A transmission electron microscope observation of 138Å period in Pb-As-S sulfosalts

Tohru OZAWA and Osamu TACHIKAWA

Mineralogical Institute, Graduate School of Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

Abstract

A small crystal fragment whose diffraction pattern shows a long period of around 138Å was found under the electron microscope, and based upon its high-resolution TEM image the essential crystal structural features were discussed. It belongs to the rathite group of lead sulfarsenites. The crystal structures of the members of this group can be interpreted as various combinations of two different structural units, namely, sartorite unit “S” with about 9.8Å in width and rathite unit “R” with about 12.6Å in width. The present material has been proved to have an ordered arrangement of RSRSR · RSRSRSR. This result is consistent with the conclusion derived by Takéuchi (1970) that the crystal structure of each member of the rathite group is constructed by a regular arrangement of S and R units. Although the 138Å period is reported for rathite-IV, the characteristics of the diffraction pattern of the present phase appear to be different from those of rathite-IV. The occurrence of the present material is discussed.

Introduction

A group of lead sulfarsenites, which Takéuchi (1970) called “rathite group”, has the crystal structural characteristics of having common two axial lengths of around 7.9Å generally along their b-axis and around $4.2 \times 2\text{Å}$ along their c-axis. About ten species belonging to this group have been described and studied chemically and crystallographically, such as dufrenoyite (Marumo and Nowacki, 1967), rathite-I (Marumo and Nowacki (1965), liveingite (rathite-II) (Engel and Nowacki, 1970), rathite-III (LeBihan, 1962; Takéuchi, 1970), rathite-IV (Ozawa and Nowacki, 1974), baumhauerite (Engel and Nowacki, 1969), baumhauerite-2a and baumhauerite- $\Psi\text{O}_3\text{abc}$ (Pring and Graeser, 1994), an unnamed 115Å phase (Ozawa and Tachikawa, 1995a, b), sartorite (Iitaka and Nowacki, 1961; Ozawa and Takéuchi, 1993; Pring, Williams and Withers, 1993). Among them rathite-IV is reported to have the longest a-axis dimension of around 138Å (Ozawa and Nowacki, 1974). The present report deals with a phase having a 138Å period observed under the electron microscope. It has, however, not been revealed whether the present material corresponds to rathite-IV or not, since the material available for the present study was only a small fragment under the electron microscope, and moreover, detailed crystal-structural data of rathite-IV is not obtained only by X-ray diffraction.

Experimental

Many of the above lead sulfarsenites are described only from Binnathal, Switzerland. It is also the case with the present material. It was originally collected in Binnathal and then came into possession of the authors by purchase. The specimen is labelled “liveingite” from Lengenbach quarry in Binnathal. Some sulfosalts and pyrite crystals are included in powdery dolomite. It is now deposited in the University Museum, the University of Tokyo.

We made TEM observations of numbers of fragments in the crushed specimen so as to study the disordering in liveingite with a 70Å period, when we found that the most objects of observations were not liveingite, but a new species having a 115Å period (Ozawa and Tachikawa, 1995a,b). And we also encountered a fragment of about one micron in size showing a still longer period in the electron diffraction. Thus, we recorded the diffraction pattern and tried the high-resolution imaging for the material using the JEM 2010 high-resolution transmission electron microscope operated at 200kV of the Electron Microbeam Analysis Facility of the Mineralogical Institute, the University of Tokyo.

Results and discussion

The crystal structural principle in the rathite group was fully elucidated by Takéuchi (1970). All the crystal structures already determined in this group (dufrenoyite, rathite-I, baumhauerite, liveingite, sartorite substructure) are constructed by two types of structural units named sartorite unit and rathite unit, although Pring and Graeser (1994) called them sartorite and dufrenoyite units and the group “sartorite group” instead of rathite group. The crystal data for these species are summarized in Table 1 including those for the species whose crystal structures are left unknown.

TABLE 1. Crystal Data of Rathite Group Minerals

	Chemical Formula	a	b	c	β	s.g.	struc.type
dufrenoyite	Pb ₁₆ As ₁₆ S ₄₀	25.74(b)	7.90(a)	8.37	90°20'	P2	RR
rathite-I	(Pb,Tl) ₁₂ As ₂₀ S ₄₀	25.16	7.94	8.47	100°28'	P2 ₁ /a	RR
rathite-III	Pb ₁₂ As ₂₀ S ₄₀	24.52	7.91	8.43	90°00'	P2 ₁	RR
baumhauerite	Pb ₁₂ As ₁₆ S ₃₆	22.80	7.89(c)	8.36(b)	97°16'	P ₁	RS
baumhauerite-2a	Pb ₂₂ Ag _{1.4} As _{34.3} S ₇₂	44.75	7.89(c)	8.48(b)	93°38'	tcl.	2×(RS)
baumhauerite-ΨO3abc	Pb _{38.1} Ag ₃ (As,Sb) _{52.8} S ₁₀₈	68.3	7.89(c)	8.48(b)	90°		4×(RS)
liveingite	Pb ₃₇ As ₅₀ S ₁₁₂	70.49(b)	7.91(c)	8.37(a)	90°08'	P2 ₁	2x(RSR)
“115A phase”	(Pb,Tl,Ag) ₆₀ As ₈₄ S ₁₈₄	115.7(b)	7.90(c)	8.37(a)	90°	P2 ₁	2×(RSRSR)
rathite-IV		138.3	7.92	8.46	90°20'	P2 ₁ /m,P2 ₁	
sartorite(subcell)	(Pb,Tl) ₄ As ₈ S ₁₆	19.62	7.89	4.19		Pbnm	SS

References: dufrenoyite, Marumo & Nowacki (1967); rathite-I, Marumo & Nowacki (1965); rathite-III, LeBihan (1962); baumhauerite, Engel & Nowacki (1969); baumhauerite-2a & -YO3abc, Pring & Graeser (1994); liveingite, Engel & Nowacki (1970); “115A phase”, Ozawa & Tachikawa (1995a & unpublished data); rathite-IV, Ozawa & Nowacki (1974); sartorite, Iitaka & Nowacki (1961)

FIG.1 The crystal structure of baumhauerite (Engel and Nowacki, 1969).

S designates sartorite unit of around 9.8Å in width and R designates rathite unit of around 12.6Å in width. large open circles represent Pb atoms, small filled circles As atoms and small open circles O atoms.

In order to elucidate the structural relationships among the species in the rathite group, Takéuchi(1970) drew three fundamental structural units, “S”, “R3” and “R1” from the known crystal structures.

“S” is “sartorite unit”, which is about 9.8Å in width corresponding to a half of the a-period of the sartorite subcell. The second “R3” is “rathite unit” found in the structure of rathite -I (Marumo and Nowacki, 1965), which is the similar structural unit to “S” but about 12.6Å in width corresponding to a half of the a-period of rathite-I. The third unit “R1” is found in the structure of dufrenoyite. It is closely similar to “R3”, but in which some As atom sites in “R3” are replaced by Pb. However, we use only “R” without subscript in this paper neglecting the difference between R3 and R1, since R3 and R1 have similar dimensions and they can not be distinguished by the present TEM images.

The crystal structure of baumhauerite (Engel and Nowacki, 1969), which is composed of the same number of S and R, is represented in Fig. 1, so as to illustrate S and R units.

The electron diffraction study of the present material (Fig. 2) showed that the fragment observed has overall a long period ordered superstructure. Fig. 3 represents the high-resolution TEM image corresponding to the diffraction of Fig. 2. S and R mean the above-mentioned S unit (9.8Å in width) and R unit (12.6Å in width). Fig.3 shows the regularly arranged lattice fringe of RSRSR·RSR·RSR. In connection with this, the unnamed 115Å phase (Ozawa and Tachikawa, 1995a,b) is reported to have an arrangement of RSRSR·RSR·RSR.

The specimen in which we found the present material is composed of 115Å phase, sartorite, baumhauerite and baumhauerite-2a except for the present 138Å phase and dolomite. The occurrence of the present material is not clear, since it was found only after the specimen containing the present material was crushed for TEM observations. It is, however,

FIG. 2. The [010] electron diffraction pattern of the 138Å phase.

R S R S R R S R S R R S R S R R S R S R S R R

FIG. 3. The [010] high-resolution TEM image of the 138Å phase, corresponding to Fig.2.

most probable that the present phase grows with intimate relations to the 115Å phase such as the overgrowth on the latter phase, because the 115Å phase was proved to have the largest volume of the sulfosalts in the specimen and also its crystal structure proved to be closely related to that of the present phase. More details of the present phase may be revealed accompanied by the study of the 115Å phase which is now being undertaken.

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