

Transformation of chernikovite and sodium autunite into lehrnerite

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ABSTRACT

Chernikovite $[(\text{H}_3\text{O})_2(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}]$ and sodium autunite $[\text{Na}_2(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}]$ were synthetically prepared from schoepite $[\text{UO}_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}]$ and transformed into synthetic lehrnerite $[\text{Mn}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}]$ by ion exchange with MnCl_2 . Chemical analysis of synthetic lehrnerite combined with TGA yields a composition that is identical with natural lehrnerite. Synthetic lehrnerite crystals are pale brown to yellow and not fluorescent.

The space group is $P2_1/n$ and the cell parameters are $a = 7.04(2)$, $b = 17.16(4)$, $c = 6.95(2)$ Å and $\beta = 90^\circ 18'$. The Mohs hardness lies between 3 and 4, and the cleavage is perpendicular on (001). The density is 3.600 g/cm^3 (measured), 3.640 g/cm^3 (calculated). The crystals are biaxial negative, $\alpha = 1.600(2)$, $\beta = 1.6055(2)$, $\gamma = 1.607(2)$, and $2V = 72^\circ$. The X-ray powder pattern shows the following strongest eight lines: $8.5542(70)(020)$, $4.9425(40)(101)$, $3.506(50)(200)$, $3.4676(50)(002)$, $2.4848(100)(202)$, $2.2227(60)(\bar{3}01)$, $1.7531(70)(361)$, $1.5716(70)(\bar{1}44)$.

INTRODUCTION

Mühlbauer (1925) described for the first time a mineral from the pegmatite of Hagendorf, Oberpfalz, Germany, as lehrnerite $[\text{Mn}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}]$. However this mineral was afterward identified as ludlamite $[\text{Fe}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}]$ by Berman (1925) with the consequence that the name lehrnerite was discredited. Recently, a new mineral from the same pegmatite was described by Mücke (1988) for which the name lehrnerite was accepted by the IMA Commission on New Minerals and Mineral Names. This mineral belongs to the uranyl-phosphate group and more particularly to the meta-uranite series. The idealized formula of this mineral is $\text{Mn}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, whereas the empirical formula was given by Mücke (1988) as $\text{Mn}_{0.99}\text{Fe}_{0.03}(\text{UO}_2)_{1.035}(\text{PO}_4)_2 \cdot 7.41\text{H}_2\text{O}$.

According to Mücke (1988), the mineral lehrnerite from Hagendorf, Oberpfalz, is always associated with decomposed zwieselite $[(\text{Fe}^{2+}\text{Mn})_2\text{F}(\text{PO}_4)]$ and corroded rock-bridgeite $[(\text{Fe}^{2+}\text{Mn})\text{Fe}_3^+(\text{OH})_5(\text{PO}_4)_3]$, whereas the rare lehrnerite analogue mineral bassetite $[\text{Fe}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}]$ sometimes occurs in decomposed zwieselite (Mücke, 1983).

According to Haase (1988), the mineral lehrnerite should be formed in an oxidizing and acid environment. It was the purpose of this work to study the genesis of lehrnerite by cation exchange, using a MnCl_2 solution, with chernikovite as well as sodium autunite as starting substances. The aim was furthermore to prepare a quantity of the pure compound sufficient to allow the accurate determination of its physical and crystallographic properties.

SYNTHESIS OF THE STARTING SUBSTANCES

Chernikovite

When chernikovite is synthesized starting from pure chemicals, a very fine powder is obtained (Moeller, 1957)

that is not well suited for crystallographic studies. We therefore tried to use schoepite as a starting material, which was solubilized in a $0.3M \text{ H}_3\text{PO}_4$ solution. The schoepite itself was also synthetically prepared by hydrolysis of uranylacetate at 100°C (Bignand, 1955). After three months, well-formed crystals were obtained, ranging in size from 0.2 to 0.3 mm. These crystals were found to show an X-ray diffraction pattern identical with those of the mineral chernikovite published by Chernikov (1958). Furthermore, their composition as determined by chemical analysis corresponds exactly with the composition of chernikovite given by Ross (1955).

Sodium autunite

The synthetically obtained chernikovite crystals were treated for two weeks with a $1M \text{ NaCl}$ solution. During this treatment, the crystals are completely transformed into sodium autunite as revealed again by X-ray diffraction as well as chemical analysis; the obtained results correspond exactly with the data published by Chernikov et al. (1957) on the mineral sodium autunite.

SYNTHESIS OF LEHRNERITE

It has to be mentioned that Fairchild (1929) already synthesized a manganese-bearing uranyl phosphate by ion-exchange experiments on sodium autunite. However, no X-ray diffraction, crystallography, or chemical composition data were given.

Earlier ion-exchange experiments in this laboratory resulted in the synthesis of a number of uranyl arsenate and uranyl phosphate minerals: meta-zeunerite $[\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}]$ (Vochten and Goeminne, 1984), meta-kirchheimerite $[\text{Co}(\text{UO}_2)_2(\text{As}_4\text{O}_{12}) \cdot 8\text{H}_2\text{O}]$ (Vochten and Goeminne, 1984), bassetite $[\text{Fe}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}]$ (Vochten et al., 1984), kahlerite $[\text{Fe}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 12\text{H}_2\text{O}]$ (Vochten et al., 1986).

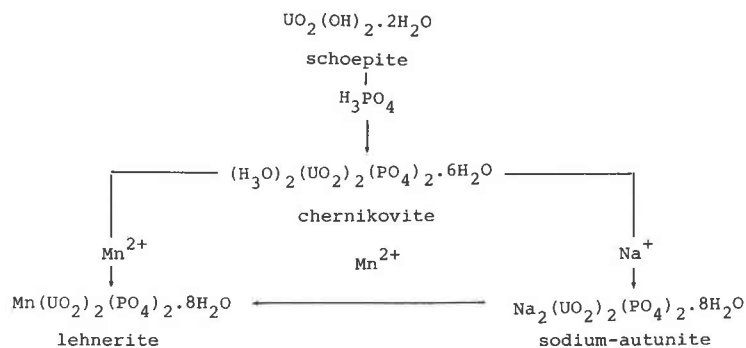


Fig. 1. Schematic representation of the synthesis of lehnerite.

In a similar way, the synthetically prepared chernikovite and sodium autunite crystals were digested with a 0.5M MnCl_2 solution in order to obtain lehnerite. It appears that at 60 °C an exchange reaction takes place that can easily be followed by the decrease of fluorescence of the crystals. Chernikovite and sodium autunite both are strongly fluorescent but lehnerite is not.

In both cases, fluorescence disappears after an exchange for one week so that complete transformation of the starting material into the uranyl phosphate lehnerite is suggested. The described reactions are represented by the scheme given in Figure 1.

CHEMICAL ANALYSIS

The lehnerite crystals obtained as described above were dissolved in 6M HCl, and their MnO, UO_3 , and P_2O_5 content was determined: MnO by atomic absorption spectrometry (AAS), UO_3 by spectrophotometry using arsenazo-III reagent (Singer and Matuchia, 1962), and P_2O_5 by spectrophotometry using vanado-molybdate reagent (Michelsen, 1957). The water content was obtained by thermogravimetric analysis on a separate sample of the air-dried crystals. The oxide and crystal chemical formulae were calculated by the residual oxygen method (Bulach, 1964).

In Table 1 the analytical results are summarized both of the synthetic lehnerite, prepared from chernikovite as described, and of natural lehnerite that was analyzed by

Mücke (1988). Both substances appear to have nearly identical chemical compositions. The same results are obtained within an error of 0.1% when analysis is performed on the crystals obtained by the exchange reaction with MnCl_2 of sodium autunite. It may therefore be concluded that lehnerite is a mineral that may be generated from chernikovite or sodium autunite by simple exchange of cations.

CRYSTALLOGRAPHY

Crystal morphology

According to Mücke (1988), natural lehnerite crystallizes in the monoclinic system with space group $C_{2h}^2(P2_1/n)$. Synthetic lehnerite should also be monoclinic, and this is confirmed by X-ray diffraction. However, the crystals should be considered as pseudomorphic after chernikovite, and since crystal habit is not altered by ion-exchange processes, their morphology remains identical with those of chernikovite. Chernikovite itself crystallizes in the tetragonal system with space group $P4_22$ (Ross and Evans, 1964). A scanning electron micrograph of synthetic lehnerite crystals is shown in Figure 2. A typical multilayer structure is clearly present, which obviously is due to the negatively charged $[(\text{UO}_2)(\text{PO}_4)]_n^-$ layers (Fig. 3). The morphology can be described by a combination of the crystal planes $\{100\}$ and $\{111\}$.

The relatively fast transformation of chernikovite and sodium autunite crystals may be explained by a diffusion-controlled process of the exchanging ions between this layer.

X-ray crystallography

X-ray diffraction data of synthetic lehnerite crystals have been obtained at 40 kV and 20 mA using a Philips PW.1140 generator and $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The powder photographs were recorded by means of a Guinier-Hägg camera with a diameter of 100 mm. Si powder (NBS-640) was used as an internal X-ray diffraction standard. The relative intensity of the diffraction lines was measured with a Carl-Zeiss Jena MD-100 microdensitometer. By taking into account the lattice parameters of natural lehnerite [$a = 7.04(2)$, $b = 17.16(4)$, $c = 6.95(2)$]

TABLE 1. Chemical analyses of synthetic and natural lehnerite

Oxide	Synthetic lehnerite from chernikovite			Natural lehnerite (Mücke, 1988)		
	Wt%	Molar quantity	Atomic ratio	Wt%	Molar quantity	Atomic ratio
MnO	7.90	0.1114	1.03	7.50	0.1057	0.99
FeO	—	—	—	0.20	0.0028	0.03
UO_3	63.10	0.2205	2.04	63.00	0.2202	2.07
P_2O_5	14.85	0.1046	1.94	15.10	0.1064	1.00
H_2O	14.44	—	7.46	14.20	0.7889	7.41
	100.29			100.00		
Empirical formula of synthetic lehnerite	$\text{Mn}_{1.03}[(\text{UO}_2)_{1.02}(\text{PO}_4)_{0.97}]_2 \cdot 7.46\text{H}_2\text{O}$					
Ideal formula of synthetic lehnerite	$\text{Mn}[(\text{UO}_2)(\text{PO}_4)]_2 \cdot 7.5\text{H}_2\text{O}$					

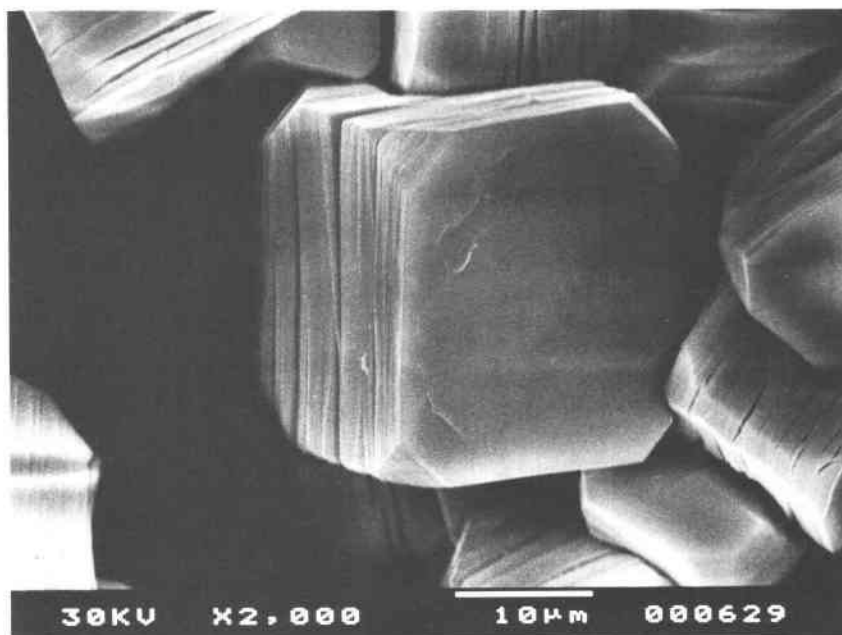


Fig. 2. Scanning electron micrograph of synthetic lehnerite crystals derived from chernikovite. Field width = 60 μm .

\AA , $\beta = 90^\circ 18'$ (Mücke, 1988)] and applying the computer program of Visser (1969), all the possible d_{hkl} values with the corresponding (hkl) values were computed. The measured and computed d_{hkl} values with their indices are summarized in Table 2.

THERMAL BEHAVIOR

Since no data on the thermal behavior of lehnerite are known, the thermal stability of synthetic lehnerite crystals was investigated by differential scanning calorimetry

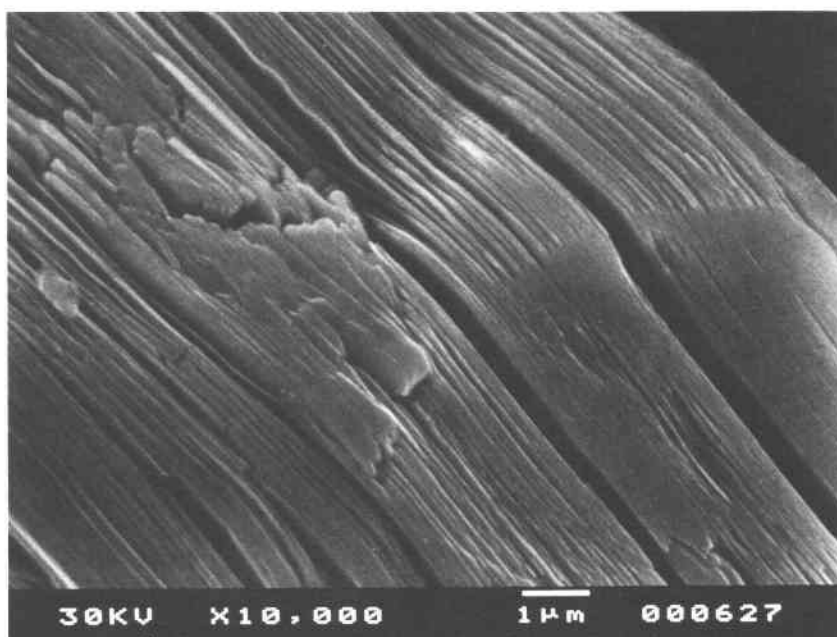


Fig. 3. Scanning electron micrograph of the multilayer structure of synthetic lehnerite crystals derived from chernikovite. Field width = 11 μm .

TABLE 2. X-ray powder-diffraction data of synthetic lehnerite

No.	d_{obs}	l	d_{calc}	h k l
1	8.5542	70	8.5800	0 2 0
2	4.9425	40	4.9588	1 0 1
3	4.7654	30	4.7639	$\bar{1}$ 1 1
4	4.3870	5	4.4165	0 3 1
5	3.5061	50	3.5200	2 0 0
6	3.4676	50	3.4750	0 0 2
7	3.4115	45	3.4058	0 1 2
8	2.9547	40	2.9699	0 3 2
9	2.5533	15	2.5374	2 4 1
10	2.4848	100	2.4794	2 0 2
11	2.4110	10	2.3820	2 2 2
12	2.2227	60	2.2269	5 0 1
13	2.1931	30	2.1976	$\bar{1}$ 7 1
14	2.1502	30	2.1554	3 2 1
15	1.7531	70	1.7536	3 6 1
16	1.6527	45	1.6529	3 0 3
17	1.5716	70	1.5715	$\bar{1}$ 4 4
18	1.5578	20	1.5600	0 11 0
19	1.3908	10	1.3908	$\bar{1}$ 7 4
20	1.3780	20	1.3785	5 0 1
21	1.3411	10	1.3402	5 3 1
22	1.3363	20	1.3363	4 8 1
23	1.2721	10	1.2720	1 11 3
24	1.2659	10	1.2652	4 8 2
25	1.2438	10	1.2439	5 6 1
26	1.2399	10	1.2399	2 4 5
27	1.2227	5	1.2217	5 5 2
28	1.2062	10	1.2060	5 0 3
29	1.1698	10	1.1706	6 1 0
30	1.1317	10	1.1317	3 11 3
31	1.1140	10	1.1144	1 15 1

Note: Guinier-Hågg camera (100 mm), $\text{CuK}\alpha$, radiation ($\lambda = 1.5406 \text{ \AA}$), 40 kV, 20 mA, exposure time 50 min.

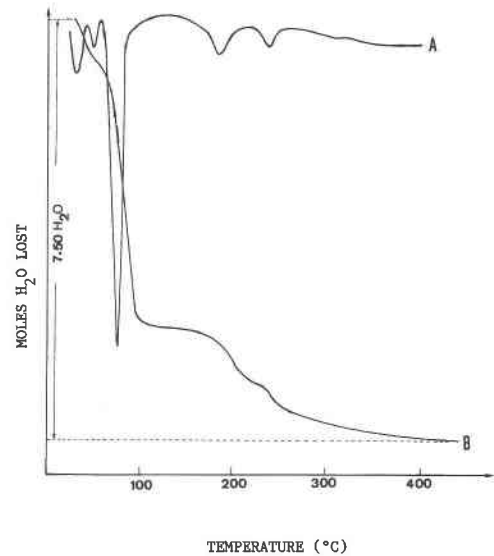


Fig. 4. Differential scanning calorimetric (A) and thermogravimetric (B) curves of synthetic lehnerite derived from chernikovite.

lehnerite even more closely related to synthetic bassettite, as described by Vochten et al. (1984), which also contains 7 molecules of water.

PHYSICAL PROPERTIES

(DSC) and thermogravimetric analysis (TGA). The analyses were performed by means of a Dupont DSC-910 and TGA-951 apparatus with an applied heating rate of $5 \text{ }^\circ\text{C}/\text{min}$ and a flow of N_2 of $20 \text{ mL}/\text{min}$.

The DSC and TGA curves are represented in Figure 4. The DSC curve shows clearly that the whole range of dehydration is characterized by endothermic peaks only. Combination of the DSC and TGA curves yields six well-defined dehydration steps, which are summarized in Table 3.

It should be noted that the water lost in the temperature range $25\text{--}40 \text{ }^\circ\text{C}$ may be surface-bound and/or zeolitic-bound water. Taking into account that zeolitic- and surface-bound water is easily lost at low temperatures, the formula of synthetic lehnerite should be written with 7 molecules of H_2O instead of 7.5. This makes synthetic

The crystals of synthetic lehnerite are pale brown to yellow and show no fluorescence under either long-wave or short-wave ultraviolet light. The synthetic crystals have a Mohs hardness between 3 and 4 and show a perfect cleavage perpendicular on [001].

For a cell volume of 838.76 \AA^3 , a molecular weight of 920 and $Z = 2$, the density is calculated as $3.640 \text{ g}/\text{cm}^3$, whereas the measured density in toluene by means of a Cahn-RG microelectrobalance is $3.600 \text{ g}/\text{cm}^3$ at 25°C . The crystals are biaxial negative with $2V = 72^\circ$ and $\alpha = 1.600(2)$, $\beta = 1.605(2)$, and $\gamma = 1.607(2)$.

Applying the Gladstone-Dale relationship with the constants given by Mandarino (1981) and the analytical composition gives a K_c value of 0.1663. The measured indices of refraction and density give a K_D value of 0.1677. This gives a value of the compatibility expression $1 - K_D/K_c$ of -0.0084 , which indicates superior compatibility on the base of density, indices of refraction, and chemical composition.

TABLE 3. Dehydration data of synthetic lehnerite as function of temperature

Temperature range ($^\circ\text{C}$)	H_2O lost (mol)
25–40	0.55
40–60	0.45
60–100	4.38
100–225	1.02
225–250	0.52
250–450	0.54
	7.46

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