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Crystal structure of dicalcium (cobalt,magnesium) diarsenate dihydrate, $Ca_2(Co_{0.532}Mg_{0.468})[AsO_4]_2 \cdot 2H_2O$, *hydrogen bonding in talmessite*

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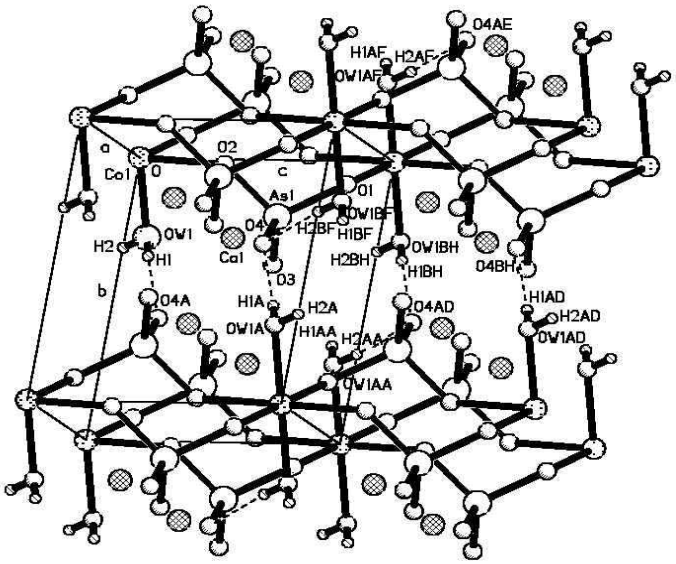

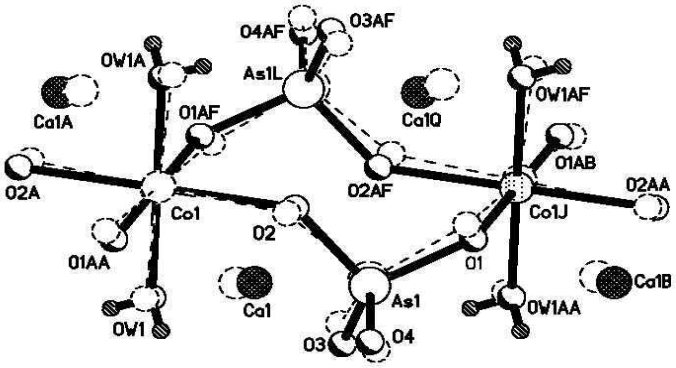

Abstract

$As_2Ca_2Co_{0.532}H_4Mg_{0.468}O_{10}$, triclinic, $P\bar{1}$ (no. 2),
$a = 5.884(1)$ Å, $b = 6.981(1)$ Å, $c = 5.564(1)$ Å, $\alpha = 97.33(2)°$,
$\beta = 108.93(2)°$, $\gamma = 108.18(2)°$, $V = 198.6$ Å^3, $Z = 1$,
$R_{gt}(F) = 0.017$, $wR_{ref}(F^2) = 0.047$, $T = 293$ K.

Source of material

The crystals were taken from a mine near Bou-Azzer, Morocco. In contrast to the crystals investigated by Dunn, Sturman and Nelen, which had much more Mg than Co [1], our samples contain according to electron microprobe analyses in the average more Co than Mg (0.579:0.473).

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Experimental details

The average I/σ of the measured X-ray intensities is 76.6. The hydrogen atoms could be refined isotropically, nevertheless the measurements were carried out at room temperature. The largest peak and hole in the difference density map were 0.778 and –0.854 e/Å^3, respectively. Despite the average $|E^2 - 1|$ equals 0.808, the adequate space group is $P\bar{1}$. The refinement in $P1$ with racemic twinning resulted in the same structure with slightly higher R-values ($R_{gt}(F) = 0.020$, $wR_{ref}(F^2) = 0.055$).

Discussion

According to Catti et al. [2] and Hawthorne & Ferguson [3] the triclinic compound of the chemical formula $Ca_2(Mg,Co)(AsO_4)_2 \cdot 2H_2O$ is called talmessite, the monoclinic one – roselite [3]; the name β-roselite [4] will not be used by us. The top figure shows the kröhnkite-type chains. According to M. Fleck the structure should be assigned to the structural type A [5], roselite to structural type D. The high significance of the hydrogen positions allows an unambiguous identification of the water molecules and the hydrogen bonding [2]. O4 is the acceptor of two hydrogen bonds originating from the two hydrogens of the water molecule. The hydrogen bond OW1–H2···O4 (2.616 Å) connects two chains within the layers parallel (101), whereas OW1–H1···O4 (2.579 Å) connects the layers. There are, however, no hydrogen bonds within the chains [5]. The bottom figure shows a least squares fit between kröhnkite-type chains of talmessite (bold lines) and roselite (dashed lines) [3]. The chains are very similar indeed. There seems to exist a solid solution seria between Mg and Co [1], whose relative content has apparently no influence on the crystal structure. There is an analysis of the miscibility in minerals, but not in crystals grown in the laboratory [1]. The average e.s.d. for metal-metal distances is 0.001 Å, for metal-oxygen and oxygen-oxygen distances 0.002 Å and for the oxygen-hydrogen distances 0.04 Å. The average e.s.d. of angles between metals with no oxygens in is 0.02°, with one oxygen 0.04° and with 2 oxygens 0.1°, in the water molecule it is 3°.

Table 1. Data collection and handling.

Crystal:	pink plate, size 0.05 × 0.175 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	107.92 cm^{-1}
Diffractometer, scan mode:	Nonius CAD4, θ-2θ-scan
$2\theta_{max}$:	59.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2318, 1159
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1141
$N(param)_{refined}$:	80
Programs:	SHELXS-97 [6], SHELXL-97 [9], SHELXTL-PLUS [8]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	0.081(8)	0.358(6)	0.126(7)	0.023(9)
H(2)	2*i*	–0.123(8)	0.302(6)	–0.031(8)	0.026(9)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1)	1*a*	0.532(2)	0	0	0	0.0072(3)	0.0070(3)	0.0086(3)	0.0024(2)	0.0036(2)	0.0018(2)
Mg(1)	1*a*	0.468	0	0	0	0.0072	0.0070	0.0086	0.0024	0.0036	0.0018
As(1)	2*i*		0.33318(3)	0.24575(3)	0.67079(3)	0.0059(1)	0.0057(1)	0.0068(1)	0.00189(7)	0.00270(7)	0.00204(7)
Ca(1)	2*i*		–0.29524(7)	0.23736(6)	0.34744(7)	0.0089(2)	0.0093(2)	0.0093(2)	0.0031(1)	0.0039(1)	0.0022(1)
O(1)	2*i*		0.3405(3)	0.1288(2)	0.9213(3)	0.0091(6)	0.0121(7)	0.0104(6)	0.0037(5)	0.0045(5)	0.0066(5)
O(2)	2*i*		0.2399(3)	0.0505(2)	0.4002(3)	0.0138(6)	0.0095(6)	0.0087(6)	0.0044(5)	0.0019(5)	–0.0009(5)
O(3)	2*i*		0.1537(3)	0.3907(2)	0.6412(3)	0.0107(6)	0.0093(6)	0.0132(6)	0.0058(5)	0.0050(5)	0.0039(5)
O(4)	2*i*		0.6411(3)	0.3849(2)	0.7158(3)	0.0061(6)	0.0103(6)	0.0123(6)	0.0001(5)	0.0040(5)	0.0023(5)
OW(1)	2*i*		–0.0463(3)	0.2744(2)	0.0737(3)	0.0085(6)	0.0073(6)	0.0092(6)	0.0013(5)	0.0025(5)	0.0017(5)

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