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Superstructures, (Si,Al) and H₂O ordering in armenite BaCa₂Al₆Si₉O₃₀ · 2 H₂O*

by Thomas Armbruster¹

Abstract

Armenite is a member of the group of double-ring silicates. Partial (Si,Al) ordering leads to orthorhombic symmetry which can be resolved with FeK α_1 Guinier powder photographs. Using single-crystal diffraction experiments superstructure reflections caused by H₂O ordering indicate a primitive lattice with $a = 13.874(2)$, $b = 18.661(2)$, and $c = 10.697(1)$ Å. The crystal structure of an optically homogeneous armenite from Rémigny (Canada) was determined and refined from X-ray single-crystal data in the space group Pnna.

Keywords: Armenite, ordering, superstructure, structure refinement, X-ray methods.

Introduction

Armenite (BaCa₂Al₆Si₉O₃₀ · 2 H₂O) together with milarite and osumilite belong to the group of double-ring silicates. This rare mineral was detected and described in several locations including: the Armen Mine, Norway (NEUMANN, 1941), Rémigny, Canada (POULIOT et al., 1984), Broken Hill, Australia (MASON, 1987), Zufuru Mine in Sardinia, Italy (BALASSONE et al., 1989) and the celsian-bearing leucocratic gneisses (FRANK, 1979) of the Simplon area in Switzerland (SENN, 1990).

Armenite when viewed under a polarizing microscope shows pseudo-hexagonal morphology formed by penetration twins with domains showing an 120° angle (NEUMANN, 1941; POULIOT et al., 1984), NEUMANN (1941) recognized armenite as a biaxial, $2 V_x = 60^\circ$ ("orthorhombic?") mineral. BAKAKIN et al. (1975) were aware of this twinning problem, but refined the structure of an armenite twin-aggregate in the space-group P6/mcc as is characteristic of other double-ring silicates. Since this study, armenite has erroneously been considered hexagonal.

A series of studies on double-ring silicates was conducted to study the relation between optical anomalies and symmetry reduction. Thin sections of milarite (KNa_{1-x} Ca₂Be_{3-x}Al_xSi₁₂O₃₀ · [H₂O])

with the space group P6/mcc revealed optical sectors in (001) and were related to partial ordering of H₂O (ARMBRUSTER et al., 1989). This study reports experiments performed on armenite from Rémigny Canada, which was kindly provided by the Museum of Natural History Bern, sample NHMB-B4468. A more detailed description of these structural investigations will be published elsewhere.

Mineralogical studies

X-ray powder diffraction of the armenite sample from Rémigny, Canada, (recorded on a Guinier camera with FeK α_1 -radiation) displays characteristic splitting of various reflections (Tab. 1). The reflections can not be indexed with a hexagonal lattice but are in agreement with a face-centered orthorhombic lattice ($k + l = 2n$). POULIOT et al. (1984) previously reported a powder diffraction pattern determined using a diffractometer with CuK α -radiation but could not resolve any splitting.

A thin section of an armenite twin was prepared perpendicular to the pseudo-hexagonal c -axis and an optically homogeneous domain was separated with the micro-drilling device of MEDENBACH (1986). This domain was studied with

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Tab. 1 Indexed powder pattern of natural orthorhombic (Pnna) armenite from Rémigny, Canada: $a = 13.874(2)$, $b = 18.661(2)$, $c = 10.697(1)$ Å and of dehydrated armenite (Amaa): $a = 14.024(3)$, $b = 18.383(3)$, $c = 10.606(2)$ Å. Intensities were calculated (Yvon et al., 1977) for a Guinier camera (FeK α_1 -radiation) using the positional parameters obtained from the structure refinement.

natural armenite						dehydrated armenite	
h	k	l	d_{calc}	d_{obs}	I_{calc}	d_{calc}	d_{obs}
0	2	0	9.330	9.291	23	9.191	9.195
0	1	1	9.280	"	34	9.188	"
2	0	0	6.937	6.927	100	7.012	7.008
0	3	1	5.377	5.388	7	5.306	5.307
0	0	2	5.349	"	4	5.304	"
2	3	1	4.2498	4.255	50	4.2312	4.2307
2	0	2	4.2357	4.247	24	4.2301	"
2	4	0	3.8711	3.8712	31	3.8437	3.8404
2	2	2	3.8569	3.8633	66	3.8427	"
0	1	3	3.5023	"	2	3.4723	3.4726
4	0	0	3.4685	3.4684	8	3.5060	3.5063
1	5	1	3.4153	3.4182	29	3.3720	3.3719
1	4	2	3.4079	3.4091	33	3.3714	"
1	1	3	3.3958	3.3961	28	3.3706	"
0	6	0	3.1100	3.1098	14	3.0638	3.0609
0	3	3	3.0934	3.0942	30	3.0627	"
4	3	1	2.9147	2.9148	61	2.9251	2.9246
4	0	2	2.9101	"	31	2.9248	"
3	4	2	2.7988	2.7986	6	2.7880	"
4	4	0	2.7834	2.7841	28	2.7875	2.7885
4	2	2	2.7781	2.7782	49	2.7871	"
0	6	2	2.6885	2.6894	28	2.6530	2.6557
0	0	4	2.6742	2.6749	15	2.6520	2.6481
0	7	1	2.5866	2.5873	7	2.5492	2.5495
0	2	4	2.5707	2.5717	6	2.5481	"
1	7	1	2.5418	2.5433	6	2.5081	"
1	5	3	2.5347	2.5336	5	2.5075	2.5081
1	2	4	2.5280	2.5272	5	2.5070	"
2	6	2	2.5072	2.5066	18	2.4814	2.4825
2	0	4	2.4955	2.4958	9	2.4805	2.4779
4	5	1	2.4722	2.4727	5	2.4677	2.4681
4	4	2	2.4694	2.4687	4	2.4675	"
0	4	4	2.3204	2.3190	1	2.2970	"
4	6	0	2.3155	2.3147	3	2.3070	2.3075
4	3	3	2.3089	2.3081	4	2.3065	"
3	5	3	2.2518	"	2	2.2376	2.2371
3	2	4	2.2469	"	2	2.2373	"
6	2	0	2.2444	"	1	2.2652	2.2640
2	8	0	2.2109	2.2104	4	2.1836	2.1826
2	4	4	2.2006	2.2006	8	2.1829	"
6	3	1	2.1242	"	9	2.1390	2.1391
6	0	2	2.1225	"	4	2.1389	"
4	0	4	2.1181	2.1172	4	2.1151	2.1152
6	4	0	2.0718	"	2	2.0834	2.0818
6	2	2	2.0696	"	4	2.0832	"
2	8	2	2.0435	2.0430	4	2.0192	2.0200
0	9	1	2.0355	2.0348	10	2.0057	2.0052
0	6	4	2.0277	2.0266	7	2.0052	"
2	9	1	1.9531	1.9527	10	1.9283	1.9282
2	6	4	1.9465	1.9474	9	1.9279	"
5	7	1	1.8920	1.8929	8	1.8864	1.8860
5	5	3	1.8889	1.8882	8	1.8862	"
0	10	0	1.8660	"	2	1.8384	1.8366
0	5	5	1.8561	"	7	1.8376	"
6	6	0	1.8556	"	4	1.8583	1.8581
6	3	3	1.8522	1.8517	8	1.8581	"
6	6	2	1.7533	1.7537	18	1.7536	1.7539
6	0	4	1.7493	1.7496	7	1.7535	"
8	0	0	1.7343	1.7339	12	1.7530	"

a spindle-stage equipped polarizing microscope and extinction data yielded an optic axial angle $2 V_x = 59.9(6)$. This result is in excellent agreement with the U-stage measurements of NEUMANN (1941) on armenite from Norway. The same isolated single-crystal from Rémigny was transferred to a precession camera (MoK α -radiation)

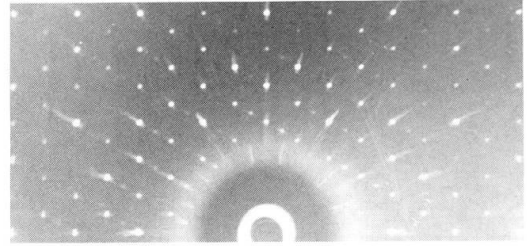


Fig. 1 hk2-layer (pseudo-hexagonal setting) of an optically homogeneous armenite from Rémigny, Canada (recorded with a precession camera, MoK α -radiation). In addition to the pseudo-hexagonal arrangement of reflections, slightly streaked superstructure reflections which characterize a primitive orthorhombic lattice can be observed. Systematic extinctions lead to space group Pnna.

where the hk2 layers (pseudo-hexagonal setting) displayed superstructure reflections (Fig. 1). This observation clearly indicates that armenite is orthorhombic and crystallizes in a primitive lattice. Systematic extinctions lead to the space-group Pnna ($\underline{a} = 13.874[2]$, $\underline{b} = 18.661[2]$, $\underline{c} = 10.697[1]$ Å). The structure of armenite was then solved in this space group by routine X-ray techniques described in a forthcoming paper. A projection along \underline{a} of the refined structure is shown in figure 2. Three different types of tetrahedra could be distinguished on the basis of T(Si,Al)-O distances. Of six symmetry distinct ring tetrahedra (T1 type), two show T-O distances characteristic of pure Si occupation whereas the remaining four indicate a Si/Al ratio of 1/1. Three tetrahedra (T2 type) connect the double-ring units to a tetrahedral framework. Two of the latter type also show a Si/Al ratio of 1/1 and one is occupied by Al. The (Si,Al) distribution is in agreement with a face-centered orthorhombic lattice. The observed primitive lattice is caused by the arrangement of H₂O molecules. In armenite, Ca is in seven-fold coordination where six oxygens of the tetrahedral framework form a distorted octahedron and one additional H₂O molecule completes the coordination. This H₂O molecule is either above or below the octahedron (in projections parallel to \underline{a} , Pnna setting).

The refined structure (Fig. 2) shows a correlation between (Si,Al) ordering and H₂O arrangement. T2 type tetrahedra connect edge-sharing CaO₇ units with the water molecule on the same height along \underline{a} and have a Si/Al ratio of 1/1. The tetrahedron which links two CaO₇ units with H₂O in opposite directions along \underline{a} , has longer T-O distances and is indicative of pure Al occupation. This Al tetrahedron is also linked to four Si tetrahedra in the double-ring units.

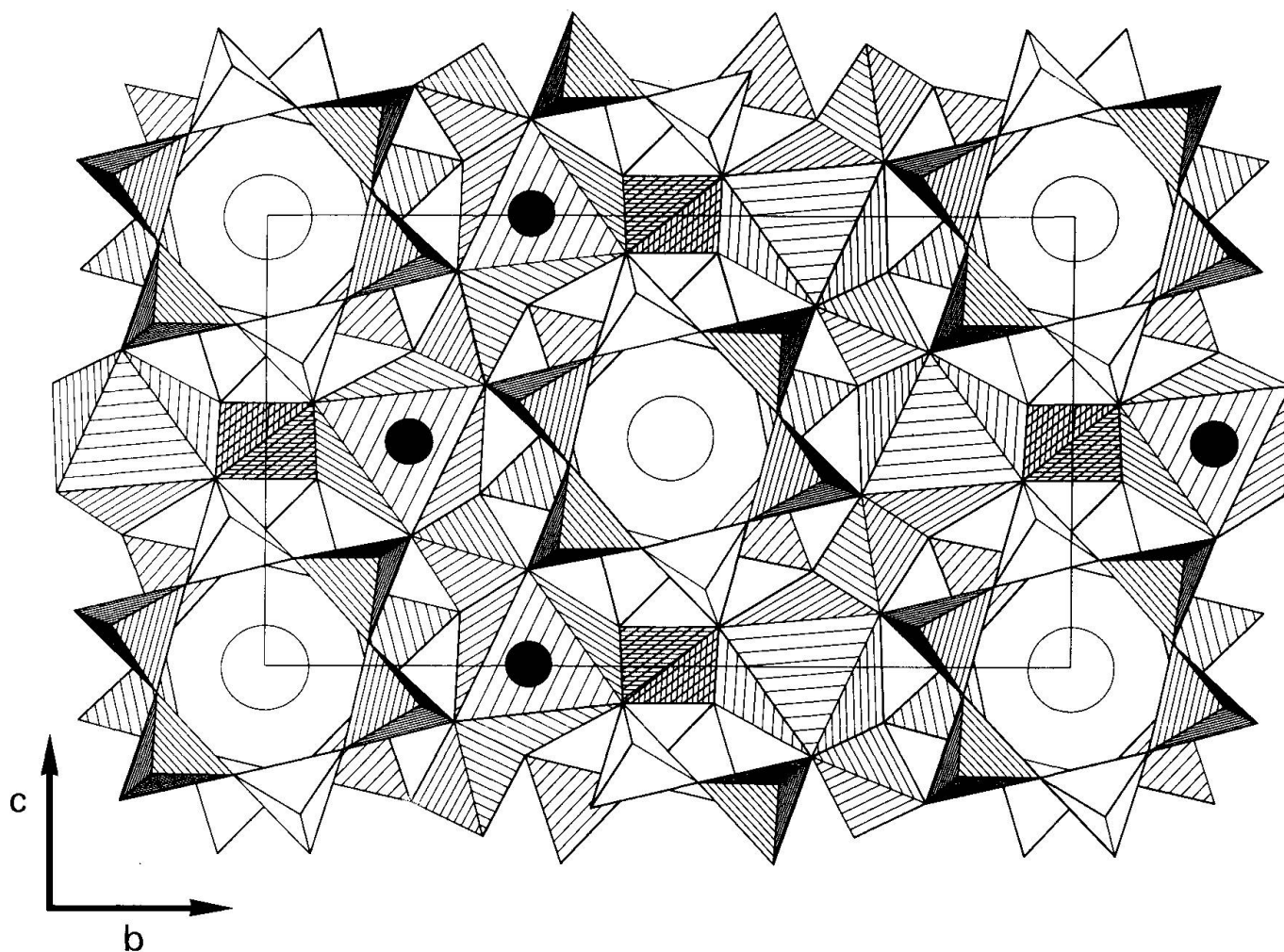


Fig. 2 Projection of the armenite structure parallel to a (setting for space group $Pnna$: $a = 13.8$, $b = 18.6$, $c = 10.7$ Å). In this projection, double-rings appear as single rings. Open tetrahedra are occupied by Si, hatched tetrahedra have Si/Al = 1/1, and cross-hatched tetrahedra are centered by Al. Ba (open circles) is shown between two adjacent double-ring units. Ca is in seven-fold coordination where six oxygens of the tetrahedral framework form a distorted octahedron and a H_2O molecule (filled circle) completes the coordination. In cases where no H_2O molecules are drawn the corresponding H_2O position is below the CaO_6 octahedron.

Previous heating experiments by NEUMANN (1941), POULIOT et al. (1984) and BALASSONE et al. (1989) showed that heating to 1000 °C expels H_2O from armenite. Our experiments on armenite single-crystals that were heated for 72 h at 1000 °C indicate that the superstructure reflections (characteristic of the primitive lattice) disappear and the crystals become metrically hexagonal. However, based on the experience of (Si,Al) order-disorder in cordierite (e.g. SCHREYER, 1966), it is not likely that these fairly moderate heating conditions are sufficient to cause complete (Si,Al) disorder within the double-ring (T1) and the linking tetrahedra (T2). Thus, armenites heated under these conditions are probably only pseudo-hexagonal and possess the same (Si,Al) arrangement as natural armenite. The corresponding space group symmetry is $Amaa$ (in a setting corre-

sponding to $Pnna$; standard setting is $Cccm$). The loss upon heating of H_2O leads to a pronounced shortening of b and c and an expansion of a : $a = 14.024(3)$, $b = 18.383(3)$, $c = 10.608(2)$ Å.

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