Structural Investigation of Adelite and Cobaltaustinite, two Members of the Adelite-descloizite Group

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Compounds crystallizing in the adelite-descloizite structure type have the formula $M1^{1+,2+}M2^{2+,3+}(OH)(X^{4+,5+,6+}O_4)$, M1 = Na, Ca, Pb; M2 = Mg, Al, Mn, Fe, Co, Ni, Cu, Zn; X = Si, P, V, As, Mo. More than a dozen of minerals belong to this group, however, investigations on synthetic compounds are rare. Compounds with accurate structure refinements exhibit space-group symmetries Pnam or $P2_12_12_1$. The deviation from the centrosymmetric parental structure is moderate. Single-crystal X-ray structure investigations were performed for adelite, $CaMg(OH)(AsO_4)$ (Palache et al., 1951) and cobaltaustinite, $CaCo(OH)(AsO_4)$ (Nickel & Birch, 1988). The acentric space group $P2_12_12_1$ was proved for both minerals: a = 7.468(1) / 7.475(1), b = 8.953(2) / 8.976(2), c = 5.941(1) / 5.916(1) Å; NONIUS four-circle diffractometer, CCD detector, capillary-optics collimator, Mo tube, graphite monochromator; program SHELXL (Sheldrick, 1996), R1 = 0.018 / 0.020, wR2 = 0.038 / 0.048; 1378 / 1364 reflections [1355 / 1342 with $F_o > 4\sigma(F_o)$] up to $2\theta = 65°$; for non-hydrogen atoms anisotropic displacement parameters were refined; the H atom was found from a difference Fourier map and was refined isotropically. The type structure exhibits $M2O_6$ octahedra (elongated tetragonal dipyramids in case of divalent Cu atoms due to Jahn-Teller distortion) edge linked to chains parallel to [001]. Each of the XO_4 tetrahedra link two such chains to a three-dimensional network.Cavities house the M1 atoms. Their coordination varies from [7] to [8] depending on the space-group symmetry. In adelite / cobaltaustinite the average M2-O and As-O bond distances are 2.0754 / 2.0867 and 1.6924 / 1.6911 Å. The average M1-O bond distance is 2.5238 / 2.5187 Å; the coordination polyhedron is a slightly distorted tetragonal antiprism. O-H is 0.85 / 0.84 Å, O-H···O is 2.766 / 2.714 Å.

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Isomorphism Peculiarities of the System Chatkalite - Mawsonite, $Cu_6FeSn_2S_8$ - $Cu_6Fe_2SnS_8$

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Mawsonite, $Cu_6Fe_2SnS_8$ is the mineral related to stannite group with the structure derivative of sphalerite type (Szymanski, 1976). Based on the formula and x-ray data similarity the rare mineral chatkalite, $Cu_6FeSn_2S_8$, found in 1981, has been assigned to the same structure type(Kovalenker et al., 1981). The chatkalite structure is not carried out till now because of its rarity and of the absence of available crystals. The element composition and the “Metals:S” ratio of these two minerals are identical, and lead to the conclusion about the isomorphous replacement Fe-Sn. For prove this idea the experimental study of the series $Cu_6FeSn_2S_8$ - $Cu_6Fe_2SnS_8$ has been carried out for the first time. Compounds $Cu_6Fe_{2-x}Sn_{1+x}S_8$, synthesized by melting the elements in necessary proportions under condensed system, have been studied using ore microscopy, x-ray, microprobe, and moessbauer spectroscopy. Although the whole isomorphous series chatkalite-mawsonite was not obtained, but end members as well as some intermediate ones have been studied. In connection with the recent results on the complex type of isomorphism in stannite type compounds, i.e. kesterite (Rusakov et al.,2001), and kuramite-stannite series (Evstigneeva et al., 2001) the valence state and the co-ordination of ^{57}Fe and ^{119}Sn in these compounds are have been studied. Moessbauer spectra of $^{57}FeFe$ under the room temperature have the ultrafine structure of paramagnetic type. Iron in chatkalite corresponds to Fe^{2+}. Mawsonite contains Fe^{3+}. Spectra of other members of the series present the superposition of two well-resolved partial spectra (Fe^{2+} and Fe^{3+}). The number of Fe^{3+} increases but of Fe^{2+} decreased as the total Fe contents increases. Moessbauer spectra of ^{119}Sn are of paramagnetic type, and present two type of Sn^{4+}: a) with strong ionic bond Sn^{4+}-S, and strong covalent bond Sn^{4+}-S. The covalence of bond Sn^{4+}-S increases, but of Fe^{2+}-S decreases as the Fe content increases. Authors thank the Russian Foundation of Basic Researches for financial support (Project _00-05-64609).

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Adelite (from Långban, Sweden)

Space group $P2_12_12_1$
a = 7.468(1) Å
b = 8.953(1) Å
c = 5.941(1) Å
V = 397.22 Å

absorption coefficient: $\mu = 9.42\ \text{mm}^{-1}$
measured reflections: 4908 ($-11 \le h \le 11$, $-13 \le k \le 13$, $-8 \le l \le 8$, $2\delta \le 65°$
unique reflections: 1378 (R(int) = 0.0213 R(sigma) = 0.0277)
total number of parameters refined: 79
weight = $1 / [\sigma^2(F_o^2) + (0.0110\times P)^2 + 0.26\times P]$ where $P = (\max(F_o^2,0) + 2\times F_c^2) / 3$
Flack x parameter = 0.015(3); considering racemic twining of 0.015(7) the Flack x parameter is reduced to 0.000(8)
wR2 = 0.0376 all 1378 data
R1 = 0.0179 for 1355 $F_o > 4\sigma(F_o)$ and 0.0188 for all 1378 data
GooF = S = 1.055
extinction coefficient: 0.0138(10)
Final difference Fourier summation: $-0.70\ e\text{Å}^{-3}$ to $0.80\ e\text{Å}^{-3}$ (close to the As atom)

Atom	x	y	z	sof	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Ca	0.63323(5)	0.66993(4)	0.47737(6)	1.00000	0.01038(16)	0.00669(16)	0.01104(16)	-0.00012(12)	0.00086(13)	-0.00049(11)	0.00937(10)
Mg	0.24093(9)	0.50504(8)	0.24576(10)	1.00000	0.0074(3)	0.0065(3)	0.0045(3)	-0.0007(2)	0.0005(2)	0.0006(2)	0.00610(14)
As	0.61594(2)	0.31858(2)	0.51671(3)	0.9312(15)	0.00567(9)	0.00523(9)	0.00509(8)	-0.00013(6)	-0.00002(6)	0.00064(5)	0.00533(6)
P	0.61594(2)	0.31858(2)	0.51671(3)	0.0688(15)	0.00567(9)	0.00523(9)	0.00509(8)	-0.00013(6)	-0.00002(6)	0.00064(5)	0.00533(6)
O1	0.43758(15)	0.43594(13)	0.4901(2)	1.00000	0.0090(5)	0.0104(5)	0.0094(6)	0.0005(5)	-0.0002(5)	0.0034(4)	0.0096(2)
O2	0.78376(18)	0.43523(15)	0.5872(2)	1.00000	0.0113(6)	0.0131(6)	0.0161(6)	-0.0001(5)	-0.0024(5)	-0.0032(5)	0.0135(3)
O3	0.35447(17)	0.72683(14)	0.2293(2)	1.00000	0.0130(6)	0.0105(6)	0.0081(5)	0.0009(5)	-0.0001(5)	-0.0018(5)	0.0105(3)
O4	0.39884(19)	0.70196(15)	0.7603(2)	1.00000	0.0146(6)	0.0103(6)	0.0087(5)	-0.0023(5)	0.0013(5)	-0.0032(5)	0.0112(3)
O5	0.10657(16)	0.57687(13)	0.5059(2)	1.00000	0.0086(5)	0.0109(6)	0.0092(5)	0.0003(5)	0.0014(6)	-0.0004(4)	0.0096(2)
H	0.009(4)	0.529(3)	0.513(5)	1.00000	0.032(8)						

Principal mean square atomic displacements U

0.0117	0.0098	0.0066	Ca
0.0077	0.0065	0.0041	Mg
0.0061	0.0051	0.0047	As1
0.0061	0.0051	0.0047	P1
0.0132	0.0094	0.0061	O1
0.0175	0.0147	0.0084	O2
0.0140	0.0098	0.0078	O3
0.0169	0.0097	0.0069	O4
0.0109	0.0103	0.0075	O5

Bond lengths (Å) and angles (°)

Ca—O5	2.2779(12)	Mg—O5	1.9516(14)	As—O2	1.6843 (13)	H—O5	0.85(3)
Ca—O4	2.4435(14)	Mg—O5	1.9661(15)	As—O4	1.6906 (12)	H—O2	1.93(3)
Ca—O2	2.4708(14)	Mg—O1	2.0888(14)	As—O3	1.6908 (13)	O5—H···O2	169(3)
Ca—O1	2.5552(12)	Mg—O4	2.1288(14)	As—O1	1.7039 (11)	O5···O2	2.7664 (0.0018)
Ca—O3	2.5733(13)	Mg—O1	2.1557(14)	O2—As—O4	103.68(7)		
Ca—O2	2.5773(15)	Mg—O3	2.1613(14)	O2—As—O3	114.77(7)		
Ca—O3	2.6012(13)			O2—As—O1	102.85(6)		
Ca—O4	2.6913(14)			O4—As—O3	112.70(6)		
				O4—As—O1	113.73(6)		
				O3—As—O1	108.76(6)		