A NEW METHOD OF SYNTHESIS OF BOLTWOODITE AND OF FORMATION OF SODIUM BOLTWOODITE, URANOPHANE, SKLODOWSKITE AND KASOLITE FROM BOLTWOODITE

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ABSTRACT

Boltwoodite has been synthesized at 185°C (1.3 MPa) from quartz, KCl and uranyl nitrate by a new method avoiding local supersaturation of silicate species in solution. Sodium boltwoodite, uranophane, sklodowskite and kasolite were synthesized from boltwoodite. Unit-cell parameters and space groups were determined from the X-ray powder-diffraction data. Infrared spectra have intense absorption bands at 3458 and 3377 cm^{-1}, which correspond to OH-stretching vibrations. Bands at 1384 cm^{-1} indicate the presence of SiO$_3$OH groups in the structures. Luminescence spectra and solubility data are reported.

Keywords: synthesis, IR and luminescence spectra, X-ray diffraction, powder method, solubility.

SOMMAIRE

Nous avons synthétisé la boltwoodite à 185°C (1.3 MPa) à partir de quartz, KCl et le nitrate d'uranyle; notre nouvelle méthode évite la sursaturation locale des espèces silicatées en solution. Les espèces sodium boltwoodite, uranophane, sklodowskite et kasolite ont ensuite été synthétisées à partir de la boltwoodite. Nous en avons déterminé les paramètres réticulaires et les groupes d'espace à partir des spectres de diffraction X (méthode des poudres). Les spectres d'absorption infra-rouge montrent des bandes intenses à 3458 et 3377 cm^{-1}, qui correspondent à l'étirement des groupes OH. L'absorption à 1384 cm^{-1} indique la présence de groupes SiO$_3$OH dans ces structures. Nous présentons aussi les spectres de luminescence et des données sur la solubilité.

(Traduit par la Rédaction)

Mots-clés: synthèse, spectre infra-rouge, spectre de luminescence, diffraction X (méthode des poudres), solubilité.

INTRODUCTION

Boltwoodite, a relatively rare secondary mineral of hexavalent uranium, was first described by Frondel & Ito (1956) from the Delta mine, San Rafael Swell, Emery County, Utah. Honea (1961) described additional localities of boltwoodite. The pale yellow to amber mineral occurs mostly as microcrystalline crusts of needle-shaped crystals in fibrous aggregates. Honea (1961), Chernikov *et al.* (1975), Strunz & Tennyson (1983) and Pu (1990) found that potassium in the structure of boltwoodite may partially be replaced by sodium, resulting in the general formula [(Na$_x$K$_{1-x}$)(H$_3$O)(UO$_2$)(SiO$_4$)·nH$_2$O], with $x <$ 0.5 for boltwoodite, and $x >$ 0.5 for sodium boltwoodite. This study presents a new method of synthesis for boltwoodite-group minerals.

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SYNTHESIS OF BOLTWOODITE

Although K^+, UO_2^{2+} and SiO_4^{4-} ions are present in groundwater, the concentration of SiO_4^{4-} is too low to contribute to the formation of boltwoodite. As boltwoodite is commonly associated with quartz, we first considered that the slow dissolution of quartz in an alkaline medium ($8 < pH < 12$) could be a source of the SiO_4^{4-} ions.

A solution of 0.35 g $UO_2(NO_3)_2 \cdot 6H_2O$ (A.R.) and 0.5 g KCl (A.R.) in 25 mL water was adjusted with KOH to a pH of 11.5. The solution was transferred into a teflon vessel in a Parr reaction bomb (Model 4760) and 3 g of chunks (*ca.* 1 cm) of synthetic hydrothermal quartz (Comptoir Sidérurgique Pan Américain, Libramont, Belgium) were added. The reaction bomb was heated at 185°C for seven days, resulting in a calculated pressure of *ca.* 1.3 MPa. After cooling to room temperature, the reaction mixture consists of fragments of quartz, a colloidal precipitate, and a crystalline phase of pale yellow needles and fine prismatic yellow crystals. The fragments of quartz were removed, and the remaining mixture was centrifuged. The colloidal precipitate and the yellow prismatic crystals were removed by washing the solid three times with 5% acetic acid, and subsequently with distilled water until acid-free. To remove smaller particles of quartz, the air-dried solid was suspended in bromoform and, after separation, again air-dried. The solid phase obtained consists of fine, pale yellow needles. Chemical analysis and X-ray diffraction (powder method) showed that the crystals consist of boltwoodite. The same experiment in a crucible of fused SiO_2 placed into the Parr reaction bomb gives identical results.

Time-dependent experiments indicate that the yield of boltwoodite increases to a maximum after seven days, and then decreases when soddyite begins to form. If the experiment is extended for 40 days or more, only crystals of soddyite are present. The slow transformation of boltwoodite into soddyite was confirmed in separate experiments under the same conditions, in which both natural and synthetic boltwoodite were suspended in distilled water.

SYNTHESIS OF BOLTWOODITE-GROUP COMPOUNDS FROM BOLTWOODITE

To obtain uranophane, sklodowskite, kasolite and sodium boltwoodite, synthetic boltwoodite was suspended in a 2 M solution of $Ca(NO_3)_2$, $MgSO_4$, $Pb(NO_3)_2$ and NaCl, respectively. The suspension was heated at 185°C (1.3 MPa) in a teflon vessel in a Parr reaction bomb for 24 hours. After cooling to room temperature, the suspension was centrifuged, and the supernatant fluid was tested for potassium using sodium tetraphenylborate. This procedure was repeated until no trace of potassium was detected. X-ray powder diffraction of the air-dried solids identified uranophane, sklodowskite and kasolite. The X-ray powder pattern of the sodium boltwoodite

TABLE 1. CHEMICAL COMPOSITION OF PRODUCTS OF SYNTHESIS

	$Na_2(UO_2)_2(SiO_4)F_2$*		Boltwoodite **		Sodium ** boltwoodite	
Na_2O	6.67	1.59			8.70	2.29
K_2O			10.11	1.85		
SiO_2	8.25	1.01	13.49	1.93	14.52	1.97
UO_3	79.85	2.06	68.86	2.07	69.16	1.97
F	5.23	2.03				
H_2O			7.50	-	7.46	-
Total	100.33		99.96		99.84	

In each case, the first column gives the proportion of the oxide or F, in wt.%, whereas the second column gives the molar proportion. The formula was calculated on the basis of nine (*) or eleven (**) atoms of oxygen.

formed could not be indexed successfully, although the diffraction lines reported by Honea (1961) and Nguyen *et al.* (1992) were present. Experiments extended to 40 days yielded well-formed yellow crystals. Electron-microprobe analysis (Table 1) and a single-crystal X-ray study (Blaton *et al.*, in prep.) revealed the composition $Na_2(UO_2)_2(SiO_4)F_2$. The lines of the X-ray powder-diffraction pattern of this compound correspond to the extra lines present in the powder pattern of the sodium boltwoodite synthesized. As the only source of F is teflon, the experiment was repeated in a crucible of fused SiO_2. The product obtained was identified by chemical analysis to be potassium-free sodium boltwoodite.

MORPHOLOGY OF THE CRYSTAL

Scanning electron micrographs show that crystals of synthetic boltwoodite and sodium boltwoodite are indistinguishable, as represented in Figure 1. Crystals are prismatic along [010] (Strunz & Tennyson 1983, Honea 1961). Most crystals occur as radial clusters, resulting in a fibrous appearance. The length of the crystals varies from 20 to 40 μm, and their width ranges from 1 to 2 μm.

CHEMICAL COMPOSITION OF SYNTHETIC BOLTWOODITE AND SODIUM BOLTWOODITE

Three well-formed crystals each of synthetic boltwoodite and sodium boltwoodite were analyzed with a Cameca SX–50 electron microprobe. The data for silicon and uranium were collected at eight different points of each crystal. Pure synthetic SiO_2 and UO_2 were used as standards. The K and Na contents were determined by Atomic Absorption Spectroscopy using a Philips PU 9200 absorption spectrometer equipped with a K/Na hollow cathode tube. The H_2O content was determined by means of a Dupont TGA 951 thermogravimetric analyzer. The formulae resulting from the analysis (Table 1), assuming Si present as SiO_4, lack 0.87
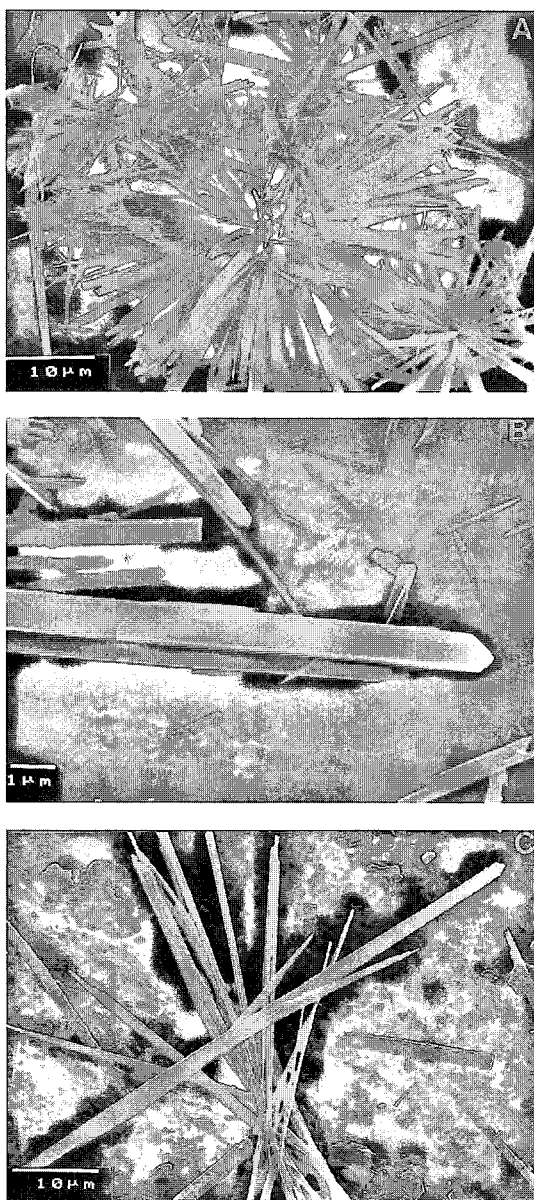
FIG. 1. Scanning electron micrographs of synthetic crystals of boltwoodite (A and B) and sodium boltwoodite (C).

ence of a (SiO_3OH) group. Bond-valence sum calculations (Brown & Altermatt 1985) for the oxygen atoms of the SiO_4 tetrahedra not involved in the U coordination, omitting the contribution of possible H-bonds, give 1.250 and 0.963 valence units (*vu*) for α-uranophane, 1.139 and 0.983 *vu* for β-uranophane, 1.150 *vu* for boltwoodite (Stohl & Smith 1981), 1.233 *vu* for sklodowskite (Ryan & Rosenzweig 1977) and 2.103 *vu* for kasolite (Rosenzweig & Ryan 1977). These calculations show that except for kasolite, the oxygen is highly undersaturated and should be defined as an (OH)-group. Accepting the SiO_3OH group, the calculated and ideal formulae are:

$$K_{0.92}(UO_2)_{1.03}(SiO_3OH)_{0.96}\cdot 1.30H_2O$$

$$K(UO_2)(SiO_3OH)\cdot H_2O$$

$$Na_{1.14}(UO_2)_{0.98}(SiO_3OH)_{0.98}\cdot 1.20H_2O$$

$$Na(UO_2)(SiO_3OH)\cdot H_2O$$

INFRARED SPECTROSCOPY

The infrared spectra of synthetic boltwoodite, synthetic sodium boltwoodite and boltwoodite from the Rössing mine, Namibia, were recorded with an ATI Mattson Genesis FTIR spectrometer. The range 4000–450 cm^{-1} was covered using the standard KBr-pellet technique. The spectra are shown in Figure 2. Table 2 contains the band maxima, relative intensities and band assignments. The low-wavenumber part of each spectrum can be divided into two regions, 1080 to 790 cm^{-1} and 625 to 450 cm^{-1}, respectively. According to Farmer (1974), Lyon (1962) and Cejka & Urbanec (1990), the former region contains the uranyl- and silicate-stretching bands, whereas the latter contains mainly bending vibrations of the silicate groups. Above 1100 cm^{-1}, only OH-vibration modes are observed. The broad, complex band in the region 3000–3500 cm^{-1} may well be associated with the stretching modes of H_2O molecules having a disordered arrangement (Ryskin 1974, White 1971). The corresponding bending vibrations lie in the region 1400–1700 cm^{-1} as relatively broad bands of moderate intensity.

The spectra of synthetic boltwoodite and sodium boltwoodite show two sharp bands in the OH-stretching region, at 3458 and 3377 cm^{-1}. Plesko *et al.* (1992) assigned these bands in the spectrum of their synthetic boltwoodite to stretching vibrations of ordered H_2O. A sharp band at 1730 cm^{-1} was assigned to the H_2O-bending mode. In our spectra, no 1730 cm^{-1} band was observed. However, both synthetic boltwoodite and sodium boltwoodite show a very sharp band at 1384 cm^{-1}, which, according to Plyusnina (1977) and Cejka & Urbanec (1990), indicates the presence of a (SiO_3OH) group. The infrared spectra of uranophane and sklodowskite also show a sharp band at 1384 cm^{-1}. Furthermore, the band at 1384 cm^{-1} is absent from the infrared spectra

and 0.82 positive charges for boltwoodite and sodium boltwoodite, respectively. Some authors (Smith *et al.* 1957, Brasseur 1962, Sobry & Rinne 1973) solved this problem by accepting the presence of oxonium ions in the structure. Crystal-structure determinations of α-uranophane (Ginderow 1988) and β-uranophane (Viswanathan & Harneit 1986) demonstrated the pres-
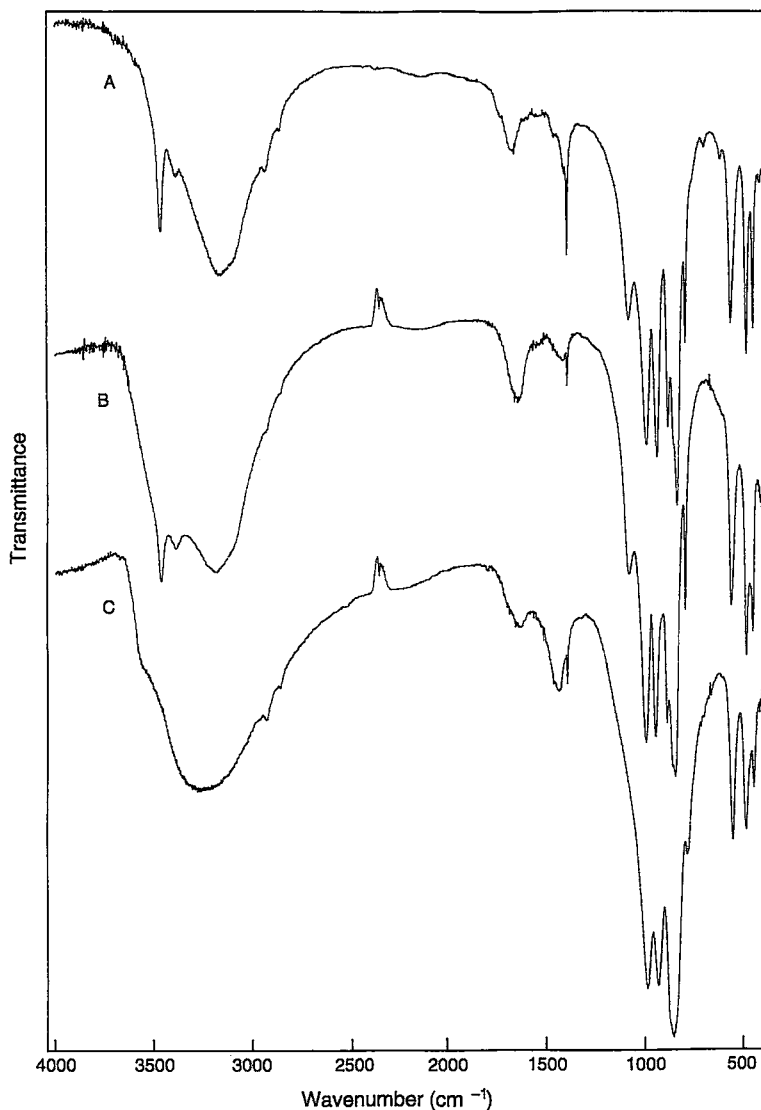
FIG. 2. Fourier-tranform infrared spectra of synthetic boltwoodite (A), synthetic sodium boltwoodite (B) and boltwoodite from the Rössing mine, Namibia (C).

of soddyite and kasolite (Rozenzweig & Ryan 1977, Demartin *et al.* 1992). The band at 1384 cm^{-1} indicates that synthetic boltwoodite and synthetic sodium boltwoodite contain (SiO$_3$OH) groups. The 1384 cm^{-1} band also is present in the spectrum of natural boltwoodite, but with a lower intensity. The sharp bands in the 3000–3500 cm^{-1} region are not present in the spectrum of boltwoodite, although they may be masked by the broad H$_2$O band.

LUMINESCENCE SPECTROSCOPY

The fluorescence spectra of synthetic boltwoodite and synthetic sodium boltwoodite were recorded at 298 and 77 K with a Perkin–Elmer MPS44B spectrofluorimeter. At room temperature, boltwoodite fluoresces very weak yellow to green under both short- and long-wave ultraviolet radiation, whereas sodium boltwoodite does not fluoresce. The optimal excitation

TABLE 2. BAND MAXIMA AND INTENSITIES
IN THE INFRARED SPECTRA

Synthetic Boltwoodite	Synthetic Sodium Boltwoodite	Boltwoodite from Rössing mine, Namibia	Assignment
3458 (s)	3462 (m)		ν SiO$_3$OH
3377 (w)	3391 (w)		ν SiO$_3$OH
3154 (s,b)	3187 (s,b)	3258 (s,b)	ν H$_2$O
1655 (m,b)	1630 (m,b)	1635 (m,b)	δ H$_2$O
1400 (w,b)	1400 (w,b)	1425 (m,b)	δ H$_2$O
1384 (s)	1384 (w)	1384 (w)	δ SiO$_3$OH
1076 (m)	1076 (w)		ρ H$_2$O
989 (vs)	987 (vs)	987 (s)	ν SiO$_4$/ν UO$_2$
937 (vs)	939 (vs)	935 (s)	
882 (w)	883 (w)		
835 (vs)	841 (vs)	854 (vs)	
790 (m)	789 (m)	782 (vw)	
561 (s)	559 (s)	555 (s)	δ SiO$_4$
482 (s)	482 (s)	486 (s)	
447 (s)	449 (m)	447 (w)	

vs: very strong, s: strong, m: medium, w: weak, vw: very weak, b: broad.

TABLE 3. SOLUBILITY OF SYNTHETIC BOLTWOODITE AT 25°C

pH	U-concentration (g.at/L)	pH	U-concentration (g.at/L)
3.81	$4.8 \cdot 10^{-3}$	7.38	$1.3 \cdot 10^{-6}$
4.31	$1.7 \cdot 10^{-3}$	7.60	$1.2 \cdot 10^{-6}$
4.81	$1.3 \cdot 10^{-4}$	11.73	$1.2 \cdot 10^{-6}$
5.75	$1.3 \cdot 10^{-6}$		

wavelength is 380 nm, with a bandpass of 20 nm, and for emission, 5 nm, and a scan speed of 120 nm/s. At low temperature, the spectra show (Figs. 3A, B) three fluorescence peaks at 508, 529, 551 nm (77 K). The intensity of fluorescence at 298 K is lower than at 77 K, a result of the decrease in quantum efficiency with increasing temperature. The calculated band-gap energy at 77 K for the most intense peak (551 nm) is 2.27 eV, which indicates that the compounds at this temperature are insulators.

SOLUBILITY OF BOLTWOODITE

The pH of several suspensions of aliquots of synthetic boltwoodite in CO$_2$-free distilled water was adjusted with KOH or HClO$_4$ to a series of pH values in the range 3.8–11.8. The suspensions were then shaken at 25°C under a N$_2$ atmosphere. After 30 days, the total U concentration of the supernatant solution had become constant. The suspensions were filtered through a 1.4 µm Millipore filter. The total U content of the solutions was determined spectrophotometrically at 662.5 nm using a Pye Unicam SP 8-00 UV/VIS spectrophotometer with Arsenazo III as the reagent (Singer & Matucha 1962). Table 3 shows the total uranium content of the solutions as a function of pH. The solubility of the synthetic bolt-woodite is relatively high in acidic solutions, decreases rapidly with increasing pH, and remains then constant above a pH of 5.75. X-ray-diffraction analysis of the
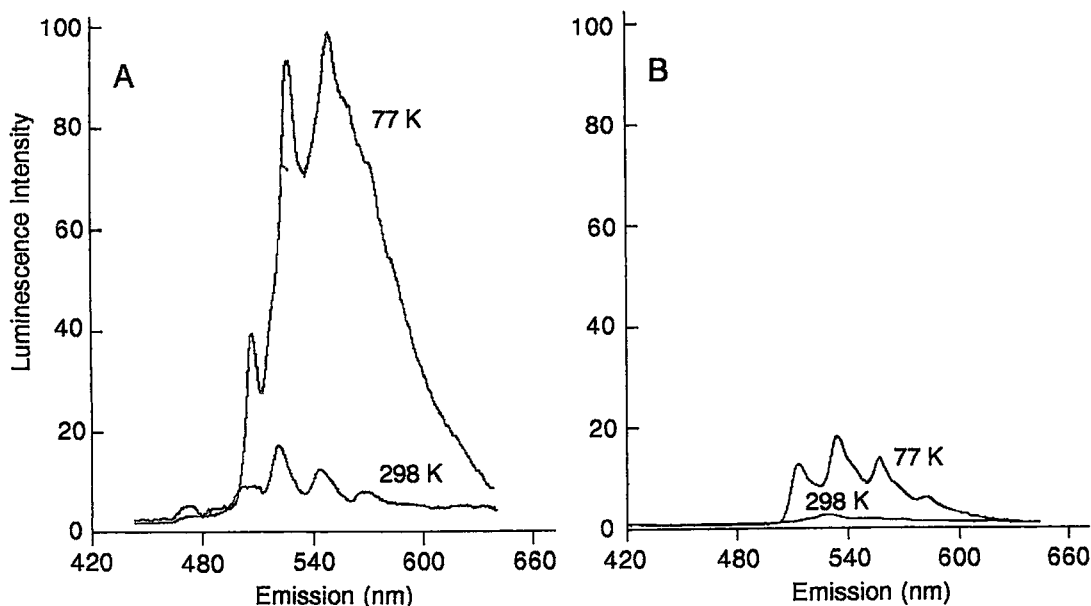

FIG. 3. Luminescence spectra of synthetic boltwoodite (A) and synthetic sodium boltwoodite (B) at 298 and 77 K.

air-dried samples after the solubility experiments showed only lines attributable to boltwoodite. The solubility value obtained is close to that for synthetic sodium boltwoodite at a pH of 4.5 (Nguyen *et al.* 1992), although those authors reported soddyite after equilibration.

The dissolution of synthetic boltwoodite can be written as

$$K(UO_2)(SiO_3OH)\cdot xH_2O \rightarrow$$
$$K^+ + UO_2^{2+} + SiO_3OH^{3-} + xH_2O$$
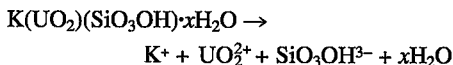
The associated solubility product is then

$$K_{SP} = [K^+][UO_2^{2+}][SiO_3OH^{3-}]$$

This equilibrium is governed by two pH-dependent systems. One of them is the formation of uranyl-hydroxo complexes (Djogic *et al.* 1986, Van Haverbeke & Vochten 1992). The second is the formation of the different monomeric and polymeric silicate species (Dent Glasser & Lachowski 1980). This equilibrium system is not yet fully known, which makes it impossible to determine the nature and the concentration of all silicate species present in solution at a given pH value. Nguyen *et al.* (1992) calculated the solubility product of synthetic sodium boltwoodite by assuming that all silicate species in solution could be considered together as $(SiO_2)_{aq}$. However, in solutions with pH below 7.5, we observed a visible gelling of silica after the period of equilibration. Because the formation of colloidal silica had probably taken place before any gelling was visible, accurate calculation of the solubility product is impossible; hence, we present only the solubility data in terms of $[U]_{total}$.

X-RAY POWDER-DIFFRACTION DATA

The X-ray powder-diffraction data of each crystalline phase (without crushing) were recorded with a Guinier-Hägg camera using CuKα_1 radiation (λ = 1.5406 Å) at 40 kV and 20 mA. 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. The unit-cell parameters (Table 4) were determined using the computer program TREOR90 (Werner *et al.* 1985). The reflections were indexed and refined with the program PIRUM (Werner 1969). The unit-cell parameters are in close agreement with those already in the literature for boltwoodite (Stohl & Smith 1981), α-uranophane (Ginderow 1988), sklodowskite (Ryan & Rosenzweig 1977) and kasolite (Rosenzweig & Ryan 1977). Although the unit-cell parameters obtained for synthetic sodium boltwoodite differ from those reported for sodium boltwoodite with a K/Na ratio of 0.30/0.70 (Chernikov *et al.* 1975), there is a close agreement if their orthorhombic cell is transformed to a monoclinic cell with half the cell volume

TABLE 4. UNIT-CELL PARAMETERS

	Blt	Sodium Blt	Urn	Skl	Ksl
a (Å)	7.0316(8)	13.931(4)	15.944(3)	17.372(2)	13.270(2)
b (Å)	7.0668(2)	6.9436(5)	7.0169(5)	7.058(5)	6.9308(9)
c (Å)	6.6633(2)	6.6749(4)	6.6828(8)	6.6216(4)	6.703(1)
β (°)	105.862(6)	103.21(1)	97.51(1)	105.890(8)	104.25(1)
$M(20)$	70	18	31	38	15
$F(20)$	81(0.0055,45)	25(0.010,79)	55(0.0059,62)	73(0.0096,29)	26(0.0179,44)

Symbols: Blt boltwoodite, Urn uranophane, Skl sklodowskite, Ksl kasolite.

(a 14.10, b 7.02, c 6.65 Å, β 103.64°). The similarities in the cell parameters of the boltwoodite-group compounds (Table 4) indicate that synthetic sodium boltwoodite has a structure consisting of uranyl silicate sheets cross-bonded by the sodium ions, and thus similar to the structure of the other members of the group.

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