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THERMAL ANALYSIS OF SYNTHESIS OF WULFENITE

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Abstract

A derivatograph was used in a thermal analysis study of the synthesis of wulfenite (lead molybdate) by the sintering of cerussite or lead oxide with molybdite. The reaction products were identified microscopically and by using a Siemens crystalloflex diffractometer. The DTA curves of mixtures of cerussite with molybdite show first the characteristic peaks of cerussite. The sharp endothermic peak at 300°C reflects the dehydration of hydrocerussite associated with cerussite. The endothermic peak at 350°C indicates the first step of cerussite decomposition, into $PbO{\cdot}PbCO_3$, and that at 400°C indicates the second step of its decomposition, into lead oxide. The formation of wulfenite takes place at 520°C in an exothermic reaction. The medium endothermic peaks at 880 and 955°C reflect the melting and volatilization of unreacted lead and molybdenum oxides. The DTA curve of sintering of molybdite with lead oxide reveals the formation of wulfenite at 500°C. The melting and volatilization of unreacted lead and molybdenum oxides appear in only one large and sharp endothermic peak at 980°C.

The resulting wulfenite is pale-yellow in thin section, and crystallizes in the tetragonal system, in the form of square tabular crystals, with distinct (011) cleavage.

Keywords: wulfenite

Introduction

Wulfenite (lead molybdate) occurs as a secondary mineral in the oxidation zones of lead deposits, often associated with cerussite, galena, anglesite, pyromorphite, vanadinite, minetite and other minerals. Wulfenite usually occurs as square and thin tabular crystals and crystalline crusts on the walls of leaching cavities. It may also occur as a pseudomorph after lead minerals in the oxidized zone, particularly cerussite [1–4].

The thermal behaviour of the starting materials, i.e. cerussite, lead oxide and molybdite, is well known [2–11]. The DTA curve of cerussite shows its dissociation in two distinct steps. The first step is a large and sharp endothermic peak at 330–400°C, representing the dissociation of cerussite into $PbO{\cdot}PbCO_3$. The second step is a small endothermic peak at 390–440°C, reflecting its decomposition into lead oxide. The small endothermic peak at 660–850°C denotes

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the volatilization and melting of lead oxide [9, 12]. The lead oxide melts at 883°C; its marked volatilization is observed at 800°C and this increases at temperatures higher than 950°C. The temperature of lead oxide dissociation is higher than 2000°C [2]. Molybdenum oxide melts at 770–795°C and boils at 1155°C. Its marked vaporization is observed at 600–650°C. Lead molybdate melts without dissociation at 1050–1065°C, with appreciable vaporization [2–4].

The present work involves a differential thermal analysis study with a derivatograph of the synthesis of wulfenite via the sintering of molybdite with cerussite or lead oxide.

Experimental techniques

Starting materials

The starting materials usually consisted of molybdite mixed with cerussite or lead oxide in particular amounts. Mixes were processed by repeated grinding in an automated agate mortar and sieved in a 200 mesh sieve.

The processed molybdite has the form of flat needles that are white with a greenish tint and an adamantine lustre. In thin sections, the crystals are colourless and elongated and striated parallel to the *c*-axis, flattened on the (010) surface and displaying strong birefringence. Cleavage is not observed. Molybdite crystallizes in the orthorhombic system and is optically positive.

Cerussite is colourless in thin sections, tabular and elongated along the *a*-axis, with distinct cleavage in directions on the (110) and (021) surfaces, and exhibits extreme birefringence and twinning on the (110) surface. It crystallizes in the orthorhombic system and is optically negative. Cerussite is associated with hydrocerussite, which is colourless in thin sections, displays a tabular form and perfect (0001) cleavage, crystallizes in the hexagonal system and is optically negative.

Apparatus

Experiments were carried out with ceramic crucibles, heated in an electric furnace, with the removal of evolved gases and vapours resulting from the sintering reaction. The temperature was regulated automatically with an accuracy of ±5 deg.

The thermal analysis study of wulfenite synthesis via the sintering of molybdite with cerussite or lead oxide was carried out with the MOM derivatograph [13]. This apparatus simultaneously records four curves, the change in temperature (T), differential thermal analysis (DTA), thermogravimetric analysis (TG) quantitatively in mg, and the derivative thermogravimetric curve (DTG) on a single sample under controlled conditions.

Ceramic crucibles and aluminium oxide as inert material were used. The mass of the mix was 500 mg; temperature range, ambient up to 1200°C, in atmospheric air; mass used in TG 20 or 100 mg; heating rate 10 deg·min^{-1}. The DTA and temperature measuring thermocouples consisted of Pt-Pt/Rh wire.

Phase identification

The phases of the products of sintering of molybdite with cerussite or lead oxide were identified both microscopically and by X-ray diffraction analysis, using a Siemens crystalloflex diffractometer. The finely-ground sintered material was mixed with sodium chloride as standard. Its peak at $2\theta=31.38°$ and 45.44° were use for corrections. Nickel-filtered copper radiation was used. The sensitivity of the experiment was 4×10^4 impl/min and the statistical error was 1.5%.

Determination of thermodynamic constants

Before the study of the synthesis of wulfenite, an attempt was made to calculate the thermodynamic constants of the reactions. The thermodynamic data given in Table 1 were used in the calculations.

Table 1 Thermodynamic data used

Thermodynamic function	Value / kcal·mol^{-1}	Reference
$\Delta F°$ $PbMoO_4$ (c)	− 226.69	[17]
$\Delta F°$ MoO_3 (c)	− 159.60	[17]
$\Delta F°$ Cerussite (c)	− 149.70	[15, 16]
$\Delta F°$ PbO (c)	− 45.05	[15, 16]
$\Delta F°$ CO_2 (g)	− 94.26	[15]

1) Synthesis of wulfenite via sintering of molybdite with cerussite
The reaction may be represented as

$$\underset{\text{cerussite}}{PbCO_3} + \underset{\text{molybdite}}{MoO_3} \rightarrow \underset{\text{wulfenite}}{PbMoO_4} + CO_2$$

The standard free energy of the reaction is

$$\Delta F°_{\text{reaction}} = \Delta F°_{PbMoO_4} + \Delta F°_{CO_2} - \Delta F°_{PbCO_3} - \Delta F°_{MoO_3}$$

$$= -226.69 - 94.26 + 149.7 + 159.6$$

$$= -11.65 \text{ kcal/mol.}$$

The equilibrium constant of the reaction of wulfenite synthesis may be calculated from the equation relating to 25°C:

$$\Delta F^{\circ} = -RT \ln K$$

$$\log K = \frac{-\Delta F^{\circ}}{4.575 \times 298} = -0.000733\ \Delta F^{\circ}$$

$$\log K = 0.000733 \times 11650 = 8.539$$

$$K = 3.46 \times 10^{8}$$

2) Synthesis of wulfenite via sintering of molybdite with lead oxide
The reaction may be represented as

$$\underset{\text{molybdite}}{MoO_3} + PbO \rightarrow \underset{\text{wulfenite}}{PbMO_4}$$

The standard free energy of the reaction is

$$\Delta F^{\circ}_{\text{reaction}} = \Delta F^{\circ}_{PbMoO_4} - \Delta F^{\circ}_{MoO_3} - \Delta F^{\circ}_{PbO}$$

$$= -226.69 + 159.6 + 45.05$$

$$= -22.04 \text{ kcal/mol.}$$

$$\log K = 0.000733 \times 22040 = 16.155$$

$$K = 1.43 \times 10^{16}$$

The equilibrium constant is large and the reaction of wulfenite synthesis may be considered in practice to be irreversible.

Results and discussion

Synthesis of wulfenite from mixed of molybdite with cerussite

The thermal analysis data on 1:1 mixes of molybdite with cerussite (Fig. 1) show firstly the characteristic peaks of cerussite. The sharp endothermic peak at 300°C reflects the dehydration of hydrocerussite associated with cerussite, the endothermic peak at 350°C the first step of cerussite dissociation into $PbO{\cdot}PbCO_3$, and the medium endothermic peak at 400°C the second step of its dissociation into lead oxide. These processes involve a marked decrease in mass (TG curve) in steps. The first is the loss of consitutional OH from hydrocerussite, due to its dehydration, and the second is the liberation of carbon dioxide resulting from cerussite dissociation. These results are consistent with the lit-

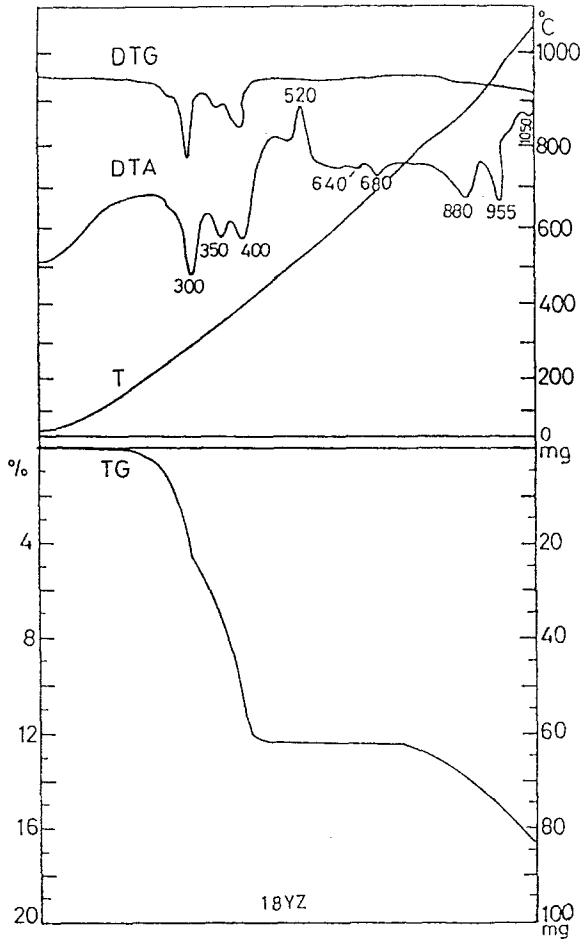

Fig. 1 DTA curve of synthesis of wulfenite by sintering of molybdite with cerussite

erature data [8–12], as the dehydration of hydrocerussite has been reported to take place at 300°C, and the steps of cerussite decomposition are denoted by two endothermic peaks, one at 330–400°C and the second at 390–440°C.

The formation of wulfenite takes place at 520°C, as demonstrated by the exothermic peak. The reaction of molybdenum and lead oxides occurs at 500–600°C, with the formation of lead molybdate [1, 13].

The medium endothermic peaks at 880 and 955°C may denote the melting and vaporization of unreacted lead and molybdenum oxides. The small endothermic peak at 1050°C indicates the melting of the wulfenite produced [1, 13]. The very small endothermic peak at 680°C may represent some vaporization of molybdite as molybdenum oxide volatilizes at 600–650°C.

Microscopic and X-ray diffraction study

The products of the runs at 300, 400, 520 and 955°C were identified microscopically and by using X-ray diffraction.

At 300°C, cerussite and molybdite are the only materials present, the hydrocerussite having disappeared completely. At 400°C, the product is composed of molybdite and lead oxide grains, indicating complete dissociation of the cerussite. At 520°C, wulfenite appears in thin sections as pale-yellow tabular crystals; it is the main constituent, together with some unreacted molybdite and lead oxide grains. This indicates the incompleteness of the reaction, due to the short time. At 955°C and 2 h, wulfenite is virtually the only material present in the product, with a very few residual grains of molybdenum and lead oxides.

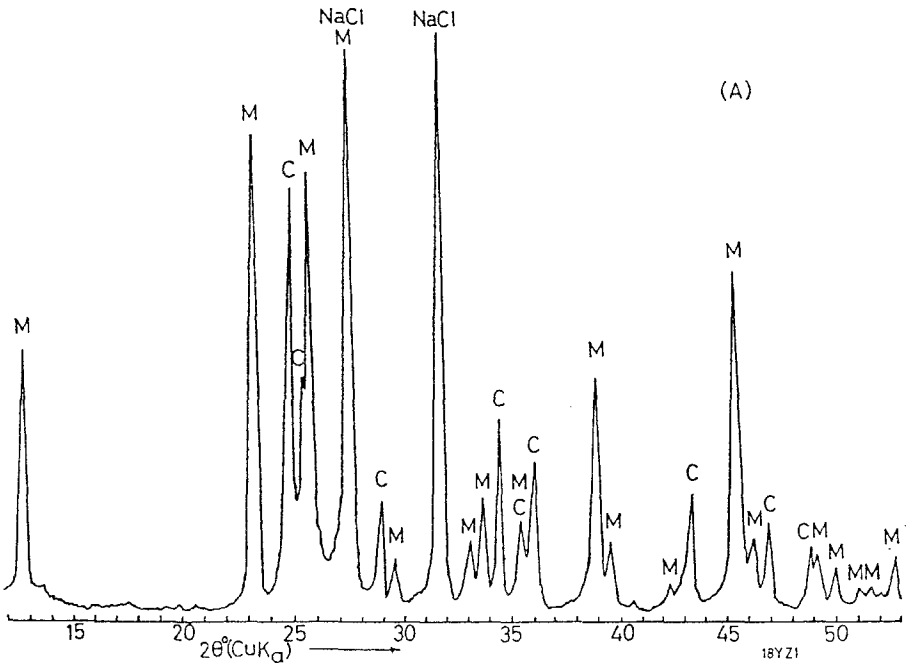

Fig. 2 X-ray powder diffraction patterns of the products of wulfenite synthesis by sintering of molybdite with cerussite; (A, B, C and D at 300, 400, 520 and 955°C respectively) C=Cerussite, M=Molybdite, P=lead oxide and W=Wulfenite

The X-ray diffraction patterns of these products are shown in Fig. 2 (A, B, C and D at 300, 400, 520 and 955°C, respectively). Wulfenite is seen to be the only product at 955°C. The molybdite and lead oxide have disappeared completely. The X-ray peaks of wulfenite are sharp and intense, suggesting good crystallinity.

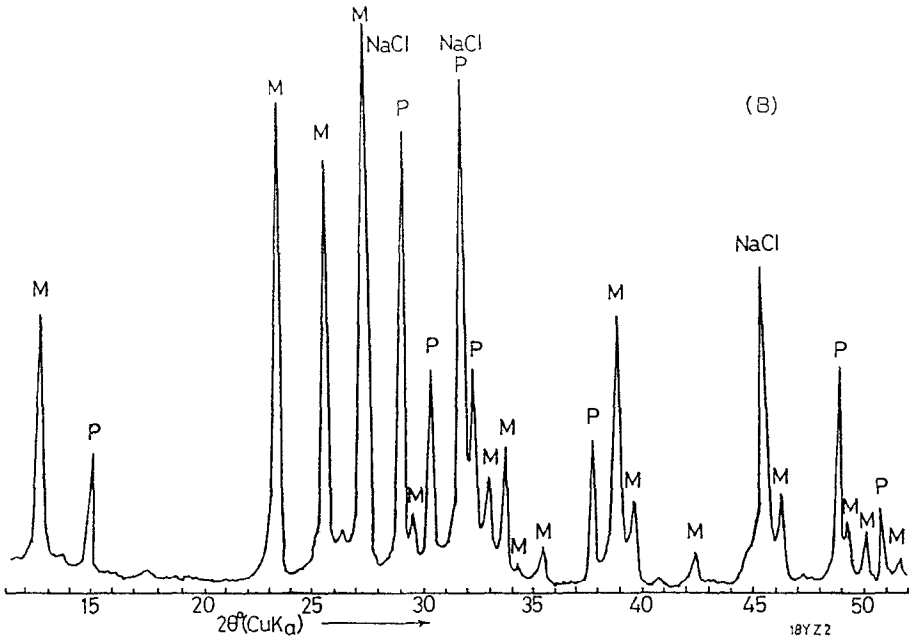

Fig. 2B

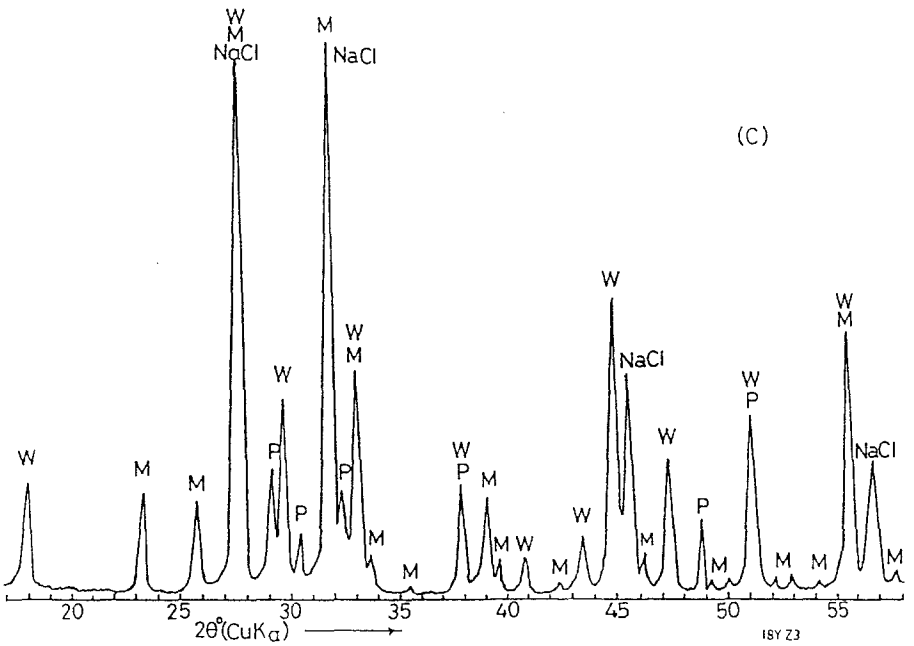

Fig. 2C

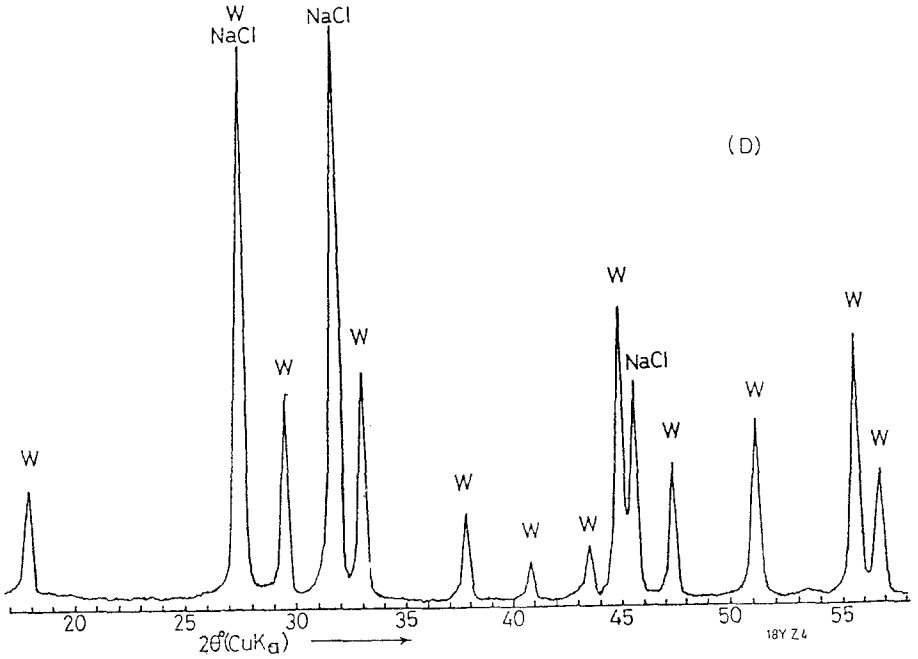

Fig. 2D

Synthesis of wulfenite from mixes of molybdite and lead oxide

The thermal analysis data on 1:1 mixes of molybdite with lead oxide (Fig. 3) indicate the formation of wulfenite at 500°C, as reflected by the exothermic peak at this temperature. The melting and volatilization of unreacted lead and molybdenum oxides are denoted by only one large and sharp endothermic peak at 980°C. The TG curve reveals a considerable decrease in mass, due to such volatilization. The small endothermic peak at 640°C may represent the beginning of vaporization of such oxides.

Microscopic study of the products of the runs at 500°C and at 950°C for 2 h shows that wulfenite is the main phase of the product at 500°C, with very few grains of molybdite and lead oxide. At 950°C, wulfenite is the only constituent in the product. The resulting wulfenite is pale-yellow in thin sections, and crystallizes in the tetragonal system, in the form of tabular crystals, with distinct (011) cleavage.

The X-ray diffraction patterns of the product as 950°C for 2 h (similarly to Fig. 2D) show only the presence of wulfenite. The X-ray diffraction results are in good agreement with the microscopic findings on thin sections of the sintering products.

The mechanism of the reaction of wulfenite synthesis via the sintering of molybdite with cerussite can be considered to be as follows:

At 350°C, the first stage of dissociation of cerussite takes place:

$$2PbCO_3 \rightarrow PbO{\cdot}PbCO_3 + CO_2$$

At 400°C, the second stage of dissociation takes place, with the formation of lead oxide:

$$PbO{\cdot}PbCO_3 \rightarrow 2PbO + CO_2$$

At 500–250°C, molybdite reacts with lead oxide to yield wulfenite:

$$MoO_3 + PbO \rightarrow PbMoO_4$$

molybdite wulfenite

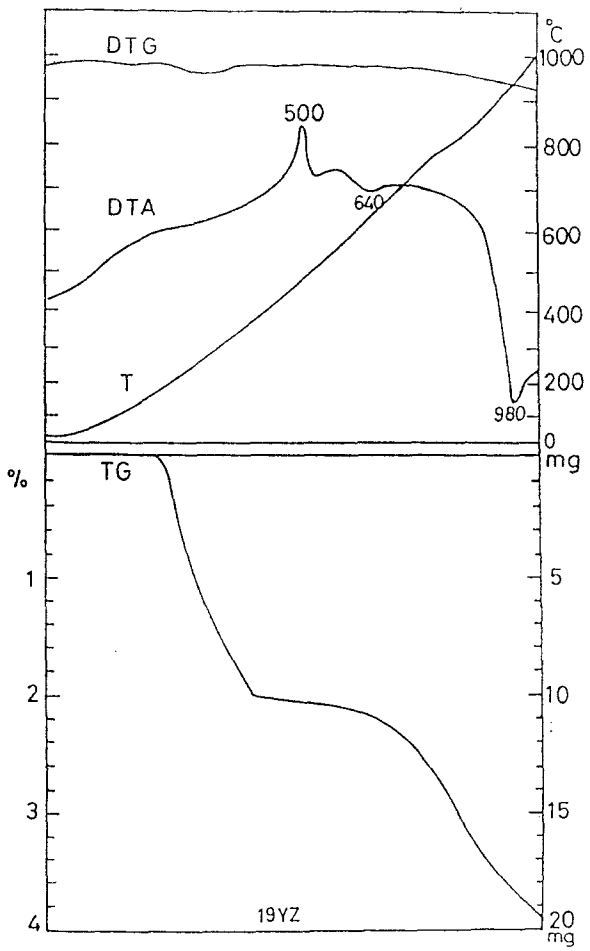

Fig. 3 DTA curve of wulfenite synthesis by sintering of molybdite with lead oxide

This study of the conditions of formation of wulfenite and its thermal stability at higher temperatures has provided good evidence concerning its genesis and occurrence in the oxidized zone of lead deposits.

General characteristics of synthetic wulfenite

The synthetic wulfenite has the following chemical composition: 61.38% PbO and 38.6% MoO_3.

Wulfenite is pale-yellow in thin sections, crystallizes in the tetragonal system, in the form of square tabular crystals, with distinct (011) cleavage, and is

Table 2 X-ray powder diffraction data of synthetic wulfenite

d /Å	*d* /Å	*I*	*I*	*h k l*
ASTM	Observed	ASTM	Observed	
4.960	4.957	11	16	1 0 1
3.244	3.243	100	100	1 1 2
3.028	3.025	22	36	0 0 4
2.718	2.723	24	22	2 0 0
2.383	2.384	8	9	2 1 1
2.212	2.213	5	6	1 0 5
2.082	2.084	7	5	2 1 3
2.021	2.022	31	30	2 0 4
1.920	1.921	14	12	2 2 0
1.787	1.786	18	18	1 1 6
1.653	1.652	25	28	3 0 3, 3 1 2
1.622	1.622	12	12	2 2 4
1.515	1.514	3	4	0 0 8
1.496	1.496	2	2	3 2 1, 3 1 4
1.411	1.411	22	12	3 2 3, 2 1 7
1.359	1.359	3	5	4 0 0

Table 3 Unit cell dimensions and axial angles of wulfenite

Mineral	*a*	*c*	α	β	γ	*V*
	Å	Å	deg. min.	deg. min.	deg. min.	$Å^3$
Wulfenite	(Tetragonal)					
Synthetic	5.4268	12.1043	90.0	90.0	90.0	356.474
	±0.0107	±0.0208	0.0	0.0	0.0	±0.003
Standard	5.435	12.11	90.0	90.0	90.0	357.72

optically negative. The crystals are transparent and have an adamantine lustre. In general, the X-ray diffraction data are consistent with the corresponding values for the natural material (Table 2). The unit cell dimensions and constants of the synthetic wulfenite are given in Table 3. It is observed that the calculated cell dimensions, constants and optic axial angles of the synthetically formed wulfenite are consistent with the corresponding data for the natural mineral.

Conclusions

This thermal analysis study of the synthesis of wulfenite by means of the sintering of molybdite with cerussite or lead oxide has revealed that the formation of wulfenite takes place at 500–520°C. The DTA curves show medium endothermic peaks at 880 and 955°C, reflecting the melting and volatilization of unreacted lead and molybdenum oxides. Wulfenite melts without dissociation at 1050°C, as indicated by the endothermic peak at that temperature. The resulting synthetic wulfenite is pale-yellow in thin sections and crystallizes in the tetragonal system, in the form of square tabular crystals, with distinct (011) cleavage.

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