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THE Mn ISOTYPE OF ANDORITE AND UCHUCCHACUAITE

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ABSTRACT

Phase relations in the system Ag_2S–MnS–Sb_2S_3 were studied between 300° and 500°C using evacuated and sealed glass capsules. Two ternary phases, $Ag_2Mn_2Sb_6S_{12}$ ($Ag_2S{\cdot}2MnS{\cdot}3Sb_2S_3$) and $Ag_{1.41}Mn_{2.82}Sb_{5.65}S_{12}$ ($Ag_2S{\cdot}4MnS{\cdot}4Sb_2S_3$) are stable in the system, and both form equilibrium assemblages with stibnite and alabandite. The phase $Ag_2Mn_2Sb_6S_{12}$ is a Mn isotype of andorite, with *a* 12.79(1), *b* 19.58(1) and *c* 4.00(1) Å. The limits of Pb-for-Mn substitution along the join andorite and its Mn isotype, $Ag_2(Pb_{1-x}Mn_x)_2Sb_6S_{12}$, are $0.40 \geq x \geq 0.95$. Uchucchacuaite is readily synthesized from its reported composition $AgMnPb_3Sb_5S_{12}$. It has an andorite-type structure and calculated unit-cell dimensions *a* 13.08(1), *b* 19.46(1), and *c* 4.27(1) Å. Uchucchacuaite forms a complete solid-solution series with andorite, whereas the solid-solution is incomplete between uchucchacuaite and the Mn isotype of andorite.

Keywords: andorite, Mn isotype, uchucchacuaite, solid-solution series.

SOMMAIRE

Les relations de phases dans le système Ag_2S–MnS–Sb_2S_3 ont fait l'objet d'études entre 300° et 500°C par synthèses dans des ampoules de verre évacuées et scellées. Deux phases ternaires, $Ag_2Mn_2Sb_6S_{12}$ ($Ag_2S{\cdot}2MnS{\cdot}3Sb_2S_3$) et $Ag_{1.41}Mn_{2.82}Sb_{5.65}S_{12}$ ($Ag_2S{\cdot}4MnS{\cdot}4Sb_2S_3$) sont stables dans le système; les deux définissent des assemblages à l'équilibre avec stibine et alabandite. La composition $Ag_2Mn_2Sb_6S_{12}$ serait l'isotype manganifère de l'andorite; ses paramètres réticulaires sont *a* 12.79(1), *b* 19.58(1) and *c* 4.00(1) Å. La substitution entre andorite et son isotype manganifère, $Ag_2(Pb_{1-x}Mn_x)_2Sb_6S_{12}$ est partielle: $0.40 \geq x \geq 0.95$. Il est facile de synthétiser l'uchucchacuaïte à partir d'un mélange ayant la composition attribuée à cette espèce, $AgMnPb_3Sb_5S_{12}$. Cette phase possède une structure semblable à celle de l'andorite, et ses paramètres réticulaires sont *a* 13.08(1), *b* 19.46(1) and *c* 4.27(1) Å. L'uchucchacuaïte forme une solution solide complète avec l'andorite, tandis qu'avec l'isotype manganifère de l'andorite, elle est incomplète.

(Traduit par la Rédaction)

Mots-clés: andorite, isotype manganifère, uchucchacuaïte, solution solide.

INTRODUCTION

Andorite is considered to be a relatively common sulfosalt of silver, and in some deposits, it forms the chief silver ore (Chace 1948). Its composition generally deviates from the ideal formula, $Ag_2Pb_2Sb_6S_{12}$, as demonstrated by Nuffield (1945), Mozgova *et al.* (1983), and Moëlo *et al.* (1989) because of substitution between $2Pb^{2+}$ and $Ag^{1+} + Sb^{3+}$ or between $3Pb^{2+}$ and $2Sb^{3+} + \square$. In the system Ag_2S–PbS–Sb_2S_3, andorite displays an extensive range of solid solution at temperatures between 300° and 500°C (Hoda & Chang 1975). The compositions of ramdohrite and fizelyite all fall into this range. Bortnikov *et al.* (1980) observed the formation of andorite solid-solution in the system, and proposed a miscibility gap between fizelyite and andorite at about 400°C in their hydrothermal experiments. A Sn isotype of andorite was synthesized, and found to form a complete solid-solution series with andorite (Chang 1987).

Andorite-like phases also were synthesized with manganese (Chang 1982), but their characterization and phase relations with andorite have not been established. Recently, a Mn-bearing andorite-type mineral, uchucchacuaite, was reported from a telescoped deposit at Uchuc-Chacua, Peru (Moëlo *et al.* 1984). Uchucchacuaite has an ideal composition $AgMnPb_3Sb_5S_{12}$ illustrating a complex scheme of replacement of Ag + Sb by Pb + Mn.

The purpose of this study is to examine the phase relations in the system Ag_2S–MnS–Sb_2S_3 and between andorite and uchucchacuaite.

Experimental Procedures

Starting compositions were prepared from reagent-grade lead, manganese, antimony, silver and sulfur; all have 99.99% or better purity, as specified by the suppliers' information. Synthesis and heat treatment were made in muffle furnaces using the conventional technique of sealed, evacuated glass capsules (Kullerud & Yoder 1959). Two to five months were used for equilibrium experiments in the temperature range 300°–500°C. As a test of the attainment of equilibrium, some samples were heated to complete melting (~800°C), quenched, ground under acetone, resealed in a new evacuated glass capsule, and annealed at the desired temperature for the same period of time as experiments with samples prepared from raw starting materials. The final assemblages of the same bulk composition treated by the two methods were found to be identical. A total of sixty-five compositions were prepared for the determination of phase relations in the system Ag_2S–MnS–Sb_2S_3 and for the synthesis of uchucchacuaite. For the determination of Mn $\rightleftharpoons$ Pb substitution, twenty compositions at a 5 mole % interval were prepared for each of the three joins under consideration.

The quenched phases were examined by X-ray powder diffraction and reflected-light microscopy. Chemical compositions of selected samples were obtained by electron-microprobe analysis. The probe was operated at a reference beam-current of 0.1 μA and 15 kV. The beam diameter was maintained at 1 μm at all times. A reference standard of synthetic PbS was used for sulfur, and pure metals were used for all other elements. The data were corrected for background and drift, and the matrix effects were corrected using a ZAF computer program. Cell dimensions were computed with a least-squares refinement program (Benoit 1987).

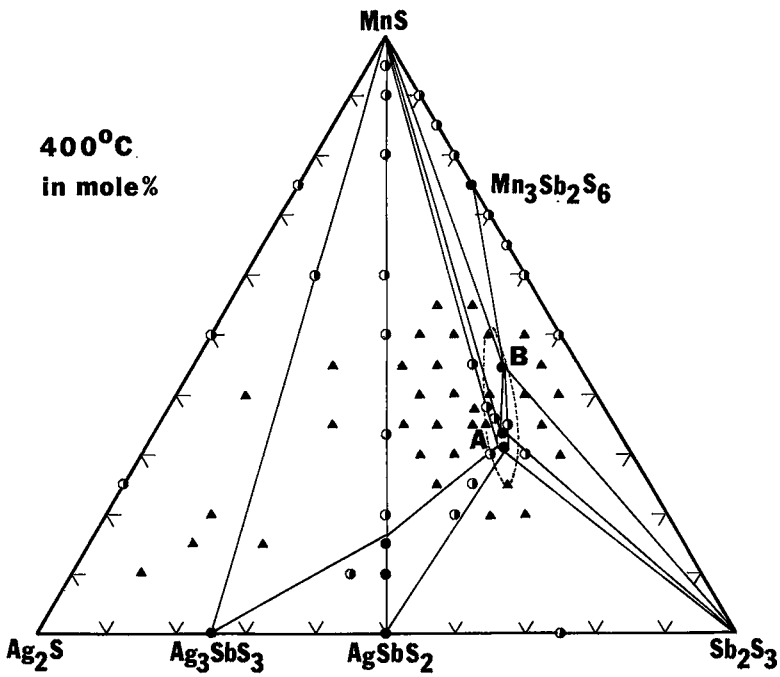

FIG. 1. Phase relations in the system Ag_2S–MnS–Sb_2S_3 at 400°C. Symbols used in the diagrams, solid triangle, half-filled circle and solid circle, represent three-phase, two-phase, and one-phase assemblages, respectively. Dashed lines mark the region of andorite solid-solution in the system Ag_2S–PbS–Sb_2S_3.

PHASE RELATIONS IN THE SYSTEM Ag_2S–MnS–Sb_2S_3

Phase relations in the system Ag_2S–MnS–Sb_2S_3 were studied in the temperature range 300°–500°C. A liquid forms from compositions having between 18 and 43 mole % Sb_2S_3 and between 58 and 80 mole % Sb_2S_3 along the join Ag_2S–Sb_2S_3 at 500°C and are present in equilibrium assemblages with Ag_2S, $AgSbS_2$, Sb_2S_3 and MnS in the ternary system. The system becomes completely solidified at 450°C. Figure 1 illustrates the phase relations in the system at 400°C. Ag_3SbS_3 and $AgSbS_2$ are stable along the join Ag_2S–Sb_2S_3, whereas $Mn_3Sb_2S_6$ exists along the join MnS–Sb_2S_3. Both Ag_3SbS_3 and $AgSbS_2$ are well-characterized phases (Keighin & Honea 1969), but the structural analysis of $Mn_3Sb_2S_6$ has not been done. The seven most intense reflections of $Mn_3Sb_2S_6$ [*d* in Å (I)] are 2.803(100), 1.849(80), 3.424(75), 2.686(50), 2.375(50), 2.056(35), and 2.537(35). A comparison with XRD data for $Pb_3Sb_2S_6$ (PDF 27–266) and $Sn_3Sb_2S_6$ (PDF 30–1368) did not result in a match. Neither stephanite (Ag_5SbS_4) nor an unnamed phase ($MnSb_2S_4$) (Harris 1989) was observed in the system.

Two ternary phases were found, designated as Phase A and Phase B for convenience. Phase A has a composition $Ag_2Mn_2Sb_6S_{12}$ ($Ag_2S{\cdot}2MnS{\cdot}3Sb_2S_3$), a compositional equivalent to andorite, and it has a small range of solid solution extending to $Ag_{2.09}Mn_{1.84}Sb_{6.08}S_{12}$. Phase B has a composition $Ag_{1.41}Mn_{2.82}Sb_{5.65}S_{12}$ ($Ag_2S{\cdot}4MnS{\cdot}4Sb_2S_3$). Electron-microprobe analysis of these synthetic phases gave $Ag_{2.20}Mn_{1.80}Sb_6S_{12}$ for Phase A and $Ag_{1.40}Mn_{2.76}Sb_6S_{12}$ for Phase B, which illustrates a fair match between the compositions prepared from raw starting materials and the compositions after heat treatment. X-ray powder-diffraction data for Phase A (Table 1) can be indexed on the basis of the unit cell of andorite, which yields *a* 12.79(1), *b* 19.58(1) and *c* 4.00(1) Å. As tabulated in Table 1, Phase B has several major reflections that match those of Phase A, but it also has many distinct ones that cannot be accounted for if an andorite unit-cell is used for indexing. Both Phase A and Phase B form equilibrium assemblages with stibnite and alabandite, and bulk compositions between Phase A and Phase B produced distinct two-phase assemblages.

At 400°C, $AgSbS_2$ can take only 17.5 mole % MnS, and the range of solid solution toward MnS is less than 5 mole % $AgSbS_2$, although MnS and $AgSbS_2$ are isostructural. This is in contrast to the extensive range of 70 mole % PbS in $AgSbS_2$ in the system Ag_2S–PbS–Sb_2S_3 (Hoda & Chang 1975).

Experiments at 300°C were conducted with a LiCl–NH_4Cl flux. Results obtained show no major change in phase relations as compared with those at 400°C. Samsonite ($Ag_8Mn_2Sb_4S_{12}$), the only known Mn-bearing sulfosalt mineral, is not a stable phase in the system at temperatures between 300° and 500°C.

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR PHASES A AND B

Phase A				Phase B	
$d_{obs.}$	$d_{calc.}$	R_I	(*hkl*)	$d_{obs.}$	R_I
6.10	6.08	5	210	-	-
5.83	5.81	5	130	5.80	5
3.89	3.88	10	240	-	-
3.57	3.54	25	121	3.57	50
-	-	-		3.50	40
3.34	3.34	50	250	3.35	50
-	-	-		3.30	60
3.21	3.22	20	340	3.21	20
3.15	3.15	30	410	-	-
2.876	2.881 / 2.873	30	311 / 430	2.883	100
2.791	2.792	100	321	2.788	40
2.675	2.678 / 2.660	10	440 / 331	2.680	60
-	-	-		2.565	30
-	-	-		2.489	20
-	-	-		2.408	50
2.342	2.338	15	351	-	-
-	-	-		2.214	80
-	-	-		2.168	60
2.138	2.141	10	511	-	-
2.044	2.045	15	531	2.046	70
-	-	-		2.031	25
-	-	-		2.007	20
1.975	1.972	25	541	-	-
-	-	-		1.966	40
1.955	1.955	10	640	1.952	60
1.933	1.936	10	1.10.0	-	-
1.847	1.870	20	621	1.855	80
1.822	1.820	10	710	-	-
-	-	-		1.805	25

SYNTHESIS OF UCHUCCHACUAITE AND EXTENT OF Mn ⇌ Pb SUBSTITUTION

Uchucchacuaite is readily synthesized from its reported composition, $AgMnPb_3Sb_5S_{12}$ ($Ag_2S{\cdot}2MnS{\cdot}6PbS{\cdot}5Sb_2S_3$) (Moëlo *et al.* 1984) in the temperature range 300°–500°C. $AgMnPb_3Sb_5S_{12}$ has an andorite-type structure, and calculated cell-dimensions are *a* 13.04(1), *b* 19.46(1) and *c* 4.27(1) Å. Cell dimensions of uchucchacuaite are *a* 12.67, *b* 19.32, and *c* 4.38 Å (Moëlo *et al.* 1984).

The extent of Mn ⇌ Pb substitution in the three andorite-type phases was studied at 400°C. Along the join andorite ($x = 1$) – uchucchacuaite ($x = 0$), there is a complete solid-solution series $Ag_{1+x}Mn_{1-x}Pb_{3-x}Sb_{5+x}S_{12}$. Electron-microprobe analysis was performed on the compositions of two members of

this series. Results are $Ag_{1.55}Mn_{0.35}Pb_{2.30}Sb_{5.55}S_{12}$ for $x = 0.65$ and $Ag_{1.25}Mn_{0.80}Pb_{2.70}Sb_{5.35}S_{12}$ for $x = 0.25$, which correlate well with the starting compositions. Calculated unit-cell dimensions of these two members are *a* 12.98(1) and 13.02(1), *b* 19.31(1) and 19.43(1), and *c* 4.24(1) and 4.27(1) Å, respectively.

Uchucchacuaite and Phase A also form a stable join, $Ag_{1+x}Mn_{1+x}Pb_{3-3x}Sb_{5+x}S_{12}$, along which solid solution is incomplete. The uchucchacuaite solid-solution extends from $x = 0$ to $x = 0.65$, which has *a* 13.00, *b* 19.45 and *c* 4.34 Å and an analyzed composition of $Ag_{1.70}Mn_{1.45}Pb_{1.05}Sb_{5.80}S_{12}$. The solid solution based upon Phase A ($x = 1$) has a restricted range to $x = 0.90$. The extent of Mn ⇌ Pb substitution along the join andorite ($x = 0$) and Phase A ($x = 1$), $Ag_2(Pb_{1-x}Mn_x)_2Sb_6S_{12}$, was determined to be $0.40 \geq x \geq 0.95$. The compositions of two andorite solid-solutions were analyzed by electron microprobe, and their cell dimensions were calculated. For $x = 0.20$, the analyzed composition is $Ag_{2.14}Pb_{1.66}Mn_{0.50}Sb_{6.16}S_{12}$, with *a* 12.91(1), *b* 19.27(1), and *c* 4.21(1) Å; for $x = 0.40$, the analyzed composition is $Ag_{1.98}Pb_{1.24}Mn_{0.84}Sb_{6.04}S_{12}$, with *a* 12.96(1), *b* 19.32(1), and *c* 4.13 Å.

Summary and Conclusions

Two ternary phases, $Ag_2Mn_2Sb_6S_{12}$ (Phase A) and $Ag_{1.41}Mn_{2.82}Sb_{5.65}S_{12}$ (Phase B), are stable in the system Ag_2S–MnS–Sb_2S_3 in the temperature range 300°–500°C. Phase A is a Mn isotype of andorite, whereas X-ray powder-diffraction data of Phase B cannot be fully indexed on the basis of an andorite unit-cell. Uchucchacuaite is readily synthesized from its reported composition, $AgMnPb_3Sb_5S_{12}$. It has an andorite-type structure with *a* 13.04(1), *b* 19.46(1) and *c* 4.27(1) Å, comparable with the cell dimensions of uchucchacuaite from Uchu-Chacua, Peru.

With the presence of uchucchacuaite in nature and the synthesis of Mn isotype of andorite, the Mn-members of the andorite isomorphous series (Moëlo *et al.* 1989) are described. The limits of Mn ⇌ Pb substitution between Phase A and andorite along the join $Ag_2(Pb_{1-x}Mn_x)_2Sb_6S_{12}$ are $0.40 \geq x \geq 0.95$, and those between Phase A and uchucchacuaite along he join $Ag_{1+x}Mn_{1+x}Pb_{3-3x}Sb_{5+x}S_{12}$ are $0.65 \geq x \geq 0.90$. Andorite and uchucchacuaite form a complete series.

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