THERMAL ANALYSIS AND X-RAY DIFFRACTION OF SYNTHESIS OF POWELLITE

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Abstract

Powellite (calcium molybdate) is an essential industrial product used as additive material to steel and for smelting of ferromolybdenum. Powellite often occurs as a secondary mineral and as pseudomorph after molybdenite in the oxidation zone of molybdenite deposits.

The present work reports a thermal analysis study of synthesis of powellite by sintering of molybdite (molybdenium oxide) with calcite or calcium oxide using a derivatograph. The reaction products were identified microscopically and by using a Siemens Crystalloflex diffractometer.

The DTA curve of sintering of molybdite with calcite shows the beginning of the reaction at 480°C with the formation of powellite. The intensive formation of powellite is represented by the medium and wide endothermic peak at 630°C. This is followed by a small endothermic peak at 790°C, representing the melting of unreacted molybdite. This is followed directly by large and sharp endothermic peak at 880°C, representing the dissociation of unreacted calcite. The wide and large endothermic peak at 1155°C represents the boiling of unreacted molybdite with appreciable vaporization.

The DTA curve of sintering of molybdite with calcium oxide shows a medium and wide endothermic peak at 525°C representing the intensive formation of powellite and also the dehydration of calcium oxide. The small endothermic peak at 730°C represents the loss of carbon dioxide due to some carbonatization of calcium oxide with carbon dioxide from air. The medium endothermic at 790°C represents the melting of unreacted molybdite.

The produced powellite is yellow in thin sections, has indistinct cleavage, crystallizes in the tetragonal system in the form of tabular crystals and is optically positive.

Keywords: DTA, synthesis of powellite, XRD

Introduction

Powellite (calcium molybdate) is an essential industrial product used as additive material to steel and for smelting of ferromolybdenum. Calcium molybdate is cheaper than ferromolybdenum, and on smelting of steel, calcium molybdate is reduced by iron where molybdenum is alloyed with steel in the form of solid solution, while calcium oxide remains in the slag [1–5]. Powellite often occurs as a secondary mineral

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in the oxidation zone of molybdenite deposits. Exogenic powellite is derived probably from the reaction of molybdenic acid formed by the oxidation of molybdenite with calcium bearing solutions. Endogenic powellite is rare [4–7].

The thermal behaviour of starting materials, i.e. molybdite, calcite and calcium oxide, is well known [1–3, 6, 8–13]. Molybdite (molybdenum oxide) melts at 770–795°C and boils at 1150–1280°C with its vaporization. Its marked sublimation is observed at 600–650°C. At higher temperatures, molybdenum oxide vaporizes in the form of $(MoO_3)_3$ or Mo_3O_9 [1, 3–6, 8, 19]. The DTA curve of calcite shows its dissociation at 830–920°C as represented by the large and sharp endothermic peak at such temperature [3, 9–11, 13]. The DTA curve of calcium oxide shows two thermal effects. The medium and wide endothermic peak at 450–525°C represents the dehydration of calcium hydroxide content. The small endothermic peak at 740°C represents the loss of carbon dioxide due to some carbonatization of calcium oxide with carbon dioxide from air [11–13, 20]. Powellite or calcium molybdate is thermally stable up to 1200–1300°C without sublimation and melts at 1520°C.

The present work illustrates simultaneous thermal analysis and X-ray diffraction study of synthesis of powellite by sintering of molybdite with calcite or calcium oxide using a derivatograph. The reaction products were identified microscopically and by using a Siemens Crystalloflex diffractometer.

Experimental techniques

Mineralogy

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

The X-ray powder diffraction pattern of the studied molybdite sample shows only the characteristic peaks of molybdite; no mineral impurity was detected. The X-ray peaks of molybdite are well-defined, narrow and intense, suggesting good crystallinity, and their data are consistent with those given in the ASTM index.

Procedure

The starting materials of powellite synthesis usually consisted of molybdite-calcite and molybdite-calcium oxide in particular amounts. Mixes were processed by repeated grinding in an automated agate mortar followed by sieving until all the powder passed through a 200 mesh sieve. Finally, the mixtures were then ground with a pestle and mortar for 1 h to achieve homogeneity.

Apparatus

Experiments were carried out using ceramic crucibles, heated in an electrical furnace in air atmosphere. The temperature was regulated automatically with an accuracy ±5°C.

The thermal analysis study of synthesis of powellite was carried out with a MOM derivatograph [14]. This apparatus simultaneously records four curves: the change of temperature of the sample (T), differential thermal analysis (DTA), thermogravimetric analysis (TG), quantitatively in mg; and the derivative thermogravimetric curve (DTG) on a single sample under controlled conditions.

The parameters during the test were as follows: ceramic crucible; inert material aluminium oxide. Mass of sample 1000 mg; temperature range, ambient up to 1200°C; in air atmosphere; mass used for TG curve 50, 100 and 200 mg, heating rate, 10°C min^{-1}, sensitivity of DTA circuit, 1/3; 1/5 and 1/10; sensitivity of DTG circuit, 1/10. The DTA and temperature thermocouples were Pt–Pt/Rh wires.

Phase identification

The phases of the products of powellite synthesis were identified microscopically and by X-ray diffraction analysis, using a Siemens Crystalloflex diffractometer. The finely ground product of sintering was mixed with sodium chloride as a standard. Its peaks at $2\theta=21.38$ and $45.44°$ were used for corrections. Nickel filtered copper radiation was used. The exposure time was 1 h. Intensities were collected to a maximum $2\theta=70°$. The sensitivity of the experiment was $4\cdot10^4$ imp min^{-1} and the statistical error was 1.5%.

Determination of thermodynamic constants

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

Table 1 Thermodynamic data used

Thermodynamic function/$\Delta F°$	Value/kcal mol^{-1}	Reference
MoO$_3$ (c)	−159.60	[15–18]
CaMoO$_4$ (c)	−344.60	[16–18]
Calcite	−269.78	[16, 17]
CaO (c)	−144.40	[15, 16]
CO$_2$ (g)	−94.26	[16, 17]

Synthesis of powellite via sintering of molybdite with calcite.

The reaction may be represented as:

$$MoO_3+CaCO_3 \rightarrow CaMoO4+CO_2$$

molybdite calcite   powellite
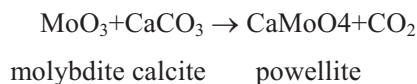
The standard free energy of the reaction ($\Delta F°$) at 25°C is:

$$\Delta F^{\circ}_{\text{reaction}} = \Delta F^{\circ}_{\text{CaMoO}_4} + \Delta F^{\circ}_{\text{CO}_2} - \Delta F^{\circ}_{\text{MoO}_3} - \Delta F^{\circ}_{\text{CaCO}_3} =$$

$$= -344.60 - 94.26 + 159.60 + 269.78 =$$

$$= -438.86 + 429.38 = -9.48 \text{ kcal mol}^{-1}$$

The equilibrium constant of the reaction (K) may be calculated from the equation relating to 25°C

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

$$\lg K = \frac{-\Delta F^{\circ}}{4.57562 \times 298} = \frac{9480}{1363.535} = 6.9525$$

$$K = 8.96 \cdot 10^{6}$$

Synthesis of powellite via sintering of molybdite with calcium oxide.

The reaction may be represented as:

$$MoO_3 + CaO \rightarrow CaMoO_4$$

$$\text{powellite}$$

The standard free energy of the reaction (ΔF°) at 25°C

$$\Delta F^{\circ}_{\text{reaction}} = \Delta F^{\circ}_{\text{CaMoO}_4} - \Delta F^{\circ}_{\text{MoO}_3} - \Delta F^{\circ}_{\text{CaO}} =$$

$$= -344.6 + 159.6 + 144.4 = -40.6 \text{ kcal mol}^{-1}$$

$$\lg K = \frac{40600}{4.57562 \times 298} = 29.7756$$

$$K = 5.96 \cdot 10^{29}$$

The equilibrium constants are large and the reactions of synthesis of powellite by sintering of molybdite with calcite or calcium oxide are considered in practice to be irreversible.

Results and discussion

Differential thermal analysis of molybdite and calcium oxide

Before the thermal analysis study of powellite synthesis by sintering of molybdite with calcite or calcium oxide, the thermal behaviour of molybdite and calcium oxide was studied. The DTA curve of molybdite (Fig. 1) shows small endothermic peak at 100°C, representing the loss of moisture content. The small, wide endothermic peak at 650°C may represent the beginning of subtimation of molybdite. The sharp, medium endothermic peak at 795°C represents its melting. This is accompanied by a gradual decrease in mass (TG curve) due to the vaporization of molybdic oxide. The vapour pressures of molybdic oxide at 650 and 800°C are 0.05 and 10.1 mm Hg, respectively,
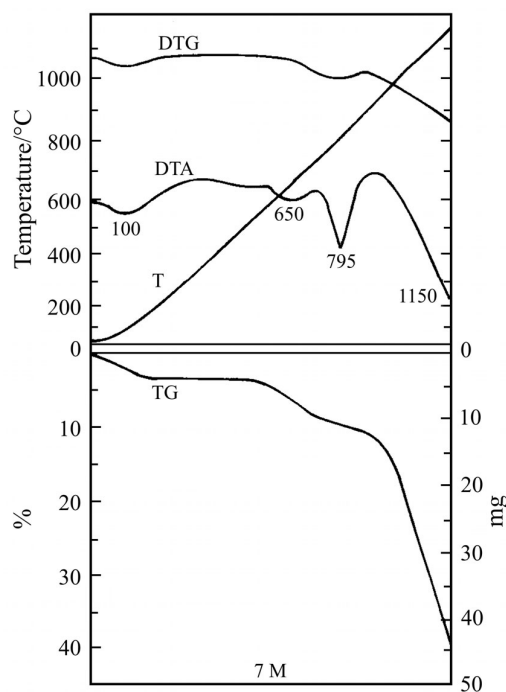
Fig. 1 DTA curve of molybdite. Mass of sample 200 mg; heating rate: 10°C min^{-1}

[1, 4, 5]. The sharp, large endothermic peak at 1150°C indicates boiling of molybdic oxide and its intensive vaporization. This vaporization is indicated by the sharp, large decrease in mass on the TG curve. Molybdic oxide has been reported [1, 4, 5, 19] to vaporize at 800–1000°C in the form of polymerized molecules, $(MoO_3)_3$ or Mo_3O_9 according to:

$$3MoO_3 \ (l) \rightarrow Mo_3O_9 \ (g)$$
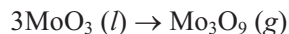
The thermal behaviour of the studied molybdite or molybdic oxide is consistent with literature data [1, 3, 4–6, 8, 19], as molybdic oxide melts at 770–795°C and boils at 1155°C with appreciable vaporization. Molybdic oxide begins sublimation at temperature lower than the melting point (at 625–650°C), where its rate is small. Remarkable vaporization is observed at the melting point 795°C. The vaporization of molybdic oxide intensively takes place with high rate at temperatures higher than 900°C. That is why the industrial purification of molybdic oxide by distillation is performed at 900–1000°C, at which the vapour pressure ranges from 53.9 to 198.8 mm Hg [4, 5, 19].

The DTA curve of calcium oxide (Fig. 2) shows a small, wide endothermic peak at 95°C, representing the loss of moisture content. The sharp, medium endothermic peak at 500°C represents the dehydration of some calcium hydroxide content in calcium oxide. The small endothermic peak at 720°C represents the loss of carbon dioxide due to carbonatization of calcium oxide with carbon dioxide from air. The TG
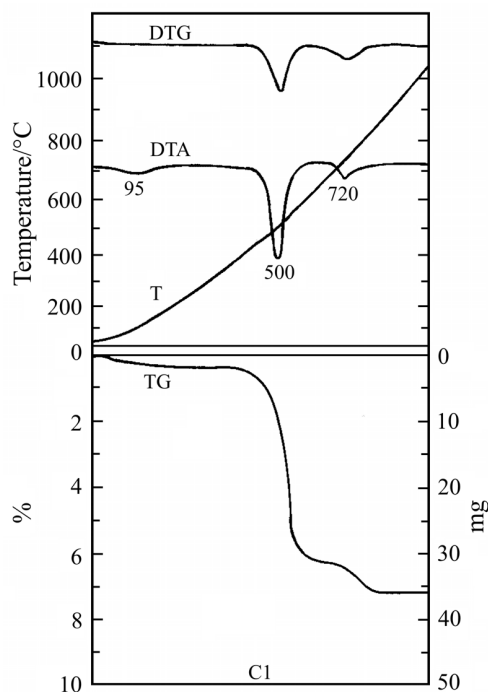
Fig. 2 DTA curve of calcium oxide. Mass of sample 500 mg; heating rate: 10°C min⁻¹

curve shows a sharp, large decrease in mass at 500°C due to such dehydration. This is followed by a small decrease in mass due to the loss of carbon dioxide.

The thermal behaviour of the studied calcium oxide agreed well with the data in [11, 12, 20], as the dehydration of calcium hydroxide was reported to take place at 450–525°C and the loss of carbon dioxide (bound by calcium oxide from air) at 660–730°C.

DTA of synthesis of powellite by sintering of molybdite with calcite

The thermal analysis data of sintering of molybdite-calcite mix of ratio 1:1 (Fig. 3) show the beginning of the reaction between molybdite and calcite at 480°C. The intensive formation of powellite is represented by the wide and medium endothermic peak at 630°C. The medium and sharp endothermic peak at 790°C represents the melting of unreacted molybdic oxide with appreciable vaporization. This is followed directly by large and sharp endothermic peak at 880°C, representing the dissociation of unreacted calcite with sharp decrease of mass.

The TG curve shows a remarkable decrease in mass in four steps. The first is the loss of carbon dioxide from the reaction of sintering of molybdite with calcite with the formation of powellite. The second is due to the vaporization of molybdic oxide during its melting. The third decrease of mass is large and sharp, due to the libration
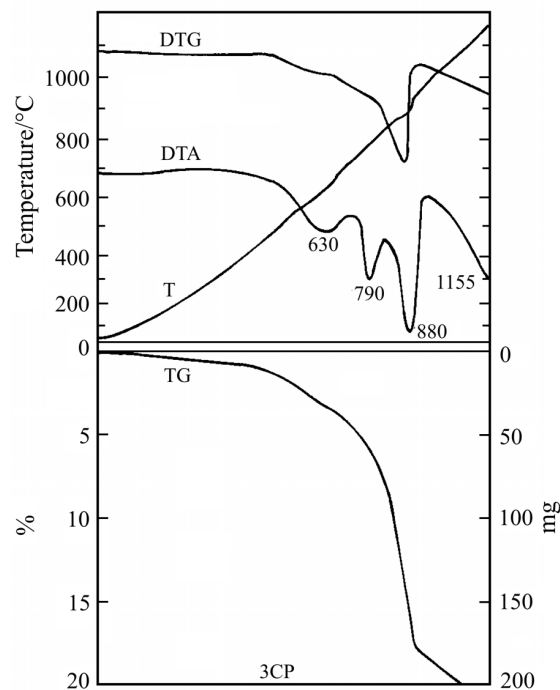
Fig. 3 DTA curve of synthesis of powellite by sintering of molybdite-calcite mix of ratio 1:1. Mass of sample 996 mg; heating rate: $10°C\ min^{-1}$

of carbon dioxide, resulting from calcite dissociation. The fourth is observed at temperature higher than 900°C due to the intensive vaporization of molybdic oxide. The vapour pressure of molybdic oxide at 900°C is 53.9 mm Hg [4, 5, 19].

Microscopic and X-ray diffraction study

The products of the runs at 480, 630 and 880°C for 1 h were identified microscopically and by using X-ray diffraction.

At 480°C, the product of sintering is composed of powellite with large amount of unreacted molybdite and calcite. This shows low rate of the reaction at such temperature. At 630°C, powellite is the main constituent of thin section, with some unreacted molybdite and calcite grains. This indicates high rate of the reaction of sintering and the intensive formation of powellite. Powellite appears in thin section as pale yellow tabular crystals. At 880°C, powellite constitutes the total composition of the product with few relict grains of molybdite and calcium oxide.

The X-ray diffraction patterns of these products are shown in Fig. 4a, b and c at 480, 630 and 880°C, respectively. At 480°C, the product shows the appearance of powellite with considerable amount of unreacted molybdite and calcite, indicating
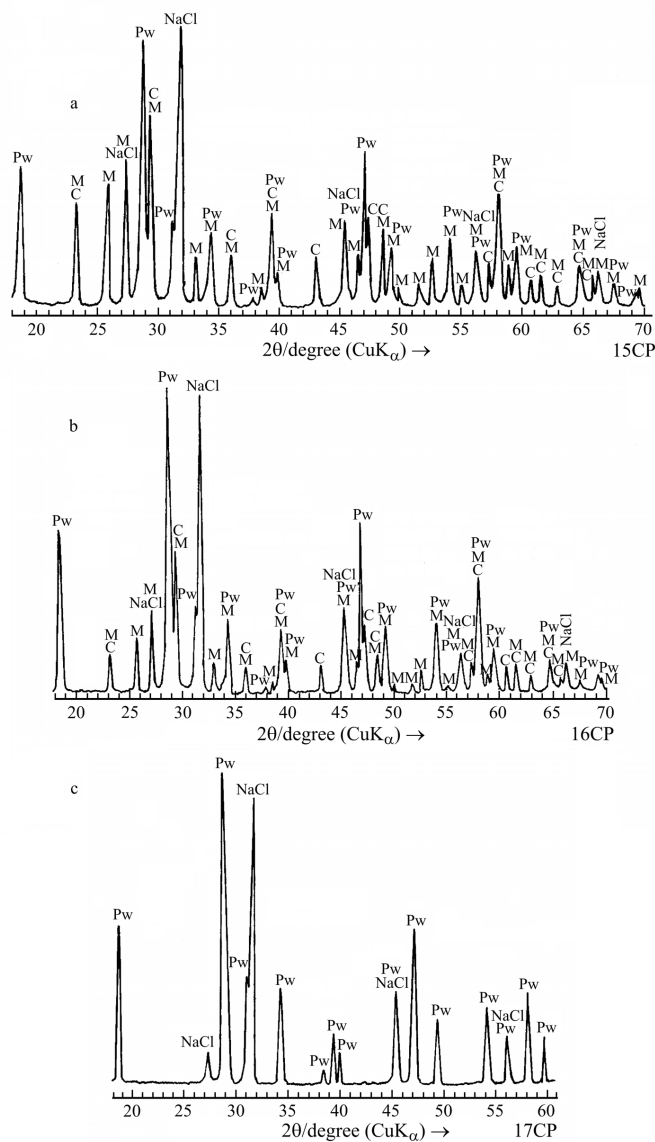
Fig. 4 X-ray diffraction patterns of the products of powellite synthesis by sintering of molybdite-calcite mix 1:1 (a, b and c at 480, 630 and 880°C respectively).
M – molybdite, C – calcite and Pw – powellite

the beginning of the reaction. At 630°C, powellite constitutes the major phase of the sintering product with small amount of molybdite and calcite.

The X-ray diffraction pattern of the end product at 880°C shows only the characteristic powellite peaks, indicating that powellite constitutes the total composition

of the product. The molybdite and calcite peaks disappeared completely, indicating completeness of the reaction and all molybdite and calcite are consumed in the formation of powellite. The X-ray peaks of powellite are sharp, well-defined and intense, suggesting good crystallinity. The X-ray diffraction study of the products of sintering is in good agreement with microscopic study of their thin sections.

DTA of synthesis of powellite by sintering of molybdite with calcium oxide

The thermal analysis study of sintering of molybdite-calcium oxide mix of ratio 1:1 (Fig. 5) shows the beginning of the reaction between molybdite and calcium oxide at 440°C. The wide and medium endothermic peak at 525°C represents the intensive formation of powellite. The dehydration of some calcium hydroxide content in calcium oxide at 500°C in masked by the reaction of formation of powellite. The small endothermic peak at 730°C represents the loss of carbon dioxide due to some carbonatization of calcium oxide with carbon dioxide from air. The medium and sharp endothermic peak at 790°C represents the melting of unreacted molybdic oxide with remarkable vaporization. The large and sharp endothermic peak at 1155°C indicates the boiling of unreacted molybdite and its intensive vaporization.

The TG curve shows a marked decrease of mass in four steps. The first step is the loss of moisture content at 105°C. The second loss at 525°C is due to the
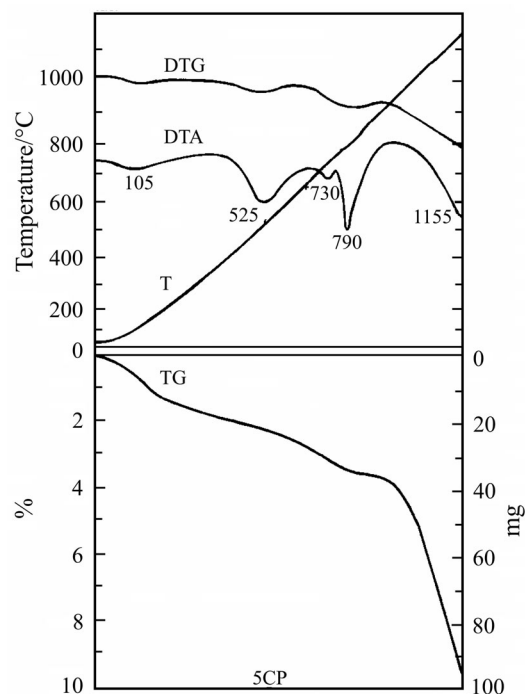

Fig. 5 DTA curve of synthesis of powellite by sintering of molybdite-calcium oxide mix of ratio 1:1. Mass of sample 1000 mg; heating rate: 10°C min^{-1}

dehydration of hydrated calcium oxide content and the beginning of sublimation of molybdite. The third decrease of mass is observed at 730°C representing the loss of carbon dioxide due to some cabonatization of calcium oxide. The fourth step is the decrease of mass due to the vaporization of the melted unreacted molybdite at 790°C. Intensive vaporization of molybdite with considerable loss is observed at the boiling point 1155°C.

The results obtained agreed very well with the data in [4, 5, 11–13, 20], as the dehydration of calcium hydroxide has been reported to take place at 450–525°C and the loss of carbon dioxide (bound by calcium oxide from air) at 660–730°C. The reaction of

Table 2 X-ray powder diffraction data of synthesized powellite

d/Å		I/I_0%		h, k, l
ASTM	Observed	ASTM	Observed	
4.76	4.75	28	34	1 0 1
3.10	3.097	100	100	1 1 2
2.86	2.854	13	15	0 0 4
2.61	2.609	16	17	2 0 0
2.38	2.377	3	3	2 0 2
2.29	2.286	10	13	2 1 1
2.262	2.261	6	7	1 1 4
1.993	1.992	5	6	2 1 3
1.929	1.927	30	37	2 0 4
1.848	1.849	13	14	2 2 0
1.694	1.693	14	15	1 1 6
1.635	1.633	5	7	2 1 5
1.588	1.588	22	22	3 1 2
1.552	1.551	9	9	2 2 4
1.438	1.439	3	4	3 2 1
1.429	1.429	2	2	0 0 8
1.386	1.385	3	3	3 0 3
1.355	1.354	4	5	3 2 3
1.339	1.338	3	3	2 1 7
1.307	1.306	4	5	4 0 0
1.260	1.261	2	2	4 1 1
1.254	1.253	7	9	2 0 8
1.249	1.248	12	14	3 1 6
1.204	1.204	5	6	3 3 2
1.188	1.187	5	6	4 0 4

molybdic oxide and calcium oxide occurs at temperature higher than 400–450°C, with the formation of calcium molybdate or powellite.

The microscopic study of the products of the runs at 440 and 525°C for 1 h shows that powellite is the major phase of the product at 440°C with some molybdite and calcium oxide grains. At 525°C, powellite constitutes the total composition of the end product. The produced powellite is pale yellow with subadamantine lustre. In thin sections, powellite is yellow, crystallizes in the tetragonal system in the form of tabular and some pyramidal crystals; with indistinct cleavage some faces are striated and is optically positive. The X-ray diffraction pattern of the product at 525°C (similar to Fig. 4c) shows only the presence of powellite.

General characteristics of the synthesized powellite

The synthesized powellite is pale yellow in hand-specimen and has sub-adamantine luster. In thin sections, powellite is yellow, has indistinct cleavage, crystallizes in tetragonal system in the form of pyramidal or tabular crystals, some faces are striated and is optically positive.

The synthesized powellite has the followed chemical composition: 71.98% MoO_3 and 28.01% CaO.

The X-ray diffraction pattern of the produced powellite (Fig. 4c) shows the characteristic and well-defined peaks of powellite, which are sharp and intense, suggesting good crystallinity. The X-ray diffraction data of the synthetic powellite are consistent with the corresponding ASTM values of the natural mineral (Table 2).

Table 3 Unit cell dimensions and axial angles of the synthesized powellite

Mineral	a/Å	c/Å	α/°C	β/°C	γ/°C	V/Å^3
Powellite	(Calcium molybdate) Tetragonal					
Synthetic	5.2287	11.4435	90.00	90.00	90.00	312.857
	0.0154	0.0303	0.00	0.00	0.00	0.026
Standard	5.23	11.44	90.00	90.00	90.00	312.917

The unit cell dimensions and constants of the synthetic powellite are given in Table 3. It is observed that the calculated cell dimensions, constants and optic axial angles of the synthesized powellite are consistent with the corresponding data of the natural mineral.

Conclusions

The thermal analysis and X-ray diffraction study of synthesis of powellite by sintering of molybdite with calcite or calcium oxide has revealed the following conclusions:

- The DTA curve of molybdite (molybdic oxide) shows three thermal effects. The small, wide endothermic peak at 650°C may represent the beginning of sublimation

of molybdite. The sharp, medium endothermic peak at 795°C indicates its melting with remarkable vaporization. The large, sharp endothermic peak at 1150°C represents the boiling of molybdite and its intensive vaporization. The TG curve reveals a sharp, large decrease in mass due to such vaporization of molybdic oxide.

- The DTA curve of sintering of molybdite with calcite shows the beginning of the reaction at 480°C with the formation of powellite. The intensive formation of powellite is represented by the medium and wide endothermic peak at 630°C. The medium and sharp endothermic peak at 790°C represents the melting of unreacted molybdite. This is followed directly by large and sharp endothermic peak at 880°C, representing the dissociation of unreacted calcite. The wide, large endothermic peak at 1155°C represents the boiling of unreacted molybdite with appreciable vaporization.

- The DTA curve of sintering of molybdite with calcium oxide shows a medium, wide endothermic peak at 525°C representing the formation of powellite and also the dehydration of calcium oxide. The small endothermic peak at 730°C represents the loss of carbon dioxide due to some carbonatization of calcium oxide with carbon dioxide from air. The medium endothermic peak at 790°C represents the melting of molybdite. At temperature higher than 800°C, intensive vaporization of unreacted molybdite is observed up to the boiling point.

The synthesized powellite is yellow in thin sections, has indistinct cleavage, crystallizes in tetragonal system in the form of pyramidal crystals, some are tabular and is optically positive.

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