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Superstructures, (Si,Al) and H₂O ordering in armenite $\text{BaCa}_2\text{Al}_6\text{Si}_9\text{O}_{30} \cdot 2 \text{H}_2\text{O}^*$

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 $\text{FeK}\alpha_1$ 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 ($\text{BaCa}_2\text{Al}_6\text{Si}_9\text{O}_{30} \cdot 2 \text{H}_2\text{O}$) 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 ($\text{KNa}_{1-x}\text{Ca}_2\text{Be}_{3-x}\text{Al}_x\text{Si}_{12}\text{O}_{30} \cdot [\text{H}_2\text{O}]$)

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 $\text{FeK}\alpha_1$ -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 $\text{CuK}\alpha$ -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

*Extended abstract of a contribution presented at the annual meeting of the SSMP, Geneva, October 4 and 5, 1990.

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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)

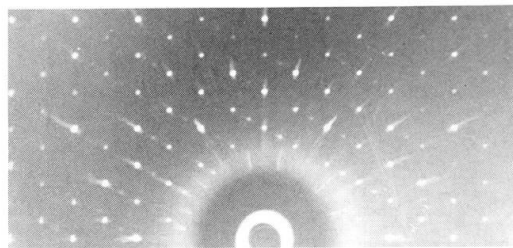


Fig. 1 hk2-layer (pseudo-hexagonal setting) of an optically homogeneous armenite from Rémigny, Canada (recorded with a precession camera, MoK α -radiation). In addition to the pseudo-hexagonal arrangement of reflections, slightly streaked superstructure reflections which characterize a primitive orthorhombic 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 ($a = 13.874[2]$, $b = 18.661[2]$, $c = 10.697[1]$ Å). The structure of armenite was then solved in this space group by routine X-ray techniques described in a forth coming paper. A projection along 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 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 a and have a Si/Al ratio of 1/1. The tetrahedron which links two CaO₇ units with H₂O in opposite directions along 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.

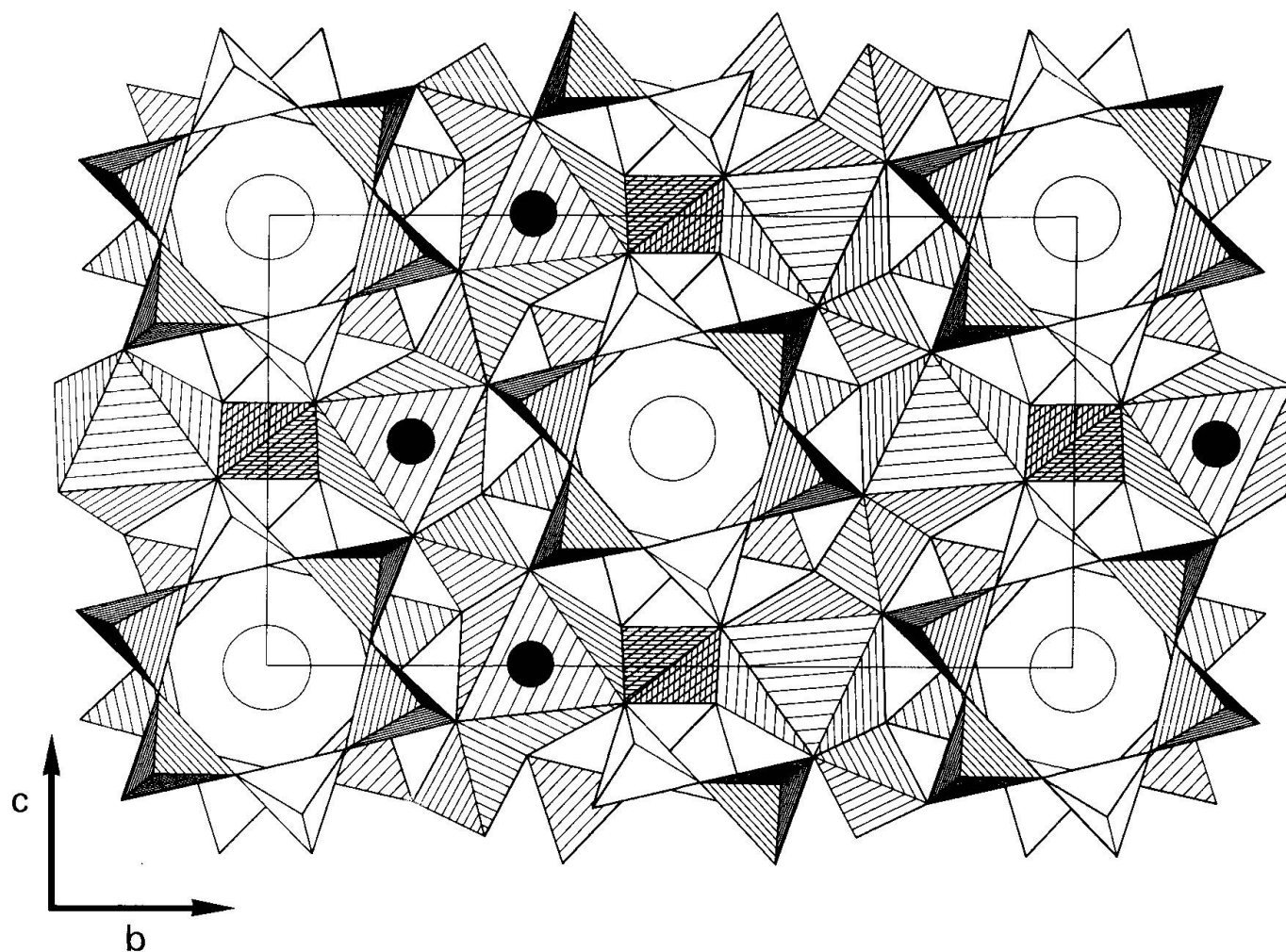


Fig. 2 Projection of the armenite structure parallel to a (setting for space group $Pnna$: $a = 13.8$, $b = 18.6$, $c = 10.7$ Å). In this projection, double-rings appear as single rings. Open tetrahedra are occupied by Si, hatched tetrahedra have $Si/Al = 1/1$, and cross-hatched tetrahedra are centered 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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