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SYNTHESIS OF LIEBIGITE AND ANDERSONITE, AND STUDY OF THEIR THERMAL BEHAVIOR AND LUMINESCENCE

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ABSTRACT

Andersonite and liebigite were synthesized starting from tetrasodium uranyl tricarbonate [$Na_4UO_2(CO_3)_3$]. Their H_2O content, studied by thermal analysis, is estimated to be 10.5 and 6 moles, respectively. From the fluorescence spectra, a bandgap energy of approximately 2.5 eV was calculated. It is not affected by temperature.

Keywords: liebigite, andersonite, syntheses, thermal behavior, fluorescence.

SOMMAIRE

Nous avons synthétisé l'andersonite et la liebigite à partir du tricarbonate uranylé de sodium [$Na_4UO_2(CO_3)_3$]. Leur teneur en H_2O, étudiée par analyse thermique, serait de 10.5 et 6 moles, respectivement. D'après les spectres de fluorescence, l'énergie calculée de la séparation entre bandes serait d'environ 2.5 eV. Elle ne semble pas affectée par la température.

(Traduit par la Rédaction)

Mots-clés: andersonite, liebigite, synthèses, comportement thermique, fluorescence.

INTRODUCTION

In the uranyl carbonate system, the liebigite group can be represented by the general formula: $R[UO_2(CO_3)_3]\cdot nH_2O$. In this formula, R represents Na_2Ca in andersonite, Ca_2 in liebigite, CaMg in swartzite, and Mg_2 in bayleyite, and n has a corresponding value of 6, 10 or 11, 12 and 18, respectively. On the basis of the stability diagrams (Alwan & Williams 1980), it may be expected that liebigite and andersonite can coexist. Associations of liebigite and andersonite have been found at the Hillside mine, Yavapai County, Arizona (Axelrod *et al.* 1951) and at Stripa, Västmanland, Sweden (Wellin 1958). Andersonite occurs by itself in the gypsum deposits of Myrthengraben, Semmering, Austria (Tufar 1967) and Jachymov, Czechoslovakia (Čejka & Urbanec 1988). Liebigite also occurs at Shinkolobwe, Shaba, Zaire (Deliens 1985), Müllenbach, Black Forest, Germany (Walenta 1977) and in the orebody of the Tono mine, Gifu, Japan (Matsubara 1976). Several syntheses of liebigite and andersonite have been described starting from pure chemicals (Blinkoff 1906, Axelrod *et al.* 1951, Bachelet *et al.* 1952, Meyrowitz & Ross 1961, Meyrowitz *et al.* 1963, Čejka 1969, Coda *et al.* 1981).

In the present paper, a new method of synthesis of andersonite and liebigite is described, starting from the complex tetrasodium uranyl tricarbonate $Na_4[UO_2(CO_3)_3]$. This method of synthesis allows the preparation of sufficient quantities of both minerals. The identity of the species was verified by X-ray diffraction and by chemical and thermogravimetric analyses.

SYNTHESIS

In this section, we discuss the synthesis of tetrasodium uranyl tricarbonate (NaUTC) and its further conversion into liebigite and andersonite.

Synthesis of tetrasodium uranyl tricarbonate

NaUTC was synthesized at room temperature according to the method of Blake *et al.* (1956), slightly modified to obtain pure crystals. These were washed with 2M NaCl. In this way, crystals free of any Na_2CO_3 were obtained. The residual NaCl was subsequently removed by dissolution in a 50/50 ethanol–water mixture. The identity of the air-dried NaUTC crystals was verified by chemical analysis and by comparison of the X-ray-diffraction data with those given by Douglas (1956).

Conversion of NaUTC into liebigite and andersonite

According to the stability fields of the minerals of the liebigite group (Alwan & Williams 1980), andersonite can only be formed at a high Na^+/Ca^{2+} concentration ratio, whereas liebigite is formed at a low Na^+/Ca^{2+} concentration ratio. This was confirmed in our experiments.

Two grams of NaUTC were dissolved in 100 mL of 0.04 M $CaCl_2$ and left to evaporate at 25°C in an open vessel. After one week, well-formed hemimorphic crystals of liebigite started to grow. After 3 weeks, typical cubic crystals of andersonite were formed as a result of the changed Na^+/Ca^{2+} concentration ratio.

The formation of liebigite can be written as:

$$2Ca^{2+} + [UO_2(CO_3)_3]^{4-} + 10H_2O \rightarrow$$
$$Ca_2[UO_2(CO_3)_3] \cdot 10H_2O$$

The tranformation of liebigite into andersonite can be represented as:

$$Ca_2[UO_2(CO_3)_3] \cdot 10H_2O + 2Na^+ \rightarrow$$
$$Na_2Ca[UO_2(CO_3)_3] \cdot 6H_2O + Ca^{2+} + 4H_2O$$

It should be mentioned that the formation of an intermediate phase, consisting of lath-like crystals, was observed, as previously reported by Meyrowitz *et al.* (1963). The study of the intermediate compound will be the subject of a separate paper. The crystals of liebigite and andersonite were hand picked.

CHEMICAL COMPOSITION

The air-dried synthetic specimens were dissolved in 6 M HCl. The Na_2O and CaO content was determined by atomic absorption spectroscopy (AAS), whereas UO_3 was determined spectrophotometrically with Arsenazo III as the reagent, the optical densities being measured at 662.5 nm (Singer & Matucha 1962). The H_2O and CO_2 contents were measured on separate samples by thermogravimetric analysis. Table 1 summarizes the results. From the composition in terms of oxides, the chemical formulae were calculated by the classic method of residual oxygen.

TABLE 1. CHEMICAL COMPOSITION OF SYNTHETIC LIEBIGITE AND ANDERSONITE

Liebigite				Andersonite			
		no. of atoms[§]	atomic ratio			no. of atoms[§]	atomic ratio
CaO[*]	15.29	0.2726	1.93	Na_2O	9.80	0.1580	2.05
UO_3	39.60	0.1384	0.98	CaO	8.92	0.1590	1.03
CO_2	18.97	0.4034	3.05	UO_3	44.29	0.1548	1.00
H_2O	26.53	-	-	CO_2	20.10	0.4568	2.96
				H_2O	16.72		
Total	100.39				99.83		
$Ca_2[UO_2(CO_3)_3] \cdot 10\text{-}11H_2O$				$Na_2Ca[UO_2(CO_3)_3] \cdot 6H_2O$			

[*] in weight %. [§] times 10^4.

X-RAY CRYSTALLOGRAPHY

X-ray-diffraction data were recorded at 40 kV and 20 mA using $CuK\alpha_1$ radiation ($\lambda = 1.54056$Å). The diffraction patterns were recorded by means of a Guinier–Hägg camera, with a diameter of 100 mm. Silicon powder (NBS640) was used as an internal standard. The relative intensities of the diffraction lines were measured with a Carl Zeiss Jena MD100 microdensitometer. Using the cell parameters of liebigite (space group *Bba*2), with *a* 16.699, *b* 17.557 and *c* 13.697Å (Mereiter 1982), and those of andersonite (space group $R\bar{3}m$), with *a* 17.902 and *c* 23.734Å (Coda *et al.* 1981), the powder patterns were indexed with the computer program of Visser (1969). For both synthetic specimens, all the observed reflections could be indexed, with $\Delta Q_{obs} \leq \Delta Q_{calc}$ ($\Delta\theta$ 0.05°), in agreement with PDF 20–1092 and 11–246.

The densities of the two synthetic minerals were measured in toluene at 25°C ± 0.1 by means of a Cahn Electrobalance RG. The measured density of andersonite is 2.834 ± 0.005 g/cm^3, which agrees with the calculated value of 2.860 g/cm^3, corresponding to $Z = 18$. For liebigite, a density of 2.416 ± 0.005 g/cm^3 was found, which corresponds to $Z = 8$.

The morphology of andersonite and liebigite crystals is shown in the electron micrographs (Figs. 1A, B). The dimensions of the liebigite crystals range from 0.1 to 0.6 mm, whereas those of andersonite range from 0.05 to 0.1 mm. The crystals of andersonite are clearly pseudocubic, and those of liebigite have a pronounced hemimorphic morphology (Mereiter 1986).

Thermal behavior

Concerning the water content of the two minerals, there is some confusion in the literature. Synthetic liebigite having 10 moles of H_2O was described by Frondel (1958), Čejka & Urbanec (1979) and Alwan & Williams (1980). Appleman (1956) and Meyrowitz *et al.* (1963) suggested a water content ranging between 10

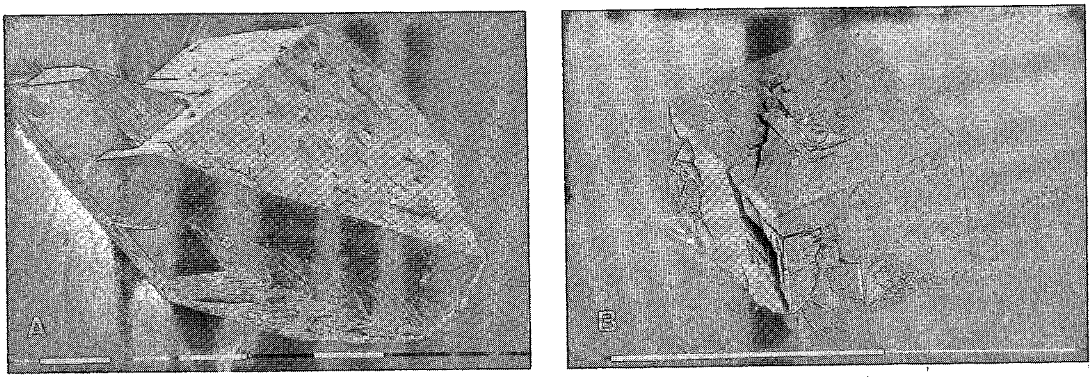

FIG. 1. SEM micrographs of synthetic crystals of liebigite (A) and andersonite (B). Scale bar: 100 μm.

and 11 moles of H_2O. For synthetic andersonite, the water content was studied by a number of investigators (Čejka 1969, Urbanec & Čejka 1979, Čejka *et al.* 1987). These authors accept a water content ranging between 5.4 and 5.8 moles of H_2O.

The thermal stability of both synthetic minerals was investigated by thermogravimetric analyses (TGA) combined with differential scanning calorimetry (DSC). A DuPont DSC910 and TGA951 apparatus was used, with an applied heating rate of 5°C/min and a flow of N_2 of 30 mL/min. In order to detect the temperature at which CO_2 is liberated, the outlet of the gas-stream was passed through a solution of $Ba(OH)_2$. The results, summarized in Table 2, show that synthetic liebigite and andersonite contain 10.53 and 5.99 moles of H_2O, respectively.

The decomposition of liebigite and andersonite as function of temperature can be represented as:

$$Ca_2[UO_2(CO_3)_3]\cdot 11H_2O \xrightarrow{25\text{–}150^\circ\text{C}} Ca_2[UO_2(CO_3)_3]\cdot H_2O \xrightarrow{150\text{–}300^\circ\text{C}} Ca_2[UO_2(CO_3)_3] \xrightarrow{300\text{–}1000^\circ\text{C}} \text{oxides}$$

TABLE 2. RESULTS OF THERMOGRAVIMETRIC ANALYSES OF SYNTHETIC LIEBIGITE AND ANDERSONITE

Liebigite			Andersonite		
Temp. interval	wt.% lost	assignment	Temp. interval	wt.% lost	assignment
25-100	24.00	9.53 H_2O	25-200	13.99	5.02 H_2O
150-300	2.53	1.00 H_2O	200-300	2.73	0.97 H_2O
300-500	14.89	2.40 CO_2	300-575	12.40	1.82 CO_2
500-650	3.06	0.49 CO_2	575-675	2.65	0.40 CO_2
650-1000	1.02	0.16 CO_2	675-1000	5.05	0.74 CO_2

Temperature interval in °C.

$$Na_2Ca[UO_2(CO_3)_3]\cdot 6H_2O \xrightarrow{25\text{–}150^\circ\text{C}} Na_2Ca[UO_2(CO_3)_3]\cdot H_2O \xrightarrow{150\text{–}300^\circ\text{C}} Na_2Ca[UO_2(CO_3)_3] \xrightarrow{300\text{–}1000^\circ\text{C}} \text{oxides}$$

Since liebigite does not contain structural cavities (Mereiter 1982), and andersonite is structurally characterized by the presence of channels along the three-fold axis (Coda *et al.* 1981), the water molecules are structurally bonded in liebigite, whereas in andersonite, zeolitic water may occur.

Luminescence spectra

Both synthetic specimens fluoresce intensely blue-green both under short- and long-wave ultraviolet radiation. The fluorescence spectra were recorded by means of a Perkin–Elmer MPS44B spectrofluorimeter at 298 and 77 K, with an excitation wavelength of 366 nm.

The slight differences in the fluorescence spectra are characterized by the mode of bonding of the U atom in the crystal structure. No phosphorescence could be detected for either specimens in a measuring interval of 2 ms. The spectra for synthetic liebigite and andersonite at 298 and 77 K are represented in Figures 2 and 3, respectively. For both specimens, the maxima of the uranyl bands at 298 and 77 K are given in Table 3. The spectra of andersonite and liebigite are very similar. The spectrum of andersonite is shifted approximately 3 nm to higher wavelengths relative to that of liebigite. Taking into account the applied amplification, liebigite fluoresces more intensely than andersonite. The intensity of fluorescence at 298 K is much lower than at 77 K, which can be explained by the fact that the quantum efficiency of fluorescence decreases with increasing temperature. This is a consequence of the fact that the increased

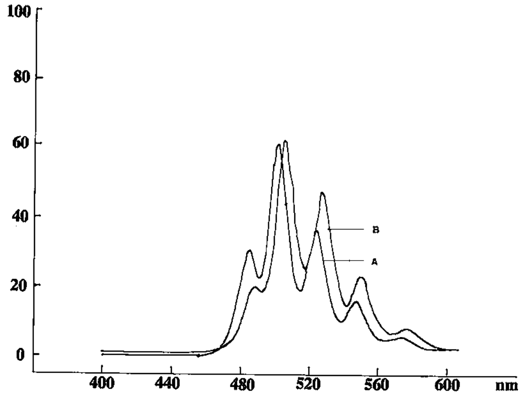

FIG. 2. Fluorescence spectra at 298 K. A. Synthetic liebigite (amplification factor 0.1). B. Synthetic andersonite (amplification factor 3.0).

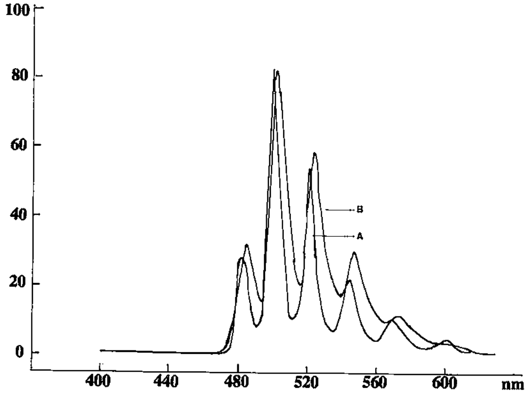

FIG. 3. Fluorescence spectra at 77 K. A. Synthetic liebigite (amplification factor 0.05). B. Synthetic andersonite (amplification factor 0.3).

TABLE 3. FLUORESCENCE MAXIMA OF SYNTHETIC LIEBIGITE AND ANDERSONITE AT 298 AND 77 K

Temp.	Specimen	Fluorescence maxima (nm)				
298	Liebigite	486	503	525	548	575
	Andersonite	489	506	528	551	578
77	Liebigite	482	500	522	544	570
	Andersonite	485	503	525	547	574

frequency of collision at elevated temperatures improves the probability for deactivation by external conversion.

In comparison with the spectra at 298 K, there exists a supplementary small band at 610 nm at 77 K. The spectrum of andersonite at 298 K is not quite identical to the one shown by Tufar (1967), as no weak peak at 407 nm could be detected in our spectrum.

Based on the relation E = hc/λ (hc = 1.9863 × 10^{23} Jm) (1 eV = 1.6021 × 10^{19} J), E can be expressed in eV as 1.24 × $10^{-6}/\lambda$. With this relation, the bandgap energy Eg between the conduction and valence band was calculated at the most intensive peak at 298 and 77 K for both synthetic species. The Eg values found for andersonite are 2.45 eV (298 K; λ = 506 nm) and 2.46 eV (77 K; 503 nm). For liebigite, Eg values of 2.46 eV (298 K; 503 nm) and 2.48 eV (77 K; 500 nm) were obtained. For both specimens, the bandgap energy is not affected by temperature. Based on the Eg values, we may conclude that liebigite and andersonite must be considered as minerals with insulator properties.

DISCUSSION

Liebigite and andersonite are easily formed from NaUTC in aqueous medium. The latter can only be obtained from a strongly alkaline Na_2CO_3 solution of polynuclear uranium hydroxides by a continuous input of CO_2.

The synthesis of liebigite and andersonite is done with an initial concentration of 0.04 M NaUTC and 0.04 M $CaCl_2$. Initially, liebigite is formed because the ratio Ca^{2+}/Na^+ is equal to one. Later, the Ca^{2+}/Na^+ value diminishes, and andersonite appears. The formation of liebigite and andersonite can be explained by a two-stage process. First, the $[UO_2(CO_3)_3]^{4-}$ complex is formed in a strongly alkaline medium. Subsequently, this complex forms both minerals when sufficient Ca^{2+} ions are present.

In natural environments, the UO_2^{2+} ions necessary for the formation of the tricarbonate complex are generated by oxidation and acid leaching of primary pitchblende. If the migration of the UO_2^{2+} ions takes place in limestone-bearing sediments, the two minerals can be formed with secondary gypsum. This is observed in most of the deposits in which these minerals occur. In some deposits, however, only liebigite is found. This cannot be explained by a difference in solubility of these two minerals. It can only be explained by an initial Ca^{2+}/Na^+ ratio that is larger than unity.

The synthesis of these minerals indicates that an intermediate phase is formed. This consists of lath-like crystals with a well-defined composition. Up to now, no such intermediate phase is reported to be present as an accessory mineral with liebigite and andersonite. Whether this intermediate phase is formed in a natural environment remains unclear.

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