Characterization of temperature-induced phase transitions in $AgSbS_2$ phases by HTXRD, DSC, EXAFS and TEM

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Abstract

Depending on the heat treatment conditions and kinetics, $AgSbS_2$ can be synthesised in different modifications. The cubic disordered form (β-miargyrite) and ordered monoclinic α-miargyrite. Another (third) phase which is different from a and β- forms was synthesised by annealing $AgSbS_2$. This new phase is called the "intermediate phase" or γ-miargyrite.

EPMA, analytical SEM and Ag and Sb X - ray images confirmed the homogeneity all of these phases. High temperature XRD experiments for β-$AgSbS_2$ showed that only the cubic form is present from room temperature up to 210 °C. From 220 °C the 1 1 1 peak shows slightly broadening while the 3 1 1 peak starts to split. Above 220 °C, the 200 and 220 peaks show clear splitting. At 240 °C a very small extra peak can just be distinguished at ~ 26.5° 2θ. As the temperature rises, this peak becomes progressively more intense and further extra peaks can be identified at about 45° and 53.5° 2θ. It is clear that extra reflections appear and therefore there is change in the translational symmetry. Between 280 °C and 300 °C there is a dramatic change in the pattern, particularly in the region 26° - 28° 2θ. The small peak at ~ 26.5 becomes very intense and sharp while the peak at 27.5° (1 1 1 cubic) has changed. The peak splitting and appearance of extra peaks must reflect the occurrence of a phase transition (β-miargyrite to a more stable, less symmetrical polymorph). This phase transition is effectively complete when peaks become sharp at ~300 °C. It is possible to index the 310 °C pattern: α-miargyrite, the stable low temperature form. However, the trace of the 111 peak vanishes at above 310 °C. Thus, it appears that only β-miargyrite is present to 220°C and that α-miargyrite is present at over 310 °C. At intermediate temperatures the phase transition takes place progressively as temperature is increased, with both more-symmetrical (β) and less-symmetrical (α) polymorphs coexisting, the former presumably decreasing in amount and the latter increasing.

DSC scans of synthetic α-miargyrite showed three endothermic reactions. An endothermic reaction beginning below 385 °C is observed and the endothermic reaction starting at 460 °C is likely to be related to the appearance of another phase which is not quenchable and only can exist between 462 °C and the melting point of $AgSbS_2$.

The EXAFS spectra were extracted from the raw data for α and β-miargyrite, along with model fits for the Ag-S distances. Ag K-edge EXAFS spectra for β-miargyrite gave a very much shorter mean Ag-S bond length (2.54 Å) than the XRD bond length (2.8282 A) and only showed 3 nearest-neighbour S atoms rather than 6 as expected for the *fcc* structure. EXAFS results for α-miargyrite gave 3 S atoms at a mean distance from of 2.47 A.

To investigate the phase transition in AgSbS2, *in situ* heating experiments were performed in the TEM. The changes in the diffraction pattern of α-AgSbS, were observed during heating of the sample up to 390 °C. During heating of the specimen to 300 °C, there was no obvious change in the bright-field image or diffraction pattern from the grain. As the temperature was increased

above 300 °C, some of the spots in the [010] pattern of the monoclinic phase became more intense than they were initially. These strong spots are close to a [110] cubic *fcc* pattern w i t h a cell parameter ~ 5.56 Å. Thus there is evidence for an emerging pseudo-cubic symmetry, suggesting an orientation relationship between the structures of the monoclinic and pseudo-cubic cells. The possible orientation relationship between the monoclinic structure and the pseudo cubic cell is: [010]$_{mono}$ // [110]$_{cubic}$ and (001)$_{mono}$ // (111)$_{cubic}$. The equivalent d-spacings are: d(020)$_{mono}$ = 2.21 Å; d(220)$_c$ =2.00 Å; d(001)$_m$ = 3.19 Å and d (1 1 1)$_c$ = 3.26 Å. Further heating of the specimen above 337 °C, resulted in a further change in the intensities of the reflections, while the diffraction patterns from other grains suggested orientation relationships between the monoclinic and cubic cells of [211]$_{cubic}$ // [010]$_{mono}$ and (111)$_{cubic}$ // (101)$_{mono}$. This orientation is different from the first one and it is not clear if there is any simple relationship between the monoclinic and cubic cells. Thus, the γ-phase structure is distinct from that of both α- and β-miargyrite. The intermediate phase appears to be monoclinic with a large cell.

Key words: EXAFS spectra, TEM, analytical SEM, HTXRD, γ-miargyrite,

Introduction

The compound $AgSbS_2$ is of considerable scientific and practical interest. $AgSbS_2$ modifications are distinguished by a high degree of non-linearity of electrical, dielectric and acoustic properties (Valiukėnas, 1980). $AgSbS_2$ has two polymorphs, a low temperature monoclinic form (α-miargyrite) and a high temperature cubic form (β-miargyrite). The monoclinic form inverts to the cubic modification at 380 °C, which is thought to be a first order phase transition (Orliukas et al., 1981). α-miargyrite has the space group A2/a, with a=13.224 Å, b=4.410 Å ,c=12.881 Å and β = 98.48°. Above the phase transition, the symmetry becomes face centered cubic, space group Fm3m with a = 5.652. α-miargyrite is the only naturally occurring form of $AgSbS_2$ and is typically found in polymetallic vein deposits. It commonly occurs as granular anhedral aggregates with galena, sphalerite, pyrargyrite, tetrahedrite, native silver, stephanite and polybasite.

The first structural determination of α-miargyrite was from Hoffmann (1938) using a Weissenberg X-ray camera who established the space group as C_{2h}^6 - A2/a. This structure was subsequently modified by Knowles (1964) who determined the space group as C1c1. Berry (Reference from Daresbury structural references) suggested a space group of C2/c (A2/a) after quenching from above 380°C, but inverts completely to the monoclinic form when slowly cooled and in material that is held slightly below the inversion temperature before quenching (Keighin and Honea, 1969). Bryndzia and Kleppa (1988) presented the enthalpy of formation of the sulphosalt α-miargyrite at 298 K (-4.1 ± 2.3 kJ/mol) from the end - member component sulphides (Ag_2S and Sb_2S_3). They determined the enthalpy of transformation of ordered monoclinic α-miargyrite to disordered cubic β-miargyrite to be 8.7 ± 1.4 kJ/mol. Bryndzia and Kleppa (1988) suggested that the driving energy for this transition may arise from the ordering of displacements of antimony and sulphur atoms forming the base of the Sb_2S_3 pyramid.

Since no in situ high temperature crystallographic studies have been undertaken on miargyrite, experiments were carried out to establish what structural changes occur upon heating.

Experimental conditions

To establish the fraction of β-miargyrite transformed to α-miargyrite, samples of synthesised β-miargyrite were heated in a horizontal tube furnace above the phase transition of α-miargyrite to β-miargyrite and held for 3-4 days to ensure that the samples were in the stability field of β-miargyritc. The temperature was dropped below the phase transition and held for different times. It took a few minutes for the temperature to drop to the desired temperature. This procedure was carried out at five different temperatures (370, 360, 350, 330 and 310°C).

X-ray diffraction was used for mineral identification, structural determinations and quantitative analyses of the fraction of β-miargyrite transformed to α-miargyrite. Quantitative measurements of both phases were performed using XRD methods.

Annealing experiments were performed on the $AgSbS_2$ samples in an attempt to understand their behaviour as a function of different cooling histories. In this case the sample was cither melted and then cooled gradually at a rate of 10°C/day to room temperature, or a mixture of pure elements with the $AgSbS_2$ stoichiometry was heated up to the melting point of $AgSbS_2$ (520°C) before being cooled to 350 °C and held at this temperature for a week, and then quenched in liquid nitrogen. An intermediate form can be synthesised using different heat treatments:

a) annealing (with a very slow cooling rate of 10°C/day);

b) quenching of $AgSbS_2$ derivation from the cubic form

Results

All of the run products synthesised above the phase transition of α to β-miargyrite appeared as homogeneous single phases, except for some samples which contained traces of pyrargyrite and stibnite. However, just below the phase transition, although the run products were chemically homogeneous, examination by XRD revealed that two phases (β and α-miargyrite) were present. At lower temperatures the only phase present was α- miargyrite, but XRD showed that below 280 °C other phases such as pyrargyrite and stibnite occasionally coexisted with α-miargyrite.

Depending on the heat treatment conditions and kinetics, $AgSbS_2$ can be synthesised in different modifications. The cubic disordered form (β-miargyrite) and ordered monoclinic α-miargyrite can be obtained by melting the starting materials at 519°C, holding the temperature above and below the phase transition temperature of miargyrite for the β and α forms respectively and then quenching in liquid nitrogen. Both α and β can also be synthesised by heating the starting materials at temperatures below and above 381°C. Another (third) phase which is different from α and β- miargyrite was synthesised by annealing $AgSbS_2$ at temperatures from the melting point and cooling very slowly (10°C/day) to room temperature. This phase is called the "intermediate phase" or γ-miargyrite.

EPMA and analytical SEM confirmed the homogeneity of α and β-miargyrite as well as of the intermediate phase. Ag and Sb X-ray images have been obtained for the intermediate phase to confirm that it is single phase and chemically homogeneous. The images showed element distribution maps of Ag and Sb in the sample in which the contrast variation reflects a homogeneous distribution of Ag and Sb in the sample.

The XRD diffraction pattern at room temperature for β-miargyrite has sharp peaks and the peak positions are consistent with the reported diffraction patterns of β-miargyrite. XRD confirmed that (β-miargyrite is face centred cubic with a galena structure, 'space group Fm3m. In β -miargyrite, S atoms occupy alternate sites with disordered Ag and Sb in the other set of sites.

Thus Ag should be 6 co-ordinated by S atoms with a bond length 2.8282 Å. The cell parameter of β miargyrite is 5.6565 Å which is slightly different from that reported the literature.

The XRD diffraction pattern at room temperature for α-miargyrite has sharp peaks and most of the peak positions are consistent with the reported diffraction pattern of α-miargyrite. XRD data shows that α-miargyrite is monoclinic, with a space group A2/a, and with cell parameters a=13.221, b=4.410, c=12.867 Å and β=98.463. In the structure of α-miargyrite there are 2 Ag sites, each coordinated by 3 nearest neighbour sulfurs with Ag(1)-S(3) distances of 2.44, 2.50, 2.58 Å (mean 2.51 Å), and Ag(2)-S(3) distances of 2.36, 2.46 Å and 2.89 Å (mean 2.57 Å) (Knowles, 1964). Note that one of the S atoms linked to Ag(2) has bonds which are significantly longer than the other two.

In Fig. 1 the observed powder diffraction pattern at room temperature for γ-miargyrite is shown. Comparison with the observed X-ray pattern of α-miargyrite showed many discrepancies (such as shoulders and an anomalous broadening at the base of some peaks). The reflections suggest that the compound has low symmetry, probably monoclinic.

High temperature XRD experiments for β-AgSbS$_2$ showed that only the β-miargyrite cubic structure is present from room temperature up to 210°C. From 220°C the 1 1 1 peak shows slightly broadening, the 200 and 220 show greater degrees of broadening while the 3 1 1 peak starts to split. Above 220°C, the 200 and 220 peaks show clear splitting (Fig. 2). At 240°C a very small extra peak can just be distinguished at ~ 26.5° 2θ. As the temperature rises, this peak becomes progressively more intense and further extra peaks can be identified at about 45° and 53.5° 2θ (Fig. 3). In a phase transition, if there is no change in the translational symmetry and the unit cell merely changes its shape, no extra reflections should appear in the diffraction pattern. It is clear in these experiments that extra reflections appear and therefore there is change in the translational symmetry. Between 280°C and 300°C (Figs. 4 and.5) there is a dramatic change in the pattern, particularly in the region 26°-28° 2θ. The small peak at ~ 26.5 becomes very intense and sharp while the peak at 27.5° (1 1 1 cubic) has changed. In addition, most of the other peaks become much sharper (e.g. 30°-33° 2θ and 43°-47° 2θ). The peak splitting and appearance of extra peaks must reflect the occurrence of a phase, the metastable, high temperature cubic (β-miargyrite to a more stable, less symmetrical polymorph. Presumably this phase transition is effectively complete when peaks become sharp at ~300°C (Fig. 5). It is possible to index the 310°C pattern: α-miargyrite, the stable low temperature form. However, the trace of the 111 peak vanishes at above 310°C (Fig. 6). Thus, it appears that only β-miargyrite is present to 220°C and that α-miargyrite is present at over 310°C. At intermediate temperatures the phase transition takes place progressively as temperature is increased, with both more-symmetrical (β) and less-symmetrical (α) polymorphs coexisting, the former presumably decreasing in amount and the latter increasing.

DSC scans of synthetic α-miargyrite showed three endothermic reactions (Fig. 7). An endothermic reaction beginning below 385°C is observed and thus is assumed to be the transition of the low temperature (α) form to high temperature (β) form (Sugaki et al., 1978). The endothermic reaction starting at 460°C is likely to be related to the appearance of another phase which is not quenchable and only can exist between 462°C and the melting point of AgSbS$_2$. A

final strong reaction at 522°C is related to the congruent melting reaction of $AgSbS_2$ (Sugaki et al., 1978). For α-miargyrite, the transition temperature differs for the heating and cooling stages. On cooling of this sample at a rate of 10°C/min, no peaks were observed; apparently the cooling rate was not slow enough to allow β-miargyrite to transform back to α-miargyrite.

The corresponding DSC curve produced for β-miargyrite has a strong exothermic reaction beginning at about 236°C and peaking at 262°C (Fig. 7). XRD of this sample at 280°C showed a distortion from the cubic form. The endothermic reaction beginning at 381°C is likely to be the inversion point from this distorted phase to the high temperature form (β-miargyrite). A weak endothermic reaction at 462°C is likely to be related to the previously mentioned higher temperature form, and the strong endothermic reaction beginning at 470°C is related to congruent melting. DSC and associated sythesis experiments show the transition temperature of α to β-miargyrite (with heating rate of 10°C /min) to be at 381°C, which agrees very well with the literature.

The EXAFS spectra which were extracted from the raw data for α and β-miargyrite, along with model fits for the Ag-S distances, are shown in Figs. 8. and 9 respectively. Ag K-edge EXAFS spectra for β-miargyrite (Fig. 8) gave a very much shorter mean Ag-S bond length (2.54 Å) than the XRD bond length (2.8282 Å) and only showed 3 nearest-neighbour S atoms rather than 6 as expected for the *fcc* structure. EXAFS results for α-miargyrite (Fig. 9) gave 3 S atoms at a mean distance from of 2.47 Å. This value agrees with the XRD data (Knowles, 1964) which showed that Ag atom (Ag1) has 3 S atoms at a mean distance of 2.47 Å (range 2.4-2.58 Å) while Ag (2) atom has 3 S atoms at a mean distance of 2.57 Å (range 2.36-2.89 Å). As expected, because of static disorder in the local Ag environment, the EXAFS bond length is slightly shorter than the XRD mean distance.

To investigate the phase transition in AgSbS2, *in situ* heating experiments were performed in the TEM. A bright-field bright image of α-miargyrite showed the electron diffraction pattern of α-miargyrite is consistent with the structure being monoclinic A2/a, a= 13.224, b=4.410, c= 12.881 and β=98.48.

The changes in the diffraction pattern of α-AgSbS, were observed during heating of the sample up to 390°C. During heating of the specimen to 300°C, there was no obvious change in the bright-field image or diffraction pattern from the grain. As the temperature was increased above 300°C, some of the spots in the [010] pattern of the monoclinic phase became more intense than they were initially. These strong spots are close to a [110] cubic *fcc* pattern with a cell parameter ~ 5.56 Å. Thus there is evidence for an emerging pseudo-cubic symmetry, suggesting an orientation relationship between the structures of the monoclinic and pseudo-cubic cells. The possible orientation relationship between the monoclinic structure and the pseudo cubic cell is: $[010]_{mono}$ // $[110]_{cubic}$ and $(001)_{mono}$ // $(111)_{cubic}$. The equivalent d spacings are: $d(020)_{mono} = 2.21$ Å; $d(220)_c = 2.00$ Å; $d(001)_m = 3.19$ Å and $d(1\overline{1}1)_c = 3.26$ Å. Further heating of the specimen above 337°C, resulted in a further change in the intensities of the reflections, while the diffraction patterns from other grains suggested orientation relationships between the monoclinic and cubic cells of $[211]_{cubic}$ // $[010]_{mono}$ and $(111)_{cubic}$ // $(101)_{mono}$. This orientation is different from the first one and it is not clear if there is any simple relationship between the monoclinic and cubic cells. As the temperature was raised to above 390 °C, the grains were subject to beam damage and became sintered.

In a different experiment, a sample of β-miargyrite which had been held at 330°C for half an hour prior to quenching in liquid nitrogen was studied. The resulting product as determined by

XRD, was a mixture of 25% monoclinic and 75% cubic forms of $AgSbS_2$. The room temperature electron diffraction patterns of the sample confirmed the coexistence of the cubic and monoclinic forms of $AgSbS_2$, but no composite grains were found, so no information is available regarding possible orientation relationships between monoclinic and cubic cells. The bright field and dark field images showed faint striations that arc likely to be related to modulated slabs of α- and β-miargyrite. Note that the term 'modulated' refers to structures that cannot be adequately defined based on the conventional simple unit cell and space group (McConnell, 1992). The cubic patterns all showed various degrees of streaking, for instance the $[110]$ diffraction pattern showing streaks parallel to C*. The $[\bar{3}11]$ diffraction pattern show streaks parallel to $g_{2\bar{3}\bar{3}}$. The diffraction patterns which were taken from α-miargyrite are the same as β-miargyrite in that they show streaks, for instance, along the [031] and ; $[\bar{2}11]$ directions. All of the patterns suggest that a modulated structure in the metastable cubic phase is the precursor to the phase transition to the stable α-miargyrite form.

Samples of the γ-phase were studied by TEM but no composite grains were found, so it is not possible to speculate on any orientation relationships between it and either α- or β-miargyrite. Firstly, the composition of the intermediate phase was checked by EDS X-ray spectra and found to be $AgSbS_2$.

The spectra were obtained from isolated areas of the foils where the beam intercepted only a single phase. The crystallographic information was obtained from the very region for which EDS compositional data was obtained but attempts to index the diffraction patterns as α-miargyrite failed. Thus, its structure is distinct from that of both α- and β-miargyrite.

The intermediate phase appears to be monoclinic with a large cell, one of the diffraction patterns obtained was pseudo-cubic, in which the d(111) spacing was tripled. The pseudo-cubic cell edge is about 2.82 Å which is significantly longer than that for β-miargyrite (2.62 Å).

XRD patterns allow some speculative attempts to index the intermediate phase to be made. It was noticed that some of the most intense peaks were similar to that for smithite ($AgAsS_2$). Although, this mineral is a stoichiometric analogue of miargyrite, it is structurally distinct with a much larger unit cell. As many peaks as possible were indexed for the unknown smithite-like $AgSbS_2$ phase. The first satisfactory results suggest that the intermediate (γ) phase is a newly-discovered metastable polymorph of AgSbS. However, many peaks present in the pattern could not be indexed from the smithite cell and are most likely from an impurity phase (e.g. α-miargyrite) in the complex mixture of phases. However, there is also the possibility that the intermediate phase has a lower symmetry than monoclinic and also does not have a smithite structure.

Conclusion

- A new phase was synthesized and called the "intermediate phase" or γ-miargyrite.
- EPMA, analytical SEM and X - ray images confirmed the homogeneity of α and β-miargyrite as well as of the intermediate phase (γ-miargyrite).
- TEM experiments showed the possible orientation relationship between the monoclinic structure and the pseudo cubic cell is: $[010]_{mono}$ // $[110]_{cubic}$ and $(001)_{mono}$ // $(111)_{cubic}$. The equivalent d-spacings are: $d(020)_{mono}$ = 2.21 Å; $d(220)_c$ =2.00 Å; $d(001)_m$ = 3.19 Å and $d(111)_c$ = 3.26 Å.

- HTXRD experiments for β-AgSbS$_2$ showed that at intermediate temperatures the phase transition takes place progressively as temperature is increased, with both more-symmetrical and less-symmetrical polymorphs coexisting.

  - The EXAFS spectra which were extracted from the raw data for α and β-miargyrite, along with model fits for the Ag-S distances, showed 3 nearest-neighbour S atoms rather than 6 as expected for the *fcc* structure. As expected, because of static disorder in the local Ag environment, the EXAFS bond length is slightly shorter than the XRD mean distance.