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EFFECTS OF SULFUR-FOR-SELENIUM SUBSTITUTION ON THE STRUCTURE OF LAPHAMITE, $As_2(Se,S)_3$

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Abstract

To evaluate the effects of the S-for-Se substitution in the As_2X_3 phases (X = S, Se), the crystal structure and chemical composition of two crystals of laphamite (LAP1, LAP2) from the type locality, the Western Middle Anthracite field, Northumberland County, Pennsylvania, U.S.A., were investigated. The unit-cell parameters are: *a* 11.891(7), *b* 9.742(5), *c* 4.274(3) Å, β 90.03(4)°, *V* 495.1(5) Å^3 (LAP1) and *a* 11.934(4), *b* 9.804(4), *c* 4.268(2) Å, β 90.32(4)°, *V* 499.4(4) Å^3 (LAP2). The refinement converged to $R1$ = 5.46% (LAP1, assuming merohedral twinning) and 5.15% (LAP2). Quantitative analysis led to the chemical formulae: $(As_{1.97}Sb_{0.03})(Se_{2.28}S_{0.64}As_{0.08})$ and $(As_{1.99}Sb_{0.01})(Se_{2.25}S_{0.71}As_{0.04})$ for LAP1 and LAP2, respectively. The crystal structure of laphamite was found to be topologically identical to that of orpiment. It is based on AsX_3 pyramids linked by the sharing of X atoms to form As_2X_3 layers parallel to (010). The refinement of the site-occupancy factor in both LAP1 and LAP2 crystals indicates Se to be disordered over the three anion positions (*i.e.*, $X1$, $X2$, and $X3$), with a marked preference for the $X3$ site and, to a lesser extent, for the $X2$ site. Both *a* and *b* parameters increase linearly as a function of the ratio Se/(S + Se), whereas the *c* parameter remains substantially unchanged. No clear trend can be observed for the angle β.

Keywords: laphamite, chemical composition, structure refinement, selenium, S-for-Se substitution.

Sommaire

Afin d'évaluer les effets d'un remplacement du Se par S dans les composés de type As_2X_3 (X = S, Se), nous avons déterminé la structure cristalline et la composition chimique de deux cristaux de laphamite (LAP1, LAP2) provenant de la localité type, le champ nommé Western Middle Anthracite, comté de Northumberland, en Pennsylvanie, aux États-Unis. Les paramètres réticulaires sont: *a* 11.891(7), *b* 9.742(5), *c* 4.274(3) Å, β 90.03(4)°, *V* 495.1(5) Å^3 (LAP1) et *a* 11.934(4), *b* 9.804(4), *c* 4.268(2) Å, β 90.32(4)°, *V* 499.4(4) Å^3 (LAP2). L'affinement a convergé à un résidu $R1$ de 5.46% (LAP1, en supposant un maclage par méroédrie) et 5.15% (LAP2). Une analyse quantitative a mené aux formules chimiques $(As_{1.97}Sb_{0.03})(Se_{2.28}S_{0.64}As_{0.08})$ et $(As_{1.99}Sb_{0.01})(Se_{2.25}S_{0.71}As_{0.04})$ pour LAP1 et LAP2, respectivement. La structure cristalline de la laphamite est topologiquement identique à celle de l'orpiment. Elle contient des pyramides AsX_3 liées par partage d'atomes X pour former des couches As_2X_3 parallèles à (010). L'affinement du facteur d'occupation du site *Se* des cristaux LAP1 et LAP2 indique que le Se est désordonné aux trois positions d'anions $X1$, $X2$ et $X3$; le Se montre une préférence marquée pour le site $X3$ et, à un degré moindre, $X2$. Les paramètres *a* et *b* augmentent de façon linéaire à mesure qu'augmente le rapport Se/(S + Se), tandis que le paramètre *c* demeure à peu près inchangé. Aucun changement systématique ne semble affecter l'angle β.

(Traduit par la Rédaction)

Mots-clés: laphamite, composition chimique, affinement de la structure, sélénium, substitution de S au Se.

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INTRODUCTION

Laphamite, $As_2(Se,S)_3$, was identified as a new mineral species by Dunn *et al.* (1986) during a study of ore minerals that arose as a result of a fire in a coal waste-dump in the Western Middle Anthracite field, Northumberland County, Pennsylvania, U.S.A. On the basis of unit-cell dimensions and stoichiometry, these authors concluded that laphamite is the selenium analogue of orpiment, As_2S_3. The following unit-cell parameters were obtained from X-ray Weissenberg and precession methods: *a* 11.86(1), *b* 9.756(9), *c* 4.265(9) Å, β 90.17°, *V* 493.5 $Å^3$, *Z* = 4 (Dunn *et al.* 1986), but a full structural study was not done at that time. On the other hand, the synthetic pure As_2Se_3 (Stergiou & Rentzeperis 1985) was proven to be isostructural with orpiment (space group $P2_1/n$).

In order to account for the effects of the S-for-Se substitution in the As_2X_3 phases (X = S, Se), the crystal structure and composition of two crystals of laphamite from the type locality are investigated here.

EXPERIMENTAL AND STRUCTURE REFINEMENTS

Two small fragments (labeled LAP1 and LAP2) of the type material (sample 163039, Smithsonian Institution, Washington, U.S.A.) were selected for a study using X-ray diffraction and electron-microprobe analysis. These fragments were mounted on an automated diffractometer (Enraf Nonius, CAD4) using Mo*K*α radiation monochromatized by a flat graphite crystal. Diffraction peaks were found to exhibit very broad profiles, probably related to the foliated character of the crystals, which split easily upon the slightest mechanical manipulation. Nonetheless, all peaks found in the peak-search routine were indexed. Unit-cell parameters, determined by centering 25 reflections ($18 < 2\theta < 25°$), were: *a* 11.891(7), *b* 9.742(5), *c* 4.274(3) Å, β 90.03(4)°, *V* 495.1(5) $Å^3$ (LAP1) and *a* 11.934(4), *b* 9.804(4), *c* 4.268(2) Å, β 90.32(4)°, *V* 499.4(4) $Å^3$ (LAP2). Collected intensity-data were reduced for Lorentz-polarization effects and corrected for absorption following the semi-empirical method of North *et al.* (1968); the values of the equivalent pairs *hkl* and $h\bar{k}l$ were averaged. Systematic absences were found to be consistent with the space group $P2_1/n$. Structure refinements were performed using the program SHELXL–97 (Sheldrick 1997) starting from the atom coordinates of orpiment (Mullen & Nowacki 1972). Scattering curves for neutral species (Ibers & Hamilton 1974) were used to refine the occupancy of the Se, S site as follows: As *versus* Sb for the metal sites, and S *versus* Se for the anion sites. The refinement of the site occupancy yielded the following formulae: $As_2(Se_{2.17}S_{0.83})$ and $As_2(Se_{2.35}S_{0.65})$ for LAP1 and LAP2, respectively. By means of anisotropic full-matrix least-squares cycles, the refinement converged to $R1$ = 19.36 and 5.15% for LAP1 and LAP2, respectively. Owing to the high *R* value for the LAP1 crystal, the possibility of twinning was taken into account. Indeed, the pseudo-orthorhombic crystal lattice provides a basis for likely twinning on either {100} or {001}, or both of them. If one of those twins does occur, the high-order reflections should, in principle, be split along a plane containing **a*** and **c***. Since the deviation of β* from 90° is expected to be rather small, the splitting, approximately parallel to **a*** or **c*** (or both) due to {100} or {001} twinning (or both), respectively, may be masked, in part, by the intrinsic broadening of the peaks. However, diffraction-intensity profiles on high-order *hk*0 and 0*kl* reflections revealed a splitting into two or more subpeaks probably related to complex twinning on both {100} and {001}. The structure was then tentatively refined following the method of Pratt *et al.* (1971). In principle, this twinning should be properly described as a case of pseudomerohedry with very low obliquity. The *R* value was lowered from 19.36% to 5.46%, thus confirming the presence of twinning. The fraction of the twin components was refined as 0.36(1) and 0.64, respectively. Experimental details are given in Table 1. Fractional coordinates and anisotropic displacement parameters of atoms are shown in Table 2. A list of the observed and calculated structure-factors is available from the Depository of Unpublished Data, on the MAC website [document Laphamite CM46_269].

CHEMICAL COMPOSITION

Preliminary energy-dispersion semiquantitative analysis (EDS), performed on the same fragments of crystals used for the structural study, did not indicate elements ($Z > 9$) other than As, Sb, S and Se. The

TABLE 1. EXPERIMENTAL DETAILS OF INTENSITY-DATA COLLECTION AND STRUCTURE REFINEMENTS

	LAP1	LAP2	Dunn *et al.* *
a (Å)	11.891(7)	11.934(4)	11.86(1)
b (Å)	9.742(5)	9.804(4)	9.756(9)
c (Å)	4.274(3)	4.268(2)	4.265(9)
β (°)	90.03(4)	90.32(4)	90.17
V ($Å^3$)	495.1(5)	499.4(4)	493.5
Z	4	4	
space group	$P2_1/n$	$P2_1/n$	
wavelength	Mo*K*α	Mo*K*α	
(mA x kV)	(26 × 50)	(26 × 50)	
2θ range (°)	2 – 60	2 – 60	
crystal size (μm)	110 × 160 × 350	180 × 240 × 420	
scan mode	ω	ω	
scan width (°)	2.8	2.8	
scan speed (°/min)	2.1	2.7	
index ranges	$-16 \le h \le 16$	$-16 \le h \le 16$	
	$-13 \le h \le 13$	$-13 \le h \le 13$	
	$0 \le l \le 6$	$0 \le l \le 6$	
no. of collected reflections	3215	3250	
independent reflections	1428	1445	
reflections with $F_o > 4\sigma(F_o)$	1173	1108	
*R*1 (%)	5.46	5.15	
largest diffraction peak and hole ($e^-/Å^3$)	2.17 – 2.08	2.16 – 1.94	

* Dunn *et al.* (1986).

chemical composition was then determined using JEOL JXA 8200 (Iowa State University) and JEOL JXA 8900 (University of Minnesota) electron microprobes. The concentrations of the major and minor elements at Iowa State University were determined at an accelerating voltage of 15 kV and a beam current of 15 nA, with 10 seconds as the counting time (5 seconds on each background), whereas those at the University of Minnesota included an accelerating voltage of 15 kV and a beam current of 25 nA, with 10 seconds as the counting time (5 seconds on the background). As standards, we employed synthetic $PtSe_2$ for Se, pyrite for S, synthetic As_2S_3 for As, synthetic Sb_2S_3 for Sb (JEOL JXA 8200) and synthetic As_2Se_3 for Se and As, Se metal for Se, pyrite for S, and metallic antimony for Sb (JEOL JXA 8900). For wavelength-dispersion analyses (WDS), the following lines were used: Se$L\alpha$, As$L\alpha$, Sb$L\alpha$, and S$K\alpha$. Problems were encountered using Se metal and synthetic $PtSe_2$ as standards for Se because of fluorescence effects, which were apparent from the ZAF corrections. The problem is that Se is strongly absorbed in the system, which should not be surprising given the fact that the major elements, As and Se, are adjacent to each other in the periodic table (atomic number of 33 and 34, respectively), and that S and Se are both in the same group (VI–A). The Se metal and $PtSe_2$ standards caused an overestimation of the presence of Se due to a high absorption-correction, which in the case of the Se metal standard was ~0.7. The problem was solved by using synthetic As_2Se_3 as the standard. It is worth noting here that Dunn *et al.* (1986) also used synthetic As_2Se_3 as the standard for Se, an accelerating voltage of 15 kV, and a beam current of 25 nA. The crystal fragments studied here were found to be homogeneous within analytical uncertainty. The average chemical composition (4–7 analyses on different spots), together with ranges in concentration of elements, are reported in Table 3. On the basis of five atoms, the chemical formulae of the laphamite crystals studied here are: $(As_{1.97}Sb_{0.03})(Se_{2.28}S_{0.64}As_{0.08})$ and $(As_{1.99}Sb_{0.01})(Se_{2.25}S_{0.71}As_{0.04})$ for LAP1 and LAP2, respectively. These compositions are slightly different from that of Dunn *et al.* (1986) because laphamite analyzed here contains ~4 wt.% less As, ~6 wt.% more Se, and ~2 wt.% less S. The overall mean number of electrons calculated for the site population obtained on the basis of the chemical data (156.9 and 155.4 *apfu* for LAP1 and LAP2, respectively) is in good agreement with those from the site-occupancy refinement (153.1 and 156.3 *apfu*). It appears, therefore, that the structure of laphamite is capable of accommodating minor amounts of As on the anion positions and, to a lesser extent, Sb on metal sites. Nevertheless, the effects of such small incorporations on the structure are expected to be negligible with respect to those caused by the incorporation of large amounts of Se on the S sites. For these reasons, in the subsequent discussion, we analyze the structural variations as a function of Se alone.

REMARKS ON THE CRYSTAL CHEMISTRY

The crystal structure of laphamite is topologically identical to that of orpiment (Mullen & Nowacki 1972). It is based on AsX_3 pyramids linked by sharing *X* atoms

TABLE 2. FRACTIONAL COORDINATES AND ANISOTROPIC DISPLACEMENT PARAMETERS OF ATOMS IN LAPHAMITE

site	*population*	*x/a*	*y/b*	*z/c*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
					LAP1						
As1	1.00 As	0.2667(1)	0.1951(2)	0.8775(4)	0.0181(6)	0.0361(9)	0.0237(8)	-0.0016(5)	-0.0025(5)	0.0035(8)	0.0260(4)
As2	1.00 As	0.4895(1)	0.3239(2)	0.3735(4)	0.0169(5)	0.0345(8)	0.0221(7)	-0.0008(5)	-0.0001(5)	-0.0009(7)	0.0245(4)
*X*1	0.42(1) S + 0.58 Se	0.4032(1)	0.1192(2)	0.5209(5)	0.0208(9)	0.038(1)	0.030(1)	0.0006(7)	-0.0003(7)	0.0001(9)	0.0296(6)
*X*2	0.26(1) S + 0.74 Se	0.3472(1)	0.4092(2)	0.0210(5)	0.0208(8)	0.036(1)	0.0261(9)	0.0018(6)	-0.0033(6)	0.0013(8)	0.0276(6)
*X*3	0.15(2) S + 0.85 Se	0.1232(1)	0.3000(2)	0.5501(4)	0.0156(6)	0.039(1)	0.0225(7)	0.0010(5)	-0.0032(6)	0.0007(7)	0.0256(5)
					LAP2						
As1	1.00 As	0.26596(6)	0.1955(1)	0.8799(2)	0.0150(3)	0.0218(5)	0.0180(4)	-0.0013(3)	-0.0010(3)	0.0015(4)	0.0183(2)
As2	1.00 As	0.48961(6)	0.3243(1)	0.3764(2)	0.0146(3)	0.0215(5)	0.0183(4)	-0.0007(3)	-0.0002(2)	-0.0013(4)	0.0182(2)
*X*1	0.37(1) S + 0.63 Se	0.40305(7)	0.1185(1)	0.5225(2)	0.0159(4)	0.0224(7)	0.0220(6)	0.0011(4)	0.0021(3)	-0.0002(5)	0.0201(3)
*X*2	0.19(1) S + 0.81 Se	0.34742(7)	0.4097(1)	0.0227(2)	0.0188(4)	0.0189(6)	0.0225(5)	0.0017(3)	-0.0026(3)	0.0007(4)	0.0201(3)
*X*3	0.09(1) S + 0.91 Se	0.12264(6)	0.2997(1)	0.5515(2)	0.0136(4)	0.0253(6)	0.0187(4)	0.0001(3)	0.0010(3)	0.0011(4)	0.0192(3)

TABLE 3. COMPOSITION OF LAPHAMITE

	wt.%	range	σ (%)	atom ratios
		LAP1		
As	43.05	42.35 – 43.51	0.51	2.05
Sb	0.94	0.82 – 1.05	0.12	0.03
S	5.76	5.16 – 5.98	0.40	0.64
Se	50.38	49.47 – 52.13	1.19	2.28
total	100.13	99.33 – 101.63	1.07	
		LAP2		
As	43.48	42.52 – 44.19	0.61	2.04
Sb	0.33	0.20 – 0.60	0.14	0.01
S	6.47	5.00 – 7.26	0.81	0.71
Se	50.51	49.23 – 52.24	1.11	2.25
total	100.79	100.26 – 101.72	0.58	

Results of electron-microprobe analyses. The proportion of atoms is calculated on the basis of five atoms per formula unit.

to form As_2X_3 layers (Fig. 1) parallel to (010). The layers, separated by interspaces due to pairs of lone electrons, are connected by weak interactions only. As with orpiment, the layered nature of the structure gives rise to a perfect {010} cleavage. The As–*X* bond distances within the layer range from 2.331(3) to 2.438(1) Å. Two long distances ranging from 3.273(3) to 3.513(5) Å complete the As coordination as an irregular AsX_5 square–pyramid having the two long distances in the bases of the pyramid. Additional long distances occur between atoms belonging to adjacent layers (As1–*X*2 = 3.534 and As2–*X*2 = 3.677 Å).

The refinement of the site-occupancy factor in both LAP1 and LAP2 crystals indicated Se to be disordered among the three anion positions (*i.e.*, *X*1, *X*2, and *X*3), with a marked preference for the *X*3 site and, to a lesser extent, for the *X*2 site. This preference is clearly driven by an intrinsic difference in the anion environment (mean $<^{II}X–As>$ distance increasing from *X*1, through *X*2, to *X*3; Table 4), which occurs even in the pure compounds. In orpiment, the mean $<^{II}X–As>$ distance is 2.268, 2.282, and 2.298 Å for *X*1, *X*2 and *X*3, respectively (Mullen & Nowacki 1972); the homologous values in the structure of the synthetic As_2Se_3 are 2.403, 2.425, and 2.446 Å (Stergiou & Rentzeperis 1985).

As shown in Figure 2, the incorporation of Se at the *X* sites causes an increase of the $<^{II}X–As>$ distance and an anisotropic expansion of the unit-cell volume. Both the *a* and *b* parameters increase linearly, whereas the *c* parameter remains substantially unchanged (Fig. 3). No clear trend can be observed in the β angle, which appears to be unrelated to the Se content. Moreover, the value close to 90° that was measured for LAP1 (open triangle in Fig. 3) should not be considered significant with complete confidence, owing to the presence of twinning.

The pronounced increase of the *a* parameter as a function of Se content is mainly related to the pref-

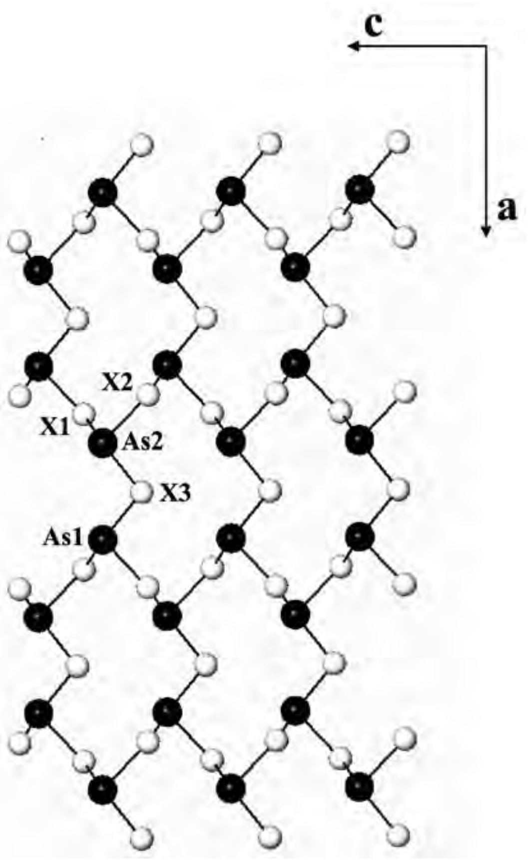

FIG. 1. Linkage of AsX_3 pyramids into a layer parallel to (010) in the structure of laphamite. The As and *X* atoms are pictured in black and white, respectively. The orientation of the structure is outlined.

TABLE 4. BOND DISTANCES (Å) AND ANGLES (°) FOR LAPHAMITE

LAP1				LAP2			
As1 -		*X*1	2.347(3)	As1 -		*X*1	2.366(2)
		*X*2	2.375(3)			*X*2	2.392(2)
		*X*3	2.431(2)			*X*3	2.430(1)
As2 -		*X*1	2.331(3)	As2 -		*X*1	2.353(2)
		*X*2	2.413(2)			*X*2	2.415(2)
		*X*3	2.429(2)			*X*3	2.438(1)
*X*1 -	As1 -	*X*2	99.55(8)	*X*1 -	As1 -	*X*2	99.37(5)
*X*1 -	As1 -	*X*3	104.1 (1)	*X*1 -	As1 -	*X*3	104.44(5)
*X*2 -	As1 -	*X*3	93.56(8)	*X*2 -	As1 -	*X*3	93.52(5)
*X*1 -	As2 -	*X*2	98.88(8)	*X*1 -	As2 -	*X*2	98.92(5)
*X*1 -	As2 -	*X*3	90.97(9)	*X*1 -	As2 -	*X*3	90.66(5)
*X*2 -	As2 -	*X*3	105.96(9)	*X*2 -	As2 -	*X*3	105.95(5)
As1 -		*X*1	3.277(3)	As1 -		*X*1	3.273(3)
		*X*3	3.496(4)			*X*3	3.496(3)
As2 -		*X*2	3.349(4)	As2 -		*X*2	3.352(4)
		*X*3	3.513(5)			*X*3	3.499(4)

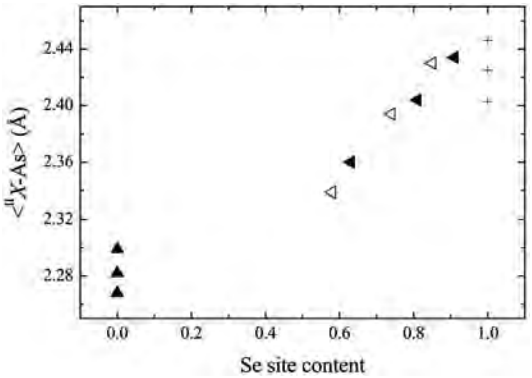

FIG. 2. The mean ^{II}X–As bond distance (X = S, Se) is plotted against the Se content in the X sites in the structure of orpiment (filled upward triangles; Mullen & Nowacki 1972), laphamite LAP1 and LAP2 crystals (open and filled leftward triangles, respectively; this study), and synthetic As_2Se_3 (filled circles; Stergiou & Rentzeperis 1985).

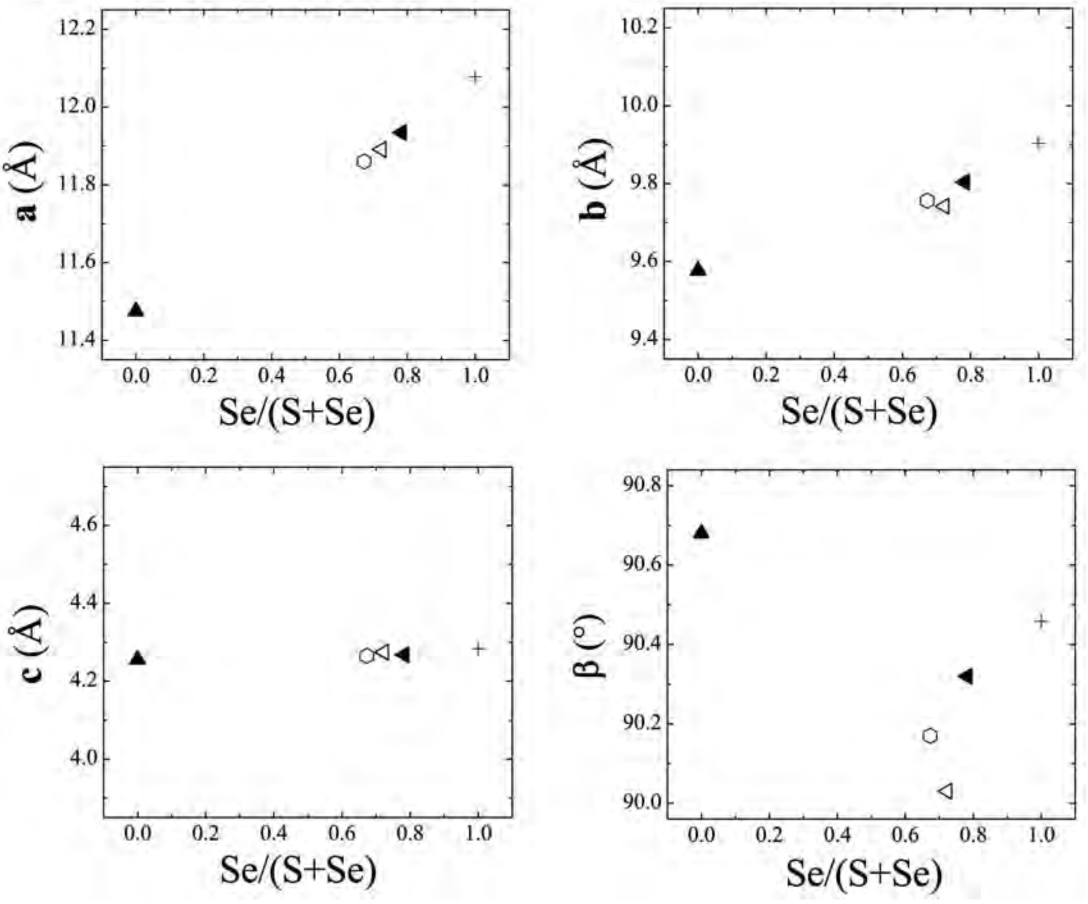

FIG. 3. Variation of the unit-cell parameters plotted against the molar ratio Se/(S + Se) along the join As_2S_3 – As_2Se_3. Symbols: filled upward triangle: orpiment (Mullen & Nowacki 1972), open and filled leftward triangles: laphamite crystals LAP1 and LAP2, respectively (this study); open circle: laphamite, original description (Dunn *et al.* 1986); filled circle: synthetic As_2Se_3 (Stergiou & Rentzeperis 1985).

erential incorporation of Se at *X*3, which causes an increase in the length of both As1–*X*3 and As2–*X*3. As a consequence, the intralayer As1–As2 distance, which is aligned along [100], increases from 3.191 to 3.324 Å along the join As_2S_3–As_2Se_3. The increase in the *b* parameter is mainly related to the lengthening of the shortest bond-distance between the sheets (*i.e.,* As1–*X*2), which ranges from 3.475 Å in orpiment, through 3.534 and 3.551 Å (LAP1 and LAP2), to 3.596 Å in synthetic As_2Se_3. Values of eccentricity, *i.e.*, the distance from centroid to central atom as defined by Balić-Žunić & Makovicky (1996), were calculated by means of the program IVTON (Balić-Žunić & Vickovic 1996) for the As1 and As2 polyhedra; eccentricity values decrease from orpiment (1.036–1.112 Å), through laphamite (0.985–1.067 and 0.930–1.039 Å for LAP1 and LAP2, respectively), to synthetic As_2Se_3 (0.907–1.018 Å). This decrease indicates a reduction in the stereochemical activity of As with increasing amounts of substitution of Se for S.

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