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## Thermal behavior of Sr-form of gordaite

### Термично поведение на Sr форма на гордаит

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**Abstract.** Cation-exchanged Sr-form of gordaite was successfully obtained from Ca-form of gordaite by an ion-exchange reaction. Data of XRD, SEM-EDS and DTA-TG-MS were used to characterize the Sr-form. Thermal decomposition of Sr-gordaite was studied for the first time in regards of thermal events and mass loss during volatile releasing. It was found similarity with Sr-gordaite and Ca-gordaite in terms of processes, type, and amount of volatiles released, but also some differences were found concerning the temperature correspondence of the volatiles evolving and the type of thermal decomposition products. The influence of the exchangeable cations (Na, Ca, or Sr) on the dehydration of the interlayer in the gordaite type structure were also established.

**Keywords:** Sr-gordaite, thermal behavior, decomposition products.

## Introduction

Zn-hydroxy-sulfate minerals as part of the minerals hydroxy-salts of various divalent cations such as Cu, Fe, Ni, Co, Cd structurally belong to the group of layered hydroxy-salt compounds. They are an important part of the development of sulfide deposits under epithermal conditions (Sillitoe, 2005). Apart from being part of the oxidation zones of sulfide deposits, zinc hydroxy salts are also found in workout mining and tailings ponds, because of the alkalization of mining wastewater. In this way, they play an important ecological role, preventing the migration of toxic Zn ions into the environment.

On the other hand, zinc hydroxy salts are one of the main phases in the patina of zinc and brass materials. The excellent resistance of brass, zinc, and galvanized steel under natural conditions is due to the formation of a protective corrosion layer of zinc hydroxy salts (zinc rust), the mineral composition of which depends on the influence of the environment. The protective effect of the corrosion layer depends on the composition, morphology, and location of the crystals, as well as on the processes of thermal decomposition – dehydration, dehydroxylation, and separation of other volatile components.

In turn, interest in the processes and products of thermal decomposition of Zn-hydroxy-sulfate minerals in the last few decades has been provoked by several specific properties. The thermal products are

important components for the hydrometallurgy of zinc and lead (Bear et al., 1986, 1987); indicators for corrosion stability (Santana et al., 2012); precursors for obtaining micro- and nanosized ZnO for various applications – catalysis, photoluminescence, ceramics, etc. (Moezzi et al., 2013).

In the present work, the object of study is cationic forms of the Zn-hydroxy-sulfate mineral, named gordaite. The gordaite structure is composed of negative charged octahedral-tetrahedral hydroxide layers  $[\text{Zn}_6^{\text{oct}}\text{Cl}_2^{\text{tet}}(\text{OH})_6(\text{SO}_4)_2\text{Zn}_2^{\text{tet}}(\text{OH})_6\text{Cl}_2]^{2-}$ . The charge is compensated by exchangeable cation-water complexes  $[\text{Na}(\text{H}_2\text{O})_6]^+$ , located in the interlayer space (Adiwidjaja et al., 1997). There are data in the literature on the products and processes of thermal decomposition of some gordaites (Stanimirova et al., 2016; Maruyama et al., 2017), but there are no data on the influence of exchangeable cations on the thermal behavior of compounds with gordaite type structure.

The present study aims to obtain an ion-exchange Sr form of gordaite and to study its thermal behavior in the context of the thermal behavior of other exchangeable forms (Ca, Na) of gordaite.

## Experimental

The Sr-form of gordaite was successfully obtained from the Ca-form by an ion-exchange reaction. The cation-



gordaites are presented in Fig. 1 (c). In the low-temperature region for Sr-gordaites (20–170 °C) a process of dehydration takes place with the realization of endo-effect 1 according to the registered mass losses (Fig. 1 c, Table 1). The dehydration is partial as 6.5H<sub>2</sub>O molecules are released at that time. The second endothermic event takes place in a narrow temperature range of 170–260 °C, as the mass losses registered by TG are associated with the release of other 7H<sub>2</sub>O molecules, which corresponds to the end of dehydration and the beginning of dehydroxylation. The course of this first stage of dehydroxylation causes the destruction of the gordaites hydroxide layer and the formation of secondary zinc hydroxy-salts – Zn<sub>3</sub>(OH)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>, 2β-Zn(OH)Cl and SrSO<sub>4</sub>. The process of dehydroxylation of the system ends within effects 3 and 4 (260–400 °C) with the sequential dehydroxylation of 2β-Zn(OH)Cl and Zn<sub>3</sub>(OH)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> (Table 1). Within endo-effect 5 (400–700 °C) the whole amount of Cl<sub>2</sub> in the structure of Sr-form is released, and in the last temperature region (700–1000 °C) within endo-effect 6, SO<sub>2</sub> and O<sub>2</sub> are released from Zn<sub>3</sub>O(SO<sub>4</sub>)<sub>2</sub>, while SrSO<sub>4</sub> remains stable at that temperatures.

Data from TG and DTA-MS analyzes show that in both cases, the observed processes of thermal decomposition are dehydration, dehydroxylation, and release of SO<sub>2</sub>, O<sub>2</sub>, and Cl<sub>2</sub> occurring in similar temperature ranges. However, the analysis of the thermal data shows a clear influence of the Sr<sup>2+</sup> on the course of the individual processes and the products of thermal decomposition.

The different cationic forms of the gordaites differ primarily in the content of the interlayer. The features (valence, size, ionic potential) caused different amounts and coordination of water molecules. The two forms (Sr and Ca) in the interlayer space have 9 H<sub>2</sub>O molecules coordinating the interlayer cation. However, the leaving of the interlayer molecules in the low-temperature region in the two forms takes place in different ways. The dehydration of the Sr-form in the 20–170 °C region is related to evolving of 6.5H<sub>2</sub>O molecules while for the Ca-form in the same region only 3.6H<sub>2</sub>O molecules are released. It could be assumed, that the facilitation of the water release for the Sr-form at the beginning of the process is due to the lower ionic potential of the Sr<sup>2+</sup> compared to that of Ca<sup>2+</sup> (Fig. 1 d). The comparison of the dehydration of gordaites forms with divalent interlayer cations (Sr<sup>2+</sup> and Ca<sup>2+</sup>) with that of gordaites, in which the compensating cation is Na<sup>+</sup>, shows the influence of valence on the process. In the Sr (or Ca)-gordaites this process occurs faster and in a narrower temperature range (20–200 °C) compared to the Na-gordaites (20–215 °C), although the hydrated coordination of Sr<sup>2+</sup> (or Ca<sup>2+</sup>) is of 9H<sub>2</sub>O molecules while the Na<sup>+</sup> is coordinated with 6H<sub>2</sub>O molecules. This is due to the presence of two Na-hydrate complexes in the interlayer space, as opposed to one Ca-hydrate complex.

The dehydroxylation process is also influenced by the interlayer cation. The first stage of dehydroxylation of gordaites is characterized by the destruction of the hydroxide layer and the formation of various

secondary phases. In contrast to the Ca-gordaites, in which after the process of the first stage of dehydroxylation both Zn and Ca secondary hydroxide phases are formed (Zn<sub>3</sub>(OH)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>, 2β-Zn(OH)Cl and Ca(OH)<sub>2</sub>), in the Sr-gordaites, the Sr<sup>2+</sup> directly forms celestine (SrSO<sub>4</sub>) without passing through the hydroxide phase. This composition of the residual material also appears to affect the dehydroxylation of the secondary Zn-hydroxy-salt compounds as well as the release of Cl from the structure. In Sr-gordaites the dehydroxylation of the secondary Zn hydroxy-salt phases is distinguished, being carried out differently in two stages. The evolving of Cl<sub>2</sub> from the Sr-gordaites is one stage process, unlike the case of the Ca-form, where the separation of Cl<sub>2</sub> is a continuing process.

*In conclusion:* the thermal behavior of Sr-gordaites was studied for the first time: (i) similarity was found with Ca-gordaites in terms of processes, type, and amount of volatiles released; (ii) differences were also found concerning the temperature correspondence of the volatiles evolving and the type of thermal decomposition products. The role and the influence of the exchangeable cations (Na<sup>+</sup>, Ca<sup>2+</sup>, or Sr<sup>2+</sup>) on the dehydration of the interlayer in the gordaites type structure were also established.

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