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THE STRUCTURE AND PHYSICOCHEMICAL CHARACTERISTICS OF A SYNTHETIC PHASE COMPOSITIONALLY INTERMEDIATE BETWEEN LIEBIGITE AND ANDERSONITE

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ABSTRACT

During the synthesis of liebigite and andersonite, starting from tetrasodium uranylcarbonate and calcium ions, an unknown stable and crystalline intermediate phase is formed at a Ca^{2+}/Na^+ ratio lying between those necessary to form the above-cited compounds. Chemical analysis of this yellow–green intermediate phase results in the formula: $Ca_{1.54}Na_{0.63}[UO_2(CO_3)_3]{\cdot}xH_2O$ ($x = 5.38$). The scanning electron micrographs show foliated lathlike crystals. From single-crystal data, the crystals are found to be orthorhombic, *a* 18.150(3), *b* 16.866(6), *c* 18.436(3) Å, space group *Pnnm*. The basic structural units consist of three $UO_2(CO_3)_3$ units. Each U atom is [8]-coordinated, resulting in a distorted hexagonal-bipyramidal polyhedron. A chemical analysis indicates that the structure is short of positive charges, which could be balanced by the presence of oxonium ions. Results of the crystal-structure analysis support this proposal, which ensures a tight fit of the water molecule that is not attached to either Na^+ or Ca^{2+} ions. The powder-diffraction spectrum calculated from the single-crystal structure corresponds very well with the measured one. The fluorescence and phosphorescence spectra are given, as well as information on the thermal decomposition, as revealed by thermogravimetric and differential scanning calorimetric analyses.

Keywords: liebigite, andersonite, synthetic phase, crystal structure, physicochemical properties.

SOMMAIRE

Au cours de nos synthèses de la liebigite et de l'andersonite, à partir de l'uranylcarbonate de tétrasodium et d'ions de calcium comme matériaux de départ, nous avons découvert une phase méconnue, stable et cristalline, ayant un rapport Ca^{2+}/Na^+ entre ceux qui s'avèrent nécessaires pour former les deux autres composés. Une analyse chimique de cette phase intermédiaire jaune-vert mène à la formule $Ca_{1.54}Na_{0.63}[UO_2(CO_3)_3]{\cdot}xH_2O$ ($x = 5.38$). D'après les photos prises au microscope électronique à balayage, il s'agit de cristaux en plaquettes ayant une structure en feuillets. Les données obtenues par diffraction X sur cristal unique montrent que cette phase est orthorhombique, *a* 18.150(3), *b* 16.866(6), *c* 18.436(3) Å, groupe spatial *Pnnm*. Les éléments structuraux fondamentaux comprennent trois unités à stoechiométrie $UO_2(CO_3)_3$. Chaque atome d'uranium possède une coordinence huit et loge dans un polyèdre hexagonal bipyramidal difforme. Une analyse chimique montre que la structure accuse un déficit de charges positives, qui pourrait être satisfait par la présence d'ions oxonium. Les résultats de l'ébauche de la structure cristalline confirment cette hypothèse, qui assure un adaptation serrée de la molécule d'eau non rattachée au Na^+ ou au Ca^{2+}. Le spectre de diffraction X (méthode des poudres) calculé à partir des résultats obtenus sur cristal unique concorde très bien avec le spectre mesuré. Nous décrivons aussi les spectres de fluorescence et de phosphorescence, de même que les résultats de la décomposition thermique par thermogravimétrie et par calorimétrie différentielle en mode balayage.

(Traduit par la Rédaction)

Mots-clés: liebigite, andersonite, phase synthétique, structure cristalline, propriétés physicochimiques.

INTRODUCTION

According to the stability diagrams of Alwan & Williams (1980), the two uranyl carbonate minerals, liebigite, $Ca_2[UO_2(CO_3)_2]\cdot10H_2O$, and andersonite, $CaNa_2[UO_2(CO_3)_2]\cdot6H_2O$, should be expected to coexist. Several syntheses of these minerals have been described (Blinkhoff 1906, Axelrod *et al.* 1951, Bachelet *et al.* 1952, Meyrowitz & Ross 1961, Meyrowitz *et al.* 1963, Čejka 1969, Coda *et al.* 1981). Meyrowitz *et al.* (1963) mentioned the formation of unknown yellow–green crystals obtained during the synthesis of liebigite from potassium carbonate, uranyl nitrate and calcium nitrate.

In a previous paper, Vochten *et al.* (1993) described a new method for the synthesis of liebigite and andersonite starting from tetrasodium uranyl carbonate $Na_4[UO_2(CO_3)_2]$ (NaUTC). As mentioned in that paper, the formation of an intermediate phase, consisting of well-formed yellow–green lath-like crystals, was observed. The X-ray powder-diffraction pattern of this phase could not be matched with that of any known compound.

For the present synthesis, two grams of NaUTC were dissolved in 100 mL of 0.04 M $CaCl_2$ and left to evaporate in an open vessel at 25°C. After one week, well-formed hemispherical crystals of liebigite started to grow. After two weeks, the formation of crystals of the intermediate phase was observed, and after three weeks, crystals of andersonite were formed. The aim of the present study was to determine the chemical composition and the crystal structure of the unknown synthetic phase, as well as some of its physicochemical characteristics.

CRYSTAL MORPHOLOGY

The scanning electron micrographs (Fig. 1) show that the crystals are orthorhombic, with a lath-like habit and faceted edges. The length of the crystals ranges from 0.6 to 1.0 mm, and their width, from 0.01 to 0.1 mm. As clearly shown in the SEM photographs, the crystals are built up of subparallel layers.

The morphology of the crystals can be considered as a combination of the forms {010} and {001}. The two other visible forms, {011} and {0$\bar{1}$1}, are barely developed. The layering in the photographs is parallel to (001).

CHEMICAL COMPOSITION

The Na, Ca and U content was determined by electron-microprobe analysis. Oligoclase (Na), wollastonite (Ca) and UO_2 (U) were used as standards. Data were collected at 12 different points. The water and carbon dioxide content was determined by thermogravimetry (TG) in combination with differential scanning calorimetry (DSC). A Dupont DSC 910 and TGA 951 apparatus was used, with an applied rate of heating of 5°C/min and a constant 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 $Ba(OH)_2$ solution. The results are shown in Figure 2. The thermal decomposition of the carbonate groups starts at approximately 300°C and is complete by 800°C, with a loss of 21% by weight, corresponding to three carbonate groups. It is clear from the TG curve that the dehydration and decarbonation steps overlap, so that it is quite difficult to

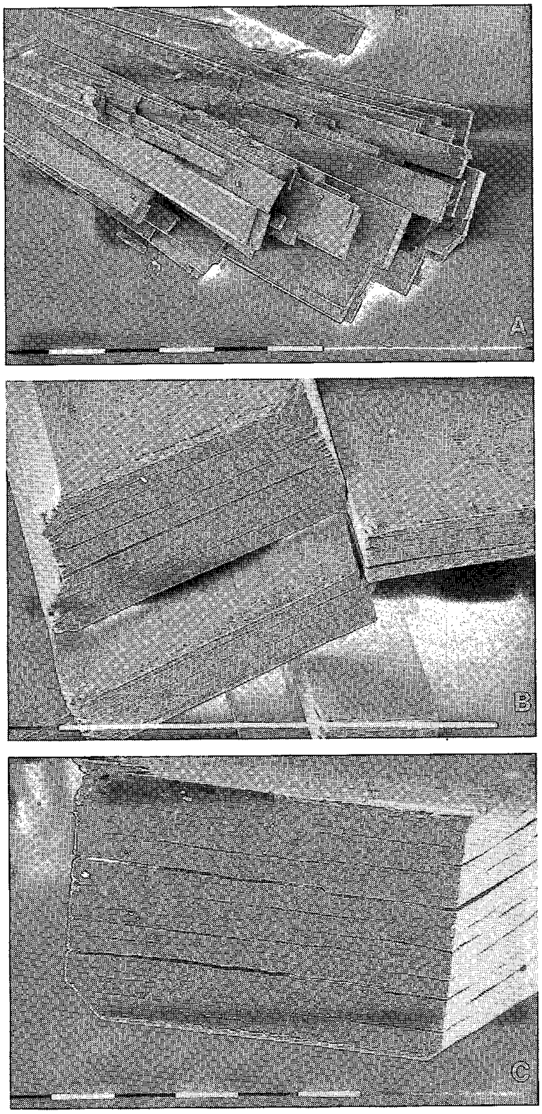

FIG. 1. Scanning electron micrographs of the intermediate phase between liebigite and andersonite. Scale bar: A, B: 100 μm; C: 10 μm.

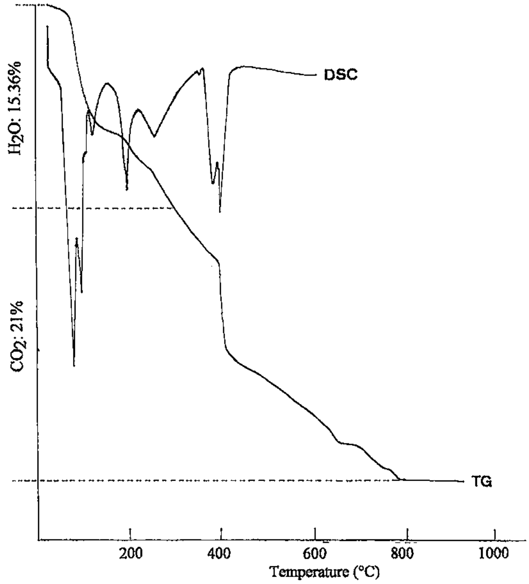

FIG. 2. Results of thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses of the intermediate phase between liebigite and andersonite.

determine the temperature intervals over which the individual molecules of water are lost. Only the total amount of water could be estimated (15.4%); it corresponds to 5.38 water molecules. Table 1 summarizes the composition in terms of oxides, from which the chemical formula is calculated by the classic "residual oxygen" method, based on 11 oxygen atoms. This leads to the formula: $Ca_{1.54}Na_{0.63}[UO_2(CO_3)_3]\cdot xH_2O$ ($x = 5.38$).

Because the electroneutrality rule is to be obeyed, the formula lacks 0.29 positive charges. This problem can be solved by the presence of a proton, associated with an oxygen atom. This could be an oxygen of UO_2 or an oxygen of H_2O, as has been suggested for other uranium minerals by Smith *et al.* (1957), Brasseur (1962) and Sobry & Rinne (1973). In this case, the formula can then be written as: $Ca_{1.54}Na_{0.63}(H_3O)_{0.29}[UO_2(CO_3)_3]{\sim}5H_2O$.

TABLE 1. CHEMICAL COMPOSITION OF THE INTERMEDIATE COMPOUND

Oxide	weight %	Atomic quantities ($\times 10^4$)	Atomic ratio
CaO	13.76	0.2453	1.54
Na_2O	3.12	0.0503	0.63
UO_3	47.22	0.1651	1.04
CO_2	21.00	0.4721	3.00
H_2O	15.36	0.8533	5.38
Total	100.46		

OPTICAL PARAMETERS

The crystals are biaxial negative, with $2V = 65°$ ($\pm 5°$), and have a positive elongation and parallel extinction. The indices of refraction are α 1.525 (± 0.005), β 1.547 (± 0.002) and γ 1.556 (± 0.002). The indices β and γ were determined by means of liquids with known index of refraction. The value of α was calculated from β, γ and $2V$. Most of the crystals are clearly twinned, as can be detected by polarizing microscopy.

LUMINESCENCE SPECTRA

Both fluorescence and phosphorescence spectra were recorded by means of a Perkin–Elmer MPS44B spectrofluorimeter at 298 and 77 K, with an excitation wavelength of 380 nm, a bandpass for excitation of 20 nm and for emission of 5 nm, and a scan speed of 120 nm/min.

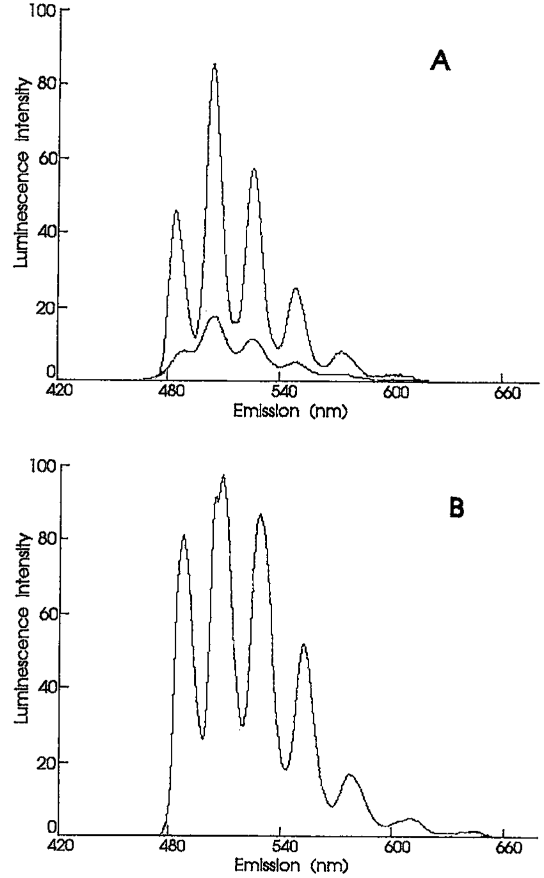

FIG. 3. Luminescence spectra of the intermediate phase between liebigite and andersonite. A. Fluorescence spectra at 77 and 298 K. B. Phosphorescence spectra at 77 K.

TABLE 2. RELATIVE INTENSITIES OF THE PHOSPHORESCENCE BANDS AT 77 K FOR LIEBIGITE, THE SYNTHETIC INTERMEDIATE COMPOUND, AND ANDERSONITE

	Phosphorescence bands in nm					
	485	505	523	550	570	600
Liebigite	68	94	100	68	25	10
Intermediate compound	8.0	10.0	8.5	5.0	2.0	0.8
Andersonite	3.5	6.5	5.0	2.2	0.8	0.4

The fluorescence spectra of the intermediate phase at 298 and 77 K are shown in Figure 3. The intensity of fluorescence at 298 K is much lower than that at 77 K, which can be explained by the fact that the quantum efficiency of fluorescence decreases with increasing temperature. The band-gap energy is calculated at the most intense peak (505 nm) as 2.46 eV, which indicates that the compound studied must be regarded as an insulator, in the same way as liebigite and andersonite (Vochten *et al.* 1993).

At 298 K, the intermediate phase shows no phosphorescence, as is also the case for liebigite and andersonite (Vochten *et al.* 1993). At 77 K, however, a well-pronounced phosphorescence could be detected for all three compounds. The phosphorescence spectrum of the intermediate phase at 77 K (Fig. 3) can be characterized by six bands (485, 505, 523, 550, 570 and 600 nm). In Table 2, the intensities of the individual phosphorescence bands are given, together with those of liebigite and andersonite. From this table, it is clear that the intensity of phosphorescence is strongly dependent on the Ca/Na ratio. A partial substitution of Ca^{2+} by Na^+ ions is reflected in a very strong decrease in the intensity of phosphorescence.

CRYSTAL STRUCTURE

The crystal chosen for data collection, a clear yellow–green lath of dimensions 0.07 × 0.11 × 0.76 mm, was mounted with the long dimension along the fiber. It exhibits a well-pronounced morphology and is not twinned when viewed in a polarizing microscope. The experimental density was determined to be 2.88 Mg/m^3 by flotation in a mixture of 1,1,2,2 tetrabromoethane and *n*-hexane. Data were collected at room temperature on a Stoe STADI4 single-crystal diffractometer equipped with Mo*K*α radiation and a perpendicular mounted graphite (002) monochromator. Accurate unit-cell parameters were obtained by least-squares refinement of measured and calculated $(\sin\theta)^2$ values (24 reflections). The θ-values are free of any zero-point error of the circles. They are obtained by measuring the ω-centers of reflections at positive and negative 2θ and taking the difference of the two ω-values as the true 2θ value (Stoe 1988b). This leads to the following parameters: *a* 18.150(3), *b* 16.866(6), *c* 18.436(3) Å, *V* 5644(3) Å^3, D_{calc} = 2.84 Mg/m^3, μ = 11.5 mm^{-1}, Z = 8. The ω-scan technique (scan width 1.05° in 35 steps plus α_1–α_2 dispersion, measuring time/step between 0.5 and 2 s) was used to collect 12 632 reflections with indices $-2 \le h \le 26$, $-2 \le k \le 24$, $-2 \le l \le 26$ and $2\theta_{max} = 60°$.

Of these measured reflections, 12 602 were accepted, and 9 014 were considered independent reflections. Of the 9 014 unique reflections (R_{int} = 0.018), 4 861 with $I \ge 2\sigma_{(I)}$ [σ(I) from counting statistics] were considered observed (Stoe 1988a). The standard deviation in intensity was computed from $\sigma^2(I) = (P + k^2B + 0.0002\,P^2)$, where P stands for peak counts, k is background to peak-scan time, and B is total background count. The intensities of three standard reflections (400, 040, 004) measured every hour showed an average decay of 7.4% over the course of the data collection. The intensities were corrected for Lorentz and polarization effects. Empirical absorption-corrections based on ψ scans (North *et al.* 1968, Stoe 1988c) were applied using nine reflections near χ = 90° in the range $8 \le 2\theta \le 36°$. Reflections were measured at 10° intervals from 0 to 360°. The minimum and maximum transmission values ranged from 0.021 to 0.068.

Systematic absences of 0*kl* for $k + l = 2n + 1$ and *h*0*l* for $h + l = 2n + 1$, as derived from Weissenberg photographs and a computer analysis of the measured data with the program SYSABS (Gabe *et al.* 1989), indicated *Pnnm* or *Pnn*2 as the space group. The centrosymmetric space-group *Pnnm* was favored by intensity statistics. The structure was successfully solved in this space group using the VAX version of the DIRDIF system (Beurskens *et al.* 1992). The automatic run located 36 atoms other than hydrogen. All other atoms were found from subsequent difference-Fourier maps. The structure was further refined with the PC version of the NRCVAX crystallographic software package (Gabe *et al.* 1989). Anisotropic least-squares refinement of *F* converged at *R* = 0.0475, R_w = 0.0562. The atoms of hydrogen were not located. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/(\sigma^2(F_o) + 0.00030\,F_o^2)$, with $\sigma(F_o)$ from counting statistics. The final refinement afforded values of S (goodness of fit) equal to 1.67 and $(\Delta/\sigma)_{max}$ less than 0.01. The crystal structure has also been refined in the noncentrosymmetric space-group *Pnn*2, resulting in a slighly higher *R* value (4.79). Based on a *R*-factor ratio test (Hamilton 1965), we cannot reject at the 5% level of significance the hypothesis that *Pnnm* is the correct

TABLE 3. THE IMPORTANT GEOMETRICAL DATA CONCERNING THE CATION–OXYGEN BONDS IN $UO_2(CO_3)_3$

	$U\text{-}O_{ap.}$	$U\text{-}O_{eq.}$	Average $U\text{-}O_{eq.}$	$C\text{-}O_{eq.}$	Average $C\text{-}O_{eq.}$	Average $C\text{-}O_{te.}$
Andersonite	1.79	2.41...2.46	2.44	1.26...1.31	1.28	1.30
Liebigite	1.78	2.39...2.45	2.43	1.28...1.31	1.29	1.25
Present compound	1.78(1)	2.41...2.47	2.44(2)	1.25...1.32	1.30(2)	1.25(2)

ap. means apical, eq. means equatorial and te. means terminal.

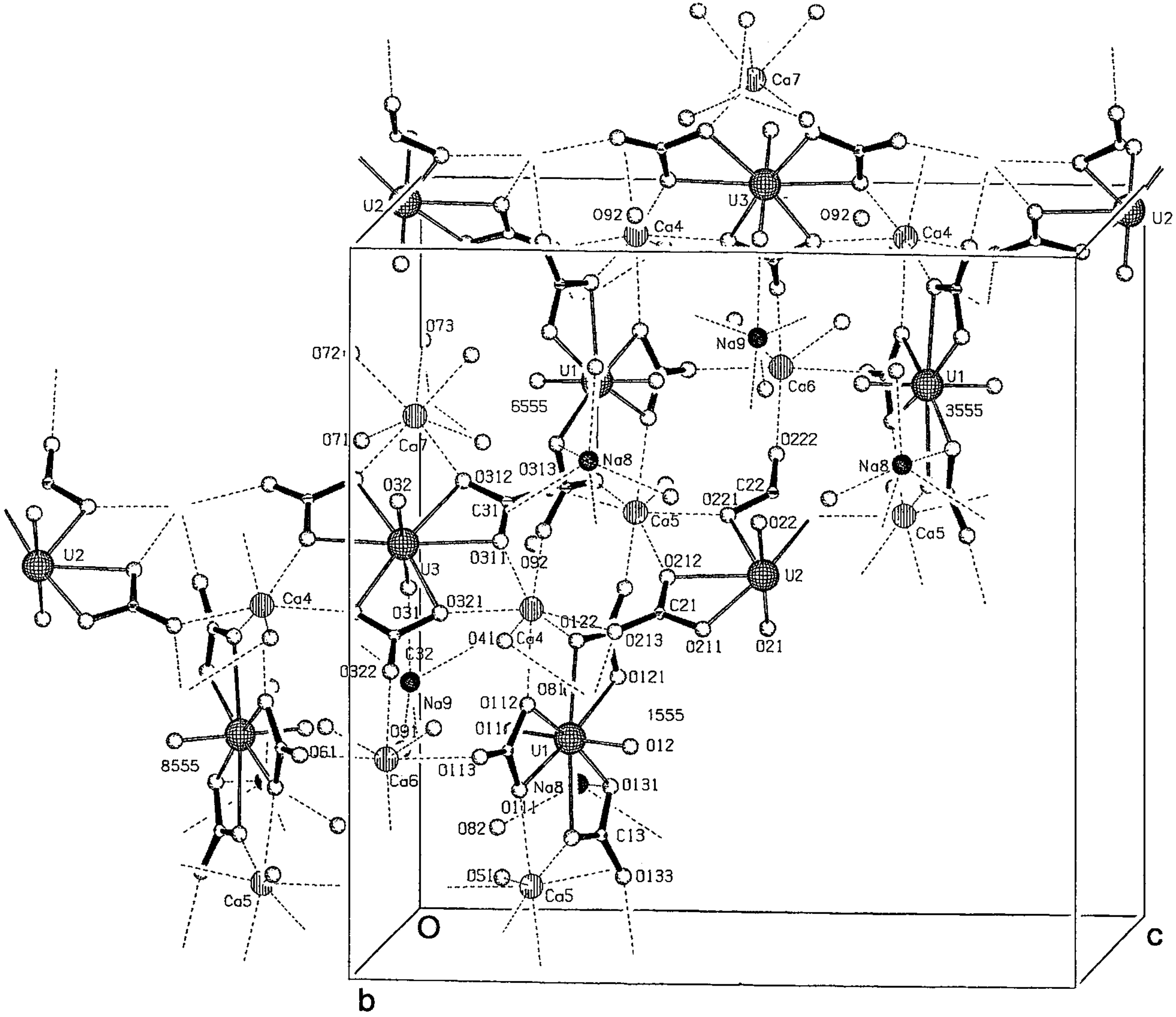

FIG. 4. View of the structure of the intermediate phase between liebigite and andersonite parallel to the *c* axis.

space-group. A similar analysis of the final difference map revealed maximum and minimum peaks corresponding to 3.6 eÅ^{-3} and –1.53 eÅ^{-3}. Atomic scattering factors were taken from International Tables for X-ray Crystallography (1974, vol. IV), and anomalous dispersion was applied for each type of atom. General calculations were performed using the PC version of the NRCVAX package, PARST (Nardelli 1983), PLATON (Spek 1990) and PLUTON (Spek 1992). Crystallographic data are summarized in Table 3. Inspection of the final difference-Fourier map reveals a positive peak at x = 0.000, y = 0.500, z = 0.034, corresponding to the maximum peak of 3.6 eÅ^{-3} in the difference map mentioned earlier. This peak contains approximately half the number of electrons of an oxygen atom and is located at a reasonable H-bonding distance (2.87 Å) from the oxygen atom of another water molecule. Voids calculated in the residual structure with the program PLATON show a cavity of 54 Å^3 at the position of the highest difference-Fourier peak, which indeed can be occupied by a water molecule, which normally occupies some 40 Å^3. This position is very near the plane of symmetry, which means that the two symmetry-equivalent positions are too close to each other. This situation is acceptable only if the electron density is distributed over two different locations, with a site occupancy of 0.5. This is a case of statistical disorder; one has to be careful in searching for small peaks in electron density in a Fourier map dominated by U atoms. Because of the small number of electrons, which gives it more the status of a residual peak, we did not include it in the refinement.

Lists of structure factors and anisotropic thermal parameters are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

The structure and numbering scheme of atoms in $Ca_3Na_{1.5}(H_3O)_{0.5}[(UO_2)_2(CO_3)_6]\cdot 8H_2O$ (M_r = 1208.47) are illustrated in the PLUTON plot (Spek 1992), shown in Figure 4. The basic structural unit consists of three $UO_2(CO_3)_3$ units. Two of them (U_2 and U_3) lie on a plane of mirror symmetry. Each U atom is [8]-coordinated. The resulting hexagonal-bipyramidal polyhedron is distorted. The two apical uranyl oxygen atoms are much closer than the oxygen atoms from the bidentate CO_3 groups in the equatorial coordination. The UO_2^{2+} ion is always nearly linear [average O–U–O angle 178.8(7)°] and has a mean bond-length of 1.78(1) Å.

The U–O carbonate bonds vary between 2.420(9) and 2.468(8) for U1, between 2.413(9) and 2.434(9) for U2, and between 2.417(9) and 2.459(10) for U3. The C–O bond lengths vary from 1.242(3) to 1.321(2), corresponding to the range reported for liebigite (Mereiter 1982) and andersonite (Coda *et al.* 1981). The CO_3 groups have the sp^2 configuration, with an average angle of 120°, but the O–C–O angle formed with the uranyl-bonded oxygen atoms invariably is smaller (between 112.7 and 116.9°) than the other ones (between 119.4 and 124.6°). The average bond-length for the oxygen atoms coordinated to U is greater (mean value: 1.299 Å) than the terminal C–O bonds (mean value: 1.249 Å), suggesting a higher p character for the latter. Table 3 summarizes the important geometrical data for the oxygen bonds in $UO_2(CO_3)_3$.

Two (Ca6, Ca7) of the four Ca polyhedra lie on the mirror plane. One of them (Ca6) is six-coordinated $[CaO_4(H_2O)_2]$. One pair of symmetry-related oxygen atoms (O113) occupies the first two coordination sites. Two other atoms of oxygen (O322 and O222) occupy the next two coordination sites. Another pair of symmetry-related water molecules (O61) occupy the positions five and six. These water molecules are at an appropriate distance from O113 and O131 for hydrogen bonding. The Ca7 atom lies in the symmetry plane and is situated in a [7]-coordinated environment, coordinated by a symmetry-related pair of carbonate oxygen atoms (O312), two pairs of symmetry-related water molecules (O71 and O72), and one water molecule (O73) lying in the plane of symmetry. Both O71 and O73 belong also to the Na9 sphere of coordination. Atom O71 also makes hydrogen bonds with other water molecules O81 and O92, and atom O73 with O82. Hydrogen bonds exist also among O72, O12 and O211. The Ca4 atom shares edges with two uranyl polyhedra (O112, O122, O311 and O321) and is coordinated to two terminal carbonate (O213, O133) oxygen atoms and one water molecule (O41). The last Ca atom (Ca5) is also seven-coordinated, shares edges with two uranyl polyhedra (O221 and O212, O132 and O111), and is also coordinated to two terminal carbonate oxygen atoms (O123, O313) and one water molecule (O51).

The Na8 and Na9 atoms are both [5]-coordinated, but the composition of the two polyhedra is different. The Na8 polyhedra can be described by $NaO_2(H_2O)_3$, with one of the water molecules (O41) at a rather large distance of 2.68 Å. The other water molecule (O81) is involved in hydrogen bonds with the oxygen atoms O121, O313 and O71. The Na9 atom lies in the plane of symmetry and is surrounded by four H_2O molecules and one apical oxygen atom O31, to give $[NaO(H_2O)_4]$. The mean Na–O distance lies between 2.44 and 2.66 Å. The Ca–O and Na–O bonding distances to water molecules are generally the longest ones in the Ca as well as in the Na spheres of coordination.

The structure contains water molecules in nine positions; two of them are special positions in the plane of symmetry.

Charge balance is achieved by OH^- substitution for O^{2-}. The single-bond character of a normal O^{2-} bond should increase, and the bond length should become larger, which has not been observed. Electrical neu-

TABLE 4. FINAL ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS (Å^2)*

label	x/a	y/b	z/c	Ueq
Ca4	0.5576(1)	0.6740(2)	0.1861(2)	0.0188(7)
Ca5	0.4370(1)	0.8206(2)	0.3147(2)	0.0199(7)
Ca6	0.7516(2)	0.5268(2)	0.0000(0)	0.0236(8)
Ca7	0.3196(2)	0.9258(2)	0.0000(0)	0.024(1)
Na8	0.6675(4)	0.5292(4)	0.2842(5)	0.054(3)
Na9	0.6787(6)	0.8640(6)	0.0000(0)	0.074(5)
U1	0.7470(3)	0.7904(2)	0.2278(2)	0.020(1)
O11	0.7413(6)	0.8380(6)	0.1422(5)	0.036(3)
O12	0.7521(5)	0.7443(6)	0.3145(5)	0.032(3)
C11	0.7493(8)	0.6377(7)	0.1558(6)	0.023(3)
O111	0.8074(5)	0.6800(6)	0.1683(6)	0.029(3)
O112	0.6892(5)	0.6703(6)	0.1808(7)	0.039(4)
O113	0.7518(6)	0.5721(5)	0.1241(5)	0.029(3)
C12	0.6085(7)	0.8569(8)	0.2719(8)	0.025(4)
O121	0.6706(5)	0.8909(6)	0.2834(6)	0.032(3)
O122	0.6120(5)	0.7909(6)	0.2368(6)	0.031(3)
O123	0.5484(5)	0.8878(6)	0.2931(7)	0.038(4)
C13	0.3853(7)	0.6383(7)	0.2372(9)	0.026(4)
O131	0.3229(5)	0.6009(5)	0.2276(6)	0.028(3)
O132	0.3826(5)	0.7030(6)	0.2703(6)	0.028(3)
O133	0.4435(5)	0.6108(6)	0.2091(6)	0.032(3)
U2	0.5122(4)	0.7210(4)	0.5000(0)	0.020(2)
O21	0.5911(7)	0.7820(9)	0.5000(0)	0.035(5)
O22	0.4334(7)	0.6571(9)	0.5000(0)	0.033(5)
C21	0.5598(7)	0.6577(8)	0.3635(8)	0.024(4)
O211	0.5780(5)	0.6272(6)	0.4254(6)	0.034(3)
O212	0.5158(5)	0.7176(6)	0.3681(5)	0.030(3)
O213	0.5828(6)	0.6300(6)	0.3045(5)	0.032(3)
C22	0.411(1)	0.855(1)	0.5000(0)	0.030(7)
O221	0.4394(5)	0.8219(6)	0.4415(6)	0.035(4)
O222	0.3636(8)	0.907(1)	0.5000(0)	0.043(6)
U3	0.4792(4)	0.763(4)	0.0000(0)	0.019(2)
O31	0.5465(7)	0.8372(9)	0.0000(0)	0.036(6)
O32	0.4122(9)	0.6852(9)	0.0000(0)	0.040(5)
C31	0.4255(7)	0.8258(8)	0.1369(7)	0.022(4)
O311	0.4743(5)	0.7699(5)	0.1330(6)	0.027(3)
O312	0.3987(5)	0.8465(6)	0.0742(5)	0.028(3)
O313	0.4084(5)	0.8599(6)	0.1939(6)	0.030(3)
C32	0.594(1)	0.643(1)	0.0000(0)	0.038(8)
O321	0.5653(6)	0.6746(6)	0.0590(6)	0.037(4)
O322	0.6371(8)	0.5867(9)	0.0000(0)	0.039(6)
O41	0.5885(6)	0.5372(6)	0.1616(7)	0.045(4)
O51	0.4115(6)	0.9604(5)	0.3423(6)	0.034(4)
O61	0.698(1)	0.4218(7)	-0.0747(7)	0.088(7)
O71	0.8640(6)	0.4719(6)	0.4171(6)	0.041(4)
O72	0.7299(6)	0.6266(9)	0.4181(6)	0.058(5)
O73	0.7261(7)	0.4682(8)	0.5000(0)	0.037(4)
O81	0.2956(6)	0.9712(7)	0.2074(6)	0.041(4)
O82	0.6137(6)	0.4667(7)	0.3906(7)	0.053(4)
O91	0.260(1)	0.747(1)	0.5000(0)	0.069(8)
O92	0.500(0)	1.000(0)	0.1561(9)	0.043(5)

$$U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

* Estimated standard deviation is shown in parentheses.

trality can also be preserved if water molecules occur in the form of oxonium ions, as was suggested by Smith *et al.* (1957), Brasseur (1962) and Sobry & Rinne (1973). Bond-valence analysis (Brown & Wu 1976, Brown 1976) of all oxygen atoms that are part of a water molecule indicates that all bond valences are within 10% of the expected value except for O51, which is 20% lower, and O71 and O73, which are 20% higher. The analysis does not show the exact position of the positive charge in the structure. Since the O92 oxygen is the only one not belonging to the sphere of coordination of the positive ions Ca^{2+} and Na^+, the positive charge most likely is located in this position.

Figure 4 shows that the $UO_2(CO_3)_3$ units form layers parallel to $(01\bar{1})$. The layers are interconnected by layers of Ca polyhedra. The sodium ions Na8 and Na9 are located near the Ca layers, and connect to the oxygen atoms of the Ca environment.

The final atomic parameters are listed in Table 4. Tables of interatomic distances and angles are available from The Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

X-RAY POWDER-DIFFRACTION DATA

X-ray powder-diffraction data were recorded at 40 kV and 20 mA, using Cu$K\alpha_1$ radiation (λ = 1.5406 Å). The diffraction pattern is recorded by means of a Guinier–Hägg camera with a diameter of 100 mm. Silicon powder (NBS–640) was used as an internal standard. The relative intensities of the diffraction lines were measured with a Carl Zeiss Jena MD–100 microdensitometer. Using the previously determined unit-cell parameters and space group, the powder patterns were indexed by the program PPLP from the IBM PC version of NRCVAX (Gabe *et al.* 1989). Nearly all the observed reflections could be indexed, with $\Delta Q_{obs} \leq \Delta Q_{calc}$ ($\Delta \leq 0.05°$). The results are given in Table 5.

COMPATIBILITY

The compatibility index $1 - (K_P/K_C)$ is calculated using the Gladstone – Dale constants (Mandarino 1981), the mean index of refraction and the density. For this index, a value of –0.004 is obtained, which indicates "superior" consistency of the data obtained for the compound.

DISCUSSION

During the synthesis, starting from NaUTC and Ca^{2+} ions, liebigite, the intermediate phase and andersonite are obtained consecutively. Therefore, the intermediate phase must be considered as a stable phase. The sequence of crystallization of the three compounds is clearly governed by the Ca^{2+}/Na^+ ratio. It is also clear that the intensity of the luminescence spectra is strongly dependent on this Ca^{2+}/Na^+ ratio.

For this phase, a deficiency in positive charge seems to exist. This deficiency can be derived from the structure determination as well as from the chemical composition. In agreement with Brasseur (1962) and Sobry & Rinne (1973), we propose the presence

TABLE 5. X-RAY POWDER-DIFFRACTION DATA FOR THE INTERMEDIATE SYNTHETIC PHASE

d(obs)	I/I_0(obs)	d(calc)	hkl
-	-	12.95	1 0 1
-	-	12.44	0 1 1
10.20	10	10.27	1 1 1
9.07	10	9.22	0 0 2
8.580	90	8.434	0 2 0
-	-	7.332	2 1 1
6.510	70	6.467	2 0 2
6.198	10	6.180	2 2 0
-	-	6.045	2 1 2
5.850	20	5.886	1 2 2
-	-	5.771	0 1 3
5.491	30	5.500	1 1 3
5.420	10	5.447	3 1 1
5.328	4	5.381	0 3 1
5.089	100	5.133	2 2 2
4.892	30	4.918	3 2 0
4.605	50	4.609	0 0 4
4.539	40	4.544	4 0 0
4.381	8	4.388	4 1 0
4.321	8	4.341	3 2 2
4.230	8	4.219	0 4 0
4.096	8	4.149	0 3 3
-	-	4.111	1 4 0
4.019	50	4.048	0 2 4
3.969	50	4.001	4 2 0
-	-	3.952	1 2 4
3.847	10	3.837	0 4 2
3.746	30	3.757	1 4 2
3.691	10	3.696	2 2 4
3.527	70	3.536	2 4 2
3.469	40	3.463	3 4 0
3.414	5	3.427	3 3 3
3.360	5	3.351	2 1 5
3.325	5	3.321	0 5 1
-	-	3.285	4 3 2
3.241	40	3.236	4 0 4
3.115	40	3.114	0 4 4
3.085	40	3.093	4 4 0
3.070	40	3.070	1 4 4
3.027	40	3.021	4 2 4
2.9113	50	2.9116	2 0 6
2.8786	50	2.8750	6 0 2
2.8532	20	2.8518	1 2 6
2.8160	30	2.8133	2 5 3
2.7561	50	2.7510	2 2 6

+ additional lines. Complete list available on request.

of oxonium ions in the structure in order to obtain electroneutrality.

Specimens in mineralogical collections in which liebigite and andersonite occur together should be re-examined, as the intermediate phase may be present.

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