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THERMAL ANALYSIS AND X-RAY DIFFRACTION OF SYNTHESIS OF SCHEELITE

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Abstract

Scheelite (calcium tungstate) is the product of one of the processing methods of wolframite by its roasting with calcium oxide or limestone or its fusion with calcium chloride, followed by acid processing of calcium tungstate with the formation of tungstic acid. Scheelite occurs in contact metamorphic deposits, hydrothermal veins and pegmatites.

The present work illustrates a thermal analysis study of synthesis of scheelite by sintering of wolframite with calcite and sintering of tungsten 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 wolframite with calcite shows the beginning of the reaction at 560°C with the formation of scheelite. The intensive formation of scheelite is represented by the medium and wide endothermic peak at 740°C. This is followed directly by a large and sharp endothermic peak at 860°C, representing the dissociation of unreacted calcite.

The DTA curve of tungsten trioxide shows three thermal effects. The sharp exothermic peak at 320°C represents the oxidation of tungsten oxide content of lower valency. The endothermic peaks at 750 and 1090°C are related to polymorphic changes of tungsten trioxide. The beginning of its sublimation is observed at temperature higher than 800°C.

The DTA curves of sintering of tungsten trioxide with calcite or calcium oxide indicate that the intensive formation of scheelite takes place by endothermic reactions at 660 and 545°C respectively. The medium and small endothermic peaks at 520 and 730°C on the DTA curve of tungsten trioxide with calcium oxide represent the dehydration of calcium oxide and the loss of carbon dioxide due to some carbonatization of calcium oxide with carbon dioxide from air, respectively.

The produced scheelite is colorless in thin sections, has distinct cleavage (101), crystallizes in the tetragonal system in the form of tabular crystals and is optically positive.

Keywords: DTA, synthesis of scheelite, XRD

Introduction

Scheelite (calcium tungstate) is the product of one of the processing methods of wolframite. Direct processing of wolframite by acid leaching is difficult. Therefore, acid processing of wolframite is intensified by preliminary roasting of wolframite with calcium oxide or limestone or its fusion with calcium chloride with the formation of scheelite. This is followed by acid processing of scheelite produced with the forma-

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tion of tungstic acid [1–5]. Scheelite occurs in contact metamorphic deposits, in hydrothermal veins, pegmatites and in placer deposits commonly associated with wolframite [1, 3, 6, 7].

The thermal behaviour of the starting materials of scheelite synthesis, i.e. wolframite, calcite, tungsten trioxide and calcium oxide, is well known [8–14, 20]. Pure wolframite does not show any thermal effect at heating up to 1000°C [11]. The DTA curve of calcite shows its dissociation as is represented by the large and sharp endothermic peak at 830–920°C [2, 8–10]. The DTA curve of lime shows medium and small endothermic peaks at 525 and 740°C representing its dehydration and the loss of carbon dioxide due to some carbonatization of calcium oxide with carbon dioxide from air [12, 13]. The DTA curve of tungsten trioxide shows four thermal effects at 300–330, 350–380, 720–750 and 1100°C. The last three effects are reversible and related to polymorphic changes of tungsten trioxide. The exothermic effect at 300–330°C is irreversible and is due to the oxidation of tungsten oxide content of lower valency. This is formed by some reduction of tungsten trioxide in the process of thermal decomposition of ammonium paratungstate [3, 4, 14, 19]. The tungsten trioxide melts at 1470 and boils at 1850°C [3, 4]. Its beginning of sublimation is observed at 800–900°C and its appreciable sublimation at 1200°C [19].

The present work illustrates a differential thermal analysis and X-ray diffraction study of synthesis of scheelite by sintering of wolframite with calcite and tungsten trioxide 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 wolframite is characterized by black colour and streak in hand-specimens, greasy to submetallic lustre, high specific gravity (7.4) and high hardness. Crystals are thick tabular to prismatic, with vertical faces often striated parallel to the *c*-axis. In polished sections, it is greyish white with faint brownish tint and has long prismatic to tabular form. Cleavage is often distinct in two directions. Twinning is common and usually of simple contact type. The crystals show low reflectivity, deep brownish red internal reflections, weak anisotropism and oblique extinction. Wolframite crystallizes in monoclinic system and is optically positive.

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

Chemical composition

The chemical composition of the studied wolframite sample is given in Table 1.

Table 1 Chemical composition of wolframite

Chemical component	Content/%
WO_3	74.81
FeO	19.20
MnO	4.35
SiO_2	0.24
SnO_2	0.32
CuO	0.11
CaO	0.44
As_2O_3	0.20
S	0.25
P_2O_5	0.05

Procedure

The starting materials of scheelite synthesis usually consisted of wolframite-calcite and tungsten trioxide-calcite or 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 scheelite was carried out with a MOM derivatograph [15]. 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 aluminum oxide. Mass of sample 1000 mg; temperature range, ambient up to 1200°C; in air atmosphere; mass used for TG curve 20, 50 and 200 mg, heating rate, 10°C min^{-1}, sensitivity of DTG 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 scheelite 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 occurring at 2θ=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 $4\cdot10^4$ impl. min^{-1} and the statistical error was 1.5%.

Determination of thermodynamic constants

Before the thermal analysis study of scheelite synthesis, an attempt was made to calculate the thermodynamic constants of the reactions. The thermodynamic data given in Table 2 were used in calculations.

Table 2 Thermodynamic data used

Thermodynamic function/ΔF^0	Value/kcal mol^{-1}	Reference
$FeWO_4$ (*c*)	–259.800	[16]
$CaWO_4$ (*c*)	–376.906	[17, 18]
Calcite	–269.908	[17, 18]
WO_3 (*c*)	–182.630	[16, 18]
CaO (*c*)	–144.353	[17, 18]
Fe_2O_3 (*c*)	–177.728	[17, 18]
CO_2 (*g*)	–94.260	[17]

Synthesis of scheelite via sintering of wolframite with calcite

The reaction may be represented as

$$2FeWO_4+2CaCO_3+0.5O_2 \rightarrow \underset{\text{Scheelite}}{2CaWO_4}+Fe_2O_3+2CO_2$$

The standard free energy of the reaction (ΔF^0) at 25°C is

$$\Delta F^0_{\text{reaction}}=2\Delta F^0_{CaWO_4}+\Delta F^0_{Fe_2O_3}+\Delta F^0_{CO_2}-2\Delta F^0_{FeWO_4}-2\Delta F^0_{CaCO_3}$$

$$=-2\times376.906-177.728-2\times94.26+2\times259.8+2\times269.908$$

$$=-1120.06+1059.416=-60.644 \text{ kcal mol}^{-1}$$

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

$$\Delta F^0=-RT\ln K$$

$$\log K=\frac{-\Delta F^0}{4.57562.298}=\frac{60644}{4.57562.298}=44.476$$

$$K=2.99\cdot10^{44}$$

Synthesis of scheelite via sintering of wolframite with calcium oxide

The reaction may be represented as

$$2FeWO_4+2CaO+0.5O_2 \rightarrow 2CaWO_4+Fe_2O_3$$

The standard free energy of the reaction (ΔF^0) at 25°C

$$\Delta F^0_{\text{reaction}}=2\Delta F^0_{CaWO_4}+\Delta F^0_{Fe_2O_3}-2\Delta F^0_{FeWO_4}-2\Delta F^0_{CaO}$$
$$=-2\times376.906-177.728-2\times259.8+2\times144.352$$
$$=-931.54+808.304=-123.236 \text{ kcal mol}^{-1}$$

$$\log K=\frac{123236}{4.57562\cdot298}=90.38$$

$$K=2.4\cdot10^{90}$$

Synthesis of scheelite via sintering of tungsten trioxide with calcite

The reaction may be represented as

$$WO_3+CaCO_3 \rightarrow CaWO_4+CO_2$$

$$\Delta F^0_{\text{reaction}}=\Delta F^0_{CaWO_4}+\Delta F^0_{CO_2}-2\Delta F^0_{WO_3}+\Delta F^0_{CaCO_3}$$
$$=-376.906-94.26+182.63+269.908$$
$$=-18.628 \text{ kcal mol}^{-1}$$

$$\log K=\frac{18628}{4.57562\cdot298}=13.662$$

$$K=4.59\cdot10^{13}$$

Synthesis of scheelite via sintering of tungsten trioxide with calcium oxide

The reaction may be represented as

$$WO_3+CaO \rightarrow CaWO_4$$

$$\Delta F^0_{\text{reaction}}=\Delta F^0_{CaWO_4}-\Delta F^0_{WO_3}-\Delta F^0_{CaO}$$
$$=-376.906+182.63+144.352$$
$$=-49.924 \text{ kcal mol}^{-1}$$

$$\log K=36.614$$

$$K=4.11\cdot10^{36}$$

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

Results and discussion

DTA of synthesis of scheelite by sintering of wolframite with calcite

The thermal analysis data of sintering of wolframite–calcite mix of ratio 1:1.25 (Fig. 1) demonstrate the beginning of the reaction at 560°C with the formation of scheelite. The intensive formation of scheelite is represented by the medium and wide endothermic peak at 740°C. This is followed directly by large and sharp endothermic peak at 860°C, representing the dissociation of unreacted calcite. These processes involve a large and sharp decrease in mass (TG curve), due to the loss of carbon dioxide, resulting from the dissociation of calcite.

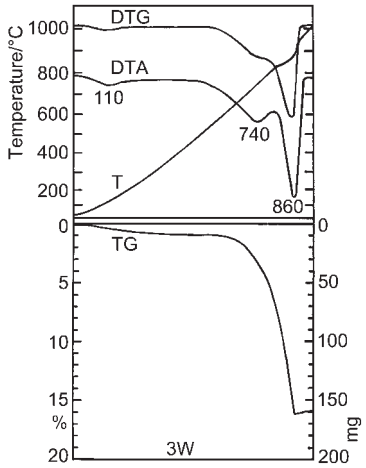

Fig. 1 DTA curve of synthesis of scheelite by sintering of wolframite–calcite mix of ratio: 1:1.25. Mass of sample 1000 mg. Heating rate: 10°C min^{-1}

The results obtained are consistent with literature data [1, 3, 4], as the reaction of wolframite and calcite takes place at 700–775°C with the formation of scheelite.

Microscopic and X-ray diffraction study

The products of the runs at 600 and 740°C during 1 h were identified microscopically and by using X-ray diffraction.

At 600°C, wolframite and scheelite constitute the main composition of the product with hematite and relict grains of unreacted calcite. At 740°C, scheelite constitutes the total composition of the product with hematite and few relict grains of unreacted wolframite.

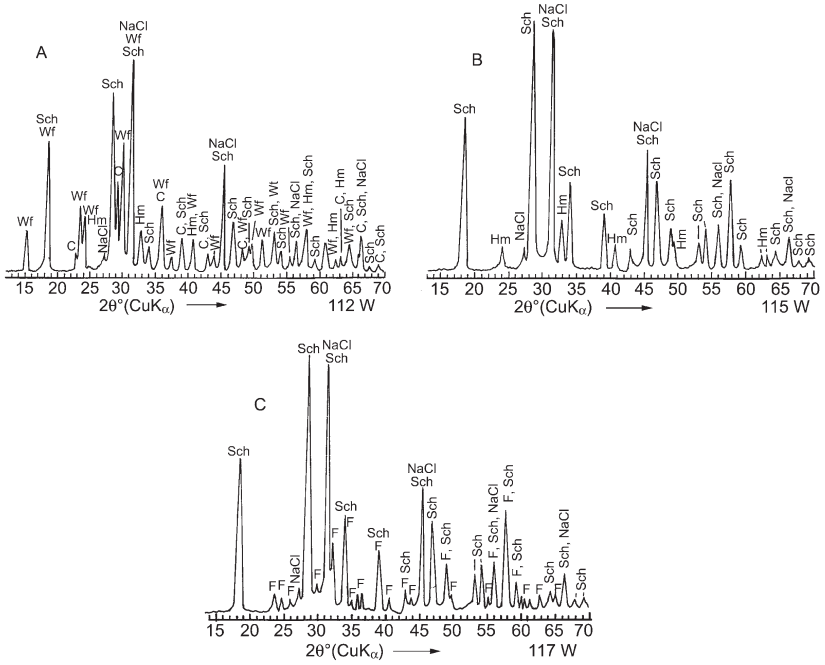

Fig. 2 X-ray diffraction patterns of the products of scheelite synthesis using wolframite–calcite mix of ratio 1:1.25. (A, B and C at 600, 740 and 1000°C respectively). Wf – wolframite; C – calcite; Hm – hematite; Sch – scheelite and F – calcium ferrite

The X-ray diffraction patterns of the products at 600, 740 and 1000°C are shown in Figs 2 A, B and C respectively. At 600°C, the product of sintering consists mainly of wolframite and scheelite with hematite and undissociated calcite. This indicates the low rate of the reaction between wolframite and calcite. At 740°C, scheelite is observed to be the main constituent of the product with hematite. The X-ray peaks of wolframite disappear completely, indicating that the relict grains of unreacted wolframite is out of the detection limit of X-ray diffraction. At 1000°C, scheelite constitutes the total composition of the product of this run with calcium ferrite of composition $Ca_2Fe_2O_5$. The X-ray peaks of scheelite are well defined, sharp and intense, suggesting good crystallinity.

Differential thermal analysis of tungsten trioxide

Before the thermal analysis study of scheelite synthesis by sintering of tungsten trioxide with calcite or calcium oxide, the thermal behaviour of tungsten trioxide was studied. The DTA curve of tungsten trioxide (Fig. 3) shows small endothermic peak at 90°C, representing the loss of moisture content. The medium and sharp exothermic peak at 320°C represents the oxidation of tungsten oxide content of lower valency.

The wide endothermic peak at 750°C represents phase transformation from alpha form to beta-one. The small endothermic peak 1090°C represents the polymorphic change of tungsten trioxide from beta to gamma-form. There is no change of the mass of the sample (TG curve). The mass is slightly decreased at temperature higher than 800°C representing the beginning of sublimation of tungsten trioxide.

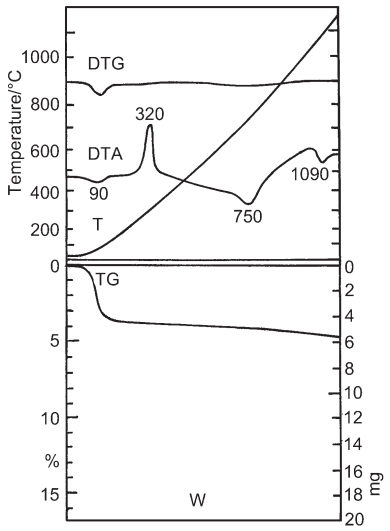

Fig. 3 DTA curve of tungsten trioxide. Mass of sample 120 mg; heating rate: 10°C min^{-1} and DTA: 1/3

The thermal data obtained of tungsten trioxide agreed well with the literature data [3, 4, 14, 19, 20], as the oxidation of tungsten oxide content of lower valency associated with tungsten trioxide takes place at 330°C. Tungsten trioxide has three crystalline forms. Alpha-form is stable up to 720–750°C, beta-form stable in the temperature range 720–1100°C and gamma-form stable at temperature higher than 1100°C. The thermal effects of these polymorphic changes are reversible [4, 14, 19]. The beginning of sublimation of tungsten trioxide is observed at temperature range 800–900°C [19] or precisely at 850°C [3] and the rate of sublimation increases at 1200°C, reaching 35% during 10 min [3, 19].

DTA of synthesis of scheelite by sintering of tungsten trioxide with calcite

The thermal analysis data of sintering of tungsten trioxide–calcite mix of ratio 1:1.25 (Fig. 4) show medium and sharp exothermic peak at 330°C, representing the oxidation of tungsten oxide content of lower valency. The beginning of the reaction between tungsten trioxide and calcite is observed at 520°C. The intensive formation of scheelite is represented by the wide endothermic peak at 660°C. The phase transformation of tungsten trioxide from alpha to beta-form at 750°C is masked by the de-

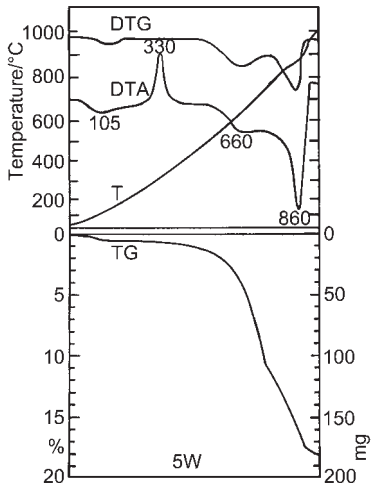

Fig. 4 DTA curve of synthesis of scheelite by sintering of tungsten trioxide–calcite mix of ratio: 1:1.25. Mass of sample 1070 mg; heating rate: 10°C min^{-1}

composition of the unreacted calcite. This is represented by the large and sharp endothermic peak at 860°C.

The TG curve shows a marked decrease in mass in three steps. The first is the loss of carbon dioxide from the reaction of sintering of tungsten trioxide with calcite with the formation of scheelite. The second is due to the liberation of carbon dioxide, resulting from calcite dissociation. The third decrease of mass is observed at 900°C due to slight sublimation of tungsten trioxide. The sublimation of tungsten trioxide does not exceed 0.1–0.2% at 900°C in air atmosphere [19].

Microscopic and X-ray diffraction study

The products of the runs at 520, 660 and 860°C during 1 h were identified microscopically and by using X-ray diffraction.

At 520°C, the product of sintering is composed of scheelite with large amount of unreacted tungsten trioxide and calcite. This indicates the low rate of the reaction at such temperature. At 660°C, scheelite is the main constituent of thin section, together with some unreacted tungsten trioxide and calcite grains. This indicates high rate of the reaction and intensive formation of scheelite, but the incompleteness of the reaction is due to the short time. Scheelite appears in thin sections as colorless tabular crystals. At 860°C, scheelite constitutes the total composition of the product with a very few residual grains of tungsten and calcium oxides.

The X-ray diffraction patterns of these products are shown in Figs 5 A, B and C at 520, 660 and 860°C, respectively. At 520°C, the product shows the beginning of the reaction and the appearance of scheelite with considerable amount of unreacted

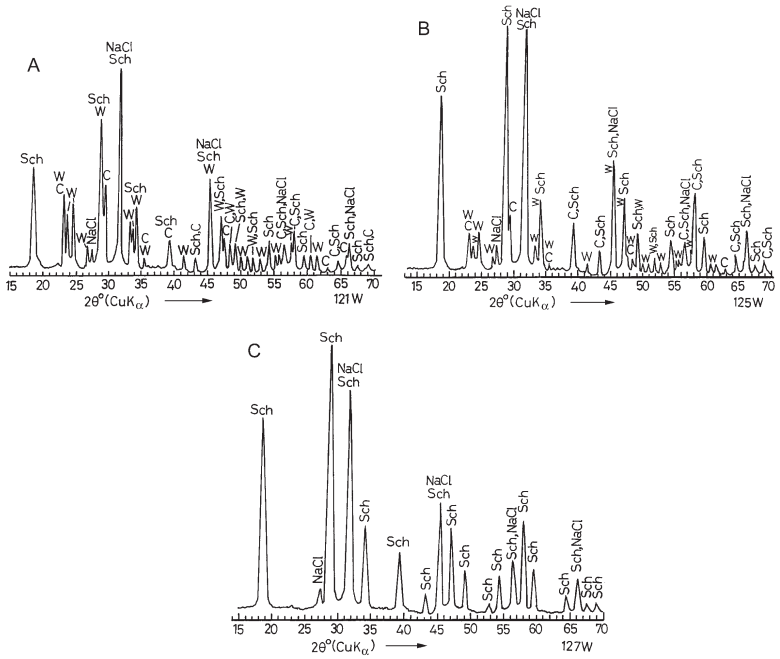

Fig. 5 X-ray diffraction patterns of the products of scheelite synthesis using tungsten trioxide–calcite mix of ratio 1:1.25. (A, B and C at 520, 660 and 860°C respectively). W – tungsten trioxide; C – calcite and Sch – scheelite

tungsten trioxide and calcite. At 660°C, scheelite constitutes the major component of the sintering product with small amount of tungsten trioxide and calcite.

The X-ray diffraction pattern of the end product at 860°C shows only the scheelite peaks, indicating that scheelite constitutes the total composition of the product. The tungsten trioxide and calcite peaks disappeared completely, indicating completeness of the reaction and all tungsten trioxide and calcite are consumed in the formation of scheelite. The X-ray peaks of scheelite 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 scheelite by sintering of tungsten trioxide with calcium oxide

The thermal analysis data of sintering of tungsten trioxide–calcium oxide mix of ratio 1.1.25 (Fig. 6) shows a medium and sharp exothermic peak at 330°C, representing the oxidation of some tungsten oxide content of lower valency. The small endothermic peak at 520°C represents the dehydration of some calcium hydroxide content in calcium oxide due to its partial hydration. The wide and large endothermic peak at 545°C represents the intensive formation of scheelite. The endothermic peak at 730°C represents the loss of carbon dioxide due to some carbonatization of calcium

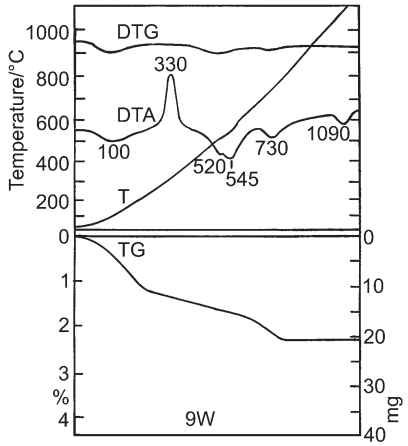

Fig. 6 DTA curve of synthesis of scheelite by sintering of tungsten oxide–calcium oxide mix of ratio: 1:1.25. Mass of sample 906 mg; heating rate: 10°C min^{-1} and DTA: 1/5

oxide with carbon dioxide from air. The phase transition of tungsten trioxide from alpha- to beta-form at 750°C is masked by the effect of loss of carbon dioxide. The small endothermic peak at 1090°C represents the phase transition of tungsten trioxide from beta to gamma-form.

The TG curve shows a marked decrease of mass in four steps. The first step is the loss of moisture content at 100°C. The second loss at 520°C is due to the dehydration of hydrated calcium oxide content. The third decrease of mass is observed at 730°C representing the loss of carbon dioxide due to some carbonatization of calcium oxide. The fourth step is the loss of mass at temperature higher than 800°C, which is due to the beginning of sublimation of tungsten trioxide.

The results obtained agreed very well with the data in the literature [12–14], 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 tungsten trioxide and calcium oxide occurs at 500–600°C, with the formation of calcium tungstate or scheelite [3, 4].

The microscopic study of the products of the runs at 500 and 550°C for 2 h show that scheelite is the main phase of the product at 500°C with some tungsten and calcium oxide grains. At 550°C, scheelite constitutes the total composition of the end product. The resulting scheelite is white with yellowish tint, colorless in thin sections and crystallizes in the tetragonal system, in the form of tabular crystals, with distinct (101) cleavage. The X-ray diffraction pattern of the product at 550°C (similar to Fig. 5 C) shows only the presence of scheelite.

This study of the conditions of synthesis and formation of scheelite and its thermal stability illustrates the thermal characteristics of processing of wolframite by its sintering with calcite and has provided good evidence concerning its genesis and occurrence in contact metasomatic deposits.

Table 3 X-ray powder diffraction data of scheelite

d/Å		I/I_0/%		*h k l*
ASTM	Observed	ASTM	Observed	
4.76	4.764	53	65	101
3.10	3.110	100	100	112
3.072	3.060	31	35	103
2.844	2.863	14	15	004
2.622	2.623	23	21	200
2.296	2.296	19	20	211
2.256	2.253	3	3	114
2.0864	2.089	5	7	105
1.9951	1.994	13	12	213
1.9278	1.928	28	35	204
1.8538	1.852	12	13	220
1.7278	1.727	5	5	310
1.6882	1.688	10	12	116
1.6332	1.633	10	12	215
1.5921	1.592	30	27	312
1.5532	1.554	14	12	224
1.4427	1.441	6	6	321
1.4219	1.421	2	2	008
1.3859	1.387	3	3	305
1.3577	1.357	4	5	323
1.3358	1.336	3	3	217
1.3106	1.311	3	3	400
1.2638	1.264	2	2	411
1.2488	1.249	13	12	316
1.2284	1.229	2	2	109
1.2074	1.208	5	5	332
1.2054	1.205	5	5	413
1.1901	1.190	4	3	404, 307
1.1728	1.172	1	1	420

General characteristics of the synthesized scheelite

The produced scheelite is white with a yellowish tint in hand-specimen and has an adamantine lustre. In thin sections, scheelite is colorless, has distinct (101) cleavage, crystallizes in tetragonal system in the form of tabular crystals and is optically posi-

tive. In polished sections, scheelite is dark-grey with very low reflectivity, yellowish white internal reflections and distinct anisotropism.

The synthesized scheelite has the following chemical composition: 80.58% WO_3 and 19.40% CaO.

The X-ray diffraction pattern of the produced scheelite (Fig. 5 C) shows the characteristic and well-defined peaks of scheelite, which are sharp and intense, suggesting good crystallinity. The X-ray diffraction data of the synthetic scheelite are consistent with the corresponding ASTM values of the natural mineral (Table 3).

Table 4 Unit cell dimensions and axial angles of the synthesized scheelite

Mineral	*a*/Å	*b*/Å	*c*/Å	α/degree	β/degree	γ/degree	*V*/Å^3
Scheelite		(Tetragonal)					
Synthetic	5.2376	5.2376	11.3458	90.00	90.00	90.00	311.243
	±0.0113	±0.0113	±0.0103	0.00	0.00	0.00	±0.214
Standard	5.246	5.246	11.349	90.00	90.00	90.00	312.330

The unit cell dimensions and constants of the synthetic scheelite are given in Table 4. It is observed that the calculated cell dimensions, constants and optic axial angles of the synthesized scheelite are consistent with the corresponding data of the natural mineral.

Conclusions

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

1. The DTA curves of sintering of wolframite with calcite show the beginning of the reaction at 560°C with the formation of scheelite. The intensive formation of scheelite is represented by the medium and wide endothermic peak at 740°C. This is followed directly by large and sharp endothermic peak at 860°C, representing the dissociation of the unreacted calcite.

The standard free energy (ΔF^0) and equilibrium constant of the reaction (K) at 298 K are –60.644 kcal mol^{-1} and $2.99 \cdot 10^{44}$ respectively. These values reflect the irreversibility of the reaction.

2. The DTA curve of tungsten trioxide shows three thermal effects. The sharp exothermic peak at 320°C represents the oxidation of tungsten oxide content of lower valency. The endothermic peaks at 750 and 1090°C are related to polymorphic changes of tungsten trioxide. The beginning of its sublimation is observed at temperature higher than 800°C.

3. The DTA curves of sintering of tungsten trioxide with calcite indicate that the intensive formation of scheelite takes place at 660°C by endothermic reaction. The phase transition of tungsten trioxide at 750°C is masked by the dissociation of calcite at 860°C.

4. The DTA curves of sintering of tungsten trioxide with calcium oxide shows a wide endothermic peak at 545°C, representing the formation of scheelite. The medium and small endothermic peaks at 520 and 730°C represent the dehydration of calcium oxide and the loss of carbon dioxide due to some carbonatization of calcium oxide with carbon dioxide from air.

The synthesized scheelite is colorless in thin sections, has distinct (101) cleavage, crystallizes in the tetragonal system in the form of tabular crystals and is optically positive.

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