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Modulated Structure of Orthorhombic Lazurite

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Abstract—The structure of the orthorhombic modification of lazurite from the deposit of the southwestern Pamirs is determined (sp. gr. *Pnaa*, $R_{hkl} = 0.068$, 1460 reflections). The character of the commensurate modulations of the displacements and the replacements of all the atoms in the structure is studied. Three types of sulfur radicals that replaced chlorine atoms in the sodalite-type structure are established.

Lazurite is a mineral sodalite group containing sulfate and sulfide sulfur atoms and known in several modifications (cubic, orthorhombic, monoclinic, and triclinic) [1, 2]. All the modifications are characterized by commensurate or incommensurate modulations of their structures. However, because of the pronounced pseudosymmetry and complexity of the diffraction patterns, X-ray diffraction studies of these minerals were carried out using only the basic reflections within the framework of the cubic sublattice, ignoring the satellite reflections [3]. Earlier, we performed a complete X-ray structure determination of the commensurately modulated structure of triclinic lazurite from the Malo-Bystrinskii deposit (the Baikal region) [4] and established the character of the modulation of the displacements and replacements of all atoms of the structure. This work was undertaken with the aim of studying the commensurately modulated structure of the orthorhombic modification of this mineral.

The results of the microprobe analysis of the samples from the Lyazhvardarinskii lazurite deposit (the southwestern Pamirs) indicate the formula $(Na_{6.47}Ca_{1.29}K_{0.08})_{\Sigma 7.84}(Si_{6.16}Al_{5.84}O_{24})(SO_4)_{1.83}Cl_{0.10}$. The presence of superstructure reflections along one of the six *hk*0 directions on the X-ray diffraction pattern from a cubic single crystal reduced the crystal symmetry to orthorhombic. The parameters of the orthorhombic unit cell related to the parameters of the cubic unit cell by the relations $a_{\text{orth}} = a_{\text{cub}}$, $b_{\text{orth}} = a_{\text{cub}}\sqrt{2}$, and $c_{\text{orth}} = a_{\text{cub}}3\sqrt{2}$ were refined on an automated Enraf-Nonius diffractometer: $a = 9.053(3)$ Å, $b = 12.837(3)$ Å, $c = 38.445(10)$ Å, $V = 4468$ Å^3, $\rho_{\text{calc}} = 2.44$ g/cm^3, sp. gr. *Pnaa*. The X-ray diffraction data were collected on the same diffractometer within a reciprocal-space octant (MoK_α radiation, graphite monochromator, $\sin\theta/\lambda \le 0.70$). A total of 1460 reflections with $|F| > 3\sigma(F)$ were measured. All the calculations were carried out using the AREN crystallographic package of programs [5].

The basic model of the structure was obtained by the direct methods and was refined by the automated procedure of successive approximations [6]. The refinement of the model alternating with calculation of difference Fourier syntheses revealed partially occupied positions for cations, anions, and anionic groups statistically distributed over the cavities. Isomorphous replacements observed in a number of positions were taken into account, as well as the correction for absorption by the irregularly shaped crystal [7]. The subsequent refinement with the anisotropic thermal parameters of the atoms reduced the *R* factor to 0.068. The atomic coordinates, thermal parameters, and occupancies of the positions are given in Tables 1 and 2. The main interatomic distances are listed in Table 3. The structure of the orthorhombic modification of lazurite was refined as a superstructure with respect to the cubic structure. Unlike the results obtained earlier [3], the allowance for satellite reflections provided reasonable thermal parameters of the atoms in the absence of statistical disorder of the framework oxygen atoms.

The framework of orthorhombic lazurite (Fig. 1) is built by Si and Al tetrahedra with the average Si–O and Al–O distances equal to Si–O = 1.58–1.61 Å and Al–O = 1.71–1.74 Å. This indicates that these tetrahedra are completely ordered. According to the chemical analysis data, the Al : Si ratio equals 35 : 37. Hence, we believe that the underestimated average distance (1.71 Å) in one of the Al tetrahedra is the consequence of the replacement of the one-eighth Al(4) atom with silicon.

Similar to triclinic lazurite with the unit cell parameter $c = 25.708$ Å, the unit cell of orthorhombic lazurite can be divided into two parts along the *z*-axis (with *z* from 0 to 0.5 and from 0.5 to 1) that differ by the character of the mutual rotation of the tetrahedra (the rotation axes are parallel to the [001] and [010] directions).

Table 1. Atomic coordinates and equivalent thermal parameters of the framework atoms in orthorhombic lazurite

Atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq}, Å^2
Si(1)	0.4779(3)	0.3718(2)	0.2092(1)	0.7(I)
Si(2)	0.2033(5)	0.75	0.25	0.6(1)
Si(3)	0.2402(4)	0.2465(3)	0.0849(1)	1.2(I)
Si(4)	0.4642(4)	0.6216(3)	0.1249(1)	1.0(1)
Si(5)	0.4730(3)	0.8788(33)	0.0401(1)	0.9(I)
Al(1)	0.2297(5)	0.25	0.25	0.6(1)
Al(2)	0.4960(3)	0.1264(3)	0.0431(1)	0.9(1)
Al(3)	−0.0124(3)	0.1280(3)	0.1263(1)	0.7(1)
Al(4)	0.4556(4)	0.6222(3)	0.2087(1)	1.0(I)
Al(5)	0.2210(4)	0.7532(4)	0.0825(1)	0.9(I)
O(1)	0.4232(11)	0.4865(6)	0.2165(2)	1.4(4)
O(2)	0.0287(9)	0.1429(7)	0.1709(2)	1.2(2)
O(3)	0.0351(16)	0.3422(10)	0.0002(2)	2.7(4)
O(4)	0.1064(14)	0.8294(11)	0.2303(3)	2.8(4)
O(5)	0.2994(11)	0.6853(10)	0.2203(2)	2.2(3)
O(6)	0.1151(10)	0.1479(8)	0.2339(2)	1.5(3)
O(7)	0.3381(10)	0.2956(7)	0.2170(2)	1.2(1)
O(8)	−0.0187(10)	0.8525(7)	0.1671(3)	1.8(3)
O(9)	0.4562(10)	0.9920(8)	0.0489(3)	1.9(3)
O(10)	0.1182(12)	0.6594(12)	0.0584(4)	4.0(3)
O(11)	0.3389(12)	0.1927(8)	0.0557(3)	2.1(4)
O(12)	0.4459(11)	0.5018(8)	0.1177(2)	1.6(3)
O(13)	0.3396(11)	0.2965(8)	0.1168(3)	1.7(3)
O(14)	0.3242(13)	0.8238(9)	0.0553(2)	2.3(3)
O(15)	0.1443(9)	0.1592(7)	0.1013(2)	1.0(3)
O(16)	0.1081(10)	0.8422(9)	0.1064(2)	1.7(3)
O(17)	0.1398(13)	0.3402(9)	0.0683(3)	2.5(3)
O(18)	0.3200(12)	0.6826(9)	0.1123(3)	2.2(3)

Table 2. Coordinates, position occupancies (*q*), and equivalent thermal parameters of the extraframework atoms in orthorhombic lazurite

Atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq}, Å^2	*q*
Ca	0.2124(6)	0.7539(5)	0.1668(1)	4.2(1)	0.80(1)
M(1)	0.248(2)	0.995(2)	0.0893(5)	4.8(3)	0.40(1)
M(2)	0.274(3)	0.7132(2)	0.0031(7)	4.2(4)	0.20(1)
Na(1)	0.211(2)	0.491(2)	0.087(5)	2.8(4)	0.40(2)
Na(2)	0.172(1)	0.503(1)	0.1020(3)	3.7(2)	0.60(2)
Na(3)	0.231(3)	−0.008(2)	0.2527(7)	5.6(5)	0.30(2)
Na(4)	0.1543(8)	0.4962(8)	0.2278(2)	2.2(2)	0.70(1)
Na(5)	0.181(2)	0.005(1)	0.0696(4)	4.7(3)	0.60(2)
Na(6)	0.202(1)	0.790(1)	−0.0021(2)	4.4(2)	0.80(2)
Na(7)	0.2992(8)	0.1773(6)	0.1691(2)	2.9(1)	1.00
Na(8)	0.276(6)	0.827(2)	0.1741(2)	6.5(9)	0.17(1)
S(1)	0.4624(7)	0.9685(4)	0.1629(1)	3.2(1)	0.81(1)
O(19)	0.447(4)	0.031(3)	0.1929(6)	8.2(7)	0.80(3)
O(20)	0.458(4)	0.033(3)	0.1346(8)	6.8(7)	0.80(3)
O(21)	0.114(2)	0.571(2)	0.1597(4)	3.1(6)	0.84(3)
O(22)	0.347(4)	0.890(2)	0.160(1)	5.8(7)	0.79(1)
S(2)	0.024(2)	−0.005(2)	−0.0085(3)	3.3(2)	0.20(1)
O(23)	0.071(5)	0.906(5)	0.009(1)	3.5(1.3)*	0.23(3)
O(24)	0.104(4)	0.103(3)	−0.0014(9)	2.1(1.1)*	0.26(3)
O(25)	0.359(5)	0.511(5)	0.040(1)	6.5(1.3)*	0.24(3)
O(26)	0.135(5)	0.027(7)	0.011(2)	4.7(1.4)*	0.20(3)
S(3)	0.023(4)	0.437(3)	0.1567(9)	6.9(8)*	0.10(1)
S(4)	0.347(6)	0.010(3)	0.143(2)	8.8(6)*	0.10(1)
S(5)	0.083(5)	0.974(4)	0.026(1)	4.1(1.3)*	0.10(3)
S(6)	0.034(9)	0.894(4)	−0.014(1)	4.5(1.5)*	0.13(3)
Cl	0.085(8)	0.052(4)	0.026(1)	4.9(1.7)*	0.09(1)

Notes: *M*(1) = $\mathrm{Ca_{0.25}Na_{0.75}}$; *M*(2) = $\mathrm{Ca_{0.5}Na_{0.5}}$; and Na(8) = $\mathrm{Na_{0.5}K_{0.5}}$.
* B_{iso}.

However, diorthogroups having the same orientations in each part of the unit cell also differ by the rotation angle, which leads to the threefold increase (not to doubling, as in case of the triclinic modification) of the unit cell parameter *c*. The above-described rotations are caused by the regular displacements of Al and Si atoms from their positions in the sodalite sublattice along the *x*- and *y*-axes and the generation of the modulation wave along the *z* direction with a period equal to the unit-cell parameter *c*. Similar to triclinic lazurite, the displacements of the Al and Si atoms in orthorhombic lazurite can be described by both the sum of the sinusoidal and rectangular waves with the coinciding phases or by the sinusoidal wave alone. In triclinic lazurite, virtually identical results were obtained, irrespective of the way of description of the displacement wave—by the sum of the sinusoidal and rectangular functions with the amplitudes of 0.25(3) and 0.05(3) Å or by the sinusoidal function with the amplitude of 0.32(2) Å. In orthorhombic lazurite, the displacements of these atoms are better described by the sum of the sinusoidal and rectangular waves (with the amplitudes equal to

0.24(1) and 0.07(1) Å, respectively) (Fig. 2) than by the sinusoidal function with the amplitude of 0.32(1) Å. In spite of the difference in the modulation wavelengths (25.7 and 38.4 Å), the amplitudes of the Al and Si displacements in orthorhombic lazurite are close to those in triclinic lazurite.

The modulation of the tetrahedral framework leads to regular changes in the shape of cuboctahedra (the cavities formed by the framework oxygen atoms) and, therefore, also to modulation of the extraframework atoms. The Ca atoms completely fill one subposition in these cavities and also occupy statistically (together with Na) two other positions, *M*(1) and *M*(2). The Na(8) position is partly statistically filled with potassium and sodium atoms (the analogous position in haüyne structure from Ariccia (Italy) is occupied by potassium [8]). All the sodium positions, except for Na(7), are split into two subpositions spaced apart by 0.7–1.2 Å and are characterized by the distances Na(1)–Na(2) = 0.70(4) Å, Na(3)–Na(4) = 1.02(2) Å, Na(5)–*M*(1) = 0.97(2) Å, Na(6)–*M*(2) = 1.20(3) Å, and Na(8)–Ca = 1.12(4) Å. Position splitting extraframework atoms in the lazurite structures are explained by positional disorder in the cavities having much larger volumes than those in sodalite [9].

Oxygen vertices of the S-tetrahedra and sulfur atoms of sulfide are involved in the coordination of all large cations. These anionic groups replacing Cl atoms in the sodalite structure are located in the vicinity of the centers of both types of crystallographically independent cavities. Localization of these groups is rather difficult because of their substantial statistical disorder of their arrangement. The predominant $[SO_4]^{-2}$ anion is localized rather reliably. Its orientation in the cavities is similar to that observed in triclinic lazurite and differs from the orientations of analogous groups in nosean and haüyne. Two additional electron-density peaks are observed in the cavity occupied by the S(1) tetrahedron. We attributed these peaks to the sulfur atoms S(3) and S(4) of sulfide. We believe that these atoms belong to

Table 3. Characteristics of the cation coordination (statistically occupied anion positions are ignored) in orthorhombic lazurite

Atom	Coordination number	Distances to the anions, Å		
		minimum	maximum	average
Si(1)	4	1.55(1)	1.62(1)	1.58
Si(2)	4	1.54(1)	1.65(1)	1.60
Si(3)	4	1.55(1)	1.65(1)	1.61
Si(4)	4	1.55(1)	1.66(1)	1.59
Si(5)	4	1.50(1)	1.62(1)	1.58
Al(1)	4	1.70(1)	1.78(1)	1.74
Al(2)	4	1.67(1)	1.77(1)	1.72
Al(3)	4	1.69(1)	1.76(1)	1.74
Al(4)	4	1.64(1)	1.79(3)	1.71
Al(5)	4	1.66(1)	1.78(1)	1.73
S(1)	4	1.36(3)	1.46(2)	1.42
S(2)	4	1.33(6)	1.62(5)	1.48
Ca	6	2.37(1)	2.79(1)	2.60
M(1)	6	2.34(1)	2.96(2)	2.63
M(2)	5	2.40(3)	2.88(3)	2.58
Na(1)	5	2.15(2)	2.82(1)	2.54
Na(2)	7	2.47(1)	3.10(1)	2.76
Na(3)	4	2.12(2)	2.57(2)	2.39
Na(4)	6	2.39(1)	3.09(1)	2.75
Na(5)	6	2.34(1)	2.85(1)	2.66
Na(6)	6	2.43(1)	2.99(1)	2.68
Na(7)	6	2.48(1)	3.10(1)	2.35
Na(8)	4	2.56(4)	2.96(4)	2.72

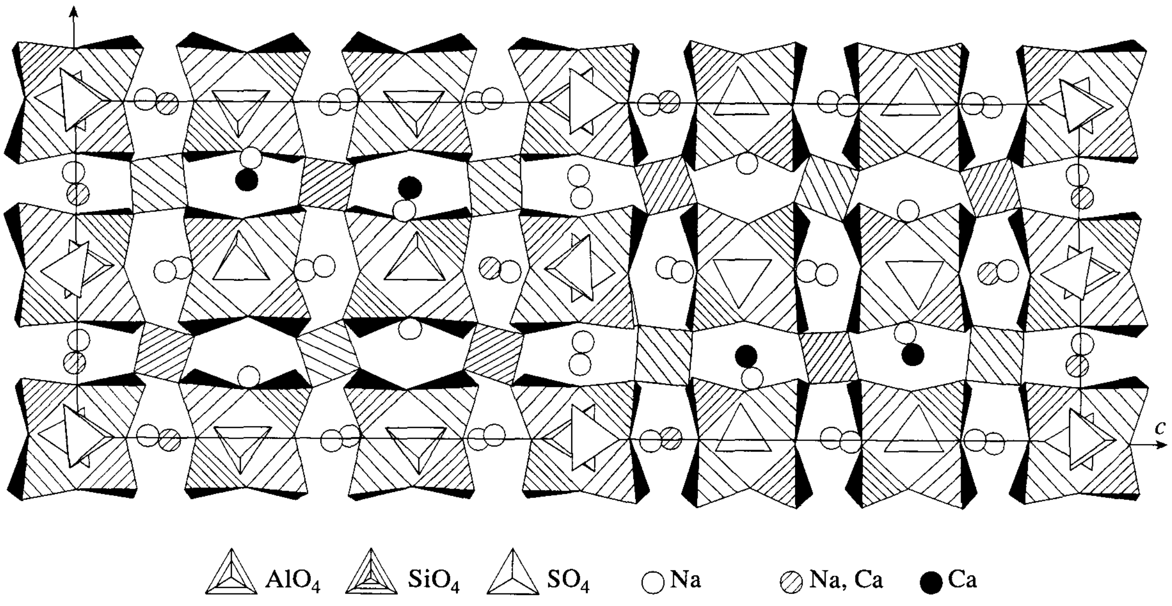

Fig. 1. Structure of orthorhombic lazurite projected onto the (100) plane with the *x* ranging from 0.1 to 0.6.

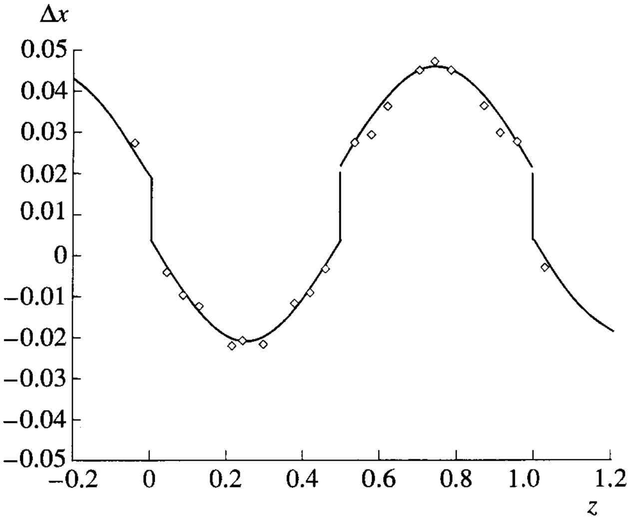

Fig. 2. Graphical representation of the displacements of the Al and Si atoms from the average or "sodalite" positions along the *z* axis. The line corresponds to the sum of the sinusoidal and rectangular functions refined by the least-squares method.

the $[S_2^{-2}]$ group with the S(3)–S(4) distance 1.81(6) Å (which is close to the value calculated from the Raman spectroscopy data [10]). The additional peaks in the cavity occupied by the S(2) tetrahedron were attributed to the Cl atom and the sulfur atoms S(5) and S(6) of sulfide. In this case, the statistical pattern is complicated by the fact that all the atoms are located around the center of symmetry. It is difficult to localize sulfur radicals by the methods of X-ray diffraction analysis because the $[S_3^{-2}]$ radical is rotated at room temperature (as was demonstrated for ultramarines [11]). However, these peaks can be rather reliably interpreted as the angular $[S_3^{-2}]$ groups with the S(6)–S(5)–S(6)' angle equal to 95(1)° and with the interatomic distances varying from 1.9(1) to 2.0(1) Å. It was also established by the electron paramagnetic resonance [11] that the blue and green colors of synthetic sodalites are associated with the presence of $[S_3^{-2}]$ and $[S_2^{-2}]$ ions partially replacing chlorine atoms. Our studies of orthorhombic lazurite from the Pamirs demonstrate that macrospecimens have blue, green, or blue-green color, which confirms our assumption that the above-described sulfur polymers enter the crystal structure of lazurite.

The crystallochemical formula of orthorhombic lazurite, which was determined by the methods of X-ray diffraction analysis is quite consistent with that established as a result of the chemical analysis and at $Z = 6$ is written as $(Na_{6.51}Ca_{1.33}K_{0.06})[Si_{6.17}Al_{5.83}O_{24}][SO_4]_{1.3}S_{0.29}(S_2)_{0.11}Cl_{0.1}$.

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