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ISOMORPHOUS SUBSTITUTION IN SYNTHETIC COBALTITE AND ULLMANNITE

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ABSTRACT

Synthetic cobaltite shows a continuous solid substitution from $CoAs_{0.86}S_{1.19}$ to $CoAs_{0.42}S_{1.58}$ at 550°C. Syntheses of $Ni(Sb, As, S)_2$ and (Ni, Co)SbS indicate that corynite is antimonian gersdorffite and willyamite is cobaltian ullmannite, and further use of these varietal names is unnecessary.

A wide range of nonmetal atom substitution in gersdorffite (NiAsS) is indicated by Yund (1962) and metal atom substitution by Klemm (1965), therefore the other minerals in the AXY sulfide subclass of cobaltite and ullmannite appear worthy of investigation. In cobaltite (CoAsS), iron and nickel may substitute extensively for cobalt as indicated by Klemm (1965) and Klemm and Weiser (1965) from both natural and synthetic materials. No data were available for compositional limits of nonmetal atom substitution. The composition of ullmannite (NiSbS) from the three chemical analyses quoted by Palache *et al.* (1944) and the ternary diagram Ni-Sb-S of Lange and Schlegel (1951) indicates Ni:Sb:S = 1:1:1. Extensive substitution of cobalt for nickel results in the variety cobaltian ullmannite (Ni, Co) SbS, and extensive arsenic substitution for antimony results in the variety arsenian ullmannite, Ni(As, Sb)S. These compounds were synthesized in the present study to define the compositional limits of ullmannite and cobaltite.

Spectrographically pure compounds from Johnson, Matthey, and Co. were used to synthesize cobaltite and ullmannite. The nickel oxide and cobalt oxide were reduced by hydrogen under red heat. Dry panning (tapping) was used to reject large metal particles because they have slow reaction rates, and fine particles because they are difficult to transfer and oxidize more rapidly. Antimony and sulfur were crushed, and their fines were discarded because of transfer difficulties. Exposure of arsenic to the atmosphere was kept to a minimum to prevent oxidation. A 0.2 g mixture of elements was transferred into an oven-dried pyrex glass sample tube. An additional 0.0001 g of sulfur, arsenic and antimony was added to compensate for the vapor of these volatile components which filled the dead space above the sample. Each tube was sealed under vacuum across the neck with the volume of less than 50 mm^3 more than half filled with a sample, so that the vapor volume was minimized and a solid plug was not required. The reaction was considered complete when the quenched sam-

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TABLE 1. UNIT-CELL DATA OF SYNTHETIC COBALTITE AND ULLMANNITE,[a] AND OTHER PHASES FORMED

Composition			Unit cell Å cobaltite	Other Phases
Co	As	S		
1.0	0.98	1.02	5.5766(3)	$CoAs_2$
1.0	0.94	1.06	5.5767(3)	$CoAs_2$
1.0	0.90	1.10	5.5767(3)	$CoAs_2$
1.0	0.86	1.14	5.5766(3)	
1.0	0.82	1.18	5.5748(4)	
1.0	0.78	1.22	5.5732(4)	
1.0	0.74	1.26	5.5716(4)	
1.0	0.66	1.34	5.5694(6)	
1.0	0.61	1.39	5.5681(6)	
1.0	0.56	1.44	5.5660(6)	
1.0	0.54	1.46	5.5658(6)	
1.0	0.52	1.48	5.5652(6)	
1.0	0.46	1.54	5.5640(8)	
1.0	0.44	1.56	5.5638(8)	
1.0	0.43	1.57	5.5623(8)	
1.0	0.42	1.58	5.5630(8)	CoS_2
1.0	0.40	1.60	5.5630(8)	CoS_2

Composition				Unit cell Å ullmannite
Co	Ni	Sb	S	
	1.0	1.1	0.9	5.9355(3)
	1.0	1.0	1.0	5.9355(3)
	1.0	0.99	1.01	5.9346(3)
	1.0	0.98	1.02	5.9344(3)
	1.0	0.96	1.04	5.9344(3)
	1.0	0.94	1.06	5.9344(3)
	1.0	0.9	1.1	5.9344(3)
				Cobaltian ullmannite
0.1	0.9	1.0	1.0	5.9260(8)
0.2	0.8	1.0	1.0	5.911(1)
0.3	0.7	1.0	1.0	5.899(3)
0.4	0.6	1.0	1.0	5.885(3)
0.5	0.5	1.0	1.0	5.89(1)
0.6	0.4	1.0	1.0	5.89(1)

[a] Numbers in parentheses indicate probable error in last figure.

ple tube did not contain any mixture of arsenic, sulfur or antimony at the top of the sample tube. The products which were ground and reheated for 5 days did not change. The unit cell was determined from a Debye-Scherrer photograph using the function of Nelson and Riley (1948).

Seventeen mixtures with compositions ranging from CoAsS to $CoAs_{0.4}S_{1.6}$ were heated at 550°C for 1 month to produce cobaltite. Their cell sizes given in Table 1 are plotted against their compositions in Figure 1 to show a continuous solid substitution for cobaltite from $CoAs_{0.86}S_{1.14}$, to $CoAs_{0.42}S_{1.58}$. Although these values plot close to a straight line, a better fit is obtained with a concave curve. The slope of this curve is shown in Figure 1 to be less than the slope of the cell size *versus* composition curve which joins CoAsS to CoS_2 (5.523 Å from Elliott, 1960).

Limited substitution of metal atoms was obtained with the simple evacuated tube method in contrast to the wide range obtained by Klemm (1965) with the LiCl-KCl melt method. Neither 001 nor 011 reflections were observed in those cobaltites produced at 550°C by the simple tube method, but both 001 and 011 reflections were recorded in cobaltites produced at 550°C by the LiCl-KCl melt method. This phenomenon is at-

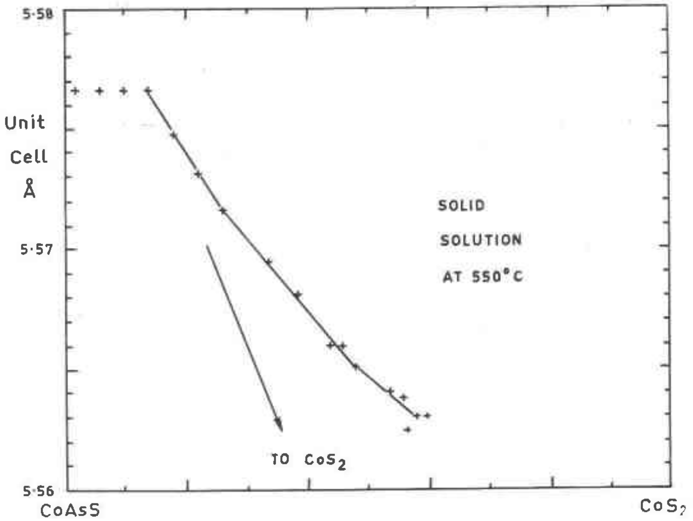

FIG. 1. Cell edge *versus* cobalite composition.

tributed to the greater mobility of atoms in an LiCl-KCl melt to allow the formation of the more ordered cobaltite ($Pca2_1$) rather than disordered cobaltite ($Pa3$).

Seven mixtures ranging from $NiSb_{1.1}S_{0.9}$ to $NiSb_{0.9}S_{1.1}$ were heated at 550°C for 1 month. Their cell sizes (Table 1) indicate little deviation from stoichiometric NiSbS. The lack of substitution of antimony for sulfur, and vice versa is explained by their large size difference.

Over forty $Ni(Sb, As, S)_2$ mixtures were heated at 550°C for 1 month. Their cell sizes are plotted in Figure 2, a ternary diagram NiS_2-$NiSb_2$-$NiAs_2$. The chemical analyses of the type variety corynite given in the original description by Zepharovich (1865) is plotted in Figure 2 and just lies within the region of antimonian gersdorffite. Corynite is used in this original sense of antiomonian gersdorffite by Hey (1964) and Palache *et al.* (1944, p. 299); however it is used in the sense of an arsenian ullmannite by Palache *et al.* (1944, p. 301), Ramdohr (1960), Ramdohr and Strunz (1967), and Berry and Thompson (1962). No recorded occurrences exist of natural or synthetic material which are intermediate between the fields of arsenian ullmannite and antimonian gersdorffite (Fig. 2); all recorded occurrences fall in these fields. Gies (1968) records both As-rich and Sb-rich phases in corynites from both Olsa (type locality) and Siegerland in accord with Figure 2. Regrettably his electron probe analyses are not given quantitatively, so they cannot be compared directly to Figure

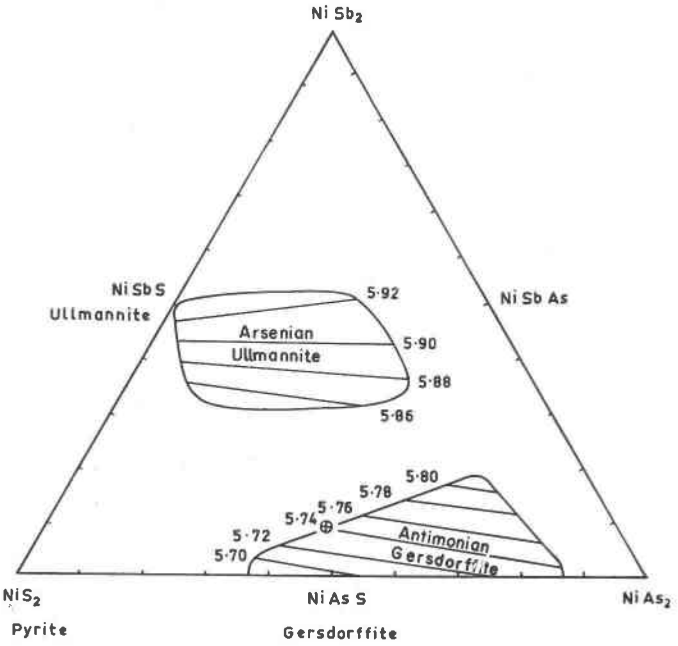

FIG. 2. A ternary diagram NiS_2-$NiAs_2$-$NiSb_2$ to show the limits of solid solution at 550°C and the associated cell dimensions (Å).
Circle with cross: Zepharovich (1865).

2. Because both synthetic and natural material indicate a distinct compositional gap between antimonian gersdorffite and arsenian ullmannite, the use of the term corynite for both sides of the compositional gap does not appear advisable. Therefore in as much as corynite is an antimonian gersdorffite, further use of this varietal name is unnecessary.

Mixtures of (Ni, Co)SbS were heated at 550°C for 1 month in an LiCl-KCl melt as described by Klemm (1965), because the simple tube method is unsatisfactory for extensive metal atom substitution. Their cell sizes given in Table 1 are plotted against their composition in Figure 3 to indicate solid solution of cubic material ranging from NiSbS to about $Ni_{0.5}Co_{0.5}SbS$ and then a distinct gap to noncubic CoSbS. The chemical analysis of the type variety willyamite given in the original description by Pittman (1896) just lies at the end of this cobaltian ullmannite regime. No recorded occurrences exist of natural or synthetic material which are intermediate between the fields of cobaltian ullmannite and CoSbS; all recorded occurrences of willyamite fall in the field of cubic

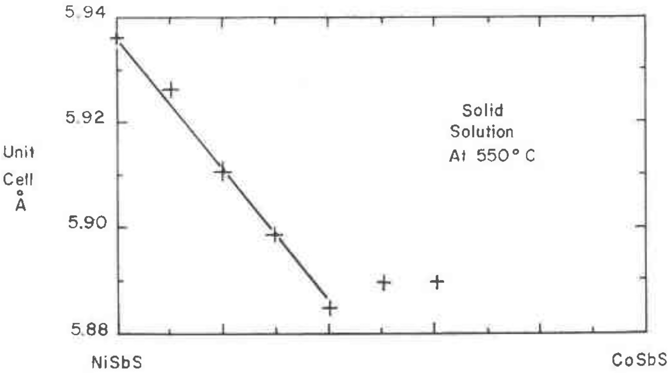

FIG. 3. Cell edge *versus* cobaltian ullmannite composition.

cobaltian ullmannite. Therefore in as much as willyamite is a cobaltian ullmannite, further use of this varietal name is unnecessary.

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