



Thermal decomposition of ktenasite

Термична декомпозиция на ктенасит

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Introduction

The ktenasite is a copper zinc hydroxy-sulfate-hydrate mineral first found by Kokkoros (1950) in the Kamariza mine, Lavrion (Greece). This mineral occurs as an alteration products of copper-zinc ores and slags. The crystal structure of ktenasite was solved by Mellini and Merlino (1978) in space group $P2_1/c$ and characterized by interrupted sheets $^2_{\infty}[(\text{Cu}, \text{Zn})_2(\text{OH})_3\text{O}]^-$ of distorted copper-zinc octahedra. Sulfate groups are connected to both sides of the octahedral sheet by corner sharing. The resultant composite tetrahedral-octahedral sheets own negative charge, which is compensating by interlayer $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ octahedra through a system of hydrogen bonds. There is a known series of minerals with ktenasite type structure: serpierite, devilline, niedermayrite, edwardsite, kobyashevite, campigliaite and others. For the first time ktenasite was synthesized by Xue et al. (2004) using simple method of mixing ZnO powder with CuSO_4 solution at room temperature and characterized by different analytical methods in order to evaluate its intercalation processes. Some data on the thermal behavior of the ktenasite can be find in that paper.

There is no detailed analysis in the literature toward the processes, the solid products and volatiles during the ktenasite thermal decomposition. It is known that the thermal decomposition of copper hydroxide sulfates and zinc hydroxide sulfates leads to the formation of CuO (Koga et al., 2008) and ZnO (Moezzi et al., 2013; Liang et al., 2015), respectively as final products with various desired properties and applications. In contrast to the detailed characteristics of the thermal decomposition of various Zn-hydroxy-salt minerals with the final product ZnO (Stanimirova et al., 2016), the ther-

mal behavior of Cu-hydroxy-salt minerals has been poorly studied.

The aim of this paper is to report preliminary data concerning the thermal behavior of the ktenasite based on analysis of decomposition processes and obtained products using combined thermal and XRD methods.

Experimental

The ktenasite was prepared by a chemical reaction between 1 g of ZnO powder and 10 ml 1M solution of CuSO_4 with periodical steering at room temperature for 7 days. The obtained suspension was filtered, washed with distilled water, and dried at room temperature.

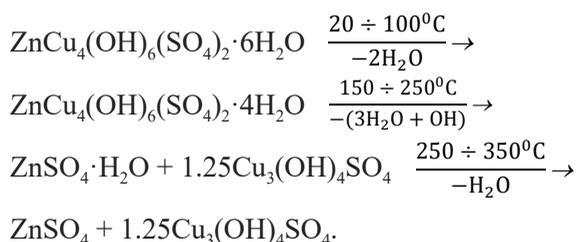
The DSC-TG analyses were carried out on apparatus SETSYS2400, Evolution, SETARAM at the following conditions: temperature range from 20 to 1000 °C, in a static air atmosphere, with a heating rate of 10 °C min⁻¹, and 10–15 mg sample mass. Simultaneous analysis of the evolved gases was performed via mass spectrometry using an OmniStar mass spectrometer connected to the TG apparatus.

The phase composition of the initial sample and products obtained during thermal decomposition was studied by powder X-ray diffractometer D2 Phaser Bruker AXS with Cu-K α radiation in steps of 0.02° s⁻¹.

Results and discussion

Data of the DSC-TG (DTG)-MS and the XRD patterns of the initial ktenasite and the products of its thermal decomposition are shown on Fig. 1A–B. The XRD data of the synthesized ktenasite (Fig. 1 B) bottom) correspond to the reference in the ICSD

rous copper hydroxy sulfate mineral and gunningite (PDF N° 74-1331), a zinc sulfate monohydrate mineral, Fig. 1B). Apparently, the departure of three more water molecules from the environment of the interlayer Zn cation enhances the interaction of Zn²⁺ cations with the sulfate groups, separating them from the hydroxide layer and forming gunningite. After this process, half of the sulfate anions remain in the hydroxide layer, as the quantitative ratios of Zn²⁺ and SO₄²⁻ in the ktenasite structure are 1:2. The calculated losses in the range of 2 and 3 endo-effects have a yield of about 3.5 H₂O (Fig. 1A). The higher amount of the water released is a result of the restructuring of the hydrate-free hydroxide layer (type brochantite Cu₄(OH)₆SO₄) into an antlerite layer (Cu₃(OH)₄SO₄), which is associated with the separation of one OH group. The gunningite losses its water molecule within endo effect 4 in the same manner and the temperature range of 250–350 °C us in the publications of Straszko et al., (1997) and Posern et al. (2014). As can see from DSC-TG curves both dehydration and partial dehydroxylation finish up to 380 °C. We take in consideration as well the presence of brochantite (5 mass % in the initial sample) and in this way 6.4 H₂O molecules leave the system up to 380 °C. Thus, the scheme of thermal decomposition in the low temperature region (1–4 endo-effect) can be described as follows:



Dehydroxylation: This process is observed with in endo-effect 5 on DSC curve in temperature interval 380–550 °C. As can expected only water is registered by MS gas-evolving method. It is known that the dehydroxylation of both brochantite and antlerite take place in this temperature region maximizing at 430 and 470 °C, respectively (Koga et al., 2008). The same tendency is observed in our investigation where the insignificant presence of brochantite explains the appearance of a shoulder to the antlerite dehydroxylation peak. The observed exothermic effect 6 at 511 °C is ascribed to the crystallization of Cu₂O(SO₄) (PDF N° 78-0612), and CuO (Uzunov et al., 1995; Koga et al., 2008). During this period the ZnSO₄ obtained after the gunningite dehydration transforms consequently into two allotropes and to the basic salt Zn₃O(SO₄) which remains stable up to 800 °C (Straszko et al., 1997). Our XRD data show the presence of Zn₃O(SO₄) (PDF N° 32-1475) as well. During this process 3.5 H₂O molecules leave the system as can estimate from the TG curve.

SO₄ degradation: This process proceeds in the temperature interval 700–1000 °C in the range of endo-effects 7 and 8 on the DSC curve. MS analysis data show the presence of SO₂ and O₂ as evolving gases. The effect 7 points the decomposition of Cu₂O(SO₄) (Koga et al., 2008) followed by the decomposition of Zn₃O(SO₄)₂ (endo-effect 8) (Straszko et al., 1997; Stanimirova et al., 2016). Tenorite (CuO) and zincite (ZnO) are obtained as final products of the thermal decomposition.

Finally, we may conclude that the thermal decomposition process of the ktenasite including different processes such as dehydration, dehydroxylation and evolving of SO₂ and O₂ is rather complicated due to the simultaneous presence of both copper and zinc in the system and this suggests further investigations to clarify the reaction mechanism of the process.

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