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Structural disorder in aikinite and krupkaite

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ABSTRACT

The nature of compositional fields in aikinite and krupkaite has been investigated by electron diffraction and high-resolution transmission electron microscopy. Variation from ideal composition in these minerals results from the disordered intergrowth of krupkaite units in aikinite and of aikinite units in krupkaite. Disordered intergrowths of the well-ordered superstructure phases such as friedrichite with aikinite and krupkaite were also observed. Contrary to earlier findings, solid solution does not appear to be a mechanism for compositional variation in natural members of the bismuthinite-aikinite series.

INTRODUCTION

Krupkaite ($CuPbBi_3S_6$) and aikinite ($Cu_2Pb_2Bi_2S_6$) are simple members of the bismuthinite-aikinite series, having structures derived from bismuthinite by ordered substitution of Bi by Pb and insertion of Cu (Fig. 1). The five other minerals in the series are superstructures based on the ordered intergrowth of bismuthinite, krupkaite, and aikinite ribbons (see Table 1). The crystal chemistry of the series has been extensively studied; structures have been determined for all members except friedrichite (see Makovicky, 1981). Over the past thirty years the nomenclature of the series has been the subject of considerable debate, with a number of systems being proposed and discarded. The current nomenclatural system is based on the naming of established ordered structures and superstructures (Mumme et al., 1976).

In contrast to the highly ordered superstructures, extensive compositional fields have been reported in natural specimens of both aikinite $Cu_{2-x}Pb_{2-x}Bi_{2+x}S_6$ ($0.0 \leq x \leq 0.34$) and krupkaite $Cu_{1-x}Pb_{1-x}Bi_{3+x}S_6$ ($-0.13 \leq x \leq 0.14$), which Harris and Chen (1976) ascribed to solid solution. However, Zak (1980) argued that the extensive nature of the compositional fields could instead result from the disordered intergrowth of compositionally distinct ribbons of aikinite, krupkaite, and bismuthinite.

Synthetic studies (Springer, 1971; Mumme and Watts, 1976) revealed complete solid solution between bismuthinite and aikinite, and, in fact, all attempts to prepare the ordered superstructures have been unsuccessful.

The degree of chemical segregation required for the formation of the well-ordered intergrowth structures seems at odds with the concept of large compositional fields due to solid solution in the end members. It was considered that the compositional fields in natural specimens could instead be due to the disordered intergrowth of end-member ribbons. An electron-micrograph study was undertaken to determine the structural nature of chemical variation in natural members of the bismuthinite-aikinite series.

MATERIAL EXAMINED

Natural specimens with compositions at the krupkaite-aikinite end of the bismuthinite-aikinite series were obtained from a number of museum collections; these included the six specimens from the Smithsonian Institution examined by Harris and Chen (1976). Details of the specimens are given in Table 2. The compositional data of Harris and Chen (1976) were considered to provide a good representation of the average compositions of the six specimens they examined. Electron-microprobe analyses were obtained for the other three specimens included in this study (Table 3).

ELECTRON MICROSCOPY

Small crystal fragments from each specimen were in turn ground under acetone in an agate mortar and dispersed onto Cu grids coated with holey C support films. Specimens were examined in either a JEM 200 CX electron microscope fitted with an ultra–high resolution top-entry goniometer (±10°), objective lens with $C_s = 1.20$ mm, and a LaB_6 filament or a Philips EM 430 electron microscope operating at 300 kV, fitted with a side entry goniometer (±40°), objective lens with $C_s = 1.90$ mm, and a LaB_6 filament. Crystal fragments projecting over holes in the C film were tilted into the [001] zone. Lattice images were recorded at magnifications between 300 000× and 500 000× using exposure times of 2–4 s. Somewhat lon-

TABLE 1. Minerals in the bismuthinite-aikinite series

Mineral	Composition	*a* (Å)	*b* (Å)	*c* (Å)	Structure*
Bismuthinite	Bi_2S_3	11.23	11.27	3.91	B
Pekoite	$CuPbBi_{11}S_{18}$	33.50	11.32	3.99	4B + 2K
Gladite	$CuPbBi_5S_9$	33.66	11.45	4.02	2B + 4K
Krupkaite	$CuPbBi_3S_6$	11.15	11.51	4.01	K
Lindströmite	$Cu_3Pb_3Bi_7S_{15}$	56.07	11.57	4.01	8K + 2A
Hammarite	$Cu_2Pb_2Bi_4S_9$	33.45	11.58	4.01	4K + 2A
Friedrichite	$Cu_5Pb_5Bi_7S_{18}$	33.84	11.65	4.01	2K + 4A
Aikinite	$CuPbBiS_3$	11.32	11.64	4.04	A

* B = bismuthinite ribbons; K = krupkaite ribbons; A = aikinite ribbons.

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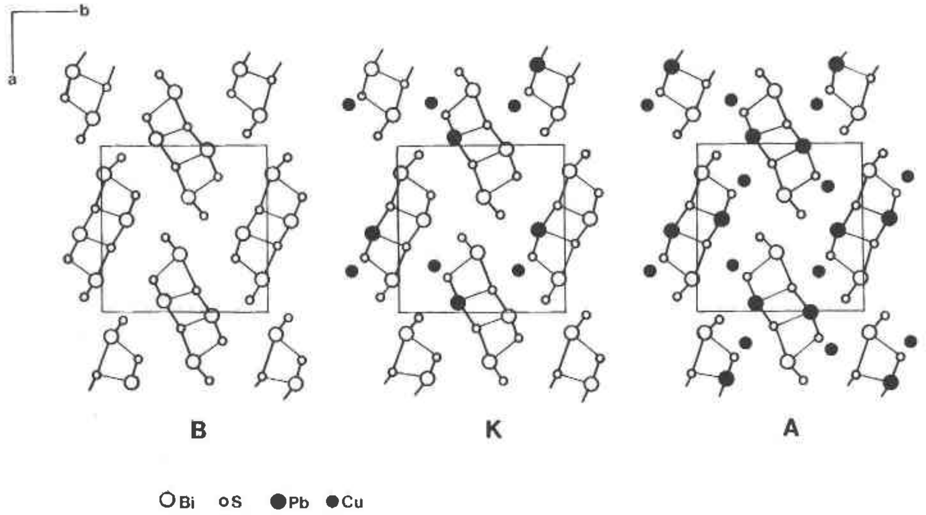

Fig. 1. The structures of bismuthinite (**B**), krupkaite (**K**), and aikinite (**A**). The bismuthinite structure (**B**) can be considered as the archetype of the group, the structure of the other minerals in the series being derived by ordered cation substitution and insertion. The structure is composed of quadruple Bi_4S_6 chains, in which half the Bi is in threefold coordination and the other half is in fivefold coordination, forming Bi_4S_6 ribbons, there being two such ribbons per unit cell. Krupkaite (K) is derived from bismuthinite by replacing one-quarter of the Bi^{3+} by Pb^{2+} and insertion of Cu^+ into half of the available tetrahedral sites in an ordered fashion. In aikinite, half the Bi^{3+} cations are replaced by Pb^{2+}, and all four tetrahedral sites are occupied by Cu. The structures of the other intermediate members are composed of ordered intergrowths of bismuthinite (B), krupkaite (K), and aikinite (A) ribbons.

ger exposure times (10–45 s) were employed to record electron-diffraction patterns so as to enhance any faint or diffuse superlattice reflections.

If the mechanism for chemical variation in krupkaite and aikinite is solid solution, then one would expect structurally homogeneous crystals. On the other hand, if the minerals adapt to compositional variation via disordered intergrowths, then considerable "stacking" disorder should be present in crystals significantly off the end-member compositions, and this disorder should be visible in the electron-diffraction patterns and the lattice images. The structural units of aikinite, krupkaite, and bismuthinite are ordered along the *a* axis in the intermediate superstructure minerals; it is therefore reasonable to expect stacking disorder to occur along this axis.

The degree of "stacking" disorder or intergrowth is reflected in the strength and nature of the superlattice reflections. Figures 2a to 2d show a series of [001] zone electron-diffraction patterns for krupkaite-aikinite minerals illustrating the four types of superlattices observed. They range from the subcell pattern free of superlattice reflections, through two states of disorder, to the formation of a well-ordered superstructure. The two states of disorder—faint continuous streaks and streaked superlattice reflections—correspond in the first case to a series of individual or pairs of foreign units in an end-member crystal, and in the second case to the disordered intergrowth of aikinite and krupkaite units with regions of a well-ordered intermediate superstructure phase. A sequence of lattice images corresponding to the four electron-diffraction patterns is shown in Figures 3a to 3d. The two types of unit are readily distinguished in the disordered images owing to contrast differences that arise from the greater concentration of interstitial Cu in aikinite.

All specimens examined in the current study gave diffraction patterns and images similar to one of the four

Table 2. Description of samples examined

Specimen no.	Name	Locality	Catalogue no.	Composition*
1	Aikinite	Lime Creek mine, Alice Arm County, British Columbia, Canada	UBC S-75-4403	$Cu_{1.7}Pb_{1.7}Bi_{2.3}S_6$
2	Aikinite	Beresov Ekaterinburg (Sverdlovsk), Ural Mountains, USSR	SAM G13565	$Cu_{1.9}Pb_{1.9}Bi_{2.1}S_6$
3	Aikinite	San Miguel di Piraciaba, Brazil	NMNH B18924	$Cu_{1.7}Pb_{1.7}Bi_{2.3}S_6$
4	Aikinite	Dobsina, Hirshkohlung, Slovakia, Czechoslovakia	NMNH R11076-2	$Cu_{1.8}Pb_{1.8}Bi_{2.2}S_6$
5	Friedrichite	Sedl, Habachtal, Salzburg, Austria	Harvard 117007	$Cu_{1.5}Pb_{1.5}Bi_{2.5}S_6$
6	Lindströmite	Silver Miller mine, Cobalt, Ontario, Canada	NMNH 106760	$Cu_{1.15}Pb_{1.15}Bi_{2.85}S_6$
7	Krupkaite	Cucomungo Canyon, Esmeralda County, Nevada, U.S.A.	NMNH 120581	$Cu_{1.11}Pb_{1.1}Bi_{2.9}S_6$
8	Krupkaite	USSR	NMNH C771	$Cu_{1.0}Pb_{1.0}Bi_{3.0}S_6$
9	Krupkaite	Balls mine, Little Cottonwood district, Utah, U.S.A.	NMNH 105571	$Cu_{1.0}Pb_{1.0}Bi_{3.0}S_6$

* Composition idealized from analyses to correspond to the general formula $Cu_xPb_xBi_{4-x}S_6$.

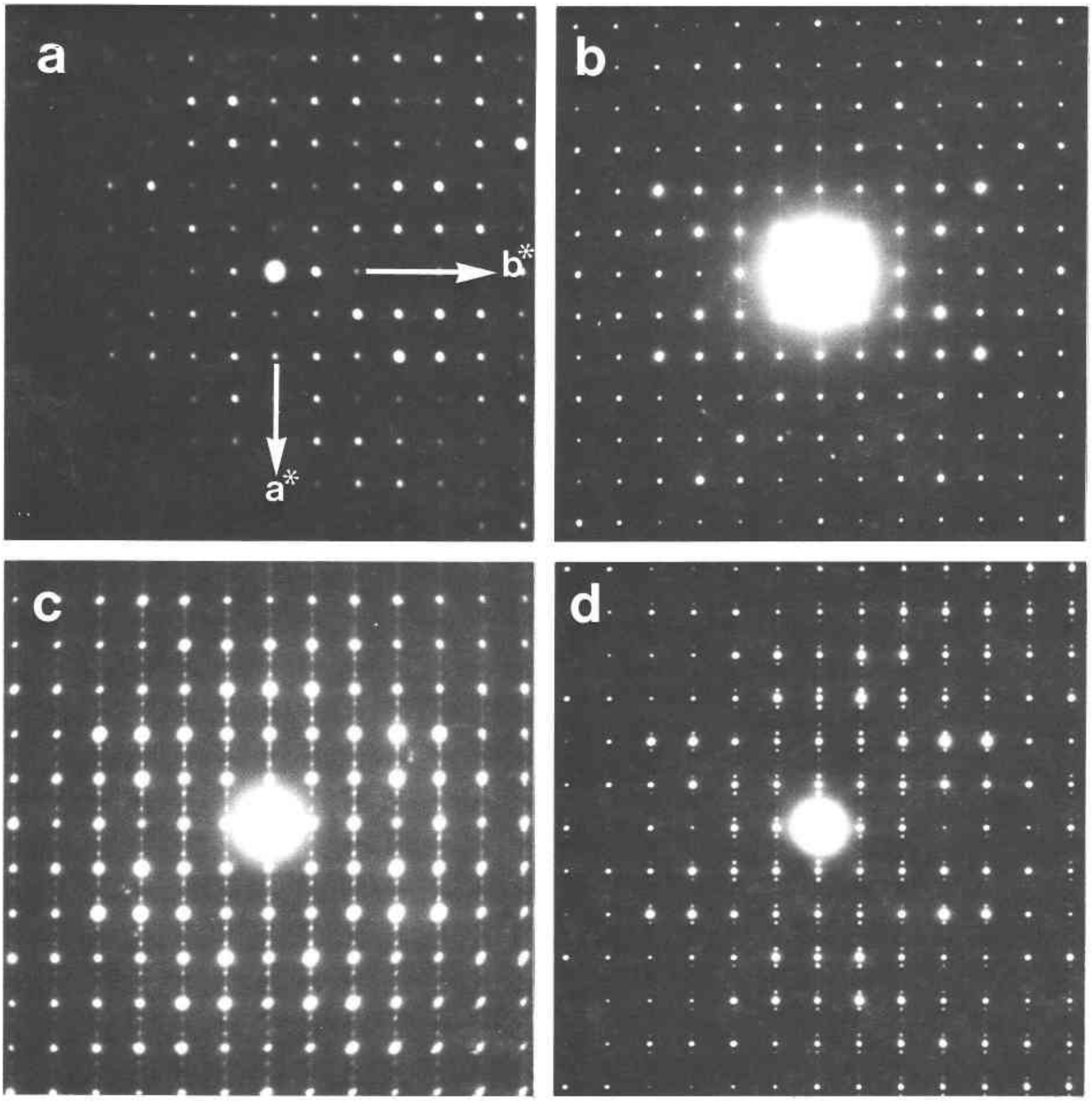

Fig. 2. Electron-diffraction patterns of krupkaite-aikinite minerals down [001]: (**a**) krupkaite, Balls mine, Utah (specimen no. 9); no superlattice intensity visible along a^*. (**b**) Aikinite, Lime Creek mine, Canada (specimen no. 1); note streaking along a^* owing to stacking disorder. (**c**) Aikinite, Dobsina, Czechoslovakia (specimen no. 4); streaked 3× superlattice reflections along a^* due to the intergrowth of friedrichite and krupkaite units in aikinite. (**d**) Lindströmite, Silver Miller mine, Canada (specimen no. 6). The sharp, well-formed 5× superlattice reflections characteristic of the minerals are clearly visible along a^*.

described and illustrated above. In a number of samples, more than one structure state was found owing to the inhomogeneity of the material. Pring and Hyde (1987) demonstrated the inhomogeneous nature of bismuthinite derivatives.

The aikinite specimens (nos. 1 and 3) are compositionally close to friedrichite $Cu_{1.7}Pb_{1.7}Bi_{2.3}S_6$, which corresponds to an aikinite to krupkaite ratio of 2:1. Electron-diffraction patterns from the specimens show faint continuous streaks of superlattice intensity along a^* (sim-

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Fig. 3. Electron micrographs of krupkaite-aikinite minerals down [001] showing the degree of ordered and disordered intergrowth: (**a**) Specimen no. 9; a region of a perfect krupkaite crystal free of aikinite intergrowth (Philips EM 430). (**b**) Specimen no. 1; an aikinite containing a disordered intergrowth of krupkaite units (K) (Philips EM 430). (**c**) Specimen no. 4; an intergrowth of friedrichite and krupkaite units in aikinite (JEOL 200 CX). (**d**) Specimen no. 6; region of a well-ordered lindströmite crystal (Philips EM 430).

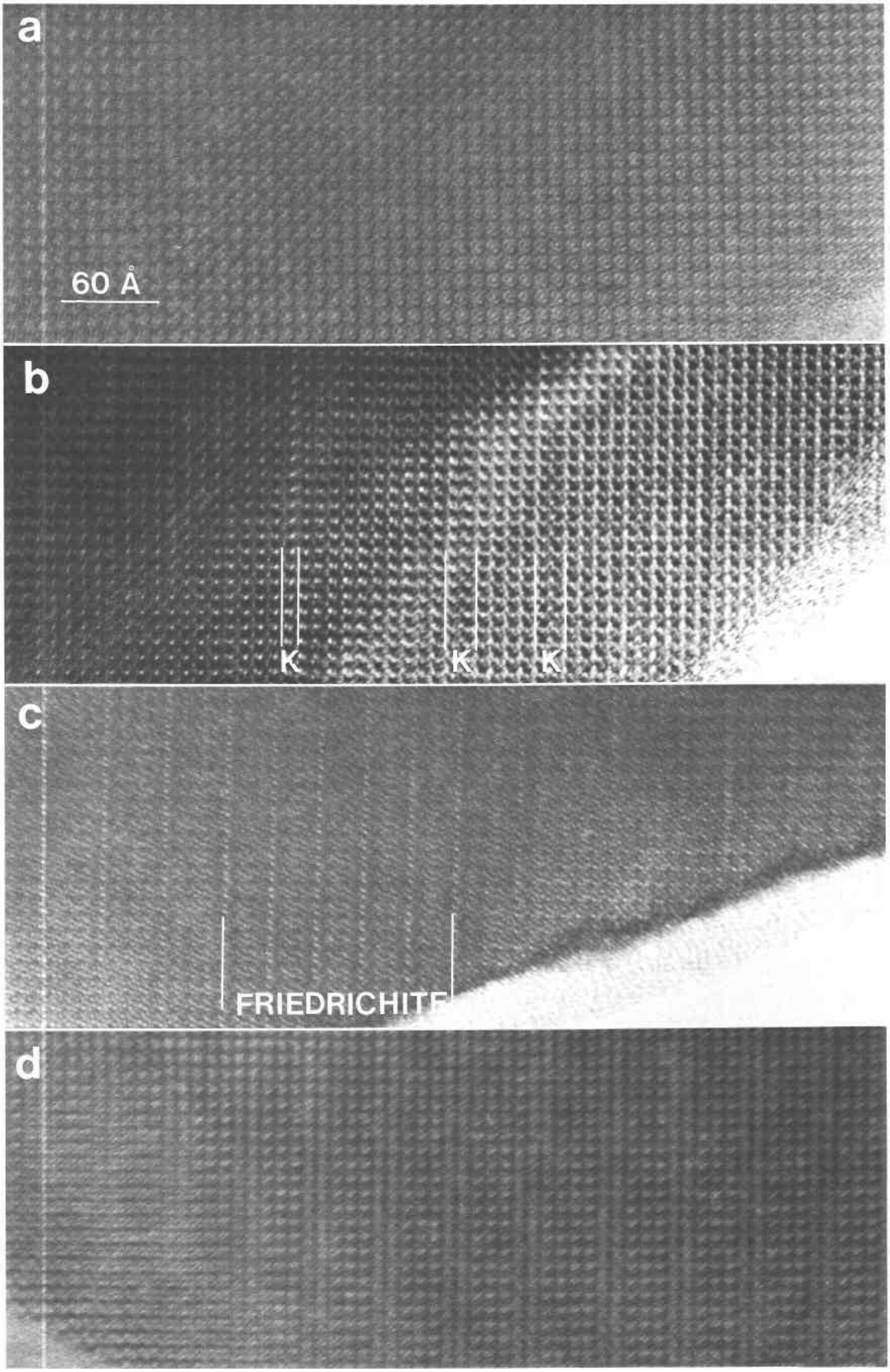
a
60 Å
b
K
K
K
c
FRIEDRICHITE
d

Table 3. Electron-microprobe analyses of krupkaite-aikinite mineral

Wt%	No. 1 UBC 5-75-4403	No. 2 SAM G13565	No. 5 Harvard 117007
Cu	10.8	12.0	10.2
	(10.7–11.0)	(10.7–14.0)	(10.0–10.3)
Pb	30.0	33.8	28.0
	(29.6–30.3)	(31.9–36.4)	(27.7–28.2)
Bi	42.4	37.6	44.7
	(41.7–42.8)	(36.7–38.2)	(44.5–45.2)
S	16.7	16.5	17.2
	(16.6–16.9)	(15.9–17.2)	(17.1–17.4)
Total	99.9	99.9	100.1
	Atomic proportions		
Cu	2.0	2.2	1.8
Pb	1.7	1.9	1.5
Bi	1.3	2.1	2.4
S	6	6	6

Note: Analyses were performed by Mr. N. G. Ware, Research School of Earth Sciences, A.N.U. Canberra, using a Cameca CAMEBAX microprobe at 25 kV with a specimen current of 50 nA. Standards used were PbS (for Pb and S) and pure metals (for Cu and Bi). The high Cu values relative to Bi and Pb are attributed to deficiencies in the ZAF correction procedure. Analyses are the average of 12 point analyses for each specimen.

ilar to Fig. 2b). The lattice images show disordered intergrowth of krupkaite units in an aikinite matrix (as in Fig. 3b). The ratio of intergrown units varies from crystal to crystal and from specimen to specimen. The average ratio of krupkaite to aikinite is approximately for specimen no. 1, 1:8, and for no. 3, 1:4. Electron-diffraction patterns and lattice images for aikinite no. 2 are also similar to Figures 2b and 3b. The composition of this specimen is closer to aikinite $Cu_{1.9}Pb_{1.9}Bi_{2.1}S_6$—an aikinite to krupkaite ratio of 9:1; the ratio of units in the image is approximately 6:1.

The composition of aikinite from Dobsina (specimen no. 4) $Cu_{1.8}Pb_{1.8}Bi_{2.2}S_6$ corresponds to a krupkaite to aikinite ratio of 1:4. Electron-diffraction patterns of the material show strong streaking along a^* with well-developed satellite reflections due to the presence of a $3a$ supercell phase (Fig. 2c). The lattice images show intergrowth of krupkaite units in aikinite with regions of well-ordered friedrichite and aikinite (see Fig. 3c).

Electron-diffraction patterns of "friedrichite" from Sedl, Austria (no. 5) (the composition of which lies between friedrichite and hammerite), gave streaked superlattice reflections rather than the expected $3a$ superlattice. A well-formed $5a$ superlattice and well-ordered images were found for lindströmite from Ontario (specimen no. 6), which is in accord with the composition $Cu_{1.15}Pb_{1.15}Bi_{2.85}S_6$ and the findings of Harris and Chen (1976) (Figs. 2d and 3d).

The three krupkaite specimens (nos. 7, 8, and 9) cover a narrow range of composition near the end-member composition. Electron-diffraction patterns of specimen no. 7, krupkaite from Nevada, are similar to Figure 2b with faint streaking along a^*. Lattice images show an intergrowth of aikinite units in a krupkaite matrix. A similar degree of disorder was observed for the Russian krupkaite (specimen no. 8). The compositions of these two specimens are $Cu_{1.1}Pb_{1.1}Bi_{2.9}S_6$ and $Cu_{1.03}Pb_{1.03}Bi_{2.97}S_6$ which correspond to aikinite to krupkaite ratios of 1:9 and 1:30, respectively. The degree of disorder in the images is consistent with these ratios.

Analyses of krupkaite from Utah (no. 9) fall at ideal composition $CuPbBi_3S_6$; electron-diffraction patterns and images show that the material is free of intergrowths (Figs. 2a and 3a).

DISCUSSION

The results of this study show that intergrowth rather than solid solution is the principal cause of the compositional fields reported for krupkaite and aikinite by Harris and Chen (1976). The inherent inhomogeneity of the natural specimens examined prevents an absolute correlation between the extent of disordered intergrowth and the degree of compositional variation, but there is in general a good agreement. If solid solution is a mechanism, it must play only a minor role in these materials formed under geologic conditions. Disordered intergrowth occurs right across the compositional range from aikinite to krupkaite with intergrowth with the ordered superstructures occurring over a large part of the central region.

The failure to prepare the ordered intermediate phases in this system synthetically has been well documented by Springer (1971), Mumme and Watts (1976), and Mariolacos (1980); instead these workers reported complete solid solution. Mumme and Watts, however, did note some evidence of Pb and Bi ordering and disordered Cu in crystals annealed at 450 °C. These findings indicate that Cu orders at much lower temperatures, although the temperature at which this occurs is yet to be established.

Phase transformations involving Cu ordering have been reported at low temperatures; as low as 75 °C in the case of digenite (Putnis, 1977). It seems probable that in nature a two-stage ordering process may occur, with Pb and Bi ordering at around 450 °C and Cu at a substantially lower temperature (200 °C?). The occurrence in nature of two structural states for the compositions of the ordered superstructures (the superstructure and a disorder intergrowth) indicates that cooling rate may be an important factor in ordering.

More rapid cooling rates could prevent complete ordering of Pb and Bi into supercells, thus resulting in a disordered intergrowth, whereas a slower cooling process allows the formation of a well-ordered superstructure. Very slow cooling processes are indicated by the complete exsolution of a superstructure phase, as observed in pekoite-gladite (Mumme and Watts, 1976).

No attempt has been made in this study to establish the ordering temperatures in the system; however, the fact that beam heating in the electron microscope does not affect the ordering state suggests that the Cu ordering temperature may be around 200 °C. Prolonged heating in the beam results in decomposition. A number of extended annealing experiments on this system are currently underway, and the results will be reported at a later date.

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