International Geology Review
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tigr20

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Version of record first published: 06 Aug 2010.

To cite this article: Jiajun Liu, Jianming Liu, Jiuling Li, Hui Xie, Jianping Wang, Jun Deng, Caixia Feng, Feng Qi & Nai Zhang (2008): Experimental Synthesis of the Stibnite-Antimonselite Solid Solution Series, International Geology Review, 50:2, 163-176

To link to this article: http://dx.doi.org/10.2747/0020-6814.50.2.163

International Geology Review, Vol. 50, 2008, p. 163–176. DOI: 10.2747/0020-6814.50.2.163

Experimental Synthesis of the Stibnite-Antimonselite Solid Solution Series

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Abstract

Experiments on the Sb-S-Se system were conducted at 300°C, and a continuous stibnite-antimonselite binary solid solution was established. By substituting S for Se, the compositions of S-rich and Se-rich endmembers were confirmed as Sb_2S_3 and Sb_2Se_3, respectively. Based on Se/(S+Se) ratios of microprobe analyses, binary stibnite-antimonselite solid solutions are defined as stibnite, selenium stibnite, sulfur antimonselite, and antimonselite. Microhardness of the stibnite subseries (Sb = 60.11–72.58, S = 13.20–27.63, and Se = 0.00–27.23 wt%) and the antimonselite subseries (Sb = 49.29–59.25, Se = 28.89–51.94, S = 0.00–12.10 wt%) varies from 112.95 to 127.72 kg/mm^2. The variation of Se concentration is continuous throughout the series, confirming a random substitution of Se for S. Crystallographic parameters obtained from the series vary as follows: a = 1.123375–1.163890 nm, b = 1.132502–1.179553 nm, c = 0.383914–0.398071 nm, D = 4.593–5.896 g·cm^{-3}, and V = 0.488425–0.546500 nm^3. As evident from the above data, the higher the Se concentration, the larger the crystallographic parameters. The Sb-S-Se binary solid solutions obey Vegard's law.

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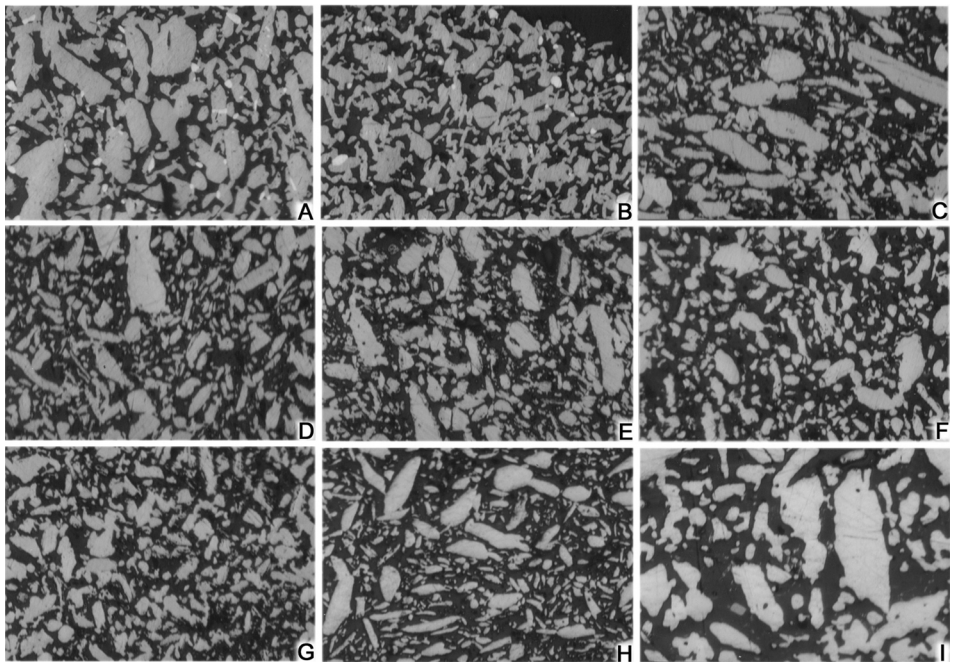

FIG. 1. Photomicrographs of synthesized phases in the stibnite-antimonselite solid solution series. All photomicrographs are in reflected light. Diagonal length of view is 1.52 mm. The small amount of brilliant white minerals in A and B are native stibnite; all the other white color minerals belong to solid solution series. A. Sb_2S_3. B. Sb_2Se_3. C. Sb_2S_3. D. $Sb_2(S_{2.5},Se_{0.5})_3$. E. $Sb_2(S_{2.0},Se_{1.0})_3$. F. $Sb_2(S_{1.5},Se_{1.5})_3$. G. $Sb_2(S_{1.0},Se_{2.0})_3$. H. $Sb_2(S_{0.5},Se_{2.5})_3$. I. Sb_2Se_3.

Introduction

IN NATURE, the substitution between antimony and bismuth forms a continuous stibnite-bismuthinite solid solution series (Li et al., 1998; Arun and Vedeshwar, 2004). Does substitution between sulfur and selenium result in a continuous stibnite-antimonselite solid solution series? This is a new subject (Liu et al., 1999, 2005).

It is well known that stibnite, Sb_2S_3, is a very common mineral. In contrast, antimonselite, Sb_2Se_3, is a new mineral found in several different localities in China in the last decade (Liu et al., 1992; Chen et al., 1993; Min et al., 1994, 1995, 1998). Also, as has been well confirmed, antimonselite, stibnite, and bismuthinite are isostructural (Hofmann, 1933; Scavnicar, 1960; Bayliss and Nowachki, 1972; Voutsas and Rentzeperis, 1984).

A series of transition minerals between stibnite and antimonselite have been discovered by the authors in Cambrian stratabound gold deposits at La'erma and Qiongmo in the western Qinling Mountains, China (Liu and Zheng, 1992; Liu, 1994; Liu et al., 1998, 1999, 2005). They were classified as a stibnite-antimonselite series (Liu and Zheng, 1992; Liu et al., 1999; Liu et al., 2005). Stibnite and antimonselite are the two end members of the series, respectively.

According to the "50% rule" of binary solid solution systems (Nickel and Grice, 2000), this series was divided into stibnite and antimonselite subseries. Furthermore, this binary system of stibnite-antimonselite can further be divided into stibnite, selenium stibnite, sulfur antimonselite, and antimonselite, based on atomic ratios of Se/(S+Se) (Liu et al., 1999; Liu et al., 2005). The limiting atomic ratios of Se/(S+Se) are <0.20, $0.20–<0.50$, $0.50–<0.80$, and ≥ 0.80, respectively.

Although the content of selenium ranges from 0.00% to 49.72% in the natural stibnite-antimonselite series, it is lack of data from 30.59% to 43.04% that puzzled the present authors (Liu et al., 1999, 2005). Apparently the variation of Se is not completely continuous in the series. Because of the extremely small size of minerals in the stibnite-antimonselite series, it is difficult to conduct research

TABLE 1. Investigated Chemical Compositions in the Sb_2S_3–Sb_2Se_3 Synthetic System

Sample no.	Ideal formulae	Desired proportion of chemical composition, g				
		Sb	S	Se	Sb_2S_3	Sb_2Se_3
99L01	Sb_2S_3	0.624	0.25			
99L02	Sb_2Se_3	0.447		0.43		
99L03-1	Sb_2S_3	0.669	0.26			
99L03-2	Sb_2S_3	0.621	0.25			
99L04-1	Sb_2Se_3	0.434		0.42		
99L04-2	Sb_2Se_3	0.456		0.44		
99L05-1	Sb_2S_3	0.651	0.26			
99L05-2	Sb_2S_3	0.619	0.24			
99L06-1	Sb_2Se_3	0.444		0.43		
99L06-2	Sb_2Se_3	0.481		0.47		
99L07	Sb_2Se_3	0.306		0.3		
99L011	Sb_2S_3	0.59	0.23			
99L012	Sb_2Se_3	0.35		0.34		
99L1	$Sb_2(S_{1.5},Se_{1.5})_3$				0.2125 (99L01)	0.3005 (99L02)
99L2	$Sb_2(S_{1.0},Se_{2.0})_3$				0.1411 (99L01)	0.3991 (99L02)
99L3	$Sb_2(S_{2.0},Se_{1.0})_3$				0.2616 (99L03-1)	0.1850 (99L04-1)
99L4	$Sb_2(S_{2.5},Se_{0.5})_3$				0.3836 (99L03-1)	0.1085 (99L04-1)
99L5	$Sb_2(S_{0.5},Se_{2.5})_3$				0.0571 (99L03-1)	0.4038 (99L04-1)
99L6	$Sb_2(S_{1.0},Se_{2.0})_3$				0.1409 (99L03-2)	0.3985 (99L04-2)
99L7	$Sb_2(S_{1.5},Se_{1.5})_3$				0.0892 (99L03-2)	0.1262 (99L04-2)
99L8	$Sb_2(S_{2.0},Se_{1.0})_3$				0.1470 (99L03-2)	0.1040 (99L04-2)
99L9	$Sb_2(S_{1.0},Se_{2.0})_3$				0.0796 (99L03-2)	0.2253 (99L04-2)
99L11	$Sb_2(S_{1.5},Se_{1.5})_3$				0.2210 (99L05-1)	0.3126 (99L06-1)
99L12	$Sb_2(S_{2.0},Se_{1.0})_3$				0.3052 (99L05-1)	0.2158 (99L06-1)
99L13	$Sb_2(S_{2.5},Se_{0.5})_3$				0.3571 (99L05-1)	0.1010 (99L06-1)
99L14	$Sb_2(S_{1.0},Se_{2.0})_3$				0.0795 (99L05-2)	0.2250 (99L06-2)
99L15	$Sb_2(S_{2.0},Se_{1.0})_3$	0.39	0.1	0.13		
99L16	$Sb_2(S_{2.75},Se_{0.25})_3$				0.4947 (99L05-2)	0.0636 (99L06-2)
99L17	$Sb_2(S_{1.3},Se_{1.7})_3$				0.1740 (99L011)	0.3217 (99L06-2)
99L18	$Sb_2(S_{0.8},Se_{2.2})_3$				0.1005 (99L011)	0.3910 (99L07)
99L19	$Sb_2(S_{0.05},Se_{2.95})_3$				0.0048 (99L011)	0.4002 (99L012)

adequately. At present, the following problems need to be addressed (Liu et al., 1999):

1. The variation of Se (43.04%–49.72%) in the antimonselite subseries is less continuous in comparison with that (0.00%–29.12%) of the stibnite subseries. Does selenium vary continuously throughout the entire series? Is the substitution of Se for S ordered or disordered? Is the series a complete solid solution or only restricted to certain proportions?

2. It is necessary to establish the relationship between Se concentration and crystallographic parameters for different Se concentrations in the stibnite-antimonselite series, so as to confirm the existence of a complete solid solution system? Because Sb_2S_3 and Sb_2Se_3 crystallize in the same structural type (Hofmann, 1933; Scavnicar, 1960;

TABLE 2. Electron Microprobe Analyses and Chemical Formulae of the Synthetic Stibnite-Antimonselite Solid Solution Series

Sample no.	Ideal formulae	Sb	S	Se	Total	Chemical formulae
99L01	Sb_2S_3	69.27	27.63	0	96.9	$Sb_{1.98}S_{3.00}$
		71.84	27.42	0	99.26	$Sb_{2.07}S_{3.00}$
		71.60	27.29	0	98.89	$Sb_{2.07}S_{3.00}$
		71.81	27.25	0	99.06	$Sb_{2.08}S_{3.00}$
		71.56	27.23	0	98.79	$Sb_{2.08}S_{3.00}$
		71.40	27.12	0	98.52	$Sb_{2.08}S_{3.00}$
		72.58	26.98	0	99.56	$Sb_{2.13}S_{3.00}$
99L05		71.47	26.21	0	97.68	$Sb_{2.16}S_{3.00}$
		71.64	27.11	0	98.75	$Sb_{2.09}S_{3.00}$
		71.98	26.47	0	98.45	$Sb_{2.15}S_{3.00}$
		71.40	26.05	0	97.45	$Sb_{2.16}S_{3.00}$
99L16	$Sb_2(S_{2.75}, Se_{0.25})_3$	70.55	25.33	4.37	100.25	$Sb_{2.06}(S_{2.80}, Se_{0.20})_{3.00}$
		69.92	25.01	5.37	100.30	$Sb_{2.03}(S_{2.76}, Se_{0.24})_{3.00}$
		68.99	24.85	7.55	101.39	$Sb_{1.95}(S_{2.67}, Se_{0.33})_{3.00}$
99L4	$Sb_2(S_{2.5},Se_{0.5})_3$	68.06	22.54	8.30	98.90	$Sb_{2.08}(S_{2.61}, Se_{0.39})_{3.00}$
		68.17	22.97	10.64	101.78	$Sb_{1.97}(S_{2.52}, Se_{0.48})_{3.00}$
		68.40	22.99	10.70	102.09	$Sb_{1.98}(S_{2.52}, Se_{0.48})_{3.00}$
		67.65	22.15	11.72	101.52	$Sb_{1.99}(S_{2.47}, Se_{0.53})_{3.00}$
		68.05	22.03	12.13	102.21	$Sb_{1.99}(S_{2.45}, Se_{0.55})_{3.00}$
		68.23	20.30	11.46	99.99	$Sb_{2.16}(S_{2.44}, Se_{0.56})_{3.00}$
		67.17	20.98	12.74	100.89	$Sb_{2.03}(S_{2.41}, Se_{0.59})_{3.00}$
		66.05	20.52	12.46	99.03	$Sb_{2.04}(S_{2.41}, Se_{0.59})_{3.00}$
		66.97	20.73	12.81	100.51	$Sb_{2.04}(S_{2.40}, Se_{0.60})_{3.00}$
99L13		70.55	18.39	12.35	101.29	$Sb_{2.38}(S_{2.36}, Se_{0.64})_{3.00}$
		66.05	20.29	13.80	100.14	$Sb_{2.02}(S_{2.35}, Se_{0.65})_{3.00}$
99L3	$Sb_2(S_{2.0},Se_{1.0})_3$	65.37	18.45	18.11	101.93	$Sb_{2.00}(S_{2.15}, Se_{0.85})_{3.00}$
		64.22	17.11	18.79	100.12	$Sb_{2.05}(S_{2.08}, Se_{0.92})_{3.00}$
		62.03	15.86	21.63	99.52	$Sb_{1.99}(S_{1.93}, Se_{1.07})_{3.00}$
		62.23	15.51	22.27	100.01	$Sb_{2.00}(S_{1.90}, Se_{1.10})_{3.00}$
		62.88	15.83	22.83	101.54	$Sb_{1.98}(S_{1.89}, Se_{1.11})_{3.00}$
		60.40	15.19	22.76	98.35	$Sb_{1.95}(S_{1.87}, Se_{1.13})_{3.00}$
		61.81	15.23	23.46	100.50	$Sb_{1.97}(S_{1.86}, Se_{1.14})_{3.00}$
99L15		61.66	14.91	23.39	99.96	$Sb_{2.00}(S_{1.83}, Se_{1.17})_{3.00}$
		62.64	14.98	23.59	101.21	$Sb_{2.01}(S_{1.83}, Se_{1.17})_{3.00}$
		61.13	14.55	23.11	98.79	$Sb_{2.02}(S_{1.83}, Se_{1.17})_{3.00}$
99L1	$Sb_2(S_{1.5},Se_{1.5})_3$	60.11	13.20	27.23	100.54	$Sb_{1.98}(S_{1.63}, Se_{1.37})_{3.00}$
		59.25	12.10	30.05	101.40	$Sb_{1.93}(S_{1.49}, Se_{1.51})_{3.00}$
		57.33	11.46	30.33	99.12	$Sb_{1.90}(S_{1.45}, Se_{1.55})_{3.00}$
		58.41	11.34	30.91	100.66	$Sb_{1.93}(S_{1.42}, Se_{1.58})_{3.00}$
99L7		56.15	10.59	28.89	95.63	$Sb_{1.99}(S_{1.42}, Se_{1.58})_{3.00}$
		57.76	11.16	31.6	100.52	$Sb_{1.90}(S_{1.40}, Se_{1.60})_{3.00}$
		57.34	10.93	31.21	99.48	$Sb_{1.92}(S_{1.39}, Se_{1.61})_{3.00}$
		59.22	11.18	32.08	102.48	$Sb_{1.93}(S_{1.39}, Se_{1.61})_{3.00}$
		59.12	10.98	31.74	101.84	$Sb_{1.96}(S_{1.38}, Se_{1.62})_{3.00}$

Table continues

TABLE 2. *Continued*

Sample no.	Ideal formulae	Sb	S	Se	Total	Chemical formulae
	$Sb_2(S_{1.5},Se_{1.5})_3$ (*cont.*)	58.65	10.48	31.48	100.61	$Sb_{1.99}(S_{1.35}, Se_{1.65})_{3.00}$
		57.83	10.58	32.42	100.83	$Sb_{1.92}(S_{1.34}, Se_{1.66})_{3.00}$
99L17	$Sb_2(S_{1.3},Se_{1.7})_3$	57.32	10.30	33.04	100.66	$Sb_{1.91}(S_{1.30}, Se_{1.70})_{3.00}$
		58.61	10.43	33.60	102.64	$Sb_{1.92}(S_{1.30}, Se_{1.70})_{3.00}$
		58.49	9.99	33.92	102.40	$Sb_{1.94}(S_{1.26}, Se_{1.74})_{3.00}$
		55.34	8.06	37.38	100.78	$Sb_{1.88}(S_{1.04}, Se_{1.96})_{3.00}$
99L2	$Sb_2(S_{1.0},Se_{2.0})_3$	55.14	7.44	37.24	99.82	$Sb_{1.93}(S_{0.99}, Se_{2.01})_{3.00}$
		55.30	7.04	39.45	101.79	$Sb_{1.90}(S_{0.92}, Se_{2.08})_{3.00}$
99L6	$Sb_2(S_{1.0},Se_{2.0})_3$	58.45	8.17	35.77	102.39	$Sb_{2.03}(S_{1.08}, Se_{1.92})_{3.00}$
		55.70	6.69	39.08	101.47	$Sb_{1.95}(S_{0.89}, Se_{2.11})_{3.00}$
		53.97	6.55	38.85	99.37	$Sb_{1.91}(S_{0.88}, Se_{2.12})_{3.00}$
		53.09	6.64	39.61	99.34	$Sb_{1.85}(S_{0.88}, Se_{2.12})_{3.00}$
		54.41	6.39	39.58	100.38	$Sb_{1.91}(S_{0.85}, Se_{2.15})_{3.00}$
		55.48	6.51	40.37	102.36	$Sb_{1.91}(S_{0.85}, Se_{2.15})_{3.00}$
		54.82	6.38	40.52	101.72	$Sb_{1.90}(S_{0.84}, Se_{2.16})_{3.00}$
99L18	$Sb_2(S_{0.8},Se_{2.2})_3$	55.53	6.27	39.99	101.79	$Sb_{1.95}(S_{0.84}, Se_{2.16})_{3.00}$
		55.32	6.35	40.86	102.53	$Sb_{1.91}(S_{0.83}, Se_{2.17})_{3.00}$
		54.94	6.18	40.61	101.73	$Sb_{1.92}(S_{0.82}, Se_{2.18})_{3.00}$
		53.47	5.00	42.02	100.49	$Sb_{1.92}(S_{0.68}, Se_{2.32})_{3.00}$
		52.91	4.87	41.41	99.19	$Sb_{1.93}(S_{0.67}, Se_{2.33})_{3.00}$
		54.64	4.47	43.45	102.56	$Sb_{1.95}(S_{0.61}, Se_{2.39})_{3.00}$
		52.67	4.02	43.64	100.33	$Sb_{1.91}(S_{0.56}, Se_{2.44})_{3.00}$
99L5	$Sb_2(S_{0.5},Se_{2.5})_3$	51.96	2.43	47.00	101.39	$Sb_{1.91}(S_{0.34}, Se_{2.66})_{3.00}$
		51.92	2.28	47.62	101.82	$Sb_{1.90}(S_{0.32}, Se_{2.68})_{3.00}$
		49.80	0.41	50.80	101.01	$Sb_{1.87}(S_{0.06}, Se_{2.94})_{3.00}$
		49.51	0.40	50.05	99.96	$Sb_{1.89}(S_{0.06}, Se_{2.94})_{3.00}$
99L19	$Sb_2(S_{0.05},Se_{2.95})_3$	50.12	0.38	50.48	100.98	$Sb_{1.90}(S_{0.06}, Se_{2.94})_{3.00}$
		49.29	0.31	51.53	101.13	$Sb_{1.83}(S_{0.04}, Se_{2.96})_{3.00}$
		49.93	0.26	50.71	100.90	$Sb_{1.89}(S_{0.04}, Se_{2.96})_{3.00}$
		49.37	0	51.17	100.54	$Sb_{1.88}Se_{3.00}$
		49.78	0	51.44	101.22	$Sb_{1.88}Se_{3.00}$
99L02	Sb_2Se_3	49.95	0	51.22	101.17	$Sb_{1.90}Se_{3.00}$
		49.31	0	51.94	101.25	$Sb_{1.85}Se_{3.00}$
		50.05	0	51.55	101.60	$Sb_{1.89}Se_{3.00}$
		49.89	0	51.72	101.61	$Sb_{1.88}Se_{3.00}$

Bayliss et al., 1972; Voutsas and Rentzeperis, 1984), formation of a continuous series of solid solutions would be expected.

In this study, we examined the possibility of formation of solid solutions, with the composition $Sb_2(S_{3-x}, Se_x)_3$, by isovalent substitution of Se^{2+} for S^{2+}. The x value was varied from 0 to 3 with a step of 0.5.

Experimental Methods

The sulfide and selenide syntheses were performed under dry experiment conditions by the conventional evacuated silica tube technique (Qian and Gunter, 1994; Li et al., 1998; Qi, 2001). The Sb_2S_3 and Sb_2S_3 series was prepared from presynthesized Sb_2S_3 and Sb_2S_3. The starting chemicals used were high-purity antimony powder, selenium powder, and sublimed sulfur, with a purity grade of 99.999% or 99.99%, respectively. We mixed Sb and S, and Sb and Se, respectively, in a molar ratio of 2:3 in a glove box under purified argon gas. The mixtures of stoichiometric amounts of the initial reagents (Table 1) were filled in a one-sided closed tube made from pure silica. The open end of the silica tube was sealed by arc welding under a purified argon atmosphere, and then heated to 300°C with a gradient of 50°C per hour in the tube furnace. The sample was kept for 72–120 hours under these conditions before the power was switched off and the

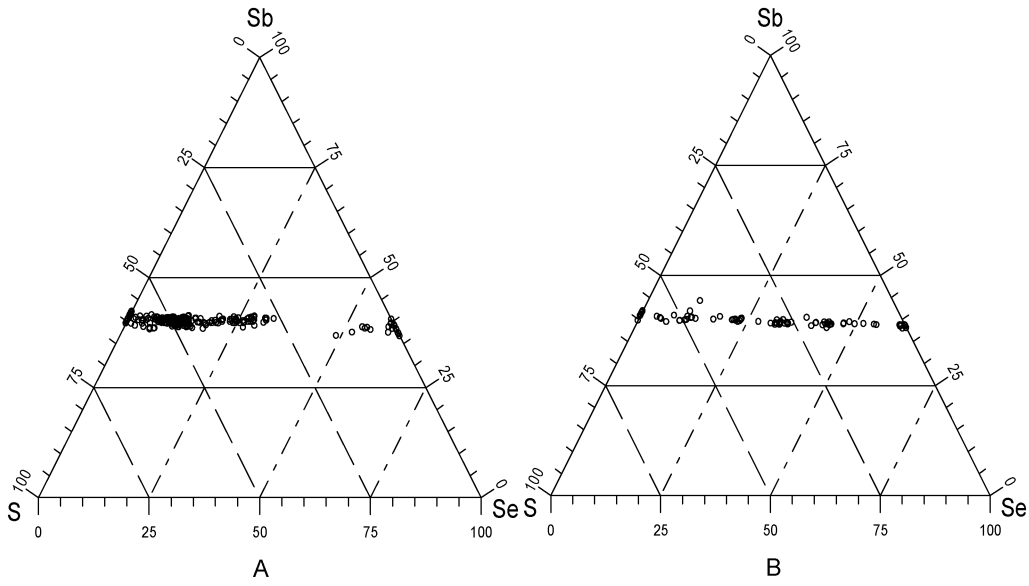

FIG. 2. Comparison of Se concentrations in the stibnite-antimonselite solid solution series between natural (A) and synthetic (B) phases. A. From La'erma-Qiongmo Au-Se deposit. B. From laboratory synthesis.

sample was allowed to cool to room temperature. After cooling, the product was taken out from the sealed silica tube, and was ground in an agate mortar under acetone in order to prevent oxidation. The mixture was again sealed in an evacuated silica tube and was reheated at a specified temperature for about 48–72 h. In order to let the solid chemical reaction reach the balanced reactive state, and to avoid the persistence of reactive materials (Figs. 1A and 1B), repeated grinding and reaction were carried out 3–4 times.

Then synthetic Sb_2S_3 and Sb_2Se_3 were weighted out and mixed in the desired proportions (Table 1). Using the same method mentioned above, various members of the stibnite-antimonselite solid solution were synthesized. Finally, the phase composition of the compounds studied and the attainment of equilibrium were examined and monitored by reflected-light microscope (Fig. 1), electron microprobe (Tables 2 and Fig. 2), and X-ray power diffraction methods (Table 3 and Fig. 3).

Results and Discussion

Physical and optical properties

Synthetic stibnite-antimonselite solid solution is lead grey in color with metallic luster, and is somewhat brittle in tenacity. Its crystal habit is acicular to anhedral granular and crystals are highly variable in size (generally 0.1–3 mm, maximum 7 mm) (Fig. 1). The transitional minerals among the stibnite-antimonselite solid solution series show no differences in their appearance. Microhardness of 25 grains of stibnite-antimonselite solid solution series ranges from 112.95 to 127.72 kg/mm^2, averaging 117.37 kg/mm^2 (for 50 g load), corresponding to a hardness of 3.30 on the Mohs scale.

Under reflected light, they are bright white to greyish white, with a yellowish tint (Fig. 1), showing strong bireflection, anisotropism, and polychroism. However, their reflectivities are a little lower than that of natural stibnite and antimonselite.

Chemical composition

Electron microprobe analysis of the synthetic stibnite-antimonselite solid solution series was performed at the Institute of Geology and Geophysics, Chinese Academy of Sciences. The apparatus used was a CAMEBEX-SX51, and the operating conditions were: accelerating voltage 15kV, probe current 20nA, electron-beam diameter 3 μm; standards: pyrite(S), native selenium(Se), InSb(Sb); ZAF correction.

The analytical results are shown in Table 2. The concentration ranges of major elements are Sb:

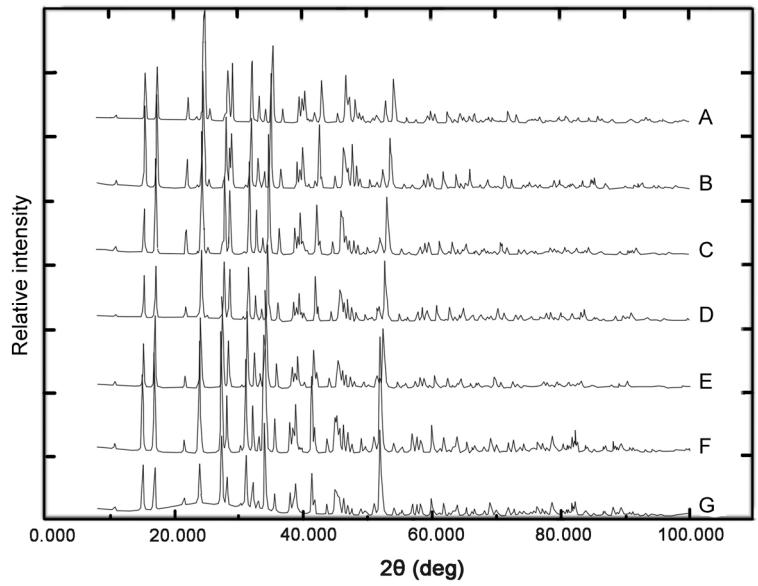

FIG. 3. X-ray powder patterns of synthetic members of the stibnite-antimonselite solid solution series. A. Sb_2S_3. B. $Sb_2(S_{2.5},Se_{0.5})_3$. C. $Sb_2(S_{2.0},Se_{1.0})_3$. D. $Sb_2(S_{1.5},Se_{1.5})_3$. E. $Sb_2(S_{1.0},Se_{2.0})_3$. F. $Sb_2(S_{0.5},Se_{2.5})_3$. G. Sb_2Se_3.

60.11–72.58 wt%, S: 13.20–27.63 wt%, Se: 0.00–27.23 wt% in the stibnite subseries. It is implicit that 0–50% of sulfur in stibnite subseries can be replaced isomorphically by selenium. The antimonselite subseries contains 49.29–59.25 wt% Sb, 30.05–51.94 wt% Se, and 0.00–12.10 wt% S. It is also implicit that 0~50% of selenium in the antimonselite subseries can be replaced isomorphically by sulfur. Therefore, the variation in Se content in the synthetic stibnite-antimonselite solid solution series is continuous. These were compared with the compositions of selenium-bearing stibnite, selenium stibnite, sulfur antimonselite, and sulfur-bearing antimonselite that were studied by the authors (Liu et al., 1998, 1999, 2005) in the La'erma-Qiongmo Au-Se deposit. Figure 2 shows that the Se contents in the synthetic series vary continuously and establishes a complete stibnite-antimonselite solid solution series. Based on the chemical components of microprobe analyses (Table 2) the formula of stibnite-antimonselite solid solution series can be written as $Sb_2(S_{3-x}, Se_x)_{3.00}$ ($0 \le X \le 3$).

X-ray powder diffraction analysis

The samples obtained were characterized by X-ray powder diffraction (XRD). The XRD analysis was carried out with a Japan Rigaku D/max-γ rotation anode X-ray energy diffractometer, using Ni-filtered Cu*K*a radiation (λ = 0.15418 nm), graphite monochromator, acceleration voltage of 40 kV, pipe current of 100 mA, continuous scanning rate 8°/min, slit DS = SS = 1°, RS = 0.15 mm, scanning model with 2θ/θ coupling. A scanning rate of 2°/min, step 0.02°, was used to record the patterns in the 2θ range 8°–100°. The obtained data were processed by powder data processing system in an HP computer work station. XRD measurement was undertaken at the X-ray Powder Diffraction Laboratory, Institute of Geology and Geophysics, Chinese Academy of Sciences.The X-ray diffraction patterns of the compounds obtained (see Table 3 and Fig. 3) are similar in the positions and relative intensities of the reflections. The X-ray powder patterns of the intermediate phases were indexed using X-ray data for Sb_2S_3 (orthorhombic crystal system, space group Pbnm) (Scavnicar, 1960; Bayliss et al., 1972) on the assumption that these phases are isostructural. The unit cell parameters were refined by the least squares method in the range of angles 2θ 10°–100°, using the LATTIC software. The results are listed in Table 4. The unit cell parameters of the stibnite end member are in substantial agreement with the theoretical value of stibnite (a = 1.1229 nm, b = 1.1310 nm, c = 0.3839 nm; JCPDS, 1967; Hurlbut et al., 1977). The unit cell parameter of the antimonselite

TABLE 3. X-Ray Powder Diffraction Data on the Synthetic Stibnite-Antimonselite Solid Solution Series

99L01 Sb_2S_3		99L4 $Sb_2(S_{2.5},Se_{0.5})_3$		99L3 $Sb_2(S_{2.0},Se_{1.0})_3$		99L1 $Sb_2(S_{1.5},Se_{1.5})_3$		99L2 $Sb_2(S_{1.0},Se_{2.0})_3$		99L5 $Sb_2(S_{0.5},Se_{2.5})_3$		99L02 Sb_2Se_3	
d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0
0.8008	8	0.8022	6	0.8125	7	0.8140	7	0.8215	6	0.8261	4	0.8261	11
						0.5894	9						
0.5668	36	0.5705	67	0.5771	32	0.5786	37	0.5847	38	0.5886	42	0.5878	50
				0.559	6	0.5248	13					0.5279	41
0.5064	50	0.5098	57	0.5151	70	0.5169	45	0.5217	61	0.5248	47	0.5248	48
												0.4164	17
0.399	23	0.4019	18	0.4055	19	0.4070	13	0.4107	11	0.4134	6	0.4134	20
0.3764	7					0.3748	8					0.3779	20
0.3639	13	0.3645	14			0.369	16						
0.3579	100	0.3610	100	0.3645	87	0.3663	59	0.3690	60	0.3717	43	0.3717	51
0.3464	14	0.3579	31	0.3610	35	0.3625	22	0.3651	21	0.3678	9	0.3681	22
		0.3477	7	0.3506	6								
0.318	9	0.3197	7	0.3225	10	0.3238	10	0.3264	9	0.3288	6		
0.3134	47	0.3158	46	0.3188	60	0.3204	52	0.3227	71	0.3250	72	0.3252	80
0.3114	36	0.3106	25			0.3188	17						
0.3056	55	0.3070	34	0.3097	44	0.3106	44	0.3131	42	0.3158	24	0.3166	40
								0.3106	7			0.2944	16
								0.2921	4	0.2942	4	0.2877	49
0.2768	59	0.2784	45	0.2806	69	0.2820	47	0.2840	66	0.2864	42	0.2866	60
												0.2824	13
0.2682	27	0.2696	20	0.2718	34	0.2731	23	0.2749	33	0.2773	21	0.2778	36
		0.2679	5			0.2718	8			0.2758	7	0.2758	18
0.2611	13	0.2624	12	0.2645	14	0.2659	12	0.2676	13	0.2699	8	0.2704	18
0.2528	77	0.2550	87	0.2574	100	0.2587	100	0.2606	100	0.2630	100	0.2626	96
		0.2535	12	0.2554	15	0.2567	14	0.2584	16	0.2605	15	0.2606	23
												0.2525	20
.2428	15	0.2445	13	0.2465	21	0.2479	17	0.2495	23	0.2516	16	0.2518	25
0.2278	28	0.2297	19	0.2317	22	0.2329	19	0.2345	21	0.2365	15	0.2366	28
				0.2296	11	0.2310	10	0.2325	11	0.2343	10	0.2345	18
0.2254	23	0.2275	12	0.2290	14	0.2302	12	0.2317	14	0.2335	11	0.2335	19
0.2233	32	0.2250	28	0.2270	34	0.2283	27	0.2298	32	0.2318	23	0.2319	35
		0.2237	7	0.2252	11	0.2265	10	0.2281	10	0.2300	5	0.2302	13
		0.2218	4	0.2236	5	0.2246	9	0.2262	5	0.2281	3		

0.2205	5	0.2202	4	0.2219	5	0.2231	5	0.2246	7	0.2265	3		
0.2155	11	0.2150	6	0.2138	40	0.2150	43	0.2165	37	0.2182	37	0.2183	49
0.2101	41	0.2119	46	0.2120	13	0.2131	15	0.2146	17	0.2162	14	0.2163	21
0.2089	12	0.2103	9										
0.1994	12	0.2010	10	0.2026	12	0.2039	11	0.2052	10	0.2068	8	0.2069	16
0.1943	49	0.1958	28	0.1972	35	0.1984	29	0.1996	27	0.2013	17	0.2014	29
0.1931	26	0.1944	20	0.1962	26	0.1977	23	0.1989	21	0.1999	16	0.2001	28
0.192	27	0.1930	14	0.1944	16	0.1971	22	0.1984	19	0.1987	12	0.1989	22
0.1886	26	0.1904	34			0.1955	18	0.1967	19				
0.1872	9					0.1934	23						
0.1860	12	0.1885	6	0.1922	13	0.1908	15	0.1947	15	0.1962	15	0.1962	24
0.1848	8	0.1878	17	0.1899	13	0.1885	9	0.1920	13	0.1935	11	0.1936	15
0.1842	5	0.1860	8	0.1874	9	0.1878	5	0.1896	8	0.1912	5	0.1913	12
0.1794	5	0.1805	8	0.1821	8	0.1833	8	0.1844	7	0.1859	8	0.1860	13
0.1788	6			0.1788	5	0.1827	5			0.1834	4	0.1836	9
0.1778	7					0.1814	5	0.1825	4				
0.1770	9	0.1773	6	0.1768	6	0.1798	5	0.1817	4				
0.176	7	0.1768	4					0.1810	4				
0.1729	26	0.1743	15	0.1758	16	0.1768	14	0.1780	9	0.1795	4	0.1797	10
		0.1737	9	0.1750	13	0.1761	15	0.1772	14	0.1787	8	0.1787	17
								0.1765	5				
0.1693	50	0.1708	39	0.1723	5l	0.1734	61	0.1745	64	0.1759	60	0.1760	100
0.1685	17	0.1700	21	0.1715	26	0.1726	35	0.1737	28	0.175	29	0.1752	40
						0.1720	8			0.1744	5		
0.1635	7	0.1647	4	0.1659	6	0.1669	8	0.1679	8	0.1695	5	0.1697	13
0.1599	6					0.1634	5	0.1644	5	0.1658	3	0.1659	9
0.1561	5	0.1573	4										
0.1554	9	0.1569	7	0.1583	7	0.1593	10	0.1603	8	0.1616	9	0.1617	15
0.1544	15	0.1554	12	0.1566	11	0.1576	15	0.1585	12	0.1598	9	0.1599	16
0.1528	11	0.1539	9	0.1551	11	0.1560	13	0.1570	11	0.1584	7	0.1585	17
				0.1547	5	0.1554	6	0.1565	5	0.1580	4	0.1581	10
0.1484	14	0.1498	15	0.1511	14	0.1521	19	0.1530	14	0.1542	15	0.1544	23
0.1479	9	0.1491	6	0.1503	6	0.1513	6	0.1522	5	0.1536	4	0.1536	10
0.1445	12	0.1457	13	0.1469	12	0.1478	16	0.1487	11	0.1499	9	0.1500	18
0.144	5	0.1442	5	0.1453	6	0.1461	6	0.1470	4	0.1469	4	0.1471	10

Table continues

TABLE 3. *Continued*

99L01 Sb_2S_3		99L4 $Sb_2(S_{2.5},Se_{0.5})_3$		99L3 $Sb_2(S_{2.0},Se_{1.0})_3$		99L1 $Sb_2(S_{1.5},Se_{1.5})_3$		99L2 $Sb_2(S_{1.0},Se_{2.0})_3$		99L5 $Sb_2(S_{0.5},Se_{2.5})_3$		99L02 Sb_2Se_3	
d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0
0.1432	8	0.1428	6	0.1438	6	0.1447	6	0.1456	6	0.1463	4	0.1464	10
0.1416	10	0.1422	4	0.1432	6	0.1440	9	0.1449	7				
0.1414	7	0.1417	8										
0.1404	10												
0.1401	10	0.1414	14	0.1426	10	0.1435	13	0.1444	10	0.1456	9	0.1456	16
						0.1432	6						
						0.1414	5						
						0.1411	5						
0.1368	5	0.1385	4	0.1398	5	0.1407	8	0.1415	6	0.1427	7	0.1427	12
0.1361		0.1370	5	0.1380	6	0.1389	7	0.1397	6	0.1410	3	0.1411	9
0.1352	8	0.1366	6	0.1374	7	0.1383	8	0.1391	7	0.1403	5	0.1404	11
		0.1363	6	0.1366	5	0.1366	6	0.1365	5	0.1376	4	0.1376	9
						0.1357	6						
0.1311	14	0.1321	12	0.1331	13	0.1340	15	0.1347	13	0.1359	9	0.1360	19
		0.1318	6	0.1328	6	0.1336	7	0.1344	6	0.1356	4	0.1357	11
0.1291	11	0.1304	8	0.1315	8	0.1324	10	0.1331	7	0.1343	5	0.1344	11
0.1255	5	0.1276	4	0.1286	6	0.1294	8	0.1302	7	0.1313	6	0.1314	14
0.1249	6	0.1266	4	0.1276	5	0.1284	6	0.1291	5			0.1303	9
0.1241	7	0.1262	6	0.1274	5	0.1282	7	0.1289	5	0.1300	7	0.1301	12
0.1227	5	0.1239	5	0.1250	5	0.1266	5			0.1284	3	0.1285	9
0.1203	7	0.1211	8	0.1220	7	0.1259	7	0.1266	4	0.1276	5	0.1277	10
						0.1242	6	0.1249	4	0.1254	3	0.1262	8
						0.1236	5	0.1241	4			0.1255	9
0.1200	7					0.1229	8	0.1236	6				
0.1193	5	0.1203	4	0.1210	6	0.1227	9	0.1234	7	0.1246	6	0.1247	15
0.1188	10	0.1200	7	0.1203	5	0.1218	10	0.1225	6	0.1236	5	0.1237	12
0.1185	5					0.1211	6	0.1218	5	0.1228	4	0.1229	9
0.1174	5			0.1193	5	0.1201	6	0.1208	5	0.1218	4	0.1219	10
0.1168	5	0.1180	5	0.1190	7	0.1198	9	0.1205	8	0.1215	9	0.1216	18
0.1156	7	0.1176	5	0.1185	5	0.1193	7	0.1200	6	0.1210	5	0.1210	12
0.1147	7	0.1158	7	0.1169	7	0.1179	6	0.1186	5	0.1193	5	0.1198	8
						0.1176	8	0.1183	6	0.1187	5	0.1194	10
						0.1170	6	0.1177	5	0.1183	3	0.1188	12

											0.1184	9
0.1131	9	0.1143	8	0.1153	5	0.1161	11	0.1168	6	0.1177	9	0.1178	19
		0.1141	5	0.1149	5	0.1157	7	0.1164	5	0.1174	4		
0.1126	6	0.1137	8	0.1147	7	0.1155	13	0.1162	8	0.1171	12	0.1172	19
0.1112	5	0.1120	5			0.1138	6	0.1144	4	0.1154	5	0.1154	10
0.108	5					0.1104	5	0.1111	4	0.1124	4	0.1124	8
												0.1121	8
0.1061	7	0.1076	5	0.1085	5	0.1090	7	0.1099	6	0.1108	7	0.1109	14
0.1059	6	0.1070	5	0.1079	5	0.1090	6	0.1092	4	0.1102	3	0.1102	8
		0.1066	4							0.1098	4	0.1099	9
0.1055	6	0.1054	5	0.1074	8	0.1081	10	0.1087	8	0.1096	5	0.1097	12
										0.1084	3	0.1084	8
0.1036	5					0.1058	5	0.1064	4	0.1079	3	0.1080	8
												0.1010	7

end member is coordinated with that of synthetic antimonselite (Sb_2Se_3): a = 1.1633nm, b = 1.1780 nm, c = 0.3985 nm and a = 1.17938(9) nm, b = 1.16478(7) nm, c = 0.39858(6) nm (Voutsas et al., 1985).

However, the unit cell parameters of natural antimonselite are a = 1.1591–1.1593 nm, b = 1.1724–1.1747 nm, c = 0.3941–0.3984 nm (Chen et al., 1993; Chen, 1994); detailed crystallographic study by Min et al. (1998) on a monocrystal of natural antimonselite gave a = 1.1588(5) nm, b = 1.1744(4) nm, c = 0.3955(2) nm. These results are close to the study on synthetic $Sb_{1.92}(S_{0.46}, Se_{2.54})_{3.00}$ carried out in this paper (Table 4). We suggest that, in nature, antimonselite contains a certain quantity of sulfur, which was proved by Liu and Zheng (1992) and Min et al. (1994) using EPMA. Inasmuch as the ionic radius of S^{2-} is less than that of Se^{2-}, it is the sulfur substitution for selenium in antimonselite that makes the unit cell parameters decrease.

It is noteworthy that, in the synthetic stibnite-antimonselite solid solution series, unit cell parameters (a, b, c values), cell volume (V), and density (D) of minerals increase in proportion to the increase of Se content and the decrease of S content (Table 4, Fig. 4). Therefore, the crystallographic parameters are linearly related to the composition, which is in accord with Vegard's law (West, 1984).

Conclusions

Experimental studies on the random substitution of sulfur and selenium in synthetic Sb-S-Se system confirm that stibnite-antimonselite constitutes a binary solid solution, which forms due to the S-Se substitution. The two end members of the series are Sb_2S_3 and Sb_2Se_3. The selenium-bearing stibnite, selenium stibnite, sulfur antimonselite, and sulfur-bearing antimonselite found in the La'erma-Qiongmo Au-Se deposit are comparable to the components of stibnite-antimonselite solid solution series revealed by laboratory experiments.

Although the experimental condition of the synthetic Sb-S-Se system cannot be compared with the conditions of formation of natural stibnite-antimonselite solid solutions, the successful synthesis under 300°C proved that this solid solution is stable under such conditions. So the authors have reached two conclusions: (1) The variation of Se concentration is continuous throughout the whole stibnite-antimonselite solid solution series, confirming the random substitution of Se for S and the existence of

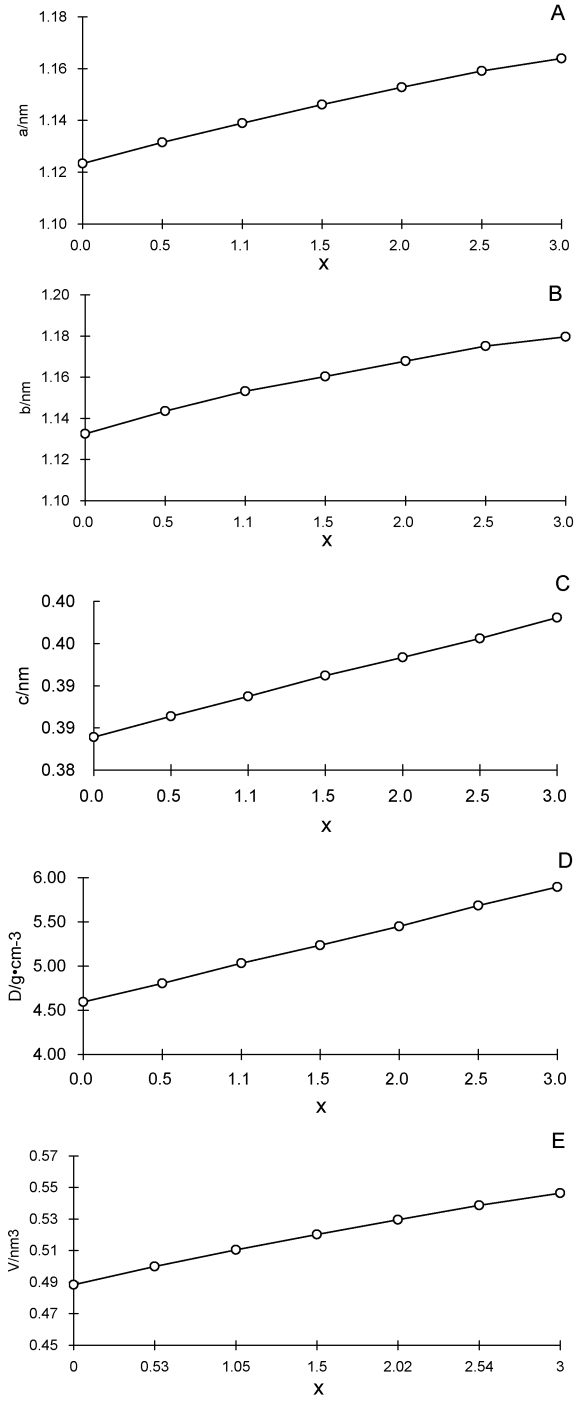

FIG. 4. Unit cell parameters *a*, *b*, and *c*, unit cell volume *V*, and mineral density *D* vs. the degree of Se substitution for S, *x*, in $Sb_2 (S_{3-x},Se_x)_{3.00}$ ($0 \le X \le 3$).

TABLE 4. Crystallographic Parameters of the Synthetic Stibnite-Antimonselite Solid Solution Series

Sample no.	Ideal formulae	Chemical formulae	Crystallographic parameters				
			a/nm	*b*/nm	*c*/nm	*D*/ g·cm^{-3}	*V*/ nm^3
99L01	Sb_2S_3	$Sb_{2.07}S_{3.00}$	1.12338	1.1325	0.38391	4.593	0.48843
99L4	$Sb_2(S_{2.5},Se_{0.5})_3$	$Sb_{2.03}(S_{2.47}, Se_{0.53})_{3.00}$	1.13151	1.14353	0.38636	4.805	0.49991
99L3	$Sb_2(S_{2.0},Se_{1.0})_3$	$Sb_{1.99}(S_{1.95}, Se_{1.05})_{3.00}$	1.13896	1.15317	0.38874	5.033	0.51058
99L1	$Sb_2(S_{1.5},Se_{1.5})_3$	$Sb_{1.93}(S_{1.50}, Se_{1.50})_{3.00}$	1.14614	1.16028	0.39119	5.234	0.52022
99L2	$Sb_2(S_{1.0},Se_{2.0})_3$	$Sb_{1.90}(S_{0.98}, Se_{2.02})_{3.00}$	1.15278	1.16779	0.39336	5.450	0.52954
99L5	$Sb_2(S_{0.5},Se_{2.5})_3$	$Sb_{1.92}(S_{0.46}, Se_{2.54})_{3.00}$	1.15915	1.17505	0.39560	5.685	0.53883
99L02	Sb_2Se_3	$Sb_{1.88}Se_{3.00}$	1.16389	1.17955	0.39807	5.896	0.54650

all possible binary compositions. (2) In stibnite-antimonselite solid solution, crystallographic parameters, including unit cell parameters (*a*, *b*, *c* values), cell volume (*V*), and density (D) of minerals, increase with Se content, which reflects Vegard's law solution behavior.

Acknowledgments

Funding for this project was jointly granted by the National Natural Science Foundation of China (Grant Nos. 40573032, 40234051, 40434011, 40273026, and 49773197) and by the 111 project (Grant No. B07011). The authors are grateful to Prof. Emil Makovicky and Dr. Changling He at the University of Copenhagen, and Prof. Nigel Cook at the University of Oslo for correcting and commenting on the manuscript. Also we thank Mr. Shiju Li and Mr. Aifu Qiu at the Institute of Geology and Geophysics, Chinese Academy of Sciences, for their contribution to this work in X-ray powder diffraction analysis.

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