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Structure determination of $Na_3DySi_6O_{15}$ and crystal chemistry of zektzerite related compounds

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Abstract

The crystal structure of $Na_3DySi_6O_{15}$ has been solved and refined to an $R_1 = 2.97\%$ ($wR_2 = 8.25\%$) for 1311 independent reflections. The compound was found to crystallize within the orthorhombic system with the space group *Cmca* ($Z = 8$) and the lattice parameters: $a = 14.590(7)$ Å, $b = 17.813(4)$ Å, $c = 10.519(2)$ Å, $V = 2734.0$ Å^3, $D_{cal} = 3.11$ g/cm^3. The structure of $Na_3DySi_6O_{15}$ is a filled variant of the zektzerite with S like corrugated double chains of $[SiO_4]$ tetrahedral, connected via Na^+ and Dy^{3+} cations and running parallel to *c*-axis. The three-dimensional network results from the packing of these chains along [100] by skewering them in rods represented by the tunnels delimited by the S shape of the silicate chains. One of the main peculiar features of the $Na_3DySi_6O_{15}$ structure is the location of Na^+ in tetrahedral sites with rather short Na–O bond lengths (2×2.243 and 2×2.262 Å).

1. Introduction

The present work is a part of a broad program of research devoted to both fundamental and applied investigations of crystalline and vitreous silicates [1]. Our interest resides mainly in compounds belonging to the ternary systems A_2O–LnO_3–SiO_2 (A = monovalent cation, Ln = rare earth). The main objectives of the study are to isolate single crystals of new phases and to solve the crystal structures, providing a better insight into the change of the structural affiliations with the variation of different parameters like temperature and chemical composition within the series of silicates $A^{I}_3LnSi_6O_{15}$, with A^{I} = monovalent cation, Ln = rare earth. Furthermore, practical applications are also sought, mainly for: (i) compounds with non-centrosymmetric space groups, due to their very important potential applications in various domains of modern technology such as non-linear optics, ferro- and piezoelectrics, SHG, etc.; (ii) rare earth doped crystals or glasses which could find interest as phosphors or laser hosts; (iii) crystalline or vitreous materials containing mobile cations such as Li^+ and Na^+ which have potential uses as super-ionic conductors, etc. [1,2]. For example, the ionic conductivity of the title compound ($\sigma_{300} = 6 \times 10^{-6}$ S cm^{-1}) was found to be more than one order of magnitude higher than that of the zektzerite crystal $NaLiZrSi_6O_{15}$ with $\sigma_{300} = 1 \times 10^{-8}$ S cm^{-1} [1,3].

A survey of the literature related to the above-mentioned ternary systems shows that there is still a need for sound and updated crystal chemical data for many of these materials. For example, $Na_3YSi_6O_{15}$, which belongs to the ternary diagram Na_2O–Y_2O_3–SiO_2, has been reported without any polymorph by Haile et al. [4] who grew the corresponding single crystals under hydrothermal conditions. On the contrary, using the flux method, Bourguiba and Dogguy [5] have succeeded in growing crystals of another crystalline variety of $Na_3YSi_6O_{15}$ which was found to be isotypic with the mineral zektzerite. Furthermore, no phase transition has been so far established between the two forms of this trisodiumyttriumhexasilicate. It is worth noting that not many structures have been resolved

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within the $A_3LnSi_6O_{15}$ systems and the structural results of the present article will indeed contribute to the general understanding of the crystal chemistry of such series in providing sound and updated crystallographic data related to one of their members, $Na_3DySi_6O_{15}$. In addition we also present a comparative structural study of analogous zektzerite compounds. Indeed, other phases chemically close to the title compound have been reported but it should be mentioned that they crystallize with structures different from the zektzerite type. For example, the dihydrate of trisodiumneodymiumhexasilicate, $Na_3NdSi_6O_{15} \cdot 2H_2O$, is characterized by corrugated layers containing four-, five-, six- and eight-membered rings [6]. The same authors have also reported different crystal structures for the potassium phases, $K_3NdSi_6O_{15} \cdot 2H_2O$, with highly corrugated $[Si_2O_5]_\infty$ layers [7] and β-$K_3NdSi_6O_{15}$ whose lattice is based on $[Si_2O_5]_n^{-2n}$ layers, connected by Nd cations [8].

Moreover, the ultimate purpose of our investigations is to understand the effect of the key chemical parameters of inserted cations (nature, size, electronegativity, etc.) on the stabilization of different structural types and the resulting physical properties (ionic conductivity, non-linear properties, etc.) of the isolated compounds. Understanding such correlations will certainly facilitate the design of appropriate physical–chemical processes for the elaboration of the device to be used for the desired practical applications.

2. Experimental

2.1. Crystal growth

Single crystals suitable for crystal structure determination were grown by a flux method using a mixture of Na_2MoO_4 and V_2O_5 (molar ratio: 4/1), with a fixed ratio: (solute weight/flux weight) = 1/10. The blend of appropriate amounts of reagent grade starting materials Na_2CO_3, Dy_2O_3, SiO_2, MoO_3 and V_2O_5, was thoroughly ground in an agate mortar, contained in a Pt crucible and submitted to the following heat treatments:

- slow heating of 50°C h^{-1} between 20°C and 850°C,
- melting at 850°C for 24 h,
- very slow cooling with a rate of 5°C h^{-1} within the range 850–530°C,
- cooling of the solid (solute + flux) with a range of 50°C to room temperature.

Colorless single crystals of $Na_3DySi_6O_{15}$ were finally extracted from the frozen melt by dissolving the flux in warmed distilled water. The recovered single crystals have the shape of platelets and an approximate size of a few hundred microns.

2.2. Crystal structure determination

Preliminary X-ray crystallography investigations, conducted using a Weissenberg and Precession photographs, have allowed to assign the orthorhombic space group *Cmca* and the appropriate unit cell parameters. The diffraction patterns were collected using an Enraf-Nonius CAD 4-F four circle diffractometer. The collected data were corrected for Lorentz and polarization effects. The DIFABS method was used for the absorption correction of the measured intensities [9]. Further experimental details of the data collection and conditions for the structure determination are summarized in Table 1. The lattice parameters were refined using

Table 1
Data collection and refinement parameters for $Na_3DySi_6O_{15}$

Crystal data	
Chemical formula	$Na_3DySi_6O_{15}$
Chemical formula weight (g)	640.01
Cell setting	Orthorhombic
Space group	*Cmca* (No. 64)
a (Å)	14.591(7)
b (Å)	17.813(4)
c (Å)	10.519(2)
V (Å^3)	2734.0(15)
Z	8
Calculated density (g cm^{-3})	3.110
Crystal shape	Platelet
Crystal size (mm)	$0.25 \times 0.15 \times 0.06$
Intensity measurements	
Diffractometer	Enraf-Nonius CAD-4
Radiation (Å)	Mo$K\alpha$ ($\lambda = 0.71069$)
Monochromator	Graphite
Temperature (K)	293
Scan method	$\omega - 2\vartheta$
Scan width	$0.8 + 0.35 \tan \vartheta$
ϑ range (deg)	3–26
Range of h, k, l	$-17 < h < +17$ $-21 < k < +21$ $0 < l < 12$
$F(000)$	2424
μ (Mo$K\alpha$) (mm^{-1})	6.173
No. of measured reflections	5247
No. of observed reflections	1394
No. of independent reflections	1394
Reflections with $I > 2\sigma(I)$	1311
Refinement	
Absorption correction	Empirical, DIFABS (Ref. [9])
No. of variables	122
Δ/ρ_{max} (e$^-$ Å^{-3})	+3.30
Δ/ρ_{min} (e$^-$ Å^{-3})	−2.49
Refinement on	SHELXS-93 (Ref. [11])
Extinction method	SHELXL-93 (Ref. [11])
Extinction coefficient	0.00058(8)
Weighting scheme	$1/[\sigma^2(F_o^2) + (0.051P)^2 + 14.20P]$ with $P = [(F_o)^2 + 2F_c{}^2]/3$
R_1	0.0297
wR_2 (F)	0.0825

the least square method and 25 independent reflections. It is also worth noticing that on the one hand, the weight of the absorption coefficient is moderate (6.2 cm^{-1}) and on the other hand the values of $R_{int} = 0.0288$ (with R_{int}, before correction = 0.0312) and $R_{sigma} = 0.0185$ are rather small. Under these conditions, very small influence (and errors) of absorption on the quality of the refinement of the title compound crystal structure are expected.

The structure was solved using the direct method to locate the heavy atoms and the Fourier difference for the remaining ones. All calculations were performed using successively the SHELXS-86 and SHELXL-93 package of programs [10,11]. The refined atomic coordinates and the thermal parameters are given in Tables 2 and 3, respectively. Selected inter-atomic distances and bond angles are given in Table 4. The bond strength and the summation of the bond strength [12] of all the ions are summarized in Table 5.

Table 2
Atomic positional parameters and equivalent isotropic displacement parameters of the structure $Na_3DySi_6O_{15}$

Atom	X	Y	Z	U_{eq}[a] (Å^2)
Na(1)	0	0.4262(3)	0.2481(3)	0.049(3)
Na(2)	0.25	0.2236(2)	0.25	0.032(2)
Na(3)	0.2381(2)	0	0	0.021(1)
Dy	0.25	−0.08940(2)	0.25	0.0061(2)
Si(1)	0.39260(7)	0.13500(6)	0.0210(1)	0.0068(5)
Si(2)	0.39004(7)	0.08259(5)	0.3002(1)	0.0057(5)
Si(3)	0.39285(7)	0.19092(6)	0.53324(9)	0.0063(5)
O(1)	0.3827(2)	0.2230(2)	−0.0134(3)	0.017(2)
O(2)	0.3370(2)	0.0855(1)	−0.0750(3)	0.012(2)
O(3)	0.3584(2)	0.1242(2)	0.1687(3)	0.012(1)
O(4)	0.1534(2)	0.0024(2)	0.1801(3)	0.014(1)
O(5)	0.3585(2)	0.1403(2)	0.4125(3)	0.012(1)
O(6)	0.3362(2)	0.1760(2)	0.6579(3)	0.014(2)
O(7)	0.5	0.1120(3)	0.0112(4)	0.016(2)
O(8)	0.5	0.0747(4)	0.2982(4)	0.015(2)
O(9)	0.5	0.1699(2)	0.5590(4)	0.016(2)

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

3. Description of $Na_3DySi_6O_{15}$ structure and discussion of the chemical bond

The projection of the $Na_3DySi_6O_{15}$ structure along [100] is given in Fig. 1. This lattice consists of a three-dimensional framework of [SiO_4] tetrahedrons and [DyO_6] octahedrons, interconnected to give three different cavities with coordination numbers of 9, 6 and 4 occupied by Na(1), Na(2) and Na(3), respectively (Fig. 2, Table 4).

3.1. The structure view

As shown in Fig. 1, the zektzerite structure could in fact be schematically regarded as a three-dimensional arrangement of double chains of [SiO_4] tetrahedrons, assembled in S-like corrugated shapes, running along [001] and packed in a foliar manner (Fig. 2) to form layers parallel to (100). The inter-foliar space is occupied by two types of M-chains made of the polyhedra around the $M(2)$, $M(3)$ and $M(4)$ interstices: (i) corrugated chains of alternating [$M(4)O_6$] octahedra and [$M(3)O_4$] tetrahedra running along [001] and serving as links between silicate sheets all along this direction; (ii) linear chains made of alternating [$M(4)O_6$] octahedra and [$M(1)O_9$] prisms sharing triangular faces and running along [100].

As can be seen from Table 6, the corrugated M-chains can contain cations of a diverse nature. In the case of the

Table 3
Anisotropic[a] thermal parameters (Å^2) for $Na_3DySi_6O_{15}$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na(1)	0.058(3)	0.035(2)	0.052(3)	−0.006(1)	0	0
Na(2)	0.033(1)	0.017(2)	0.046(1)	0	0.024(1)	0
Na(3)	0.017(1)	0.034(2)	0.012(1)	0.013(1)	0	0
Dy	0.0062(2)	0.0092(2)	0.0029(2)	0	0.00010(7)	0
Si(1)	0.0066(5)	0.0105(5)	0.0032(5)	−0.0008(5)	−0.0009(4)	−0.0005(4)
Si(2)	0.0047(5)	0.0092(5)	0.0033(6)	−0.0012(4)	−0.0001(4)	−0.0012(3)
Si(3)	0.0067(5)	0.0090(5)	0.0032(5)	−0.0009(4)	0.0015(3)	−0.0010(4)
O(1)	0.030(2)	0.009(1)	0.011(1)	−0.002(1)	0.001(1)	−0.001(1)
O(2)	0.015(2)	0.015(1)	0.007(1)	0.001(1)	−0.007(1)	−0.003(1)
O(3)	0.010(1)	0.019(1)	0.006(1)	0.002(1)	−0.001(1)	0.004(1)
O(4)	0.016(1)	0.014(1)	0.011(1)	0.001(1)	0.000(1)	0.004(1)
O(5)	0.011(1)	0.017(1)	0.008(1)	−0.005(1)	−0.001(1)	0.001(1)
O(6)	0.016(2)	0.017(1)	0.008(1)	−0.000(1)	0.005(1)	−0.005(1)
O(7)	0.008(2)	0.027(2)	0.012(2)	0.000(2)	0	0
O(8)	0.006(2)	0.026(2)	0.012(2)	−0.001(2)	0	0
O(9)	0.010(2)	0.022(2)	0.016(2)	−0.003(2)	0	0

[a] $U_{ij} = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Table 4
Selected inter-atomic distances (Å) and bond angles (deg) for the Na$_3$DySi$_6$O$_{15}$ structure

Si(1)–O(2) = 1.566(3)	O(2)–Si(1)–O(1) = 110.8(2)	O(2)–O(1) = 2.619(1)
Si(1)–O(1) = 1.615(3)	O(2)–Si(1)–O(7) = 108.5(2)	O(2)–O(7) = 2.588(4)
Si(1)–O(7) = 1.623(2)	O(1)–Si(1)–O(7) = 108.5(2)	O(1)–O(7) = 2.628(5)
Si(1)–O(3) = 1.643(3)	O(2)–Si(1)–O(3) = 112.8(2)	O(2)–O(3) = 2.672(4)
	O(1)–Si(1)–O(3) = 107.4(2)	O(1)–O(3) = 2.625(3)
	O(7)–Si(1)–O(3) = 108.9(2)	O(7)–O(3) = 2.657(2)
⟨Si(1)–O⟩ = 1.618	⟨O–Si(1)–O⟩ = 109.45	⟨O–O⟩ = 2.631
Si(2)–O(4) = 1.577(3)	O(4)–Si(2)–O(8) = 108.9(2)	O(4)–O(8) = 2.592(3)
Si(2)–O(8) = 1.611(1)	O(4)–Si(2)–O(3) = 114.1(2)	O(4)–O(3) = 2.695(6)
Si(2)–O(3) = 1.636(3)	O(8)–Si(2)–O(3) = 108.0(2)	O(8)–O(3) = 2.627(5)
Si(2)–O(5) = 1.632(3)	O(4)–Si(2)–O(5) = 111.2(2)	O(4)–O(5) = 2.648(2)
	O(8)–Si(2)–O(5) = 110.2(2)	O(8)–O(5) = 2.659(2)
	O(3)–Si(2)–O(5) = 104.3(2)	O(5)–O(3) = 2.580(6)
⟨Si(2)–O⟩ = 1.614	⟨O–Si(2)–O⟩ = 109.45	⟨O–O⟩ = 2.633
Si(3)–O(6) = 1.573(3)	O(6)–Si(3)–O(1) = 111.5(2)	O(6)–O(1) = 2.635(1)
Si(3)–O(1) = 1.617(3)	O(6)–Si(3)–O(9) = 109.1(2)	O(6)–O(9) = 2.609(1)
Si(3)–O(9) = 1.630(2)	O(1)–Si(3)–O(9) = 110.8(2)	O(1)–O(9) = 2.674(2)
Si(3)–O(5) = 1.636(3)	O(6)–Si(3)–O(5) = 113.1(2)	O(6)–O(5) = 2.678(4)
	O(1)–Si(3)–O(5) = 105.1(2)	O(1)–O(5) = 2.581(3)
	O(9)–Si(3)–O(5) = 107.2(2)	O(9)–O(5) = 2.629(4)
⟨Si(3)–O⟩ = 1.614	⟨O–Si(3)–O⟩ = 109.45	⟨O–O⟩ = 2.634
Na(1)–O(9) = 2.655(6)	Na(2)–O(6) = 2.392(4) × 2	Na(3)–O(2) = 2.243(3) × 2
Na(1)–O(8) = 2.698(7)	Na(2)–O(3) = 2.523(4) × 2	Na(3)–O(4) = 2.262(3) × 2
Na(1)–O(4) = 2.724(4) × 2	Na(2)–O(5) = 2.763(3) × 2	
Na(1)–O(7) = 2.812(5)		
Na(1)–O(2) = 3.002(4) × 2		
Na(1)–O(6) = 3.163(3) × 2		
⟨Na(1)–O⟩ = 2.882	⟨Na(2)–O⟩ = 2.559	⟨Na(3)–O⟩ = 2.252
Dy–O(6) = 2.213(3) × 2		
Dy–O(2) = 2.237(3) × 2		
Dy–O(4) = 2.280(3) × 2		
⟨Dy–O⟩ = 2.243		

Table 5
Bond strengths and summation[a] of bond strengths for ions in Na$_3$DySi$_6$O$_{15}$

Ion	Na(1)	Na(2)	Na(3)	Si(1)	Si(2)	Si(3)	Dy	$\sum$cal.
O(1)				1.02		1.02		2.04
O(2)	0.04 × 2c		0.30 × 2c	1.17			0.53 × 2c	2.04
O(3)		0.14 × 2c		0.95	0.96			2.05
O(4)	0.08 × 2c		0.28 × 2c		1.13		0.47 × 2c	1.96
O(5)		0.07 × 2c			0.97	0.96		2.00
O(6)	0.02 × 2c	0.20 × 2c				1.15	0.56 × 2c	1.93
O(7)	0.06			1.00 × 2a				2.06
O(8)	0.09				1.03 × 2a			2.15
O(9)	0.10					0.98 × 2a		2.06
$\sum$cal.	0.53	0.82	1.16	4.14	4.09	4.11	3.12	

[a] 2a and 2c stand for the anionic and cationic multiplicity, respectively.

mineral tuhualite, for example, the chains are made of [Fe^{III}O$_6$] octahedra and [Fe^{II}O$_4$] tetrahedra. Such low-dimensional arrangement of paramagnetic cations like Fe^{2+} and Fe^{3+}, with the electronic configurations ($t_{2g}{}^4\ e_g^2$) and ($t_{2g}{}^3\ e_g^2$), respectively, will be very interesting to investigate in order to determine the type of magnetic interactions that take place both within and between the chains. Indeed, the present structural work will be extended to the study of magnetic coupling within appropriate zektzerite compounds.

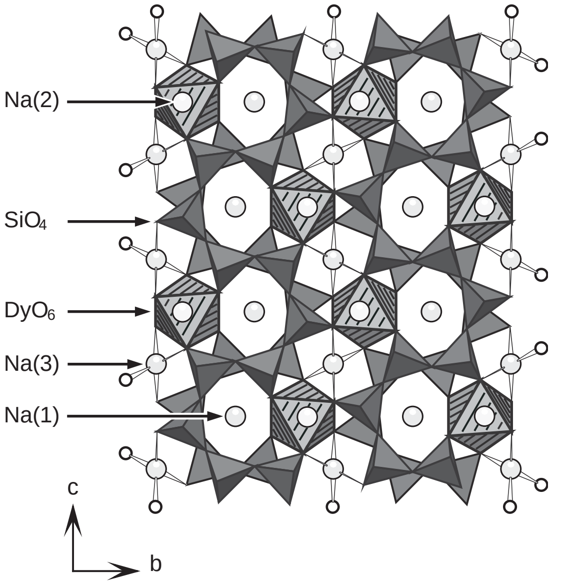

Fig. 1. Projection of the $Na_3DySi_6O_{15}$ structure along [100] direction.

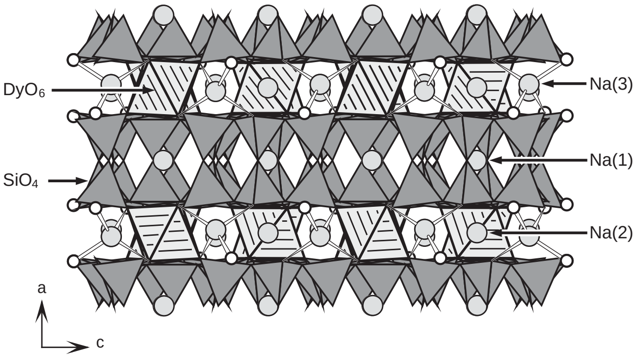

Fig. 2. Projection of the $Na_3DySi_6O_{15}$ structure along [010] direction.

3.2. The chemical bond in [SiO_4] tetrahedra

As expected the silicon ions are tetravalent (Table 5) and are located in tetrahedral sites (Fig. 1, Table 4). In addition, the mean $\langle$Si–O$\rangle$ bond lengths are almost identical in all silicon sites: $\langle$Si(1)–O$\rangle$ = 1.618 Å; $\langle$Si(2)−O$\rangle$ = 1.614 Å; $\langle$Si(3)–O$\rangle$ = 1.614 Å. The analysis of the bond angles shows that the mean values $\langle$O−Si−O$\rangle$ are all equal to 109.45° (whatever tetrahedron is considered around Si(1), Si(2) or Si(3)), which is very close to the ideal value 109.5° for a regular tetrahedron. However, with regard to inter-atomic distances, [Si(1)O_4] tetrahedra appear as the most distorted since Si(1)–O distances lie within the range 1.566(3)–1.643(3) Å while the two others Si(2)–O and Si(3)–O extend within narrower domains, ranging from 1.577(3) to 1.632(3) Å and 1.573(3) to 1.636(3) Å, respectively. Due probably to the corrugation of the silicate double chains, the angular deformations behave in the opposite direction to the bond lengths: when the values of the former tend to get close, the others are inclined to spread (Table 4).

3.3. The coordination sphere of dysprosium

The structural refinement has resulted in an octahedral environment for the dysprosium cations (Tables 4 and 5). The values of the O–Dy–O angles, show a rather deformed site since they range between 83° and 94°. Furthermore, within this coordination sphere the mean bond length $\langle$Dy–O$\rangle$ = 2.243 Å is compatible with the average values given in the literature and the sum of the ionic radii [18] of O^{2-} and Dy^{3+} in the octahedral site: $R_{(Dy)} = r(Dy^{3+}) + r(O^{2-}) = 0.912 + 1.40 = 2.312$ Å. It is also worth noting that the octahedra [DyO_6] and the tetrahedra [Na(3)O_4] sharer edges O(2)–O(4) and form corrugated mixed chains of Dy and Na(3) polyhedra running along [001] direction as shown in Fig. 1.

3.4. The sodium coordination spheres

The coordination spheres of the sodium cations (Fig. 3) were delimited by oxygen ligands corresponding to Na–O lengths shorter than the shortest distance between a given sodium ion and its nearest neighbor cation. In the case of the $Na_3DySi_6O_{15}$ structure, the distances to be considered for the three sodium atoms Na(1), Na(2) and Na(3), are the lengths Na(1)–Si(2) = 3.261 Å, Na(2)–Si(2) = 3.281 Å and Na(3)–Dy = 3.076 Å, respectively. In accordance with such relative distances, as expected, the coordination numbers of Na(1), Na(2) and Na(3) were found to be equal to 9, 6 and 4, respectively. The same respective coordination spheres were identified for these atoms using the valence calculations according to Brown and Altermatt [12], as shown in Table 5.

While the valence bond values of the other cations (Table 5) are consistent with results formerly reported for analogous silicates [5,13–17], the value calculated for Na(1) appears to be particularly of low (0.53). This apparent discrepancy can probably be ascribed to the high values of the thermal parameters of Na(1) as can be seen from Table 2. It is also worth noting that our results and those of the literature are totally consistent. As a matter of fact, using the structural data of Bourguiba and Dogguy [5] for β-$Na_3YSi_6O_{15}$, and by Haile et al. [6] for $Na_2LiYSi_6O_{15}$, the calculations of the valence bond strength for the same atom Na(1) gave 0.52 and 0.56, respectively. Indeed, these values could be considered identical to ours. The coordination sphere of Na(1) could be approximated to a distorted tricaped trigonal prismatic cavity, as illustrated in Fig. 3. The axis of the triangular prism is directed parallel to [100].

The cavities where Na(2) ions are located could be connected with a highly distorted octahedra with O–Na(2)–O angles varying within the range 58–172°.

Table 6
Crystallographic data of zektzerite related compounds of the type $M(1)M(2)M(3)M(4)Si_6O_{15}$

Compound/mineral $M(1)M(2)M(3)M(4)$	Tuhualite $(Na,K)Fe_2$ H_2O	Synthetic NaNaMgMg	Zektzerite NaLiZr	Emeleusite NaNaLiFe	Synthetic NaNaLiY	Synthetic β-Na_3Y	Synthetic Na_3Dy
Synthesis route	nat. cryst.	glass cryst.	nat. cryst.	nat. cryst	glass cryst.	flux	flux
Reference	[14]	[15]	[13]	[16]	[17]	[5]	(this work) [1,2]
a (Å)	14.31	14.165	14.330	14.004	14.505	14.744(8)	14.590
b (Å)	17.28	17.59	17.354	17.337	17.596	17.844(8)	17.813
c (Å)	10.11	10.205	10.164	10.072	10.375	10.610(3)	10.519
V ($Å^3$)	2499.96	2542.7	2527.61	2445.3	2648.01	2791.4	2734.0
Space group	*Cmca*	*Cmca*	*Cmca*	*Cmca*	*Cmca*	*Cmca*	*Cmca*
Z	8	8	8	8	8	8	8
Molar mass (g)	552.18	503.09	529.65	517.26	550.33	566.37	640.01
D (g/cm^3)	2.89	2.629	2.81	2.81	2.84	2.71	3.11
Silicate group							
⟨Si–O⟩ (Å)	1.618	1.611	1.613	1.612	1.612	1.624	1.615
⟨Si–O–Si⟩ (deg)	151.53	153.24	151.46	153.06	149.75	150.2	150.08
⟨O–Si–O⟩ (deg)	109.43	109.45	109.43	109.46	109.45	109.45	109.45
⟨O–O⟩ (Å)	2.63(5)	2.62(3)	2.63(3)	2.62(4)	2.62(6)	2.64(4)	2.632
Other cationic cavities							
$M(1)$	Vacant	Na(1)	Vacant	Na(1)	Na(1)	Na(1)	Na(1)
Coordination number		9		9	9	9	9
Electronegativity [15]		0.93		0.93	0.93	0.93	0.93
Ionic radius (Å) [14]		1.38		1.38	1.38	1.38	1.38
⟨$M(1)$–O⟩ (Å)		2.80		2.73	2.876	2.89	2.88
⟨O–$M(1)$–O⟩ (deg)		i.p.		i.p.	i.p.	i.p.	i.p.
$M(2)$	Na	Na(2)	Na	Na(2)	Na(2)	Na(3)	Na(2)
Coordination number	6	10	10	10	10	10	6
Electronegativity [15]	0.93	0.93	0.93	0.93	0.93	0.93	0.93
Ionic radius (Å) [14]	1.16	est. 1.41	est. 1.41	est. 1.41	est. 1.41	est. 1.41	1.16
⟨$M(2)$–O⟩ (Å)	2.576	2.804	2.787	2.745	2.846	2.89	2.56
⟨O–$M(2)$–O⟩ (deg)	92.83	i.p.	i.p	i.p	i.p.	i.p.	92.37
$M(3)$	Fe^{II}	Mg(1)	Li	Li	Li	Na(2)	Na(3)
Coordination number	4	4	4	4	4	8	4
Electronegativity [15]	1.83	1.31	0.98	0.98	0.98	0.93	0.93
Ionic radius (Å) [14]	0.63	0.57	0.59	0.59	0.59	1.18	0.99
⟨$M(3)$–O⟩ (Å)	2.00	1.965	1.959	1.989	2.01	2.73	2.25
⟨O–$M(3)$–O⟩ (deg)	110.83	85.275	110.55	110.86	108.65	i.p.	110.04
$M(4)$	Fe^{III}	Mg(2)	Zr	Fe^{III}	Y	Y	Dy
Coordination number	6	6	6	6	6	6	6
Electronegativity [15]	1.83	1.31	1.33	1.83	1.22	1.22	1.22
Ionic radius (Å) [14]	0.64	0.72	0.72	0.64	0.90	0.90	0.912
⟨$M(4)$–O⟩ (Å)	2.02	2.096	2.074	1.984	2.23	2.244	2.243
⟨O–$M(4)$–O⟩ (deg)	89.88	90.06	90.03	90.03	90.01	90.05	90.15
Nature of polyhedra in corrugated chains	$[Fe^{III}O_6]$–$[Fe^{II}O_4]$	$[Mg(2)O_6]$–$[Mg(1)O_4]$	$[ZrO_6]$–$[LiO_4]$	$[Fe^{III}O_6]$–$[LiO_4]$	$[YO_6]$–$[LiO_4]$	$[YO_6]$–$[Na(2)O_8]$	$[DyO_6]$–$[Na(3)O_4]$

nat. cryst.: Natural crystals (minerals); glass cryst.: Crystallization from glasses; flux: Crystals grown by flux method; Electronegativity: Electronegativity according to Pauling scale [19]; i.p.: Irregular polyhedron; est.: Estimated value from Shannon's Table [18].

The form of these interstices results from the corrugation of $[SiO_4]$ tetrahedral chains, also arranged in a manner that gives rise to infinite tunnels running parallel to the [100] direction (Fig. 1).

The environment of the Na(3) cations appears to be one of the main original features of the $Na_3DySi_6O_{15}$ structure, since it corresponds to a sodium cation located in a tetrahedral site. Indeed, although such a low coordination number of Na(I) is not unknown in oxides, it is however not very frequent compared to the octahedral environment or bigger interstices. The angles O–Na(3)–O vary within the range 94–129.3° with a

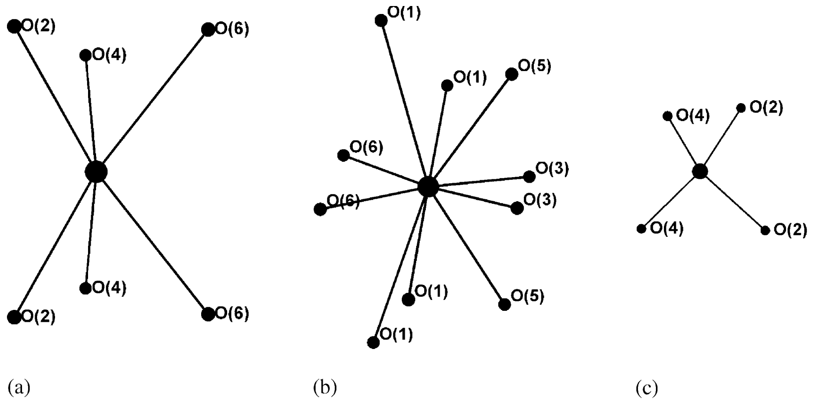

Fig. 3. Environment of sodium cations Na(1): (a); Na(2): (b); Na(3): (c).

mean value ⟨O–Na(3)–O⟩ equal to 110.1° (Table 4) which corresponds to that of an almost regular tetrahedron (109.5°).

The analysis of the chemical bond shows that the Na–O lengths lie within the following ranges: 2.655(6)–3.163(3) Å for Na(1)–O; 2.392(4)–2.763(3) Å for Na(2)–O and 2.243(3)–2.262(3) Å for Na(3)–O. The corresponding mean values $\langle \mathrm{Na(1)–O} \rangle = 2.882$ Å, $\langle \mathrm{Na(2)–O} \rangle = 2.559$ Å and $\langle \mathrm{Na(3)–O} \rangle = 2.252$ Å fit rather well the appropriate sum of ionic radii $R = [r(\mathrm{Na}^+) + r(\mathrm{O}^{2-})]$, where the value of $r(\mathrm{Na}^+)$ is adapted to the coordination number of Na^+, according to the Shannon scale [18]. As a matter of fact, the direct correspondence between the values of $R_{(\mathrm{Na(2)})} = 1.16 + 1.40 = 2.56$ Å and that of $\langle \mathrm{Na(2)–O} \rangle = 2.559$ Å tend to confirm the ionic character of the bond Na(2)–O. In the case of Na(1) cations, a slight discrepancy was observed between the values of $\langle \mathrm{Na(1)–O} \rangle = 2.883$ Å and the corresponding sum $R_{(\mathrm{Na(1)})} = 1.38 + 1.40 = 2.78$ Å. This difference could be attributed to the high values of the anisotropic thermal parameters of Na(1) (Table 2) which do not permit a good definition of the inter-atomic distances. It is also worth noticing that if we consider Na(1) in a dodecahedral coordination with an ionic radius [14] $r^{\mathrm{XII}}(\mathrm{Na}^+) = 1.53$ Å, the calculated value of $R^{\mathrm{XII}}_{(\mathrm{Na}+)} = 1.53 + 1.40 = 2.93$ Å will fit better with the measured mean distance $\langle \mathrm{Na(1)–O} \rangle = 2.882$ Å. Considering this adjustment and the low value of the valence bond (0.53) for a nine-fold coordination site given in Table 5, it appears that the true coordination number of Na(1), although difficult to establish, is probably between 9 and 12. Since the large thermal vibration amplitudes are often indicative of a high ionic mobility, the sodium cations Na(1) are probably the most inclined to enhance the ionic conductivity of $\mathrm{Na_3DySi_6O_{15}}$. However, the position of these cations is sandwiched between two filled sites occupied by Dy^{3+} ions. Therefore an enhancement of the ionic conductivity of the title compound by creating vacancies in the coordination cavities of the dysprosium cations might be expected. Due to the apparent role played by the dysprosium coordination sphere in the stability of the structural edifice (linkage between silicate chains and tunnels as shown in Fig. 1), it does not seem possible to create many point defects on Dy sites. An improvement of the ionic conductivity of $\mathrm{Na_3DySi_6O_{15}}$ comes more likely from the reduction of Na(2) content. The resulting vacancies could then enhance their own mobility within the tunnels they occupy along the [100] direction (Fig. 1).

4. Crystal chemical analysis of zektzerite related compounds

4.1. Representative crystal chemical formula and typical symmetry of zektzerite structurte

The materials crystallizing with the zektzerite ($\mathrm{NaLiZrSi_6O_{15}}$) [13] structural type can be described by the general chemical formula (Eq. (1)), as suggested by Ghose and Wan [13]:

$$M(1)M(2)M(3)M(4)\mathrm{Si_6O_{15}}, \qquad (1)$$

where $M(1)$, $M(2)$, $M(3)$ and $M(4)$ represent the four types of interstices available in the lattice.

Indeed, some of these sites can be either void or occupied by various cations. As shown in Table 6, the cations that have already been inserted in the zektzerite structure can be monovalent (Li^+,Na^+), divalent (Mg^{2+},Fe^{2+}), trivalent (Fe^{3+},Y^{3+}, Dy^{3+}) and also tetravalent (Ti^{4+}, Zr^{4+}, Sn^{4+}) [1]. All compounds so far isolated tend to crystallize within the orthorhombic system ($Z = 8$) and the centro-symmetric space group *Cmca* (Table 6). In addition, the steric effect does not seem to be the only parameter that determines site occupation in the zektzerite lattice. For example, even cations as large as Na^+ have been found in tetrahedral cavities.

4.2. Typical cationic distribution

Furthermore, taking into account that Si^{4+} ions, as expected, are always located in tetrahedral cavities, a survey of the literature results shows that the other cations are distributed in the lattice as follows:

(i) The octahedral $M(4)$ sites are normally occupied by the most highly charged cations (other than Si^{4+}) in the lattice. Typical examples are known for Mg^{2+}[11], Fe^{+3} [10,12], Y^{3+} [4,13] and Zr^{4+} [9].

(ii) The coordination sphere of $M(3)$ is normally tetrahedral, except in the case of β-$Na_3YSi_6O_{15}$ where it seems to be cubic [4]. The analysis of the chemical bond around the occupying atom Na(2), shows that this site contains four short Na(2)–O lengths, is corresponding to a tetrahedral environment. This tiny site is regularly occupied by small cations like Li^+ [9,12,13], Mg^{2+} [11] and Fe^{2+} [10], which are known to enter both octahedral and tetrahedral cavities. Therefore, it is striking that even Na^+ could enter such narrow cavities and correctly fit the corresponding chemical bonds. This rather rare tetrahedral coordination for Na^+ cations constitutes one of the most original aspects of the $Na_3DySi_6O_{15}$ structure. It is also worth noting that this atypical tetrahedral coordination of Na^+ has been reported for other silicates like $Na_3NdSi_6O_{15} \cdot H_2O$, as reported by Haile et al. [16].

(iii) The coordination number of $M(2)$ seems to be rather flexible since it can vary between 6 and 10. The analysis of the crystal structure given in Fig. 1, shows that this is not very surprising. As a matter of fact, the $M(2)$ interstices are located within the main tunnels of the zektzerite lattice. The coordination number within these large cavities is expected to be more difficult to define since it could be readily modified even under minor constraints which could result from residual mechanical tensions, thermal history (annealing time, etc.), slight change of the ionic radius, etc. Indeed, the number of close neighbors is rather high and even a small twist, tilt or elongation of the adjoining $[SiO_4]$ tetrahedral, for example, could result in a significant change in the coordination number of the cations located in $M(2)$. The effect of $[M(4)O_6]$ octahedron size and chemical bond could also be of importance since this polyhedron is the one that closes the ring of the S-like corrugated silicate chains (Fig. 1). Table 6 lists compounds where $M(2)$ sites are hosting rather large cations like Na^+, either in a small or large coordination environment (6 or 10).

(iv) The $M(1)$ cavity (Table 6) appears to be an appropriate one for a nine-fold coordination site, although the present investigations (Section 3.1) tend to suggest a coordination number higher than 9. These interstices, which sandwich $[M(4)O_6]$ octahedra in the lattice, could also be totally empty as in the natural minerals such as tuhualite $(Na,K)Fe_2Si_6O_{15}$–0.5 H_2O [10], and zektzerite $NaLiZrSi_6O_{15}$ [9]. The existence of such empty cavities probably reveals their lesser importance in the mechanical stabilization of the zektzerite structure. Due to their size, as found in β-$Na_3YSi_6O_{15}$ [4], $Na_2Mg_2Si_6O_{15}$ [11], $Na_2LiFeSi_6O_{15}$ [12] and $Na_2LiYSi_6O_{15}$ [13], such sites are apparently more appropriate for large cations like Na^+ (Table 6).

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