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# Synthetic Argentojarosite: Physical Properties and Thermal Behavior

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## Abstract

Artificial argentojarosite, $Ag_2Fe_6(OH)_{12}(SO_4)_4$, prepared in connection with U. S. Bureau of Mines research on refractory silver ores, has been synthesized in considerably greater quantities than in previous studies. As a result, a detailed study of its thermal decomposition, optical properties, and physical properties was possible by a combination of chemical analyses, differential thermal analyses, X-ray diffraction, and optical techniques. Cell dimensions are $a = 7.347\ (\pm.010)$, $c = 16.580\ (\pm.053)$; refractive indices are $\epsilon = 1.789$–$1.790$, $\omega = 1.889$–$1.890$. Twenty-nine observed X-ray diffraction reflections including reflection indices, relative intensities, and observed and calculated *d*-spacings are listed.

## Introduction

An appreciable fraction of the silver in some low-grade ores is refractory to conventional cyanidation. Recent studies have shown that ores of this type are also refractory to the more severe treatment sequence involving the electrolytic oxidation procedure developed by the Bureau of Mines, followed by cyanidation.[1] According to electron microprobe data, the silver often occurs as argentojarosite and as varieties of oxide and sulfide minerals. After leaching, some silver-bearing minerals are depleted, but jarosite is usually unaffected. Unfortunately, pure samples of argentojarosite are rarely found because argentojarosite is generally closely associated with one or more of the following minerals: potassium jarosite, plumbojarosite, iron oxides, and fine-grained silica. Thus, in an attempt to learn more about the nature of argentojarosite to aid in increasing the extraction of silver from refractory ores, synthetic argentojarosite was prepared and its physical properties and thermal behavior were studied.

Synthesis of argentojarosite was reported by Fairchild (1933); however, the yield was too small for a complete analysis. Silver was determined to be 19.1 percent $Ag_2O$ compared with a theoretical 20.3 percent. Refractive indices were determined as $\epsilon = 1.785$, $\omega = 1.880$, which agreed with the refractive indices of the natural mineral. In contrast to Fairchild's work, the present syntheses gave good yields. Complete chemical analyses, refractive indices, cell dimensions, and specific gravity were obtained, and a comprehensive thermal study of the synthetic argentojarosite was performed.

Differential thermal analyses of this synthetic argentojarosite gave approximately the same peaks as for the natural argentojarosite studied by Kulp and Adler (1950). However, extensive weight loss experiments performed at fixed temperatures, coupled with X-ray diffraction analyses of the products obtained at various temperatures, resulted in a somewhat different interpretation of the differential thermal analysis peaks from that of Kulp and Adler (1950).

Chemical analyses of jarosites frequently reveal that the amount of water is greater than theoretical, and the alkali metal content is lower than theoretical (Brophy, Scott, and Snellgrove, 1962; Kubisz, 1961). We obtained these same results. Brophy and Sheridan

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[1] B. J. Scheiner, D. L. Pool, J. J. Sjoberg, and R. E. Lindstrom, Extraction of silver from refractory ores, Reno Metallurgy Research Center, Bureau of Mines, U. S. Department of the Interior, to be published.

(1965) attributed the "excess" water to hydronium ions. However, by considering the total volatile material, we conclude that hydronium ions may not adequately explain the apparent discrepancy.

## Synthesis of Argentojarosite

Fairchild (1933), in his synthesis of argentojarosite, started with a saturated solution of $Ag_2SO_4$ mixed in a 1:3 *M* ratio of $Ag_2SO_4$ and $Fe_2(SO_4)_3$, plus a 20 percent excess of the latter, in 1.5–3 *N* $H_2SO_4$. These reactants were heated in a sealed tube for three days at 110°–200°C. The crystals that formed were washed with water and dried.

In the present work, synthetic argentojarosite was prepared by a method similar to that used by Brophy *et al* (1962) to make jarosite and natrojarosite. Due to the limited solubility of $Ag_2SO_4$, low concentrations were necessary. Samples were prepared under the following two conditions:

1. *Preparation in 0.2 N* $HNO_3$. 3.27 g (10.5 millimoles) $Ag_2SO_4$ was dissolved in a boiling solution containing 100 millimoles $HNO_3$ in 437 ml $H_2O$. 63 ml hot 0.5 *M* $Fe_2(SO_4)_3$ solution was added to the $Ag_2SO_4$ solution. The mixture was refluxed at 97°C for approximately 200 hours. A mustard-colored precipitate was filtered off, washed thoroughly with water, and dried over anhydrous $CaSO_4$. The yield was 73 percent based on total Ag content of the mixture.

2. *Preparation in 0.2 N* $H_2SO_4$. 3.27 g (10.5 millimoles) $Ag_2SO_4$ was dissolved in 430 ml boiling $H_2O$. 63 ml hot 0.5 *M* $Fe_2(SO_4)_3$ solution and 5.7 ml 17.6 *N* $H_2SO_4$ (100 meq) were added to the $Ag_2SO_4$ solution. The total volume was 500 ml. The mixture was refluxed and the product recovered as above. The yield was 86 percent based on total Ag content of the mixture.

Elemental analyses for these two samples are reported in Table 1. X-ray diffraction patterns for both products were identical with no evidence of unreacted $Ag_2SO_4$ or $Fe_2(SO_4)_3$.

TABLE 1. Elemental Analyses of Synthetic Argentojarosite Samples (Wt Percent)

| | Calculated for $Ag_2Fe_6(OH)_{12}(SO_4)_4$ | Sample prepared in $HNO_3$ | Sample prepared in $H_2SO_4$ |
|---|---|---|---|
| Ag | 18.94 | 17.12 | 17.10 |
| Fe | 29.41 | 29.4 | 29.1 |
| S | 11.26 | 11.0 | 11.4 |
| O | 39.33 | 40.2 | 42.6 |
| H | 1.06 | 1.08 | 1.34 |

TABLE 2. Physical Properties of Argentojarosite

| | 1 | 2 | 3 |
|---|---|---|---|
| Refractive index: | | | |
| $\epsilon$ | 1.789-1.790 | 1.785 | 1.785 |
| $\omega$ | 1.889-1.890 | 1.882 | 1.905 |
| $\omega-\epsilon$ | .099- .101 | .097 | .120 |
| Cell dimensions: | | | |
| a | 7.347 ±.010 | - | 7.22 |
| c | 16.580 ±.053 | - | 16.40 |
| Specific gravity: | | | |
| Obs | 3.62 ±.11 | 3.65 | 3.80 |
| Calc | 3.660 | - | - |

1. Sample EGB-6-42-3 ($H_2SO_4$ prep).
2. Larsen and Berman, 1934, p. 91.
3. Winchell and Winchell, 1961, p. 171.

## Physical Properties

Physical properties of the artificial argentojarosite prepared in this study are summarized in Table 2. Optical properties were obtained by using standard oil immersion grain mount techniques on a polarizing microscope.

The material was quite homogeneous and very fine grained, with individual crystals ranging from less than a micron to nearly 10 microns in diameter. Most grains were euhedral cube-like rhombohedrons, approximately 3–7 microns across.

Maximum observed refractive index was $\omega$ = 1.889–1.890, while the minimum observed was $\epsilon$ = 1.789–1.790, giving a birefringence of $\omega - \epsilon$ = ~0.100. Excellent interference figures were obtained, confirming that the material was uniaxial negative. Individual crystals showed a strong yellow color in the grain mounts but only weak pleochroism. The bulk powder was deep yellow to yellowish brown in color.

## X-Ray Diffraction and Density Measurements

X-ray powder diffraction measurements were made on a modified General Electric XRD-5 Diffractometer[2] using a Cr target X-ray tube ($\lambda$ = 2.29092Å). Powder smears on glass slides were scanned at 2° $2\theta$/min for identification, while the scans used for obtaining lattice parameters were run at 0.2° $2\theta$/min, with tungsten metal (*a* = 3.16516Å @ 25°C) as an internal standard. Figure 1 shows a typical scan of the synthetic argentojarosite; Table 3 lists 29 indices, corresponding relative intensities, observed *d*-spacings, and calculated *d*-spacings. The major peaks were initially indexed by analogy to existing

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[2] Reference to specific brand names is for identification only and does not imply endorsement by the Bureau of Mines.

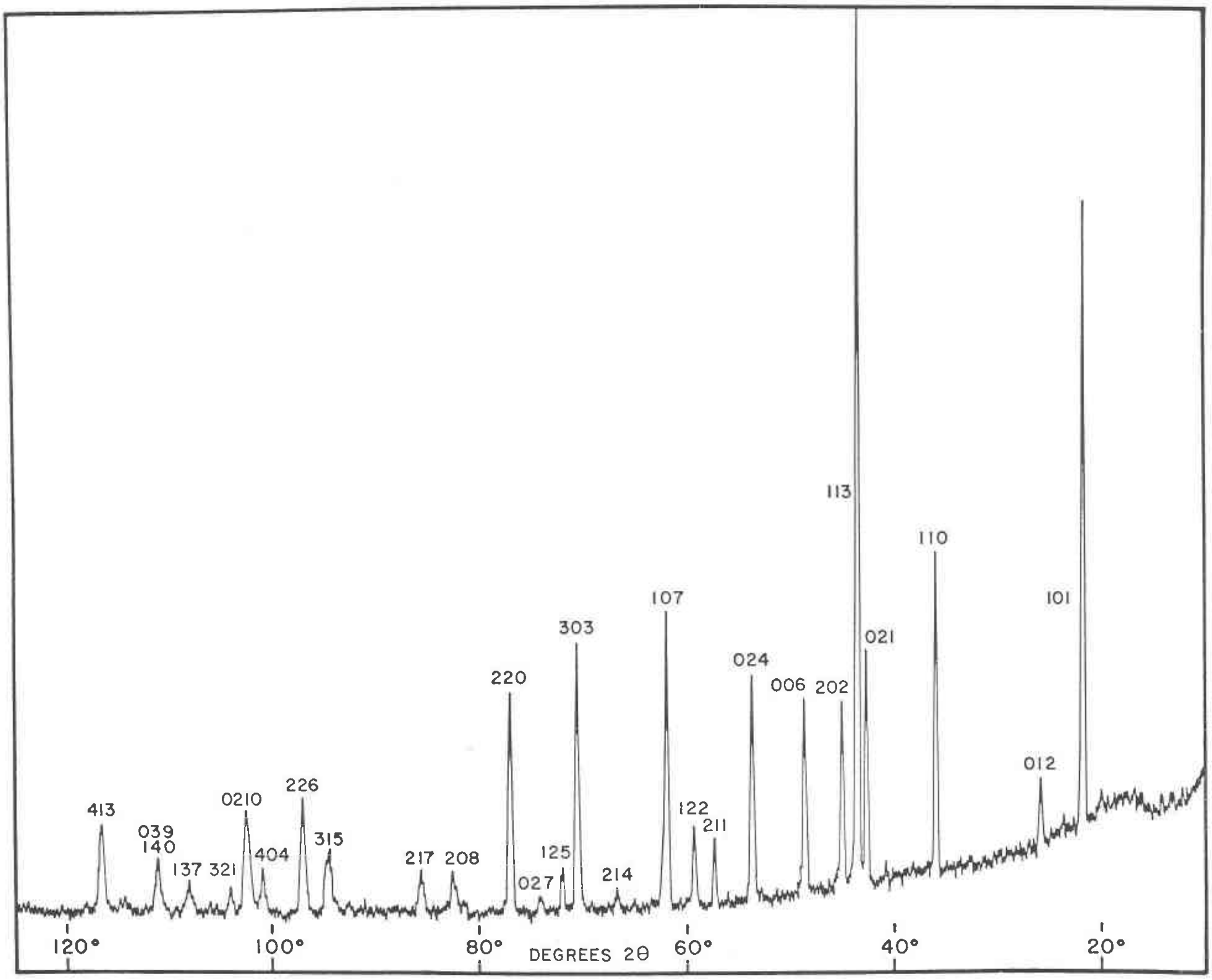

FIG. 1. X-ray diffractometer pattern of synthetic argentojarosite (Cr$K\alpha$).

ASTM cards for jarosite (Card No. 10-443) and natrojarosite (Card No. 11-302). These were later confirmed and other minor peaks indexed by comparing *d*-spacings calculated from possible *hkl* combinations and the refined *a* and *c* values. Using a Wang 700 Programmable calculator, *a* and *c* unit cell dimensions were computed for over 65 possible line pair combinations. The average *a* value obtained was 7.347 ±0.010Å while the *c* value was 16.580 ±0.053Å.

The calculated density was 3.660, which agrees closely with values reported in the literature. Because of the size and very fine-grained nature of the sample, obtaining a measured density proved fairly difficult; however, by using a Beckman Air Comparison Pycnometer (Model 930) calibrated with measured steel ball bearings that bracketed the sample volume, a value of 3.62 ±0.11 was obtained, which agrees quite well with the calculated density of 3.660 g/cm³.

## Thermal Behavior

Differential thermal analysis (DTA) and weight loss experiments were performed on the synthetic argentojarosites. A typical DTA scan, shown in Figure 2, was obtained on a R. L. Stone differential thermal analyzer (Model KA-2H). Since the DTA runs used only approximately 50 mg, a number of larger samples (300 mg) were heated to constant weight at 200°, 350°, 500°, and 800°C so that chemical analyses and X-ray diffraction identification could be performed.

Correlation of the weight loss data (Table 4) with the X-ray diffraction data of the decomposition products indicates that thermal decomposition of synthetic argentojarosite proceeds as follows:

(1) At 200°C, only a small loss in weight occurred, probably due to adsorbed moisture as the X-ray pattern still showed the presence of the jarosite structure.

(2) At 350°C, the samples darkened and very slowly lost weight (averaging 9.3 percent loss) as the jarosite structure disappeared. This decrease in weight closely corresponds to the removal of hydroxide groups as water, with the subsequent destruction of the jarosite crystal structure, as summarized by the probable reaction:

$$Ag_2Fe_6(OH)_{12}(SO_4)_4 \rightarrow Ag_2SO_4 + Fe_2(SO_4)_3 + 2Fe_2O_3 + 6H_2O\uparrow. \qquad \langle 1 \rangle$$

The exact nature of the decomposition products formed at 350°C could not be determined by X-ray diffraction because only a poor, rather complex pattern was obtained.

(3) When heated at 500°C for a short time, the samples appeared unchanged. However, on prolonged heating, they very slowly attained constant weight with a weight loss averaging 23.5 percent. The probable reaction is:

$$Ag_2SO_4 + Fe_2(SO_4)_3 + 2Fe_2O_3 \rightarrow Ag_2SO_4 + 3Fe_2O_3 + 3SO_3\uparrow. \qquad \langle 2 \rangle$$

X-ray diffraction analyses of the solid products formed at 500°C confirmed the presence of only $Fe_2O_3$ and $Ag_2SO_4$.

(4) Finally, prolonged heating at 800°C decomposed silver sulfate into Ag (metal) plus $SO_3$ and $O_2$, thus:

$$Ag_2SO_4 + 3Fe_2O_3 \rightarrow 2Ag + 3Fe_2O_3 + SO_3\uparrow + 1/2O_2\uparrow. \qquad \langle 3 \rangle$$

The presence of silver metal and iron oxide was also confirmed by X-ray diffraction. This compares favorably with Hegedüs and Fukker (1956) who found that $Ag_2SO_4$ decomposed in air above 790°C.

## DTA Interpretation

With weight loss and X-ray diffraction data as a basis, the DTA curve (Fig. 2) was interpreted as follows: The large endothermic peak from 400°–480°C corresponds to the decomposition of the argentojarosite into $Ag_2SO_4$ and other products. X-ray diffraction scans on samples that had been heated in the DTA to approximately 500°C gave only poor patterns; however, peaks were present that coincided with some of the peaks for silver sulfate, iron oxide, and a number of iron sulfate compounds. The fact that the first DTA peak does not occur closer to 350°C, as would be expected from the weight loss studies, is probably due to a time lag problem involving the reaction rates of decomposition. The DTA runs were made at ~10–15°/min while many hours were required to achieved equilibrium in the weight loss experiments. Kulp and Adler (1950) incorrectly assigned the 450° peak to the decomposition of $Ag_2SO_4$ while, in fact, $Ag_2SO_4$ merely undergoes an

TABLE 3. X-ray Powder Diffraction Data for Artificial Argentojarosite

| hkl | I/Io | d(obs) | d(calc) |
|---|---|---|---|
| 101 | 50 | 5.98 | 5.9403 |
| 003 | (1) | 5.55 | 5.5266 |
| 012 | 6 | 5.08 | 5.0474 |
| 110 | 30 | 3.681 | 3.6735 |
| 104 | (1) | 3.479 | 3.4730 |
| 021 | 20 | 3.127 | 3.1244 |
| 113 | 100 | 3.062 | 3.0593 |
| 202 | 15 | 2.972 | 2.9702 |
| 006 | 20 | 2.763 | 2.7633 |
| 024 | 30 | 2.524 | 2.5237 |
| 211 | 5 | 2.380 | 2.3800 |
| 122 | 8 | 2.309 | 2.3097 |
| 107 | 30 | 2.218 | 2.2197 |
| 214 | 2 | 2.079 | 2.0801 |
| 303 | 25 | 1.9794 | 1.9801 |
| 125 | 3 | 1.9454 | 1.9468 |
| 027 | 1 | 1.9000 | 1.8998 |
| 220 | 20 | 1.8366 | 1.8368 |
| 208 | 4 | 1.7352 | 1.7365 |
| 217 | 4 | 1.6860 | 1.6875 |
| 315 | 4 | 1.5594 | 1.5578 |
| 226 | 8 | 1.5286 | 1.5297 |
| 404 | 5 | 1.4847 | 1.4851 |
| 0210 | 8 | 1.4690 | 1.4703 |
| 321 | 5 | 1.4537 | 1.4541 |
| 137 | 3 | 1.4143 | 1.4151 |
| 039<br>140 | 4 | 1.3892 | 1.3908<br>1.3885 |
| 413 | 6 | 1.3464 | 1.3466 |

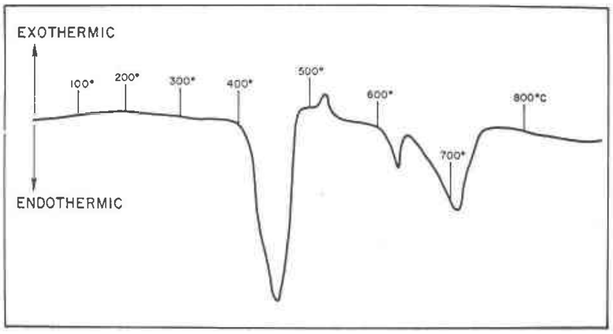

FIG. 2. Differential thermal analysis curve of synthetic argentojarosite (heating rate approximately 10°C/min.).

TABLE 4. Loss in Wt Percent on Heating to Constant Weight

| | Theory | $HNO_3$ prep | $H_2SO_4$ prep |
|---|---|---|---|
| Loss in weight (percent): | | | |
| @200° C, 18 hrs 1 mm Hg (as adsorbed moisture) | - | 0.21 | 0.42 |
| @350° C, 21 hrs 650 mm Hg (as bonded water) | 9.49 | 10.21 | 8.36 |
| @500° C, 47 hrs 650 mm (as $SO_3$ from $Fe_2(SO_4)_3$) | 21.08 | 22.66 | 24.40 |
| @800° C, 90 hrs 650 mm (as $SO_3$ + $O_2$ from $Ag_2SO_4$) | 8.44 | 5.85 | 6.38 |
| Total weight loss (excluding adsorbed moisture) | 39.01 | 38.72 | 39.14 |

endothermic inversion near this temperature (432°C, Barshad, 1952). Thus, the 450° peak we observed is probably a double peak, partly due to breakdown of the argentojarosite structure into various iron sulfate compounds and $Ag_2SO_4$, and partly due to the inversion of the $Ag_2SO_4$ just formed.

Kulp and Adler (1950) attributed the small exothermic peak at 510°C to the crystallization of $Fe_2O_3$ formed during the argentojarosite breakdown. In our study, the exact nature of this small peak could not be determined; however, $Fe_2O_3$ was present in all samples heated to approximately 500°C, both in the DTA and in the weight loss experiments. It appears, though, that $Fe_2O_3$ is formed, at least in part, directly from the initial breakdown of the argentojarsite.

The endothermic peak at about 630°C probably corresponds to the melting of $Ag_2SO_4$ formed earlier. A DTA run on pure $Ag_2SO_4$ gave endothermic peaks for both the inversion point at ~430°C and the melting point at ~650°C.

Kulp and Adler (1950) assigned the 720°C peak to the decomposition of $Fe_2(SO_4)_3$, which is apparently correct. In spite of the weight loss data, $Fe_2(SO_4)_3$ would probably be present because of the short time span of the DTA run. $Fe_2(SO_4)_3$ produced during the 450°C decomposition of the argentojarosite apparently did not have time to convert completely to $Fe_2O_3$. DTA runs on pure $Fe_2(SO_4)_3$ did show a large peak at about 720°C, while samples of the artificial argentojarosite that had been heated to constant weight at 500°C showed only the 450° and 630° peaks for $Ag_2SO_4$.

### "Excess" Water

Alternate ways (I and II) of representing the composition of argentojarosite are:

| I | Percent, by weight |
|---|---|
| Adsorbed water | 0.42 |
| $Ag_2O$ | 18.37 |
| $Fe_2O_3$ | 41.60 |
| $SO_3$ | 28.46 |
| Sum | 88.85 |
| Remainder | 11.15 |

| II | |
|---|---|
| Total volatiles | 39.56 |
| Ag | 17.10 |
| $Fe_2O_3$ | 41.60 |
| Sum | 98.26 |
| Remainder | 1.74 |

The numbers are calculated from the elemental analyses in Table 1 and the weight loss data in Table 4 for the $H_2SO_4$ preparation.

If the remainder in listing I is taken as structurally bonded water, it represents an excess of 1.66 percent water above the theoretical value of 9.49 percent. Brophy and Sheridan (1965) postulated that jarosites contained hydronium ions. Thus they subtracted the theoretical amount of water from the remainder and calculated the difference as $H_3O^+$, which in the above instance would be 1.66 percent $H_3O^+$. Since $H_3O^+$ is a cation, its amount was added to the alkali metal or silver, and by so doing, corrected for both the low alkali metal content and the high water content. Thus, in listing I, $Ag_2O$ plus $H_3O^+$ equal 20.03 percent as compared with the theoretical value of 20.34 percent for $Ag_2O$.

The total volatile material in listing II was determined by loss in weight measurements and represents all adsorbed water, bonded water, $SO_3$, $O_2$, and any other volatile material. The remaining 1.74 percent was non-volatile at 800°C, thus excluding the presence of hydronium ions in the solid products. X-ray patterns did not indicate the presence of unreacted $Ag_2SO_4$ or $Fe_2(SO_4)_3$ in the synthetic argentojarosite, and in any case, any adsorbed Ag or Fe salts would be included in the sum of listing II. Spectrographic analysis of the argentojarosite showed Al, Mg, Pb, and Mo, all at less than 0.005 percent, and Si at 0.01 percent, with 23 other elements undetected.

Since the values in listings I and II are based on only a few analyses, no attempt has been made in this report to explain the significance involved other than to point out that any discrepancies from theoretical values, that in one case were interpreted as "excess" water, can also be interpreted as unidentified solid impurities.

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