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THERMAL AND INFRARED SPECTRAL ANALYSES OF SABUGALITE

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The thermal decomposition and infrared spectrum of sabugalite were studied. The infrared spectrum was interpreted on the basis of site and factor symmetry analysis and correlated with the X-ray powder diffraction data. The dehydration of sabugalite is characterized by three endotherms. The anhydrous phase decomposes at 440–680 °C. On the basis of the infrared spectrum in Nujol, oxonium ions are postulated in the structure of sabugalite. The infrared spectrum in a KBr disk is probably influenced by the sample preparation mode. Sabugalite does not form a meta I hydrate. Its first new partly dehydrated phase is isostructural with metaautunite II.

Sabugalite, $HAl(UO_2PO_4)_4 \cdot 16–20\ H_2O$, has been described in several deposits, and synthetized by several authors. The space group of the tetragonal mineral has been determined as D_{4h}^{17}–14/mm, $Z = 1$ [1], and that of its monoclinic synthetic analogue as C_{2h}^{3}–C2/m, $Z = 2$ [2]. Sabugalite is the first stable lower hydrate of the fully hydrated tetragonal uranospathite [3] and is classified as a metaautunite type uranium mica [4]. In this paper, the thermal decomposition (combined TG and DTA) and IR spectrum (Nujol or KBr disk) of sabugalite were studied and compared with recently published data on its synthetic analogue [2]. Interpretation of the IR spectrum of sabugalite was based on site and factor group analysis. The paper forms part of the scientific reassessment of secondary uranium minerals from the collections of the National Museum in Prague.

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Experimental

Sabugalite (National Museum in Prague, inv. no. 54063, Margnac deposit, Haute-Vienne, France) was identified by using X-ray diffraction analysis. The symmetry of the sabugalite was calculated to be monoclinic, which corresponds with that of its synthetic analogue [2]. Thermal analysis was carried out by use of (a) a Stanton Redcroft TG 750 Thermobalance (10 deg·min^{-1}, dynamic air atmosphere, 10 ml·min^{-1}), and (b) micro-DTA by Blažek (9 deg·min^{-1}, static air atmosphere, reference material Al_2O_3). IR spectra were measured with Perkin–Elmer spectrophotometers (Model 225: Nujol; and Model 325: KBr disk).

Results and discussion

Thermal analysis

Sabugalite undergoes dehydration in three steps, characterized by endotherms at 191, 244 and 320° (Figs 1 and 2). All these endotherms, however, are not always observed [5–7]. The dehydration of synthetic sabugalite is also characterized by endotherms, at 50, 120 and 175° in the DSC curve [2]. Sabugalite undergoes dehydration nearly continuously in the range 20–440°. In agreement with the three endotherms, three dehydration steps can be observed: $\simeq 9\ H_2O$ (up to 150°), $\simeq 4.5\ H_2O$ (150–270°) and $\simeq 3\ H_2O$ (270–440°). Ambartsumyan et al. [5] also

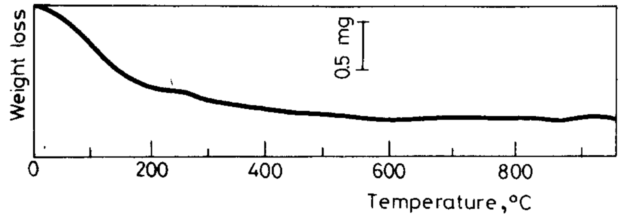

Fig. 1 TG curve of sabugalite (sample mass: 7.335 mg)

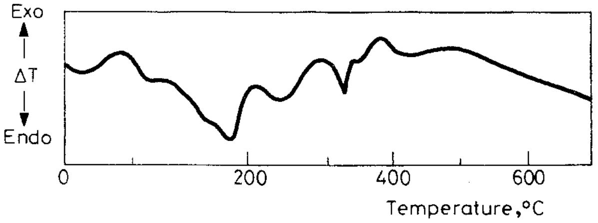

Fig. 2 DTA curve of sabugalite (sample mass: 7 mg)

observed the nearly continuous dehydration of sabugalite in the range 20–500°: 7 H_2O (up to 100°), 4.5 H_2O (100–200°) and 4.5 H_2O (200–300°), with full dehydration at 500°. Synthetic sabugalite [2] is dehydrated in the range 20–220°: 4 H_2O up to 65°, 7 H_2O (65–126°) and 5 H_2O (126–220°), with a narrow plateau between 65° and 100°. The first dehydration step is not connected with any changes in the sabugalite structure. Thus, these water molecules can be classified as zeolitic. The first new crystalline dehydrated phase of sabugalite does not correspond to a meta I hydrate, but is isostructural with metaautunite II. The dehydration processes of sabugalite are presumed to overlap. Decomposition of the anhydrous phase in the range 440–675° and the last dehydration step also seem to overlap. The anhydrous phase loses oxygen during decomposition and is transformed into crystalline phases whose X-ray powder diffraction data are temperature-dependent. U_3O_8 and phases in the systems UO_3–P_2O_5 and Al_2O_3–P_2O_5 are formed [8].

IR spectroscopy

Site and factor group analysis of some uranium micas has been given previously [9, 10]. In the IR spectrum of sabugalite (Fig. 3), a weak absorption band at 810 cm^{-1} is assigned to the symmetric stretching vibration $\nu_1 UO_2^{2+}$. The doubly degenerate bending vibration $\nu_2 UO_2^{2+}$ splits into two components (absorption bands at 254 and 298 cm^{-1}). A sharp absorption band at 915 cm^{-1} is assigned to the antisymmetric stretching vibration $\nu_3 UO_2^{2+}$. Activation of the symmetric stretching vibration $\nu_1 PO_4^{3-}$ and the doubly degenerate bending vibration $\nu_2 PO_4^{3-}$ was not observed in the IR spectrum measured in a KBr disk. Very weak absorption

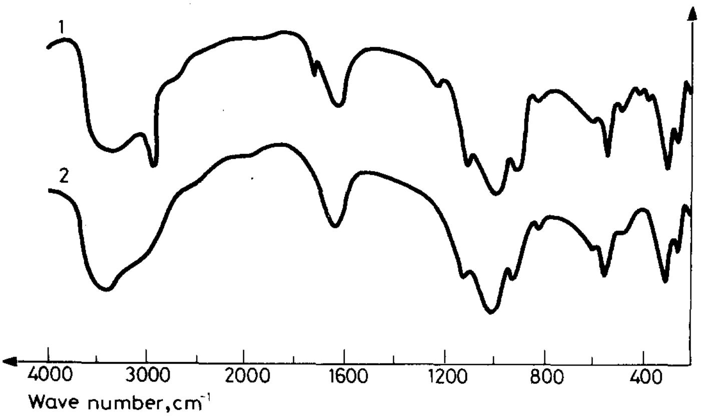

Fig. 3 Infrared spectra of sabugalite (1 — Nujol, 2 — KBr disk)

bands at 365 and 397 cm^{-1} and a shoulder at 965 cm^{-1} in the IR spectrum in Nujol, however, could be assigned to these vibrations. Two very intense absorption bands at 995 and 1123 cm^{-1} relate to the antisymmetric stretching vibration $\nu_3PO_4^{3-}$. Absorption bands at 470 and 542 cm^{-1} are assigned to the bending vibration $\nu_4PO_4^{3-}$. A weak absorption band at 585 cm^{-1} can probably be assigned to vibration modes of water molecules. An absorption band at 1640 cm^{-1} with a shoulder at 1665 cm^{-1} (KBr disk), and that at 1634 cm^{-1} (Nujol), relate to the bending vibration δH_2O. An intense absorption band at 3400 cm^{-1}, with shoulders at 3100, 3240 and 3580 cm^{-1}, was assigned to the stretching vibration νOH. Kubisz [11] assumes that $H_9O_4^+$ ions are present in the interlayer space of sabugalite. The stretching vibrations (ν_1, ν_3) H_3O^+ should be observed at approx. 2500–3400 cm^{-1}, and the bending vibrations (ν_2, ν_4) at approx. 950–1140 and 1670–1750 cm^{-1}, respectively [12]. The distinction between H_3O^+ and H_2O entities appears difficult in the region of νOH. The bending vibration $\nu_2H_3O^+$ may be partly overlapped by the vibration $\nu_3PO_4^{3-}$. The bending vibration $\nu_4H_3O^+$ is the only one which should be observed unambiguously if H_3O^+ ions are present. The OH stretching band associated with the intersquare hydrogen bond between the oxonium ion and a water molecule is clearly observed at 2760 cm^{-1} [13]. In the infrared spectrum of sabugalite (KBr disk, Fig. 3), absorption bands were found neither at 1700–1750 nor at 2700–3000 cm^{-1}. Absorption bands at 1735 and 2965 cm^{-1} (Nujol) and a shoulder at 2720 cm^{-1} in the IR spectrum (Nujol) are consistent with the vibrations ν_4, ν_1 and $\nu_3H_3O^+$, respectively [13, 14]. The difference between the IR spectra may be caused by the KBr disk preparation, probably connected with structure changes and/or partial dehydration. The presence of oxonium ions or their hydrates in the interlayer space of sabugalite can be inferred from these observations. This assumption is supported by the fact that sabugalite (Smolný vrch deposit, Czechoslovakia) contains 0.2–0.3% of K^+ ions [15]. K^+–H_3O^+ substitution is evident. Sabugalite can therefore generally be characterized by the formula

$$(H_3O^+)Al(UO_2PO_4)_4 \cdot 15H_2O \text{ or } (H_9O_4^+)Al(UO_2PO_4)_4 \cdot 12H_2O.$$

Uranosphatite is in fact fully hydrated sabugalite. Oxonium ions can also be expected in this mineral.

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Zusammenfassung — Die thermische Zersetzung und das IR-Spektrum von Sabugalit wurden untersucht. Das IR-Sektrum wird auf der Grundlage von Site- und Faktor-Symmetrie-Analysen interpretiert und mit Pulver-Röntgenbeugungsdaten korreliert. Die Entwässerung von Sabugalit ergibt 3 endotherme Effekte. Die wasserfreie Phase zersetzt sich bei 440 bis 680 °C. Auf Grund des IR-Spektrums in Nujol werden Oxonium-Ionen in der Struktur des Sabugalit vermutet. Das IR-Spektrum in KBr-Tabletten wird wahrscheinlich durch die Probenpräparation beeinflusst. Sabugalit bildet kein Metal-Hydrat. Seine erste teilweise entwässerte Phase ist isostrukturell mit Metaautunit II.

Резюме — Изучено термическое разложение и ИК спектры сабугалита. ИК спектры интерпретированы на основе фактор-группового анализа и коррелировались с данными рентгеноструктурного анализа. Дегидратация сабугалита характеризуется тремя эндотермами. Безводная фаза разлагается в интервале температур 40–80°. Согласно ИК спектра в нуйоле, в структуре сабугалита предположено наличие оксониевых ионов. ИК спектр в таблетке из бромистого калия возможно затрагивается способом получения образца. Сабугалит не образует мета I гидрата. Его первая новая частично дегидратированная фаза является изоструктурной с фазой метааутунит II.