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A thermal and mass spectrometric study of synthetic johannite $[Cu(UO_2)_2(SO_4)_2(OH)_2] \cdot 8H_2O$

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Abstract

The course of the thermal decomposition of synthetic johannite, $[Cu(UO_2)_2(SO_4)_2(OH)_2] \cdot 8H_2O$, was investigated by means of simultaneous TG–DTA–MS (thermogravimetry–differential thermal analysis–mass spectrometry). The dehydration and dehydroxylation processes (60–450°C) fall into four stages, the temperatures of which are influenced by the transport phenomena. Firstly, the four water molecules not coordinated by Cu^{2+} cations are released, followed by release of the water molecules (in two steps) that are coordinated by Cu^{2+} cations. Then, dehydroxylation takes place which may partly overlap with the last stage of dehydration. Further heating of the fully anhydrous compound results in a release of small amounts of oxygen at approx. 490 and 520°C, accompanied by corresponding exotherms on the DTA curve. This suggests the formation of new crystalline phases such as α-UO_2SO_4, β-UO_2SO_4 and UO_{3-x}. Decomposition of the anhydrous compound ($CuO \cdot 2UO_3 \cdot 2SO_3$ or $CuO + 2UO_2SO_4$) is characterized by the evolution of SO_3 (in two steps) and oxygen. Small exotherms at 655 and 688°C in argon and air, respectively, mark the onset of SO_3 evolution and can be assigned to the formation of crystalline CuU_3O_{10}. The presence of oxygen, formed both in the course of the decomposition reaction and as a result of SO_3 dissociation, causes the inhibitive influence of the oxygen content in the atmosphere over the sample on the course of decomposition.

INTRODUCTION

Johannite is well-known secondary mineral of uranium. It has been the subject of a number of studies, the most recent being by Čejka and Urbanec [1]. After some corrections concerning the water content were

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made, a new formula, $Cu[(UO_2)_2(SO_4)_2(OH)_2] \cdot 8H_2O$, was introduced [2]. This formula holds for both synthetic and natural johannite, as demonstrated in refs. 3 and 4, and 4 and 5, respectively. The thermal analysis and infrared spectra of natural and synthetic johannite are described in detail in ref. 4.

In this paper, the thermal decomposition of synthetic johannite is investigated by simultaneous TG–DTA–MS, consisting of thermogravimetry (TG), differential thermal analysis (DTA) and mass spectrometry (MS). The influence of certain experimental conditions on the course of the thermal decomposition of synthetic johannite is demonstrated; in particular, the sample weight, and the flow rate and composition of the gaseous atmosphere over the sample were investigated.

EXPERIMENTAL

Johannite was synthesized using a method described by Čejka et al. [4]. Samples of johannite were analyzed by thermoanalytical methods, thermogravimetry (TG), differential thermal analysis (DTA) and evolved gas analysis (EGA), employing the Netzsch STA-429 simultaneous thermal analyzer, coupled with a Balzers QMG-311 quadrupole mass spectrometer. The samples (20, 50 and 100 mg) were heated from ambient temperature up to 1200°C at a heating rate of 15°C min^{-1} in dynamic and static atmospheres of air, argon, carbon dioxide and air, respectively, with α-Al_2O_3 as a reference material.

The volatiles released on heating were drawn off continuously in a stream of carrier gas, via a heated capillary, into the mass spectrometer for analysis. The MS analyses were carried out with the following parameters: ionization by electron impact (EI), ionization current 1 mA and ionization energy 70 eV. The mass spectrometer was programmed to operate in a selected ions monitoring regime (SIM). Thus, a temperature profile of H_2O^+, SO_2^+ and O_2^+ current intensities has been obtained, reflecting the evolution of the volatiles of interest.

RESULTS AND DISCUSSION

TG–DTA curves of natural and synthetic johannite using both single and combined techniques are reproduced in papers by Čejka and coworkers [3,4,6], together with their detailed interpretation. In this study, a somewhat different view is presented. The thermal decomposition of synthetic johannite was investigated under different experimental conditions, showing the influence of single parameters such as the sample weight, and the composition and condition (dynamic or static) of the gaseous atmosphere over the sample. The overall picture was clarified by the use of

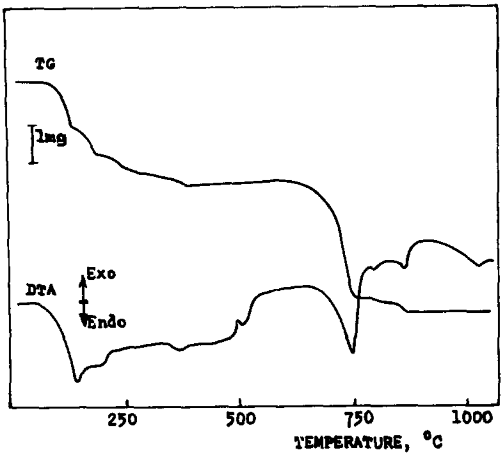


Fig. 1. TG–DTA curves of synthetic johannite recorded simultaneously in a flow of argon: sample weight, 20 mg; heating rate, 15°C min^{-1}; flow rate, 75 ml min^{-1}.

evolved gas analysis (EGA) via a mass spectrometer (EGAMS), see Figs. 1–6.

Gradual dehydration and dehydroxylation take place in the range 60–450°C (Table 1). In all the cases presented, there are four distinguishable mass losses on the TG curves (Table 1), confirmed by the EGAMS measurement of the released water profile (see Figs. 2 and 6). The sample measured in a static atmosphere of air (50 mg) is the only one that gives a DTA trace with four distinct endotherms (Fig. 3); the other measurements yield only three endotherms. The third endotherm at about 390°C can be

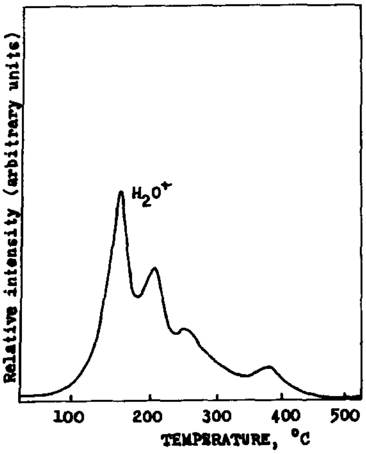


Fig. 2. EGAMS of synthetic johannite in a flow of air, water release profile: sample weight, 50 mg; heating rate, 15°C min^{-1}; flow rate, 75 ml min^{-1}.

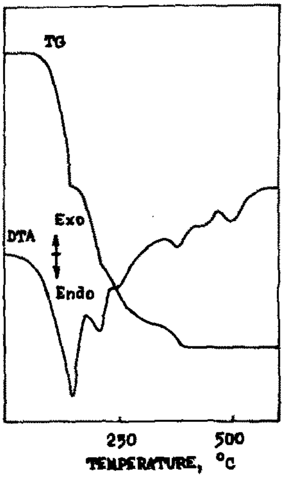


Fig. 3. TG–DTA curves of synthetic johannite recorded simultaneously in a static atmosphere of air: sample weight, 50 mg; heating rate, 15°C min^{-1}.

assigned to the dehydroxylation. While the first and second mass decreases on the TG curves are well separated, with corresponding endotherms appearing on the DTA curves, the third mass decrease represents the sum

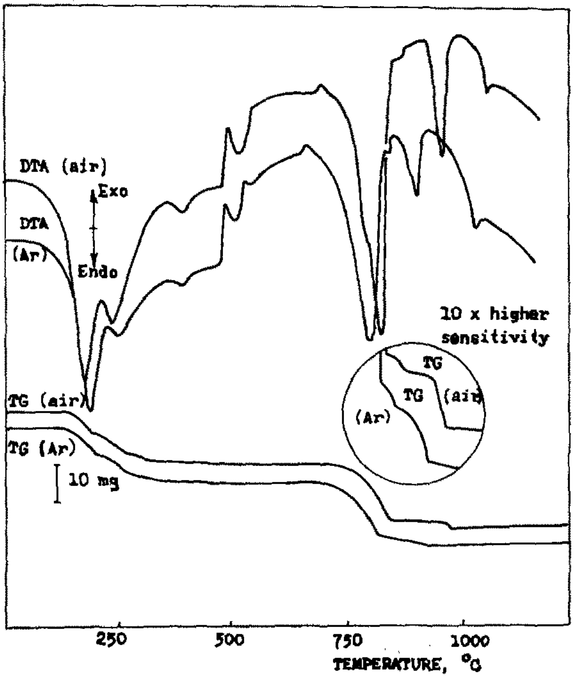


Fig. 4. TG–DTA curves of synthetic johannite recorded simultaneously in a flow of argon and air: sample weight, 100 mg; heating rate, 15°C min^{-1}; flow rate, 75 ml min^{-1}.

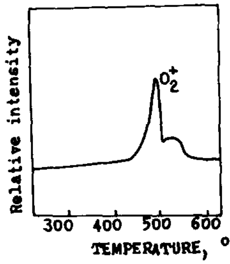
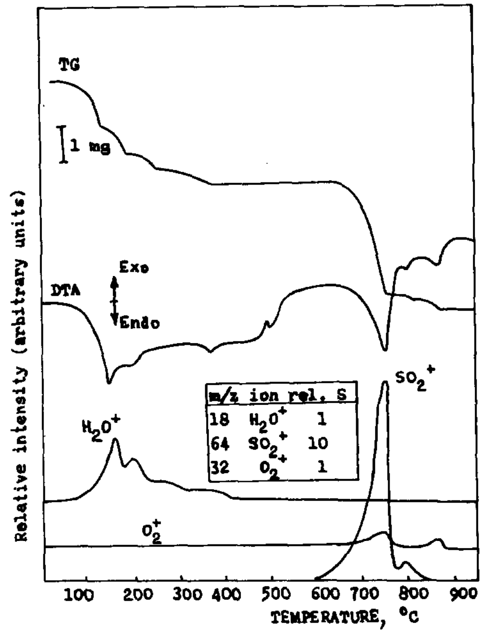


Fig. 5. EGAMS of synthetic johannite in a flow of argon, oxygen evolution profile: sample weight, 150 mg; heating rate, 20°C min^{-1}; flow rate, 75 ml min^{-1}; high sensitivity.

of the last dehydration step and the dehydroxylation, as these processes partly overlap. Increasing the sample weight shifts the individual dehydration steps to higher temperatures, as a result of the transport phenomena (water diffusion through the sample layer). Simultaneously, the amount of water released in the second dehydration step increases, while the total water released from the overlapping processes of dehydration and dehydroxylation decreases. As previously described [4], the first mass loss is attributed to the four water molecules in the johannite structure that are not coordinated by Cu^{2+} cations, being bonded only by hydrogen bonds. Thereafter, the remaining water molecules, coordinated by Cu^{2+} are re-



m/z	ion	rel. S
18	H_2O^+	1
64	SO_2^+	10
32	O_2^+	1

Fig. 6. TG–DTA–MS curves of synthetic johannite recorded simultaneously in a flow of argon: sample weight, 20 mg; heating rate, 15°C min^{-1}; flow rate, 75 ml min^{-1}.

TABLE 1

Dehydration and dehydroxylation of synthetic johannite

Sample weight (mg) Atmosphere	TG temperature range (°C)	DTA endotherm (°C)	Loss of H_2O molecules
20	60–140	140	4.0
Dynamic air	140–185	185	2.0
	185–400	–	2.6
20	60–140	140	4.0
Dynamic argon	140–185	185	2.0
	185–400	–	2.6
50	60–155	155	4.0
Static air	155–225	220	2.3
	225–420	255 and 395	2.3
100	60–175	165	4.0
Dynamic air	175–240	230	2.6
	240–430	385	2.2
100	60–175	170	4.0
Dynamic argon	175–250	240	3.0
	250–430	390	1.8

leased in two steps, the second of which may partly overlap with the dehydroxylation.

After completion of dehydration and dehydroxylation, a fully anhydrous "compound" is formed, consisting of one or possibly more X-ray-amorphous phases. No measurable mass change was observed in the range 450–650°C, as can be seen from the TG traces. However, this temperature interval is characterized by two exotherms at 485 and 530°C on the DTA curve (Fig. 4) connected with the formation of new crystalline phases: α-UO_2SO_4 and its transition to β-UO_2SO_4. The location of these exotherms is not significantly influenced by the composition of the gas over the sample. Figure 5 depicts a high-sensitivity EGAMS measurement of the released oxygen profile ($m/z = 32$) during a thermal decomposition of synthetic johannite in a flow of argon (150 mg, heating rate 20°C min^{-1}). A large sample weight, with a high sensitivity and high heating rate, makes it possible to detect small amounts of oxygen released in two steps with maxima at 490 and 520°C. This might be caused by the formation of UO_{3-x} phases such as $UO_{2.89}$. The oxygen evolution occurs in a temperature range where crystalline phases of uranyl sulphate are formed.

The decomposition of the anhydrous compound, with a probable composition of $CuO \cdot 2UO_3 \cdot 2SO_3$ or $CuO + 2UO_2SO_4$, takes place between 660°C + and approx. 900°C, and is accompanied by a gradual release of both SO_3 and O_2 (Fig. 6). The decomposition is preceded by a small

TABLE 2

Decomposition of the anhydrous phase [$CuO \cdot 2UO_3 \cdot 2SO_3$]

Sample weight (mg) Atmosphere	TG temperature range (°C)	DTA endotherm (°C)	Mass loss (mg)	Interpretation
20	600–770	665	2.9	1.80 SO_3
Dynamic air	920–940	935	0.25	0.40 O_2
20	580–755	746	3.1	1.9 SO_3
Dynamic argon	755–800	795	0.1	0.06 SO_3
	800–865	860	0.25	0.40 O_2
100	670–820	810	15.2	1.85 SO_3
Dynamic air	820–880	860	0.5	0.15 SO_3
	910–970	945	1.5	0.45 O_2
100	650–820	790	15.1	1.84 SO_3
Dynamic argon	820–835	835	0.6	0.16 SO_3
	835–900	892	1.5	0.45 O_2
100	650–810	790	15.6	1.90 SO_3
Dynamic CO_2	810–835	835	0.6	0.16 SO_3
	835–900	893	1.5	0.45 O_2

exotherm on the DTA curve, the temperature of which depends on the oxygen content in the atmosphere over the sample (688°C in air, 665°C in argon), as shown in Fig. 4. The onset of SO_3 evolution observed by the EGAMS measurements, occurs at the same temperature as that observed for the onset of the DTA exotherm discussed. The results of the X-ray powder diffraction analysis suggest that the exotherm might be assigned to the formation of crystalline CuU_3O_{10}. The exotherm has not been reported in previous works. However, it is difficult to offer a more thorough investigation into such a complex solid state reaction system than that reported recently [4].

The SO_3 evolution takes place in two steps following the same general trend at a given heating rate: the higher the sample weight and/or oxygen content in the atmosphere over the sample, the higher the temperature of the maximum rate of SO_3 evolution. The overall course of the decomposition of the anhydrous compound is given in Table 2. The influence of sample weight on the position of the decomposition temperatures is connected with transport phenomena, i.e. the diffusion of SO_3 and O_2 through the bulk of the sample. Figure 4 demonstrates the influence of atmosphere (oxygen content) on the course of the thermal decomposition of synthetic johannite (sample weight 100 mg). The general pattern is clear from Table 2. Concerning the last decomposition step of the anhydrous compound, the decomposition temperature dependence on the oxygen content of the carrier gas is attributable to the fact that the evolved oxygen must overcome the partial pressure of oxygen over the sample. The temperature dependence on the oxygen partial pressure observed in the first and second step of the anhydrous compound decomposition, is caused by dissociation of the evolved SO_3 ($SO_3 \rightarrow SO_2 + 0.5O_2$) which is hindered by the oxygen already present over the sample. Unhindered dissociation of SO_3 leads to a more rapid removal of the reaction product and, consequently, to a shift in the decomposition temperature.

Indeed, the application of EGAMS has demonstrated the presence of SO_2 and O_2 (in molar ratio of approx. 2:1) in the off-gas stream. Figure 6 shows the complex results of the TG–DTA–MS simultaneous measurement of synthetic johannite in a stream of argon (sample weight 20 mg). Tiny amounts of oxygen released at about 490 and 520°C are not registered because of the low sample weight and measurement sensitivity applied.

CONCLUSIONS

The investigation into the thermal decomposition of synthetic johannite presented in this paper confirms the results published in previous works [1–6]. Furthermore, the application of evolved gas analysis and simultaneous TG–DTA–MS measurements has elucidated some aspects of the process.

Small amounts of oxygen released at approx. 490 and 520°C (unpublished hitherto) suggest the formation of UO_{3-x} phases.

A small exotherm at 688°C in argon and at 665°C in air atmosphere (not published previously) can be assigned to the formation of crystalline CuU_3O_{10}.

The influence of different experimental conditions on the course of the thermal decomposition of synthetic johannite has been discussed, with reference to the sample weight, and the oxygen content and conditions (dynamic and static) of the gaseous atmosphere over the sample.

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