

## The crystal chemistry of sogdianite, a milarite-group mineral

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### ABSTRACT

The crystal structure of sogdianite, hexagonal,  $a = 10.053(1)$ ,  $c = 14.211(2)$  Å,  $V = 1243.8(4)$  Å<sup>3</sup>, space group =  $P6/mcc$ ,  $Z = 2$ , has been refined to an  $R$  index of 2.0% using 607 observed ( $|F_o| > 5 |F|$ ) reflections collected with an automated four-circle diffractometer using MoK $\alpha$  X-radiation. Site-scattering refinement and electron-microprobe analysis indicate the composition  $(\text{Zr}_{0.76}\text{Ti}_{0.38}\text{Fe}_{0.73}^{3+}\text{Al}_{0.13})_{\Sigma=2}(\square_{1.15}\text{Na}_{0.85})_{\Sigma=2}\text{K}[\text{Li}_3\text{Si}_{12}\text{O}_{30}]$ . The T2 tetrahedron is completely occupied by Li, and all Al occurs at the octahedrally coordinated A site. The <A-O> bond length is compatible with all Fe being in the trivalent state. There is no significant positional disorder of the A-group cations, in accord with the absence of H<sub>2</sub>O in sogdianite. Single-crystal X-ray precession photographs of sogdianite show the presence of diffractions that are incommensurate with the sogdianite diffraction pattern. The relative intensity of the incommensurate diffractions increases with the degree of apparent alteration of sogdianite (clear turbid murky), suggesting that sogdianite is altering to, or possibly exsolving, a second phase, probably zektzerite.

### INTRODUCTION

Sogdianite, written as  $(\text{K},\text{Na})_2(\text{Li},\text{Fe}^{2+})_3(\text{Zr},\text{Ti},\text{Fe}^{3+})\text{Si}_{12}\text{O}_{30}$  by Fleischer and Mandarino (1995), was first described from Dara-i-Pioz, Tajikistan, by Dusmatov et al. (1968) and its structure was reported by Bakakin et al. (1975). It is a milarite-group mineral (Forbes et al. 1972; Černý et al. 1980; Hawthorne et al. 1991), one of several reported from Dara-i-Pioz, of the general form  $\text{A}_2\text{B}_2\text{C}[\text{T}_2\text{T}_1\text{O}_{30}](\text{H}_2\text{O})_x$  where A = Zr, Fe, Ti; B = Na,  $\square$  (vacancy); C = K; T1 = Si; T2 = Li for sogdianite itself. The general structural arrangement has the  $P6/mcc$  space group and the non-silicate T2 tetrahedra link the 12-membered double-rings of silicate tetrahedra into a  $[\text{T}_2]_4$  4-connected three-dimensional framework (Hawthorne and Smith 1986), following the general scheme of Zoltai (1960). This structure-type is of considerable interest for two reasons. First, it shows a very wide range of occupancy of the T2 site [T2 = Li, Be, B, Mg, Al, Si, Mn<sup>2+</sup>, and Zn] and the A site (Al, Fe<sup>3+</sup>, Sn<sup>4+</sup>, Mg, Zr, Fe<sup>2+</sup>, Ca, Na, Y, and REE). Second, some species are optically uniaxial, whereas others show “anomalous” biaxial behavior (Janeczka 1986; Neumann 1941). As a result, there has been extensive structural work on these minerals, summarized by Hawthorne et al. (1991). Armbruster et al. (1989) and Armbruster and Czank (1992) have done extensive work on the response of the milarite-type structure to temperature and the role of H<sub>2</sub>O in those species in which it occurs. As part of our general interest in both the milarite-group minerals and the role of light lithophile elements in minerals, we report here on the crystal chemistry of sogdianite.

We dedicate this paper to Gene Foord, mineralogist *par excellence* and an inspiration to all of his colleagues.

### SAMPLE DESCRIPTION AND PROVENANCE

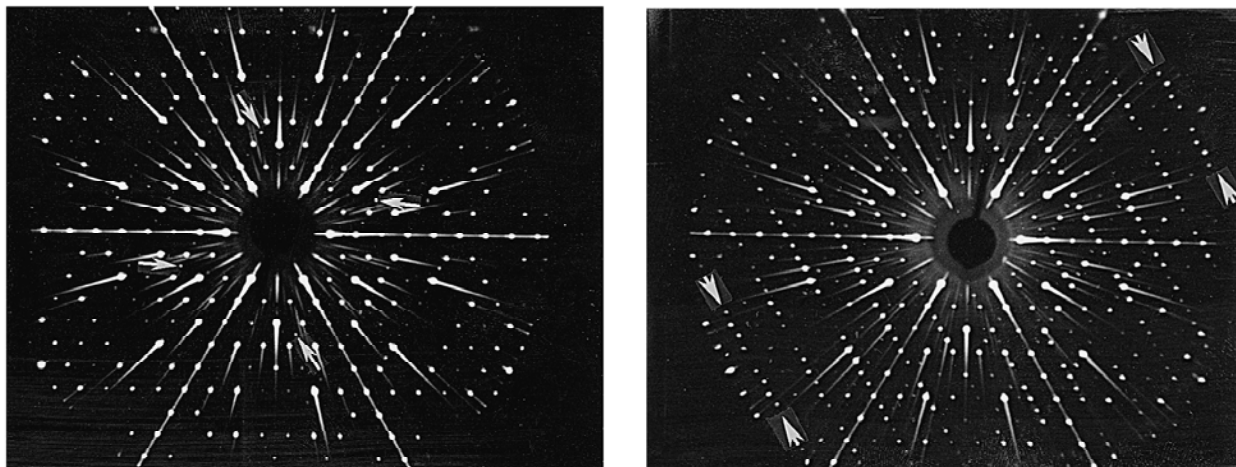
The sogdianite-bearing sample from Dara-i-Pioz consisted of a platy mass about 1.5 cm  $\times$  1.5 cm  $\times$  0.2 cm in glassy quartz associated with white perthitic microcline having a greenish tint. This sogdianite mass is partly surrounded by a discontinuous dark margin up to about 1 mm thick that consists largely of fine-grained aegirine in subhedral grains and prisms up to 0.5 mm long. Fine-grained (0.1–0.5 mm) leucosphenite occurs in an aggregate with microcline, minor aegirine and quartz between the aegirine margin and a coarse microcline grain. Albite grains are scattered throughout the microcline and probably resulted from exsolution. The purple color of sogdianite is distributed in patches. In thin section, the sogdianite masses appear as mosaic aggregates of nearly parallel platelets. The largest mass as a whole has a thick outer zone riddled with what appear to be exsolution blebs and a core free of such blebs, but locally clouded; a second mass lacks any blebs.

The exact provenance of the sample is unknown; however, it is possibly from a group-3 type-1 pegmatite which has been found only as boulders in an old moraine (Belakovskiy 1991; Grew et al. 1993). The group-3 type-1 pegmatites are presumed to have originated as cores of pegmatites similar to the highly mineralized group-2 pegmatites which are found in situ at Dara-i-Pioz.

### EXPERIMENTAL METHODS

Precession photographs of good-quality pink sogdianite crystals are compatible with  $P6/mcc$  symmetry except for a small number of very weak diffractions visible on  $\{hk0\}$  pho-

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**FIGURE 1.** Zero-level ( $hk0$ ) precession photographs of pink sogdianite crystals. **(left)** Clear crystal showing a small number of weak reflections (indicated by the white arrows) that violate hexagonal symmetry. **(right)** Murky crystals showing many intense reflections that violate hexagonal symmetry; the high-order rows of reflections (indicated by white arrows) show that the reflections violating hexagonal symmetry are not commensurate with the hexagonal cell of the sogdianite structure.

tographs (Fig. 1 left). The distribution of these diffractions violates hexagonal symmetry, raising the possibility that sogdianite is of orthorhombic or lower symmetry. However, careful examination indicates that the “violating” diffractions are not quite commensurate with the hexagonal pattern of diffractions. This prompted further precession photography on less attractive material, and as shown in Figure 1 right, other crystals show much more intense additional diffractions that have a very non-hexagonal distribution. Belakovskiy (1991) reported that sogdianite is replaced by zektzerite at Dara-i-Pioz, and zektzerite is orthorhombic, in accord with the additional diffractions recorded in Figure 1. Boggs (1987) also reported oriented intergrowths of sogdianite and zektzerite from a pegmatite in the Golden Horn batholith, Washington, U.S.A.

### X-ray data collection

The crystal used for the collection of the X-ray intensity data is pink and of good optical quality in transmitted light. This crystal was ground to a (approximate) sphere in a wind tunnel and then mounted on a Nicolet R3m automated four-circle diffractometer. Thirty-three reflections were centered using graphite-monochromated MoK X-radiation, and least-squares refinement of the setting angles produced the cell dimensions given in Table 1. Reflection intensities were measured to a maximum  $2\theta$  angle of  $60^\circ$  ( $0 \leq h \leq 12, 0 \leq k \leq 12, 20$

$l \leq 20$ ) according to the experimental procedure of Hawthorne and Groat (1985); other information pertinent to data collection is given in Table 1. Psi-scan data were collected and used to calculate an ellipsoidal shape for the crystal, which was then used for absorption corrections to the whole intensity data set. Data were then corrected for Lorentz, polarization and background effects, and then averaged and reduced to structure factors. A reflection was considered as observed if its intensity exceeded that of five standard deviations based on counting statistics; final numbers of observed reflections are given in Table 1.

### Electron-microprobe analysis

Subsequent to the collection of the x-ray intensity data, the crystal was mounted in epoxy, ground, polished, and carbon-coated for chemical analysis with a Cameca SX-50 electron microprobe operating in the wavelength-dispersion mode with an excitation voltage of 15 kV and a specimen current of 20 nA. The standards used were albite (Na, Si), kyanite (Al), orthoclase (K), fayalite (Fe), diopside (Ca), titanite (Ti), and zircon (Zr). No other elements were observed in energy-dispersion spectra obtained from the crystal. Data reduction was done according to the  $(Z)$  method (Pouchou and Pichoir 1984, 1985), and the chemical composition (mean of 10 points) is given in Table 2. The unit formula was calculated on the basis

**TABLE 1.** Miscellaneous refinement data for sogdianite

$a$ (Å)	10.053(1)	crystal size (mm)	0.32
$c$	14.211(2)	Radiation	MoK
$V$ (Å <sup>3</sup> )	1243.8(4)	Monochromator	graphite
Space group	$P6/mcc$	$R(\text{az})\%$	1.5
$Z$	2	Total $ F $	
		No. of $ F_c $	
		$R(\text{merge})\%$	
		$R\%$	
		$wR\%$	

Notes:  $R = (|F_o| - |F_c|) / |F_o|$ ;  $wR = [w(|F_o| - |F_c|)^2 / |F_o|^2]^{1/2}$ ,  $w = 1 / \sigma^2 F [1 - \exp(-0.7(\sin \theta / \lambda)^2)]$ .

**TABLE 2.** Chemical composition (wt%) and unit formula (apfu) for sogdianite

Composition	Formula	Site		
SiO <sub>2</sub>	68.87(43)	Si	12.02	T1
Al <sub>2</sub> O <sub>3</sub>	0.64(2)	Al	0.13	A
TiO <sub>2</sub>	2.90(37)	Ti	0.38	A
ZrO <sub>2</sub>	8.76(35)	Zr	0.75	A
Fe <sub>2</sub> O <sub>3</sub>	5.46(19)	Fe	0.72	A
Na <sub>2</sub> O	2.52(6)	Na	0.85	
K <sub>2</sub> O	4.48(3)	K	1.00	C
(Li <sub>2</sub> O)	Li	3	T2	
Sum	97.70			

Notes: Mn, Mg, Ca, F, V, Cr, Sc, Ba, Sr, and Cs not detected. Li calculated by difference. Sum of A cations is 1.98.

**TABLE 3.** Final atomic parameters for sogdianite

	x	y	z	$U_{eq}^*$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
A	1/3	2/3	1/4	40(1)	36(2)	36(2)	47(2)	0	0	18(1)
B	1/3	2/3	0.0192(4)	251(23)	179(18)	179(18)	395(59)	0	0	90(9)
C	0	0	1/4	194(2)	187(3)	187(3)	210(4)	0	0	93(2)
T1	0.11664(4)	0.35485(4)	0.11056(2)	69(1)	67(2)	75(2)	66(2)	-7(1)	0(1)	37(1)
T2			1/4	144(20)	133(19)	183(35)	132(16)	0		91(18)
O1	0.1325(2)	0.3971(2)		191(6)	302(8)	194(7)	73(5)	0	0	120(6)
O2	0.2211(1)	0.2778(1)	0.13506(6)	154(4)	145(4)	187(5)	194(4)	-13(3)	-15(4)	131(4)
O3	0.16186(9)	0.5041(1)	0.17134(6)	111(3)	114(4)	99(4)	126(3)	-36(3)	-16(3)	56(3)

\*  $U_{ij} \times 10^4$ .

of 30 anions with Li set equal to 3.0 apfu (atoms per formula unit) as indicated by the site-scattering refinement.

### Structure refinement

Scattering curves for neutral atoms together with anomalous dispersion corrections were taken from the *International Table for X-ray Crystallography* (Ibers and Hamilton 1974). *R* indices are of the form given in Table 1 and are expressed as percentages. The SHELXTL system of programs was used for the computational procedures.

Refinement was initiated using the atomic positions of milarite in space group *P6/mcc* (Hawthorne et al. 1991) together with site occupancies suggested by the ideal formula of sogdianite. Full-matrix refinement of all variables for an isotropic-displacement model converged to an *R* index of 4.1%. Upon conversion to an anisotropic-displacement model, the B cation(s) showed exaggerated anisotropy. This was taken as evidence for significant displacement of the cation off the special position: the electron density was modeled as a split site with an anisotropic-displacement factor (Kimata and Hawthorne 1989). This gave the same *R* index as was obtained for the ordered anisotropic-displacement model, but we prefer the split-site model on physical grounds. Full-matrix least-squares refinement of all variables (including site scattering and an isotropic-extinction correction) converged to an *R* index of 2.0%. Final atomic parameters are given in Table 3, refined site-scattering values in Table 4, and selected interatomic distance and angles in Table 5; structure factor tables are listed in Table 6<sup>1</sup>.

In a study of roedderite, Armbruster (1989) recorded a significant number of  $0kl$ ,  $l = 2n$  reflections with intensities  $>6\sigma(F_o)$ , compatible with space-group symmetry *P6<sub>2</sub>c*. He refined the structure in *P6<sub>2</sub>c* but with all positions except Na constrained to obey *P6/mcc* symmetry. We observed six reflections of the sort  $0kl$ ,  $l = 2n$  with  $|F_o| > 6\sigma(F_o)$ ; however, they did not correspond to the strong reflections reported by Armbruster (1989). These are probably due to the presence of intergrown zekzerite.

### SITE POPULATIONS

The T1 site is completely occupied by Si, as indicated both by the unit formula (Table 2) and by the  $\langle T1-O \rangle$  distance of

1.612 Å (Table 5). Bakakin et al. (1975) assigned Li + Al to the T2 site. However, our site-scattering refinement for the T2 site gives 8.8(3) epfu and a  $\langle T2-O \rangle$  distance of 1.957 Å, conformable with complete occupancy of T2 by Li (9.0 epfu). It was shown by Hawthorne et al. (1991) that Al can occur at the A, T1, and T2 sites in the milarite-type structure. For the sogdianite crystal studied here, the minor Al (0.13 apfu) must occur at the A site, as the T1 site is completely occupied by Si and the T2 site is completely occupied by Li. By analogy, Al occurs at the A site and Li at the T2 site in sugilite (Armbruster and Oberhänsli 1988).

The A site is occupied by Zr, Fe<sup>3+</sup>, Ti, and Al, and there is very close agreement between the refined site-scattering and the site populations assigned from the unit formula (Table 4). The marginal difference in the refined site-scattering values [58.8(2) electrons] and predicted site-scattering (59.4 e) could

**TABLE 4.** Refined site-scattering (SREF) values (epfu) and assigned site populations (apfu) for sogdianite

	SREF	Site population	Predicted site scattering
A	58.8(2)	0.76 Zr + 0.73 Fe + 0.38 Ti + 0.13 Al	59.4
B	9.6(4)	1.15 □ + 0.85 Na	9.4
C	19.2(2)*	1.00 K	19
T1	168	12.00 Si	168
T2	8.8(3)*	3.00 Li	9

\*Fixed at ideal occupancy in last refinement cycle.

**TABLE 5.** Selected interatomic distances (Å) and angles (°) in sogdianite

A-O3	×6	2.019(1)	B-O1	×3	2.454(2)
			B-O3	×3	2.738(4)
O3-A-O3a	×6	92.3(1)	$\angle B-O$		2.596
O3-A-O3b	×3	91.0(1)			
O3-A-O3c	×3	84.6(1)	C-O2	×12	3.033(1)
$\angle O3-A-O3$		90.1			
T1-O1		1.615(1)	T2-O3	×4	1.957(1)
T1-O2		1.624(2)			
T1-O2d		1.620(1)	O3-T2-O3e	×2	110.3(1)
T1-O3		1.588(1)	O3-T2-O3f	×2	133.5(1)
		1.612	O3-T2-O3c	×2	87.9(1)
			$\angle O-T2-O$		110.6
O1-T1-O2		109.4(1)			
O1-T1-O2d		110.6(1)	B-Bg		0.55(1)
O1-T1-O3		109.7(1)			
O2-T1-O2d		104.0(1)	T1-O1-T1		153.4(1)
O2-T1-O3		112.7(1)	T1-O2-T1		152.3(1)
O2d-T1-O3		110.4(1)	T1-O3-T2		116.6(1)
$\angle O-T1-O$		109.5			

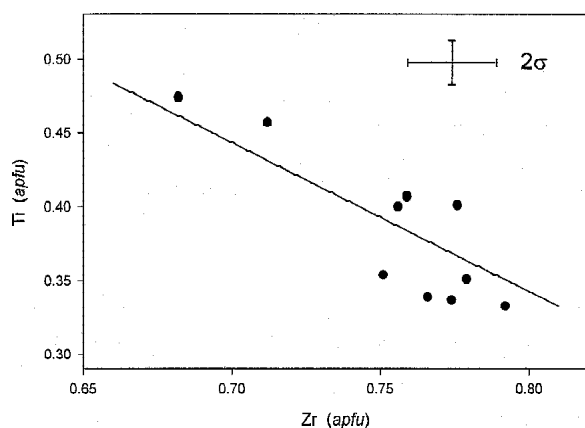
Notes: a: 1-y, 1-y+x, z; b: y-x, y, 1/2-z; c: x, 1-y+x, 1/2-z; d: x-y, x, z; e: -x, 1-y, z; f: -x, y-x, 1/2-z; g: x, y, -z.

<sup>1</sup>A copy of Table 6, document item AM-99-008 contact the Business Office, of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the American Mineralogist web site at <http://www.minsocam.org>.

be due to variation in Ti—Zr contents. The refined site scattering necessarily provides average Ti and Zr contents for the entire crystal, whereas the predicted site-scattering is based on Zr and Ti values from EMPA, which is arrived at from ten random point analyses from a single polished surface through the crystal. In Figure 2, Ti apfu is plotted against Zr for the 10 electron-microprobe compositions. There is a reasonable inverse correlation ( $r^2 = 0.74$ ), where the total Zr + Ti remains relatively constant. Because of the large electron difference between Zr (40 e) and Ti (22 e), minor Zr—Ti chemical variation encountered during EMPA can easily perturb the predicted site-scattering value. Considering this difficulty, the agreement in Table 4 is good. Hawthorne et al. (1991) showed that there is a well-developed correlation between  $\langle A-O \rangle$  and the constituent-cation radius of the A-group cations; the site populations derived here are in accord with this relation. In particular, the  $\langle A-O \rangle$  distance indicates that only  $Fe^{3+}$  ( $r = 0.645 \text{ \AA}$ ) and not  $Fe^{2+}$  ( $r = 0.78 \text{ \AA}$ ) is present at the A site.

In several milarite-group minerals, there is significant positional disorder at the A site (Kimata and Hawthorne 1989). Armbruster et al. (1989) proposed that this disorder, which produces a splitting of the A-site along the  $\bar{c}$  axis, is related to interaction between the A cations and  $H_2O$  at the B site. In sogdianite, the B site is occupied by ( $\square + Na$ ) and there is no positional disorder at the A site, in accord with this explanation. Further evidence for the absence of significant  $H_2O$  (or any other scattering species) at the B site is the relative agreement between the total scattering at the B site [9.6(4) e] and that predicted by the presence of 0.85 Na (9.4 e). If appreciable  $H_2O$  were present at B, the refined site-scattering value would be in excess of that observed; it is not, and therefore no  $H_2O$  is present at B.

The B site is occupied by vacancy and Na, and the C site is completely occupied by K; the refined site-scattering values and the observed bond-lengths are in accord with this assignment.



**FIGURE 2.** Variation in Ti as a function of Zr content in the sogdianite crystal analyzed here. The solid line was drawn by eye with a slope of 1.0, corresponding to Ti—Zr substitution with  $Fe^{3+}$  and Al constant.

**TABLE 7.** End-member formulae for the Li-bearing members of the milarite group

	A*	B*	C	T2†	T1‡
Brannockite	$Sn^{4+}$	$\square$	K	Li	Si
Berezanskite	$Ti^{4+}$	$\square$	K	Li	Si
Sogdianite	$Zr^{4+}$	$\square$	K	Li	Si
Sugilite	$Fe^{3+}$	Na	K	Li	Si
Darapiosite	$Mn^{2+}$	Na	K	$Zn_2Li_1$	Si
Dusmatovite	$Mn^{2+}$	K	K	$Zn_2Li_1$	Si

\*Multiplicity of 2.

†Multiplicity of 3.

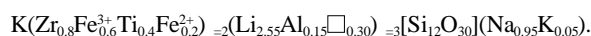
‡Multiplicity of 12.

### THE CHEMICAL FORMULA OF SOGDIANITE AND RELATED LI-BEARING MINERALS

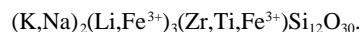
The chemical formula of sogdianite originally written by Dusmatov et al. (1968) as



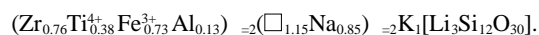
was modified by Bakakin et al. (1975) to



Fleischer and Mandarino reformulated it as



The first and third of these forms do not correspond to the milarite-type structure. The formula of the sogdianite crystal we examined may be written in the following way to produce optimum agreement with both SREF and EMPA data:



The general formula may thus be written as



The ideal end-member formula has Zr dominant at the A site,  $\square$  dominant at the B site (Table 7). These Li-bearing members of the milarite group may thus be divided into two subgroups: (1) those with  $\square$  at the B site; (2) those with (Na,K) at the B site. The crystal examined in this work is therefore a solid solution primarily between sogdianite (So) and sugilite (Su) with minor berzanskite (Be) and the Al-equivalent of sugilite (Sa):  $So_{0.38}Be_{0.19}Su_{0.37}Sa_{0.06}$ .

### ACKNOWLEDGMENTS

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