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STRUCTURES OF INORGANIC COMPOUNDS

Average Structure of Cubic Lazurite with a Three-Dimensional Incommensurate Modulation

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Abstract—Three-dimensional incommensurately modulated cubic lazurite from the Malo-Bystrinskoe deposit (the Baikal region) was studied by the methods of X-ray diffraction analysis. The *a* parameter of the cubic unit cell is 9.077(1) Å. The calculations performed within the sp. gr. *P*23 ($R = 0.056$, 309 independent reflections) provided detailed information on the average structure of the mineral (the satellite reflections were ignored). *© 2002 MAIK "Nauka/Interperiodica".*

INTRODUCTION

Like hauyne and noseane, lazurite of the complex composition $(Na,Ca,K)_{7-8}Si_6Al_6O_{24}(SO_4, S, Cl)_2 \cdot nH_2O$ belongs to the sodalite group. The minerals of this group are of particular interest because their X-ray diffraction patterns have, in addition to the Bragg reflections from the cubic sublattice, satellite reflections indicative of the modulation of the crystal structure. Lazurites are characterized by a wide variety of incommensurate and commensurate modulations of the structure. As a result, the symmetry of the crystal structures of various lazurite specimens change from cubic to triclinic [1–3]. In all cases, it is difficult to understand and adequately describe the character of superstructural distortions and, especially, the X-ray diffraction pattern of cubic lazurite. The intensities of the satellite reflections and the presence of high-order (up to the fourth order) satellites show that cubic lazurite is characterized by a three-dimensional incommensurate modulation with a pronounced amplitude and nontrivial wave functions. To solve the difficult problem of finding and refining the modulation parameters, it is necessary to obtain reliable information on the basis structure of cubic lazurite considered in this article.

EXPERIMENTAL

We studied cubic lazurite from the Malo-Bystrinskoe deposit (the Baikal region). The X-ray diffraction data were collected from a pale-blue poorly-faceted single crystal. The fragments of the X-ray diffraction pattern measured within the total sphere of the reciprocal space were combined into one set of the integrated intensities of 5778 main reflections of which 3688 reflections had $I > 3\sigma(I)$.

The systematic absences indicated three possible space groups of the diffraction class $m\bar{3}m$ or two space groups of the lower-symmetry diffraction class $m\bar{3}$. However, the centrosymmetric space groups $Pm3m$ and $Pm\bar{3}$ are inconsistent with the structural model in which sulfur-tetrahedra are located at inversion centers, whereas the acentric space group $P432$ rigidly fixes the positions of the O atoms along the z-axis. Using the main reflections, we can describe the symmetry of cubic lazurite by the sp. gr. $P\bar{4}3m$. However, the presence of satellite reflections is indicative of a lower symmetry and requires the transition from the group $P\bar{4}3m$ to the subgroup $P23$, because some *hkl* and *khl* reflections have considerably different intensities and cannot belong to one group of equivalent reflections within the diffraction class $m\bar{3}m$ (the merging R factor exceeded 7%). Averaging the intensities of the equivalent reflections within the diffraction class $m\bar{3}$ ($R_{\text{int}} = 0.031$), we arrive at 309 independent reflections. It should be noted that, although the satellite reflections were ignored, the main reflections comprised the most intense but small fraction of the overall set of rather strong reflections (the total numbers of reflections, together with the satellite reflections, were 220–908 and 40–214 before and after averaging, respectively).

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All the computations were performed by the AREN and JANA crystallographic program packages [4, 5]. The atomic coordinates of cubic hauyne [6] (transformed from the sp. gr. $P\bar{4}3n$ to the sp. gr. $P23$) were used as the starting model for the refinement. The relatively high initial R factor indicated that the starting model was rather rough. The additional S(2), Na(2), and Ca positions and the mixed M(Na,Ca) position were localized from Fourier syntheses. The thermal parameter of one of the O atoms determined at this stage was twice as large as that of another oxygen atom, O(1), which provided evidence that the former position can be split. Actually, the difference electron-density synthesis contained an additional peak at a distance of 0.776(6) Å from the O atom characterized by a large thermal parameter and also four positions occupied by sulfide sulfur atoms. The refinement of the occupancies of the positions statistically occupied by O(2') and O(2'') atoms and all the positions occupied by intraframework cations with due regard for the mixed occupancy of the M position reduced the R factor to 9% and 5.6% in the isotropic and anisotropic approximations, respectively. The crystallographic characteristics and the details of the X-ray diffraction study are indicated in Table 1. The atomic coordinates, thermal parameters, multiplicities, and occupancies of the positions are listed in Table 2. The interatomic distances are given in Tables 3 and 4.

Table 1. Crystallographic data and details of the X-ray diffraction experiment

Characteristic	Data and conditions
Unit-cell parameter, Å	$a = 9.077(1)$
Unit-cell volume, Å^3	$V = 747.9(3)$
Density, ρ_{calcd}, g/cm^3	2.306
Sp. gr.	$P23$
Radiation; λ (Å)	MoK_α; 0.71073
Crystal dimensions, mm	0.30 × 0.36 × 0.44
Diffractometer	Oxford Xcalibur four-circle diffractometer, κ geometry, CCD detector
$\sin\theta/\lambda$, Å^{-1}	0.11–0.72
Ranges of the indices of measured reflections	$-10 < h < 12$, $-12 < k < 10$, $-12 < l < 12$
R_{int} for equivalent reflections	0.031
$R_{e.s.d.} = \Sigma(\sigma_I)/\Sigma(I)$ upon averaging	0.0021
Total number of reflections	5778 reflections including 3688 reflections with $I > 3\sigma(I)$
Number of independent reflections	309 $I > 3\sigma(I)$
Software for diffractometer	CrysAlis RED (Version 1.167);
Programs for structural computations	AREN, JANA
Number of parameters refined	101
Extinction parameter E	0.0001112
R; R_w-factors upon anisotropic refinement	0.056; 0.046

RESULTS AND DISCUSSION

The basis structure (Fig. 1) calculated from the main reflections, with no account for the satellite reflections, is the superposition of all unit cells with their particular atomic arrangements. As a consequence, the thermal parameters of the atoms are overestimated, and the statistically occupied positions in the average structure are split. As can be seen from Tables 2 and 3, the Si and Al positions in such a structure cannot be distinguished; the position of one of the two O atoms involved in the formation of the tetrahedral framework is split into two subpositions, whereas the positions of the intraframework sulfide sulfur forms the pairs with rather short spacings between them. The sulfate sulfur atoms occupy the positions 1a and 1b with the coordinates (0 0 0) and (1/2 1/2 1/2), respectively, whereas in the structures of hauyne [6] and cubic lazurite [7] described within the sp. gr. $P\bar{4}3n$ they occupied the single (0 0 0) position. In the hauyne structure, the position of the oxygen atom involved in the environment of a sulfur atom is split. As a result, the S-tetrahedron has two statistically occurring orientations. The sulfide sulfur atoms occupy the 6i and 6f positions and are located in the same cavities as the SO$_4$-tetrahedra, thus competing with the sulfate sulfur atoms or their oxygen environment (Table 4).

Large Na and Ca cations occupy the positions 4e along the body diagonals of the cubic unit cell. Their polyhedra are formed not only by the O(1), O(2'), and O(2'') atoms but also by the $O_{S(1)}$ and $O_{S(2)}$ atoms surrounding the sulfate sulfur atoms and the anions of S(3)–S(6) sulfide sulfur. Allowance for the statistical filling of the anionic subpositions (Table 4) reduces the coordination numbers of the cations, which is reflected in the polyhedron names in Table 3.

According to the microprobe analysis, the composition of the mineral can be written ($Z = 1$) as $(Na_{6.41}Ca_{1.36}K_{0.04})_{\Sigma 7.81}(Si_{6.09}Al_{5.91})_{\Sigma 12}O_{24}[(SO_4)_{1.73} \times Cl_{0.17}]_{\Sigma 1.90}$. Then, it follows that the Na/Ca ratio is inconsistent with the electroneutrality of the formula. The X-ray structure study provides a more balanced formula with some coefficients being rounded off (within the experimental error of the determination of the occupancies) and allowance for the Cl atoms detected by microprobe analysis, namely, $Na_{6.2}Ca_{1.7}(Al_6Si_6O_{24})[(SO_4)_{0.85}S^{2-}_{0.9}Cl_{0.1}]$. Since the character of incorporation of sulfur atoms into lazurite structures can hardly be determined by chemical meth-

Table 2. Atomic coordinates, multiplicities (Q), and occupancies (q) of the positions and equivalent thermal parameters

Atom	x/a	y/b	z/c	Q	q	B_{eq}, Å^2
T(1)	0.5	0.2499(1)	0	6	1	3.2(1)
T(2)	0.5	0	0.2499(1)	6	1	3.6(1)
O(1)	0.3509(3)	0.3512(3)	0.0163(5)	12	1	7.8(2)
O(2')	0.1466(3)	0.1464(3)	0.5355(3)	12	0.68(1)	4.3(1)
O(2")	0.1508(6)	0.1521(6)	0.4502(6)	12	0.32(1)	3.2(2)
M	0.7547(3)	0.7547(3)	0.7547(3)	4	0.36(2)	5.1(3)
Ca	0.8150(3)	0.8150(3)	0.8150(3)	4	0.27(2)	5.0(3)
Na(1)	0.2585(3)	0.2585(3)	0.2585(3)	4	0.44(1)	4.4(1)
Na(2)	0.2019(5)	0.2019(5)	0.2019(5)	4	0.24(1)	3.1(2)
Na(3)	0.3253(6)	0.3253(6)	0.3253(6)	4	0.32(1)	5.7(2)
Na(4)	0.6872(5)	0.6872(5)	0.6872(5)	4	0.37(1)	6.6(2)
S(1)	0	0	0	1	0.51(1)	9.3(2)
S(2)	0.5	0.5	0.5	1	0.37(1)	8.1(2)
$O_{S(1)}$	0.8996(9)	0.8996(9)	0.8996(9)	4	0.51(1)	11.4(2)
$O_{S(2)}$	0.3930(8)	0.3930(8)	0.3930(8)	4	0.37(1)	10.4(3)
S(3)	0.1522(87)	0.5	0.5	6	0.06(1)	19.3(4)
S(4)	0.2589(30)	0	0	6	0.07(1)	8.7(7)
S(5)	0.2683(97)	0.5	0.5	6	0.03(1)	10.3(8)
S(6)	0.1471(42)	0	0	6	0.05(1)	11.6(6)

Note: $T = Si_{0.5}Al_{0.5}$; $M = Na_{0.6}Ca_{0.4}$.

Table 3. Interatomic distances (Å)

Tetrahedra					
T(1)–O(1)	1.643(3) × 2	T(2)–O(1)	1.639(2) × 2	S(1)–$O_{S(1)}$	1.578(8) × 4
O(2')	1.658(3) × 2	O(2')	1.660(3) × 2	$O_{S(1)}$–$O_{S(1)}$	2.58(1)
O(2")	1.709(6) × 2	O(2")	1.693(6) × 2	S(2)–$O_{S(2)}$	1.682(8) × 4
				$O_{S(2)}$–$O_{S(2)}$	2.75(1)
Nine-vertex Ca-polyhedron		Ten-vertex M-polyhedron		Seven(nine)-vertex Na-polyhedron	
Ca–S(6)	2.399(6) × 3	M–$O_{S(1)}$	2.278(9)	Na(1)–$O_{S(2)}$	2.113(8)
S(4)	2.468(8) × 3	O(2')	2.359(4) × 3	O(2")	2.217(6) × 3
O(2')	2.585(4) × 3	O(1)	2.735(5) × 3	O(1)	2.499(5) × 3
O(1)	2.807(4) × 3	O(2")	3.015(6) × 3	O(2')	2.896(4) × 3
		S(4)	3.151(3) × 3	S(5)	3.101(4) × 3
Ten-vertex Na-polyhedron		Nine-vertex Na-polyhedron		Nine-vertex Na-polyhedron	
Na(2)–O(2")	2.345(7) × 3	Na(3)–S(5)	2.30(2) × 3	Na(4)–S(5)	2.44(1) × 3
O(1)	2.550(6) × 3	O(2")	2.503(8) × 3	O(2')	2.540(6) × 3
S(6)	2.639(8) × 3	S(3)	2.7(1) × 3	S(3)	2.8(1) × 3
S(4)	2.643(7) × 3	O(1)	2.824(7) × 3	$O_{S(2)}$	2.862(9) × 3
$O_{S(2)}$	3.004(9)	O(2')	2.985(7) × 3	O(2")	2.986(7) × 3
$O_{S(1)}$	3.04(1) × 3			O(1)	3.027(6) × 3
O(2')	3.110(5) × 3				

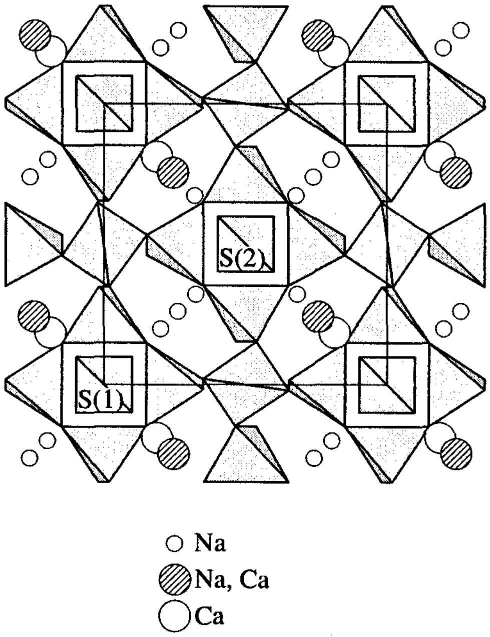

Fig. 1. Framework of the Si- and Al-tetrahedra in the average structure of cubic lazurite; the Na- and Ca-cations (circles) and the SO_4-anions (tetrahedra) are located in the framework cavities.

ods, we singled out two types of sulfur atoms proceeding from crystallochemical considerations—sulfide sulfur atoms are not tetrahedrally coordinated with oxygen atoms, but are involved in the anionic environment of Na and Ca cations (Fig. 2). The differences in the Na/Ca ratio revealed in the comparison of our results with the microprobe-analysis data can be explained by their inavoidable distortions in the consideration of the modulated structure as an average model.

Table 4. Selected distances (Å) between the statistically occupied positions

Position	Distance
O(2'), O(2")	0.777(6)
S(5), S(3)	1.1(3)
S(6), S(4)	1.01(4)
S(1), S(6)	1.33(1)
S(2), S(5)	2.10(1)
S(1), S(4)	2.35(3)
S(5), $O_{S(2)}$	1.78(5)
S(6), $O_{S(1)}$	1.36(1)
Na(1), Na(2)	0.89(1)
Na(1), Na(3)	1.05(1)
Na(2), Na(3)	1.94(1)
M, Ca	0.948(4)
M, Na(4)	1.061(6)
Ca, Na(4)	2.009(5)

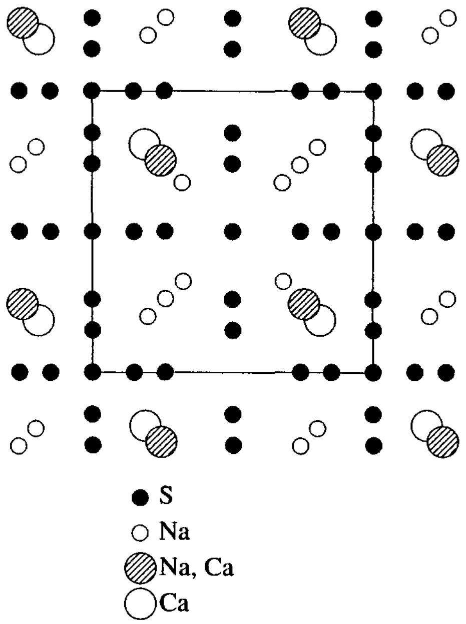

Fig. 2. Distribution of sulfide sulfur atoms around the intraframework cations.

Thus, we manage to solve the lazurite structure for the first time within the sp. gr. *P*23, which provided more detailed information on the mineral structure. Using these data, next we plan to examine the modulated structure with due regard for satellite reflections.

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REFERENCES

1. A. N. Sapozhnikov, V. G. Ivanov, A. Ya. Medvedev, and L. N. Matveeva, Izv. Akad. Nauk SSSR, Neorg. Mater. **27** (4), 811 (1991).
2. V. G. Evsyunin, R. K. Rastsvetaeva, A. N. Sapozhnikov, and A. A. Kashaev, Kristallografiya **43** (6), 1057 (1998) [Crystallogr. Rep. **43**, 999 (1998)].
3. V. G. Evsyunin, A. N. Sapozhnikov, A. A. Kashaev, and R. K. Rastsvetaeva, Kristallografiya **42** (6), 1014 (1997) [Crystallogr. Rep. **42**, 938 (1997)].
4. V. I. Andrianov, Kristallografiya **32** (1), 228 (1987) [Sov. Phys. Crystallogr. **32**, 130 (1987)].
5. V. Petricek and M. Dusek, *JANA2000: The Crystallographic Computing System* (Institute of Physics, Prague, 2000).
6. V. G. Evsyunin, A. N. Sapozhnikov, R. K. Rastsvetaeva, and A. A. Kashaev, Kristallografiya **41** (4), 659 (1996) [Crystallogr. Rep. **41**, 622 (1996)].
7. I. Hassan, R. C. Peterson, and H. D. Grundy, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. **41**, 827 (1985).

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