 (±2)	14.323(4)	17.328(5)	10.167(3)	14.215(5)	17.049(12)	9.926(9)
	V = 2523.3			V = 2405.6		
330 (±5)				14.244(7)	17.057(9)	9.930(10)
				V = 2412.6		(0.291%)
420 (±5)	14.348(10)	17.350(10)	10.187(14)			
	V = 2535.9		(0.499%)			
630 (±10)	14.367(10)	17.372(11)	10.203(8)	14.268(8)	17.082(11)	9.941(12)
	V = 2546.5		(0.918%)	V = 2422.9		(0.719%)
892 (±8)	14.395(15)	17.399(13)	10.213(10)	14.290(7)	17.109(10)	9.939(9)
	V = 2557.9		(1.317%)	V = 2430.0		(1.013%)

\* Values in ( ) following the cell dimension are E.S.D.'s  
 Values in ( ) following the cell volumes are the volume  
 expansion, in %, between 12°C and the stated temperature.

In both structure types are not yet known, hence it may not be practicable to distinguish between the two on the basis of cation content. Moreover, despite major differences in anion constitution, the two families have geometrically similar unit cell sizes and shapes. This similarity extends to the placement of many of the constituent atoms within the unit cell. In the absence of a reliable crystal-structure determination, the overall distribution of powder X-ray intensities is a better guide to the correct classification than a comparison of unit cell sizes. This is partially true because the A-centering is characteristic of chains rather than rings, as the latter cannot be accommodated in an A-centered cell of the zektzerite dimensions. Thus, symmetry as well as a comparison of powder intensities lead us to conclude that euelesite is a member of the sechser-doppelkette family and is isostructural with zektzerite.

Osumilites and milarites have also been frequently reported to occur as devitrification products of Li-containing glass-ceramics. In view of the pronounced similarities between the two structure types we feel that the validity of these reports requires careful scrutiny.

Isostructural sechser-doppelkette phases have also been synthesized containing trivalent ions. We have successfully synthesized phases in the series  $\text{LiNaM}^{3+}\text{Si}_4\text{O}_{15}$ , where  $\text{M}^{3+} = \text{Fe, Cr, Sc, In, Y, (Yb + Lu), Er, Ho, Dy, Gd}$  and Sm: a more detailed report will be given in a subsequent paper. However, all appear to be sechser-doppelkette phases. This ability to accommodate such a large range of sizes of trivalent ions is remarkable, and could not have been anticipated from any of the crystal structure determinations which have been made thus far. Our exploration of the synthetic members of this family continues, but it seems possible to anticipate that more examples of sechser-doppelkette minerals remain to be discovered in nature.

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The synthesis and stability of the Sc-containing phase and 14 other isostructural phases will be described in a forthcoming issue of *Proc. Brit. Ceram. Soc.* (no. 28).