

THERMAL AND IR SPECTROSCOPIC CHARACTERIZATION OF KAMOTOÏTE

Irma Lía BOTTO^a, Alejandro Cesar GARCÍA^a and Michel DELIENS^b

^a *Química Inorganica, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata (1900), Argentina and*

^b *Section de Mineralogie et Petrographie, Institut Royal des Sciences naturelles de Belgique, B 1040 Bruxelles, Belgium*

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Kamotoïte-(Y), a new uranyl and rare earth carbonate, has been studied by thermal treatment. The mineral has also been characterized by IR spectroscopy and the presence of the bidentate binding of carbonate to uranyl ion has been confirmed. Likewise, the U–O bond length in the uranyl group can be estimated by IR measurements.

Kamotoïte-(Y) $[4 \text{UO}_3(\text{Y, Nd, Gd, Sm, Dy})_2\text{O}_3 \cdot 3 \text{CO}_2 \cdot 14.5 \text{H}_2\text{O}]$ is a new uranyl and rare earth carbonate which was recently found in a Cu–Co deposit of Kamoto, Souther Shaba, Zaire¹. It occurs as a crust of elongated bright yellow blades on a uranoninite matrix. This mineral belongs to the monoclinic system, space group $P2_1/a$ and $Z = 4$ (ref.¹). As part of the scientific reassessment of secondary uranium minerals, some works about the crystal chemistry of natural and synthetic uranyl carbonates have been recently published^{2–10}.

This note is a contribution to the chemistry of natural Kamotoïte using IR spectroscopy and thermal analysis. By means of the former technique, the presence of expected entities such as OH^- , UO_2^{2+} , CO_3^{2-} , H_2O can be confirmed together with some information about the type of bonding within the solid structure.

EXPERIMENTAL

The Kamotoïte sample issued from the mineralogical collection of the Musee Royal de l'Afrique Centrale, Tervuren, Belgium.

The chemical analysis was performed by electron microprobe. The IR spectra were recorded with a Perkin–Elmer 580B spectrophotometer using the KBr pellet technique.

The TG and DTA study was carried out by using a Rigaku CN 8002 L2 thermoanalyzer. The measurement was performed under N_2 stream (0.4 l/min). The temperature was raised to 700°C (heating rate 10°C/min). The specimen was analyzed against $\alpha\text{-Al}_2\text{O}_3$ as reference.

RESULTS AND DISCUSSION

Infrared Absorption Spectroscopy

From the spectroscopic point of view and considering the Kamotoïte chemical formula, two important types of atomic groups can be inferred from the structure. They are related to the U—O and C—O bonds. First, the uranyl UO_2^{2+} group ($D_{\infty h}$ symmetry) has¹¹ four normal vibrations, but only three are fundamentals:

- ν_1 (700–900 cm^{-1}) symmetric stretching vibration (Raman active),
- ν_2 (180–350 cm^{-1}) doubly degenerate bending vibration (IR active),
- ν_3 (850–1 000 cm^{-1}) antisymmetric stretching vibration (IR active).

The decrease of uranyl symmetry can result in the splitting of the ν_2 vibration and in the activation of the ν_1 symmetric stretching mode.

The other group CO_3^{2-} (point group symmetry D_{3h}) has¹¹ four fundamentals, when it is considered as a free ion:

- ν_1 (1 050–1 115 cm^{-1}) symmetric stretching vibration (Raman active),
- ν_2 (835–880 cm^{-1}) out of plane bending vibration (IR active),
- ν_3 (1 250–1 610 cm^{-1}) doubly degenerate stretching vibration (IR and Raman active),
- ν_4 (670–770 cm^{-1}) doubly degenerate in plane bending vibration (IR and Raman active).

Likewise, the CO_3^{2-} group can be considered as coordinated to the metal ion in two ways (as unidentate or as bidentate ligand); so, a lowering from the D_{3h} symmetry can be expected^{12,13}. In this case, the space group is $P2_1/a$ and $Z = 4$, consequently, the site symmetry can be supposed as C_1 . Table I shows the correlation between the free ion and the site symmetry for the CO_3^{2-} group.

Fig. 1 shows the IR spectrum of Kamotoïte. From Table I, the ν_1 stretching mode becomes IR active whereas the ν_3 and ν_4 vibrations split into two absorption bands. It is well known that the ν_3 C—O band has a very marked splitting in the case of bidentate ligand than in the case of unidentate complexing¹². However, the symmetry of the specie does not vary whether the ligand is unidentate or bidentate.

The presence of a weak band at 1 120 cm^{-1} corresponding to the ν_1 mode, confirms a low symmetry of the CO_3^{2-} group in the Kamotoïte. Some intense absorption bands at 1 355 and 1 540 cm^{-1} were assigned to the ν_3 antisymmetric stretching C—O. In particular, the large splitting of this mode really confirms the bidentate binding of the CO_3 group to the uranyl ion^{12,13}. This last group presents the ν_3 antisymmetric vibration at 910 cm^{-1} , in agreement with the literature data^{14–16}. In this same region, the CO_3^{2-} out of plane bending vibration (ν_2) appears as a shoulder of the ν_3 UO_2^{2+} mode (probably located at 865 cm^{-1}) as well as the ν_1 UO_2^{2+} symmetric stretching (at 830 cm^{-1}).

According to McGlynn's expression¹⁷, it is possible to calculate the ν_1 value, knowing the ν_3 position ($\nu_1 = 21 + 0.89\nu_3$). The value of 831 cm^{-1} agrees very well with the experimental data.

The low region of the spectrum cannot be assigned so clearly. For this reason, it is interesting to compare the IR data with those presented for some other related natural uranyl carbonates^{3,14-16}. Besides, for comparative purposes, the synthetic $\text{Sr}_2(\text{UO}_2)(\text{CO}_3)_3 \cdot 8 \text{H}_2\text{O}$ is taken as reference¹⁸. This compound shows only a U coordination of $\text{UO}_2(\text{CO}_3)_3$ type. Although the Kamotoite cannot show this type of polyhedra as unique group because of its stoichiometry, the IR spectra of both compounds present a great similarity, mainly between 700 and 1700 cm^{-1} . However, in the low region, some differences are evident. The bands located at 505 ,

TABLE I
Correlation for CO_3^{2-} vibrations

Vibration	Free ion ^a		Site symmetry ^b	
	specie	activity	specie	activity
ν_1	A'_1	R	A	IR, R
ν_2	A''_2	IR	A	IR, R
ν_3	E'	IR, R	$2A$	IR, R
ν_4	E'	IR, R	$2A$	IR, R

^a Point group D_{3h} ; point group C_1

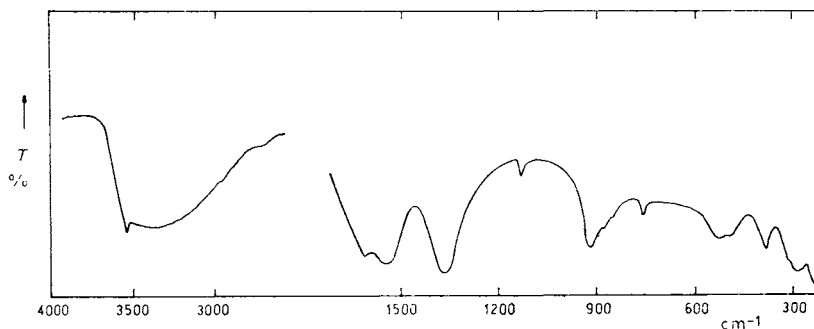


FIG. 1
IR spectrum of Kamotoite

470 and 352 cm^{-1} could be attributed to a U—O bond length of $2.1\text{--}2.5\text{ \AA}$ (ref.¹⁹, $1\text{ \AA} = 10^{-10}\text{ m}$). Notwithstanding, some bands assigned to water librations are usually observed in this region²⁰. Between $200\text{--}300\text{ cm}^{-1}$ there are three types of

TABLE II
Interpretation of the IR absorption spectrum of Kamotoïte

Wavenumber, cm^{-1}	Assignments
3 540 sh	
3 370 vs	$\nu(\text{O-H})$ stretch.
1 620 s	$\delta(\text{H}_2\text{O})$ bend.
1 540 vs	
1 355 vs	$\nu_3(\text{CO}_3^{2-})$ antisym. stretch.
1 120 w	$\nu_1(\text{CO}_3^{2-})$ sym. stretch.
910 s	$\nu_3(\text{UO}_2^{2+})$ antisym. stretch.
865 sh	$\nu_2(\text{CO}_3^{2-})$ out-of-plane bend.
830 sh	$\nu_1(\text{UO}_2^{2+})$ sym. stretch.
745 w	$\nu_4(\text{CO}_3^{2-})$ in plane bend.
505 m	
470 sh	H_2O libration, $\nu(\text{U-O})_{\text{II}}$
352 m	
310 sh	$\nu_2(\text{UO}_2^{2+})$ bend.?
270 sh	
255 s	$\nu(\text{U-O}(\text{CO}_3^{2-})), \text{CO}_3^{2-}$ librations
215 m	

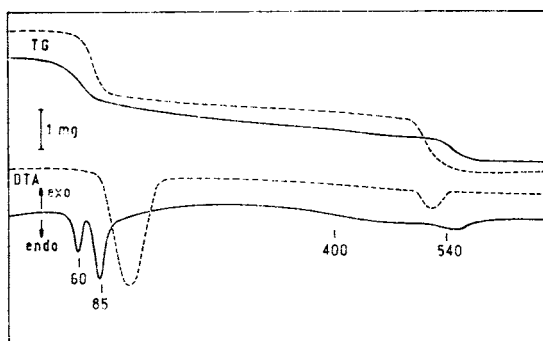


Fig. 2

TG and DTA curves for Kamotoïte (—) and synthetic $\text{Sr}_2(\text{UO}_2)(\text{CO}_3)_3 \cdot 8\text{ H}_2\text{O}$ (-----)

bands: the U—O(CO₃) stretching (270 cm⁻¹) and the librations of CO₃ groups (215 cm⁻¹). Table II gives the assignment of all the present bands.

$$R_{(U-O)} = 0.895 + 81.2 \nu_3^{-2/3} \quad (\text{ref.}^{21}), \quad (1)$$

$$R_{(U-O)} = 0.975 + 74.75 \nu_3^{-2/3} \quad (\text{ref.}^{22}), \quad (2)$$

$$R_{(U-O)} = 1.236 + 50.02 \nu_3^{-2/3} \quad (\text{ref.}^{23}). \quad (3)$$

The result obtained shows a value of 1.77 Å, which is in good agreement with the U—O distances in some other uranyl compounds.

Thermal Analysis

The TG and DTA curves of Kamotoite are shown in Fig. 2. For comparative purposes, the curves for Sr₂(UO₂)(CO₃)₃·8 H₂O are also included in the same figure.

As it occurs in other natural and synthetic uranyl carbonates, two decomposition processes result from the heating of the Kamotoite^{2,3,5,24}. It dehydrates at 85°C although the synthetic compound presents a dehydration process at 110°C. The loss of water evidently depends on the crystal structure. The second weight-loss is observed at 540°C. It corresponds to the release of CO₂. A similar process occurs in the reference compound at 490°C. The product of the pyrolysis of the Kamotoite is a mixture of Ln₂O₃ and UO₃, which is detected at 700°C. No mixed compound is then formed. A physical mixture of the stoichiometric quantities of both oxides shows an IR spectrum similar to that observed after the pyrolysis of mineral.

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