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The crystal structure of emeleusite, a novel example of sechser-doppelkette

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Abstract

Emeleusite, $Na_2LiFe^{III}Si_6O_{15}$, is orthorhombic, space group Acam with $a = 10.072(3)$ Å, $b = 17.337(6)$ Å and $c = 14.004(3)$ Å, $Z = 8$. X-ray data were collected on a four-circle diffractometer to give 563 independent reflections with $I > 3\sigma(I)$. The structure was solved by means of Patterson technique followed by Fourier syntheses and refined by least squares to $R_w = 0.043$.

The structure consists of corrugated double silicate chains with a six tetrahedral repeat (sechser doppelkette). The double silicate chains are linked by chains of Na(2) polyhedra and chains of alternating Li tetrahedra and Fe octahedra. Na(1) is located on the mirror plane coordinated by nine oxygens.

Emeleusite is isostructural with tuhualite, zektzerite and $Na_2Mg_2Si_6O_{15}$, and more distantly related to the milarite group.

Introduction

Emeleusite, $Na_2LiFe^{III}Si_6O_{15}$, is a new mineral occurring as a minor constituent of a peralkali trachyte dyke on Igdlutalik Island in Julianchåb district of South Greenland (UPTON *et al.*, 1978). It is orthorhombic, and euhedral crystals show the forms: {100} {010} {001} {110} {101} {011}. Emeleusite can form pseudohexagonal penetration triplets with {110} as the twin planes, the single individuals are tabular parallel to {010} and strongly elongated after [100].

UPTON *et al.* noted that the chemistry and the X-ray data of emeleusite indicated a close relationship to tuhualite,

$(Na,K)_2Fe_2^{II}Fe_2^{III}Si_{12}O_{30} \cdot H_2O$, (MERLINO, 1969) and zektzerite, $LiNaZrSi_6O_{15}$, (DUNN *et al.*, 1977 and GHOSE and WAN, 1978). The present paper confirms that emeleusite is isostructural with tuhualite and zektzerite, and also with the synthetic compound $Na_2Mg_2Si_6O_{15}$ (CRADWICK and TAYLOR, 1972).

The axial setting of emeleusite given by UPTON *et al.* differs from the ones quoted for tuhualite, zektzerite and $Na_2Mg_2Si_6O_{15}$, the $a\ b\ c$ for emeleusite corresponds to $c\ b\ a$ for tuhualite and others. The original orientation of emeleusite will be maintained in this paper, because this setting is the best way to manifest the pseudohexagonal symmetry ($b \sim 2a \sin 60°$) and to explain the triplets with the c axis as pseudo six-fold axis.

Experimental

Lattice type and space group were determined from Weissenberg photographs using Cu$K\alpha$-radiation. The unit cell dimensions and their standard deviations were determined from least-squares refinement based on reflections measured on a four-circle diffractometer. For data collection a single crystal of dimensions $0.05 \times 0.05 \times 0.05\,\mathrm{mm}^3$ was used. A total of 1213 independent reflections with $\theta < 25°$ was measured on the four-circle diffractometer (CAD-4F) using monochromatized Mo$K\alpha$-radiation and ω-scan technique. Of these 563 reflections with $I > 3\sigma(I)$ (counting statistics) were used in the least-squares refinement of the structure. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Crystal data

Crystal system: orthorhombic

Unit cell: $a = 10.072(3)$ Å, $b = 17.337(6)$ Å, $c = 14.004(3)$ Å

Cell content: $8(Na_2LiFe^{III}Si_6O_{15})$

Calculated density: 2.81 g/cm³

Absorption coefficient: $\mu(\mathrm{Mo}K\alpha) = 19.7\ \mathrm{cm}^{-1}$

Systematic absences:	hkl	for	$k+l$	odd
	$h0l$	for	h	odd
	$0kl$	for	l	odd

Space group: no. 64 Acam (or no. 41 Aba2).

Determination and refinement of the structure

The crystal structure was determined by means of Patterson technique followed by Fourier-syntheses in the centrosymmetric space group Acam. The structure was refined by a full-matrix least-squares procedure with all atoms except Fe and Na kept isotropic. The atomic scattering factors and the anomalous scattering corrections for Fe are from *International tables* (1974). The ratio between observations and variables was 563/64 and the final $R = \Sigma|F_o - F_c|/\Sigma F_o$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$ were 0.049 and 0.043 respectively. The weight function is, besides a scale factor, of the form $w = xy$ with

$$x = \begin{cases} (a\lambda/\sin\theta)^2 & \text{if } \sin\theta/\lambda > a \\ (a\lambda/\sin\theta)^{-2} & \text{otherwise} \end{cases} \quad \text{and } y = \begin{cases} 1 & \text{if } F_o > b \\ (F_o/b)^2 & \text{otherwise} \end{cases}$$

The constants $a = 0.4207$ and $b = 113.91$ were determined to give a distribution of $w(|F_o| - |F_c|)^2$ as uniform as possible (NIELSEN, 1977). A subsequent normal probability plot of the weighted residuals resulted in a correlation coefficient of 0.996 indicating an almost

Table 1. *Final atomic positional and isotropic thermal parametres*
Standard deviations in parentheses. U multiplied by 100. The form of the temperature expression is: $\exp(-2\pi^2\Sigma_{ij}h_ih_ja_i{}^*a_j{}^*U_{ij})$

Atom	x	y	z	U
Na(1)	0.2516(18)	0.4145(4)	0.5000	
Na(2)	0.2500	0.2243(3)	0.2500	
Li	0.0	0.0	0.2518(19)	0.5(4)
Fe	0.2500	0.4137(1)	0.2500	
Si(1)	0.4867(2)	0.1322(1)	0.6137(2)	0.39(6)
Si(2)	0.1923(2)	0.0716(1)	0.6140(2)	0.37(5)
Si(3)	0.4579(2)	0.3107(1)	0.6140(2)	0.50(6)
O(1)	− 0.0032(6)	0.2230(4)	0.1385(5)	1.3(2)
O(2)	0.4123(6)	0.4203(4)	0.1702(5)	0.9(1)
O(3)	0.3340(7)	0.1116(4)	0.3606(5)	1.4(2)
O(4)	0.3371(7)	0.4944(4)	0.3306(5)	0.9(2)
O(5)	0.0861(7)	0.1379(3)	0.3570(5)	0.9(2)
O(6)	0.1757(6)	0.3332(4)	0.1664(5)	1.1(2)
O(7)	0.5136(11)	0.1209(6)	0.5000	1.5(2)
O(8)	0.1885(11)	0.0535(6)	0.5000	1.5(2)
O(9)	0.4319(10)	0.3205(6)	0.5000	1.4(2)

Table 2. *Anisotropic thermal parameters* (Å^2) *for* Na *and* Fe
Standard deviations in parentheses. U_{ij} multiplied by 100. The form of the temperature factor expression is: $\exp(-2\pi^2\sum_{ij}h_ih_ja^*_ia^*_jU_{ij})$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na(1)	1.7(3)	2.5(4)	6.6(5)	−0.2(3)	0.0	0.0
Na(2)	4.2(4)	1.2(3)	2.8(4)	0.0	−2.1(4)	0.0
Fe	1.2(1)	0.8(1)	0.9(1)	0.0	0.0(1)	0.0

normal distribution of the weighted residuals. The final positional and thermal parameters are listed in Tables 1 and 2. A list of observed and calculated structure factors may be obtained from the authors on request.

Description of the structure

A stereoscopic view of the emeleusite structure is shown in Fig. 1. The essential feature in the structure is the formation of double silicate chains running in the [100] direction and corrugated in an S-like manner with a six tetrahedral repeat, thus forming a Sechser-Doppelkette in accordance to the classification of silicates by LIEBAU (1972).

The double chain is developed during condensation of two single chains across a mirror plane, and all the tetrahedra take part in this condensation. The bridging oxygens on the mirror plane are O(7), O(8) and O(9), hereafter referred to as group A. As a consequence of the corrugation of the double chain three distinct rings of four Si tetrahedra can be observed.

Each single chain consists of three different silicons lying on a plane parallel to the mirror plane, and connected by six different oxygens, of which the z parameters (Table 1) fall into two groups:

group B: O(1) 0.3615(5), O(3) 0.3606(5) and O(5) 0.3570(5)

group C: O(2) 0.3298(5), O(4) 0.3306(5) and O(6) 0.3336(5)

Parallel to the double chains, at $z = 0.25$, another plane is located, containing Li, Fe and Na(2). Finally, the Na(1) is situated in the middle of the triangle composed of the A oxygens. It is evident that there exists a marked planarity in the atomic arrangement, and the

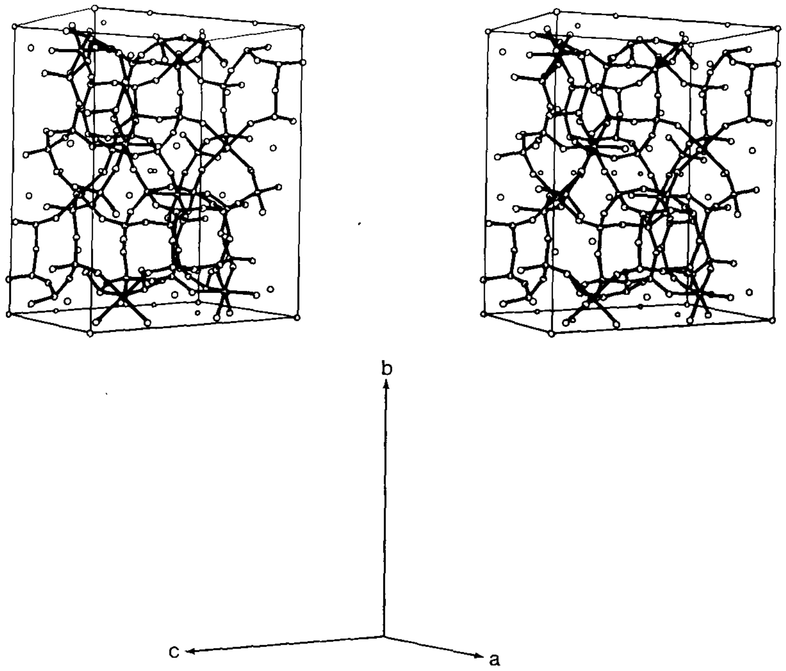

Fig. 1. Stereoscopic view of the emeleusite structure. Lines are drawn from oxygen to silicon and iron, while there are no lines from oxygen to lithium (small spheres) and sodium

emeleusite structure can be considered as a layered sequence parallel to (001):

O(A) Na(1)
Si
O(B)
O(C)
Li Fe Na(2)

The individual polyhedra

The three distinct Si tetrahedra all have three Si—O bond lengths at 1.62—1.63 Å and one Si—O bond length at 1.58 Å (Table 3). The short distances involve the C oxygens, which are linked to only one silicon, while the longer distances involve the A and B oxygens, shared by two silicons. It is not possible to state any difference between the Si—O(A) bond lengths and the Si—O(B) bond lengths as it is in the case of zektzerite (Ghose and Wan, 1978). The O—Si—O angles vary from 103° to 115°, the three smallest angles involve oxygens of group B only. The Si—O—Si angles vary from 147° to 152° for angles including the B oxygens, and from 156° to 158° for angles including the A oxygens. It is interesting to note that the larger Si—O—Si angles are not associated with shorter Si—O bond lengths as predicted by Tossell and Gibbs (1977). According to their calculations, the Si—O—Si angles are, in addition, dependent on the charge balance of the bridging oxygen, but in the case of emeleusite there is practically no difference in the sums of the electrostatic valencies received by the A oxygens and the B oxygens (Table 4).

Li is surrounded by four oxygens composing a highly distorted tetrahedron. The Li—O bond lengths are 1.98 Å and 2.00 Å, and the O—Li—O angles are from 85° to 136°. Fe is situated in a nearly regular octahedron made by the C oxygens. The Fe—O distances are 1.97—2.00 Å and the O—Fe—O angles are 85°—94°. The Li tetrahedra and the Fe octahedra share edges, O(2)—O(4), thereby forming a chain in the [100] direction.

Na(2) is irregularly coordinated by ten oxygens within 3.10 Å, two at 2.35 Å, four at 2.63—2.69 Å and four at 2.99—3.08 Å. The Na(2) polyhedra share edges, O(1)—O(1), thus forming a chain in

Table 3. *Interatomic distances* (Å) *and angles* (°)
Standard deviations in parentheses

Si(1)—O(1)	1.620(7)	Fe—O(2)	1.983(7) (× 2)
Si(1)—O(2)	1.579(7)	Fe—O(4)	2.000(7) (× 2)
Si(1)—O(3)	1.619(8)	Fe—O(6)	1.969(7) (× 2)
Si(1)—O(7)	1.627(4)		
		Na(1)—O(2)	2.901(8) (× 2)
Si(2)—O(3)	1.626(8)	Na(1)—O(4)	2.879(8) (× 2)
Si(2)—O(4)	1.575(7)	Na(1)—O(6)	2.821(8) (× 2)
Si(2)—O(5)	1.623(7)	Na(1)—O(7)	2.475(14)
Si(2)—O(8)	1.628(3)	Na(1)—O(8)	2.483(13)
		Na(1)—O(9)	2.440(13)
Si(3)—O(1)	1.623(7)		
Si(3)—O(5)	1.620(7)	Na(2)—O(1)	2.990(7) (× 2)
Si(3)—O(6)	1.581(7)	Na(2)—O(1)	3.075(7) (× 2)
Si(3)—O(9)	1.627(4)	Na(2)—O(3)	2.632(8) (× 2)
		Na(2)—O(5)	2.686(7) (× 2)
Li—O(2)	1.999(16) (× 2)	Na(2)—O(6)	2.345(8) (× 2)
Li—O(4)	1.979(16) (× 2)		

Table 3 (*Continued*)

O(1)—Si(1)—O(2)	112.7(4)	O(2)—Li—O(2)	110.3(13)
O(1)—Si(1)—O(3)	105.3(4)	O(2)—Li—O(4)	136.0(3) (× 2)
O(1)—Si(1)—O(7)	108.1(4)	O(2)—Li—O(4)	85.3(3) (× 2)
O(2)—Si(1)—O(3)	111.9(4)	O(4)—Li—O(4)	112.3(13)
O(2)—Si(1)—O(7)	108.3(5)		
O(3)—Si(1)—O(7)	110.4(5)	O(2)—Fe—O(2)	173.3(3)
		O(2)—Fe—O(4)	90.2(3) (× 2)
O(3)—Si(2)—O(4)	114.8(4)	O(2)—Fe—O(4)	85.2(3) (× 2)
O(3)—Si(2)—O(5)	102.8(4)	O(2)—Fe—O(6)	93.6(3) (× 2)
O(3)—Si(2)—O(8)	108.5(5)	O(2)—Fe—O(6)	91.1(3) (× 2)
O(4)—Si(2)—O(5)	110.8(4)	O(4)—Fe—O(4)	91.2(3)
O(4)—Si(2)—O(8)	108.4(4)	O(4)—Fe—O(6)	89.6(3) (× 2)
O(5)—Si(2)—O(8)	111.5(5)	O(4)—Fe—O(6)	176.2(3) (× 2)
		O(6)—Fe—O(6)	89.8(3)
O(1)—Si(3)—O(5)	103.8(3)		
O(1)—Si(3)—O(6)	111.9(4)	Selected angles from the Na(1) polyhedron	
O(1)—Si(3)—O(9)	110.5(5)		
O(5)—Si(3)—O(6)	115.2(4)	O(2)—Na(1)—O(2)	110.5(3)
O(5)—Si(3)—O(9)	108.4(5)	O(4)—Na(1)—O(4)	111.0(3)
O(6)—Si(3)—O(9)	107.0(5)	O(6)—Na(1)—O(6)	111.4(3)
		O(2)—Na(1)—O(4)	58.4(2) (× 2)
Si(1)—O(1)—Si(3)	146.6(5)	O(2)—Na(1)—O(6)	59.1(2) (× 2)
Si(1)—O(3)—Si(2)	151.5(5)	O(4)—Na(1)—O(6)	58.8(2) (× 2)
Si(2)—O(5)—Si(3)	148.5(5)	O(7)—Na(1)—O(8)	118.4(5)
Si(1)—O(7)—Si(1)	156.3(7)	O(7)—Na(1)—O(9)	123.7(5)
Si(2)—O(8)—Si(2)	157.6(7)	O(8)—Na(1)—O(9)	117.9(5)
Si(3)—O(9)—Si(3)	157.9(7)	O(4)—O(2)—O(6)	59.4(2)
		O(2)—O(4)—O(6)	60.3(2)
		O(2)—O(6)—O(4)	60.3(2)

Table 4. *Coordination of oxygen*

Group	Oxygen atom	Coordinated atoms	e.s.v. sum
B	O(1)	Si(1), Si(3), Na(2), Na(2)	2.20
C	O(2)	Si(1), Li, Fe, Na(1)	1.86
B	O(3)	Si(1), Si(2), Na(2)	2.10
C	O(4)	Si(2), Li, Fe, Na(1)	1.86
B	O(5)	Si(2), Si(3), Na(2)	2.10
C	O(6)	Si(3), Fe, Na(1), Na(2)	1.71
A	O(7)	Si(1), Si(1), Na(1)	2.11
A	O(8)	Si(2), Si(2), Na(1)	2.11
A	O(9)	Si(3), Si(3), Na(1)	2.11

the [100] direction. Na(2) is located in front of the channels formed by the corrugation of the silicate double chains.

Na(1) has within a distance of 2.90 Å nine oxygen neighbours, six C oxygens (av. 2.87 Å) and three A oxygens (av. 2.47 Å). The C oxygens constitute a nearly regular trigonal prism with the threefold axis in the [001] direction. The O(C)—O(C)—O(C) angles are 60.3 °, 59.4 ° and 60.3 °, while the average angle of O(C)—Na(1)—O(C) is 58.7 °. The directions [Na(1)—O(A)] point *c.* 17 ° away from the prism edges, which means that the A oxygens are not located at the centres of the prism faces as it is stated for $Na_2Mg_2Si_6O_{15}$ (CRADWICK and TAYLOR, 1972).

Coordination of oxygen

Table 4 gives the bond strengths received by the individual oxygen atoms calculated according to Pauling's electrostatic valence rule. It is shown that the A and B oxygens are overbonded, while the C oxygens are underbonded, in particular O(6). This phenomenon is reflected in the variation of cation-oxygen distances, for instance the shortest bond lengths in the Si tetrahedra are those involving the C oxygens, and in the Na(2) polyhedra the Na(2)—O(6) bond length is clearly shorter than the Na(2)—O(B) bond lengths. In the Na(1) polyhedra the trigonal prism is composed of the C oxygens, of which the O(6) is significantly closer to the sodium atom than the other two.

Relationship to other structures

Emeleusite is isostructural with tuhualite, $(Na,K)_2Fe_2^{II}Fe_2^{III}Si_{12}O_{30}\cdot H_2O$, zektzerite, $NaLiZrSi_6O_{15}$, and $Na_2Mg_2Si_6O_{15}$. All phases have the double silicate chains equally corrugated, their unit cell parameters containing the double chain direction are: emeleusite $a = 10.07$ Å, tuhualite $c = 10.11$ Å, zektzerite $c = 10.16$ Å and $Na_2Mg_2Si_6O_{15}$ $c = 10.21$ Å. Their chemistry presents the following variation:

Coordination	9	10	4	6
Emeleusite	Na(1)	Na(2)	Li	Fe^{III}
Tuhualite		Na(2)	Fe^{II}	Fe^{III}
Zektzerite		Na(2)	Li	Zr
$Na_2Mg_2Si_6O_{15}$	Na(1)	Na(2)	Mg	Mg

The Na(1) position is vacant in tuhualite and zektzerite. The Na(2) polyhedra, the Li,Fe^{II},Mg tetrahdra and the Mg,Fe^{III},Zr octahedra are very similar in shape in the different phases.

As to the question of describing emeleusite as a tektosilicate with a ratio tetrahedral cations/oxygens in agreement with the classification proposed by ZOLTAI (1960), which has been done in the descriptions of tuhualite, zektzerite and $Na_2Mg_2Si_6O_{15}$, the present authors prefer to restrict the term tektosilicate to structures, where all oxygens are shared by two cations in tetrahedral positions. In emeleusite the O(6) is involved in one tetrahedron only, so emeleusite should be considered as an inosilicate.

Several structural patterns in the emeleusite structure type can be found in the structures of osumilite (BROWN and GIBBS, 1969) and other minerals from the milarite group. These minerals are hexagonal with $a \sim 10$ Å and $c \sim 14$ Å and have six-fold double rings of (Si,Al) tetrahedra. The major part of the other cations are located in layers parallel to (001) between the double rings, and chains of alternating tetrahedra and octahedra can be detected along the *a* axis. The unit cell parameters of emeleusite show the pseudohexagonal symmetry, and the dimensions ($a \sim 10$ Å, $b \sim 2a \sin 60^\circ$ and $c \sim 14$ Å) are identical with those of the milarite group. The twin operations with {110} as twin planes give rise to slightly distorted hexagonal double rings of Si tetrahedra across the twin planes. It appears from the description of the emeleusite structure that a marked planarity exists in the atomic arrangement parallel to (001), and that the Li tetrahedra and the Fe octahedra form chains in the *a* axis direction.

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