

Article

Extending the mineralogy of U^{6+} (I): Crystal structure of lepersonnite-(Gd) and a description of the new mineral lepersonnite-(Nd)

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Abstract

Two uranyl carbonate silicate minerals have been studied in detail, lepersonnite-(Gd) and the new mineral lepersonnite-(Nd). Both minerals originate from Katanga province in the Democratic Republic of Congo (Africa): lepersonnite-(Gd) from the Shinkolobwe mine (type locality) and lepersonnite-(Nd) from the Swambo mine (type locality) and Shinkolobwe mine. Each occurs as radial to acicular aggregates composed of long prismatic, thin crystals, as the products of hydration–oxidation weathering of uraninite. A detailed description of the chemical and physical properties of lepersonnite-(Nd) is provided, including the thermal analysis of the -(Gd) member. Moreover, Raman and infrared spectroscopy data are provided for both minerals. The crystal structure of lepersonnite-(Gd) has been solved based on 3D electron diffraction data. According to the best dataset at 95 K, lepersonnite-(Gd) is orthorhombic, with $a = 11.838(134)$ Å, $b = 15.822(333)$ Å, $c = 39.147(190)$ Å and $V = 7353(282)$ Å³ ($Z = 4$). The dynamic refinement of the crystal structure ($R_{\text{obs}}/wR_{\text{obs}} = 0.1204/0.1088$ and $R_{\text{all}}/wR_{\text{all}} = 0.1204/0.1088$ for 3090/50507 observed/all reflections and 247 refined parameters) revealed a large complex sheet structure with structural units defining a new lepersonnite topology. It contains infinite sheets of uranyl polyhedra, planar CO₃ groups, protonated Si-tetrahedra, and Gd³⁺ polyhedra, and a thick interlayer hosted with H₂O and partially occupied Ca²⁺ sites. Based on the structure refinement, bond-valence considerations, and new electron microprobe data, we infer that the ideal formula of lepersonnite-(Gd) is $[\text{Ca}_{0.5}\text{Gd}_{0.5}(\text{H}_2\text{O})_{18}(\text{OH})_{1.5}][\text{Gd}(\text{UO}_2)_{12}(\text{SiO}_3\text{OH})_2(\text{CO}_3)_4(\text{OH})_{10}\text{O}_2(\text{H}_2\text{O})_5]$. On the basis of their closely related powder X-ray diffraction patterns and the similar behaviour of Nd and Gd, we expect the two minerals to adopt the same structures, apart from Ca, which was absent in lepersonnite-(Nd). The ideal formula for lepersonnite-(Nd) is $[\text{Nd}(\text{H}_2\text{O})_{18}(\text{OH})_2][\text{Nd}(\text{UO}_2)_{12}(\text{SiO}_3\text{OH})_2(\text{CO}_3)_4(\text{OH})_{10}\text{O}_2(\text{H}_2\text{O})_5]$.

Keywords: lepersonnite-(Gd); lepersonnite-(Nd); rare-earth elements; new mineral; crystal structure; 3D electron diffraction; complexity
(Received 15 January 2025; revised 16 April 2025; accepted 17 April 2025; Accepted Manuscript published online: 14 July 2025)

Introduction

The mineral lepersonnite, now lepersonnite-(Gd), reflecting the dominance of Gd over other REE, was discovered at the famous Shinkolobwe mine in the Democratic Republic of Congo in Africa and described by Deliens and Piret (1982).

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Associate Editor: Oleg I Siidra

We dedicate this paper to Michel Deliens, our dear friend and colleague, on the occasion of his 85th birthday.

Cite this article: Plášil J. *et al.* (2025) Extending the mineralogy of U^{6+} (I): Crystal structure of lepersonnite-(Gd) and a description of the new mineral lepersonnite-(Nd). *Mineralogical Magazine* 89, 549–565. <https://doi.org/10.1180/mgm.2025.29>

Based on the original description, the chemical formula assigned to lepersonnite-(Gd) and accepted by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA-CNMNC) is $\text{Ca}(\text{Gd,Dy})_2(\text{UO}_2)_{24}(\text{SiO}_4)_4(\text{CO}_3)_8(\text{OH})_{24} \cdot 48\text{H}_2\text{O}$. The assumed symmetry of the mineral based on the original Weissenberg X-ray photographs is orthorhombic ($Pnmm$ or $Pnm2_1$). Attempts by Deliens and Piret to obtain X-ray-diffraction data suitable for deciphering the crystal structure were unsuccessful and recent attempts have failed as well (at least those known to/or conducted by the corresponding author). Here, we report on the first determination of the crystal structure of lepersonnite-(Gd), which has been accomplished using three-dimensional electron diffraction

(3D ED) techniques. This first reliable structure model provides insights into important features concerning the crystal chemistry of this mineral and related phases. The structure determination has also been essential for the description of the new mineral lepersonnite-(Nd), which has been approved by the IMA-CNMNC with symbol Lps-Nd (IMA 2021-066, Plášil *et al.*, 2021). There are two co-type specimens of lepersonnite-(Nd). One cotype is deposited in the Musée d'Histoire Naturelle, Luxembourg (specimen no. WPV020). The second cotype specimen is deposited in the Musée royal de L'Afrique centrale, Tervuren, Belgium (specimen no. RGM11529.1). Along with the description of the new mineral, we provide new analytical data for lepersonnite-(Gd). According to the mineral classification based on Strunz and Nickel (2001), lepersonnite-(Gd) and lepersonnite-(Nd) are classified as 5.EG.10: Uranyl carbonates with SiO_4 .

Occurrences

Lepersonnite-(Gd) was originally described by Deliens and Piret (1982) from the Shinkolobwe mine in the Democratic Republic of Congo in Africa. The holotype, which is deposited in the Musée royal de L'Afrique centrale in Tervuren, is also the type specimen for bijvoetite-(Y), described at the same time. Lepersonnite-(Gd) forms globular crystal aggregates and crusts of pale-yellow colour, composed of prismatic, transparent, but mostly translucent crystals. The matrix of the specimen consists of massive uraninite (pitchblende) and dolomite cemented by massive uranyl-oxide hydroxy-hydrate minerals (the authors refer to curite and becquerelite).

Both minerals, lepersonnite-(Gd) and -(Nd), and their mineral associations are displayed in Fig. 1a,b. The new data for lepersonnite-(Gd) were obtained from the specimen from the Shinkolobwe mine. Initially, a larger specimen with approximate

dimensions of $25 \times 15 \times 10$ cm was trimmed to inspect and study the mineral makeup. In addition to abundant lepersonnite-(Gd) (Fig. 1a), we identified, based on single-crystal and powder X-ray diffraction, the following minerals within the specimen: bijvoetite-(Y) (scarce crystals with typical habits) (Fig. 1c), oursinite (relatively abundant pale yellowish-green prismatic crystals) (Fig. 1d), becquerelite (partially massive, partially in crystals up to 0.5 cm in length) (Fig. 1e), sklodowskite (abundant greenish-yellow crystals), and uranophane, with massive to blocky uraninite in the matrix. The new analytical data for lepersonnite-(Gd) and the crystals used for electron diffraction study were obtained from part of this specimen deposited by one of the authors (JP) in the mineralogical collections of the National Museum in Prague. Two larger pieces originating from this specimen are deposited in the collections of the Musée d'Histoire Naturelle, Luxembourg, and at the Department of Geology, Muséum cantonal des Sciences naturelles in Lausanne, Switzerland (specimen no. 088310).

Lepersonnite-(Nd) was found on three specimens originating from the Swambo deposit, which is situated 36 km to the west of Shinkolobwe, near the Mindigi mine in the Democratic Republic of Congo (Africa). The samples studied comprise two cotype specimens, one deposited in the Musée d'Histoire Naturelle, Luxembourg (specimen no. WPV020), the second cotype specimen is deposited in the Musée royal de L'Afrique centrale, Tervuren, Belgium (specimen no. RGM11529.1) and the third is a specimen deposited in the collection of the Department of Geology at the Muséum Cantonal des Sciences Naturelles in Lausanne, Switzerland (specimen no. 079986) and originates from Shinkolobwe mine.

The uranium-bearing mineralisation at Swambo is accompanied by cobalt, nickel and other precious metals in the orebody. The oxidation zone is strongly developed, with massive uraninite still present throughout the oxidation zone (Derricks and Oosterbosch,

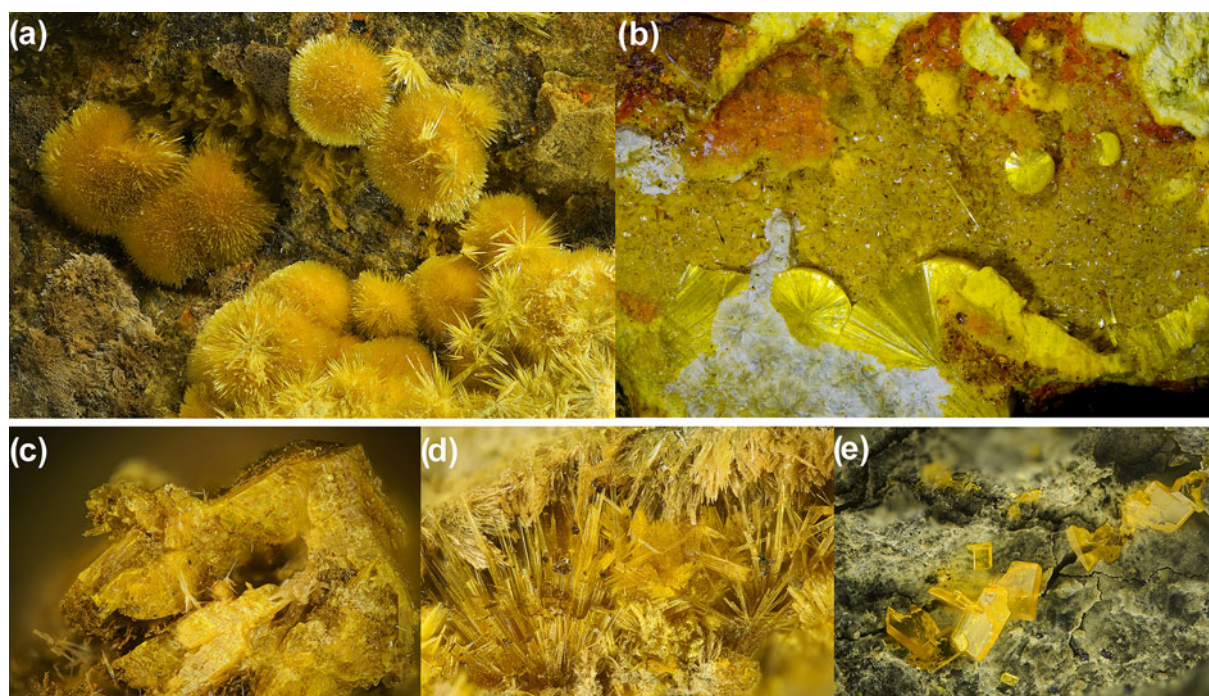


Figure 1. Minerals studied: (a) acicular aggregates of lepersonnite-(Gd) crystals (field of view, FOV = 5 mm; personal collection of SW) and (b) radial aggregates of lepersonnite-(Nd) crystals with a crust of soddyite (bipyramidal flattened yellow crystals), orange curite (needle-like crystal) and whitish studtite (cotype specimen no. WPV020, Luxembourg; FOV = 8.9 mm; photo by Eddy Van der Meersche), and some of the associated minerals: (c) bijvoetite-(Y) (FOV = 0.8 mm); (d) oursinite (FOV = 5 mm); and (e) becquerelite (FOV = 5 mm). Photos except for lepersonnite-(Nd) courtesy of Stephan Wolfsried.

1958). The Swambo mine is the type locality for the mineral swamboite-(Nd) (Deliens and Piret, 1981; Plášil *et al.*, 2017). Associated minerals on the two cotype specimens are soddyite, swamboite-(Nd), curite, studtite and gold.

The specimen labelled originally as 'lepersonnite-(Gd)' from Shinkolobwe mine, deposited in the collection of the Department of Geology at the Muséum Cantonal des Sciences Naturelles in Lausanne, Switzerland (specimen no. 079986) has been found, according to EDXS and PXRD analyses, to be lepersonnite-(Nd). The specimen originates from a collection of the renowned specialist in Katanga minerals, Mr. Gilbert Joseph Gauthier (1924–2006). In it, lepersonnite-(Nd) is associated with curite, quartz and relics of uraninite. Thus, after the Swambo mine, Shinkolobwe is the second known locality for this mineral.

Physical and optical properties of lepersonnite-(Nd)

Lepersonnite-(Nd) occurs in radial sprays and subparallel aggregates of needle-like crystals (Fig. 1b) growing on a crust of soddyite, present as small bipyramidal flattened crystals. Crystals have a yellow colour and a very pale yellow streak. The mineral is non-fluorescent in SW and LW ultraviolet light. Its Mohs hardness is estimated at 1.5 based on scratch tests. Lepersonnite-(Nd) is brittle; multiple cleavages have been observed, but it is hard to determine the crystallographic orientations due to the intergrown nature of crystal aggregates. The fracture is irregular. Optically, lepersonnite-(Nd) is biaxial (–), with $\alpha = 1.621(3)$, $\beta = 1.657(3)$, $\gamma = 1.677(3)$ (measured in white light), $2V$ (meas.) = $68(5)^\circ$ and $2V$ (calc.) = 72.0° . Dispersion was not observed. Optical orientation is $X = a$, $Y = c$ and $Z = b$. Lepersonnite-(Nd) is pleochroic, with $X = \text{yellow}$, $Y = \text{yellow}$ and $Z = \text{light yellow}$; $X \approx Y > Z$. We emphasise that the interference figure is quite diffuse, which could be due to twinning. Lepersonnite-(Nd) is soluble in dilute hydrochloric acid (10%), releasing CO_2 and leaving a residue of amorphous silica.

Chemical composition

Lepersonnite-(Gd)

The lepersonnite-(Gd) investigated (sample RO-548) occurs as fan-shaped aggregates of acicular crystals, homogeneous under back-scattered electron (BSE) images. Quantitative chemical electron microprobe analyses (EPMA, 13 points) were carried out using a Jeol JXA 8530 FE electron microprobe at the Geological Institute of Slovak Academy of Sciences, Banská Bystrica, Slovak Republic. Experimental conditions were: wavelength-dispersive spectroscopy mode, accelerating voltage 15 kV, beam current 15 nA and beam diameter 10 μm . Standards (element, emission line) were: baryte (S, $K\alpha$ and Ba, $BaL\alpha$), apatite (P, $K\alpha$), GaAs (As, $L\alpha$), orthoclase (Si, $K\alpha$ and K, $K\alpha$), thorianite (Th, $M\alpha$), UO_2 (U, $M\beta$), albite (Al, $K\alpha$ and Na, $K\alpha$), YPO_4 (Y, $L\alpha$), LaPO_4 (La, $L\alpha$), CePO_4 (Ce, $L\alpha$), PrPO_4 (Pr, $L\beta$), NdPO_4 (Nd, $L\alpha$), SmPO_4 (Sm, $L\alpha$), EuPO_4 (Eu, $L\alpha$), GdPO_4 (Gd, $L\alpha$), TbPO_4 (Tb, $L\alpha$), DyPO_4 (Dy, $L\alpha$), HoPO_4 (Ho, $L\alpha$), ErPO_4 (Er, $L\alpha$), TmPO_4 (Tm, $L\alpha$), YbPO_4 (Yb, $L\alpha$), LuPO_4 (Lu, $L\alpha$), diopside (Ca, $K\alpha$, and Mg, $MgK\alpha$), hematite (Fe, $K\alpha$), rhodonite (Mn, $K\alpha$), crocoite (Pb, $M\beta$), celestite (Sr, $L\alpha$), fluorite (F, $K\alpha$) and tugtupite (Cl, $K\alpha$). Peak counting times were 20 s for all elements and 10 s for each background. Matrix correction by ZAF software was applied to the data. Inter-*REE* coincidences were corrected by empirically determined correction factors (Åmli and Griffin, 1975). Water and CO_2 contents were calculated based on thermogravimetric

analysis (see below) and stoichiometry derived from the crystal structure analysis. The high analytical total (Table 1) is probably caused by the partial loss of H_2O in the vacuum during the deposition of the conductive carbon coating and in the microprobe chamber. The empirical formula (calculated on the basis of $U = 12$ atoms per formula unit) is $(\text{Ca}_{0.33}\text{Ba}_{0.02}\text{Sr}_{0.02}\text{Pb}_{0.01}\text{Mn}_{0.01})_{\Sigma 0.39}(\text{Gd}_{0.43}\text{Y}_{0.22}\text{Dy}_{0.20}\text{Nd}_{0.12}\text{Sm}_{0.12}\text{Eu}_{0.09}\text{Tb}_{0.08}\text{Er}_{0.07}\text{Ce}_{0.03}\text{La}_{0.01}\text{Pr}_{0.01}\text{Ho}_{0.01}\text{Tm}_{0.01})_{\Sigma 1.39}(\text{UO}_2)_{12}(\text{CO}_3)_4(\text{SiO}_3\text{OH})_{1.68}\text{O}_2(\text{OH})_{11.92} \cdot 22.98 \text{H}_2\text{O}$. The calculated density for the empirical formula ($Z = 4$) and unit-cell parameters refined from powder X-ray diffraction data is $4.05 \text{ g}\cdot\text{cm}^{-3}$, which corresponds closely to the measured density of $4.0 \text{ g}\cdot\text{cm}^{-3}$ for the holotype sample (Deliens and Piret, 1982).

Lepersonnite-(Nd)

Electron probe microanalyses (7 points on a homogeneous aggregate of crystals) were performed at the Masaryk University in Brno (Czech Republic) on a Cameca SX-100 electron microprobe operating in WDS mode. Analytical conditions were 15 kV accelerating voltage, 10 nA beam current, and 10 μm beam diameter. Raw X-ray intensities were corrected for matrix effects with a $\phi\rho(z)$ algorithm "PAP" (Pouchou and Pichoir, 1991). Inter-*REE* coincidences were corrected by empirically determined correction factors. The high analytical total is probably attributable to the partial loss of H_2O in the vacuum during the deposition of the conductive carbon coating and in the microprobe chamber, which resulted in higher concentrations of the remaining constituents. No other elements were detected. Because insufficient material is available for directly determining H_2O and CO_2 , they have been calculated based on analogy with lepersonnite-(Gd) and charge balance. Analytical data are given in Table 1. The empirical formula (calculated on the basis of $U = 12$ apfu) is $\text{Ca}_{0.02}(\text{Nd}_{0.76}\text{Sm}_{0.38}\text{Ce}_{0.26}\text{Gd}_{0.18}\text{Eu}_{0.16}\text{Pr}_{0.11}\text{Dy}_{0.05}\text{Y}_{0.02}\text{Er}_{0.01})_{\Sigma 1.92}(\text{UO}_2)_{12}(\text{CO}_3)_4(\text{SiO}_3\text{OH})_{1.98}\text{O}_2(\text{OH})_{11.86} \cdot 23\text{H}_2\text{O}$. The calculated density for the empirical formula ($Z = 4$) and unit-cell parameters obtained from powder X-ray diffraction data is $4.12 \text{ g}\cdot\text{cm}^{-3}$.

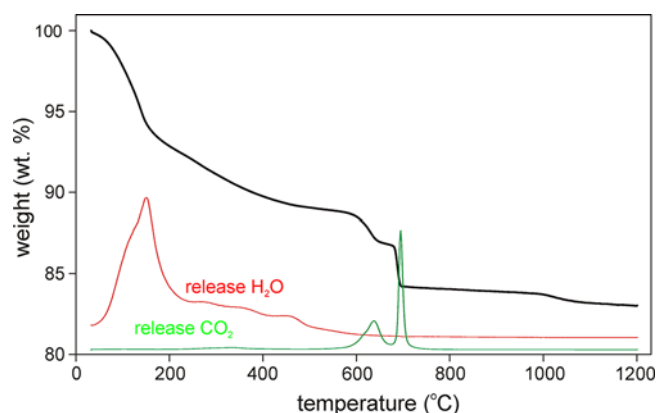
Thermogravimetric analysis

Thermogravimetric (TG) data on lepersonnite-(Gd) were collected at the University of Chemistry and Technology (Prague, Czech Republic) using a Thermobalance SETSYS (Setaram, France) equipped with a mass spectrometer GSD 320 03 OmniStar (Pfeiffer Vacuum, Austria). A sample weighing 19.537 mg was analysed between 30 and 1200°C in air with a heating rate $10^\circ\text{C}\cdot\text{min}^{-1}$. The collected thermogravimetric curve is shown in Fig. 2. Three main weight loss steps can be identified: (1) between 30 and 610°C ; (2) between 610 and 700°C ; and (3) between 700 and 1200°C . The first step (11.50 wt.%) corresponds to the loss of ca. 28.8 H_2O groups. The second weight loss (4.30 wt.%) is connected to the dominant loss of CO_2 (ca. 3.90 wt.% $\approx 4 \text{ CO}_2$) in two distinct steps partly accompanied by the loss of a small fraction of H_2O (ca. 0.4 wt.%, $\approx 1 \text{ H}_2\text{O}$). The loss of both chemical constituents is documented by mass spectrometry. The total observed weight loss, 15.80 wt.% in the range 30– 700°C , is comparable with the contents 4.02 wt.% CO_2 and 12.12 wt.% H_2O (total 16.14 wt.%) given for lepersonnite-(Gd) by Deliens and Piret (1982). The third step of weight loss (1.17 wt.%) corresponds to the partial reduction of uranyl groups, the greyish black end-product is U_3O_8 with an admixture of cubic $\text{REEO}_{1.86}$ phase.

Table 1. Chemical composition (wt.%) of lepersonnite-(Gd) and lepersonnite-(Nd)

	Lepersonnite-(Gd)						Lepersonnite-(Nd)				
	Norm.	Mean	Range	S.D.	Ideal		Norm.	Mean	Range	S.D.	Ideal
CaO	0.41	0.42	0.39–0.47	0.03	0.61	CaO	0.02	0.02	0.00–0.03	0.00	
MnO	0.02	0.02	0.00–0.05	0.02							
SrO	0.04	0.05	0.00–0.11	0.03							
BaO	0.07	0.07	0.00–0.27	0.08							
PbO	0.06	0.06	0.03–0.09	0.02							
Y ₂ O ₃	0.54	0.57	0.51–0.65	0.05		Y ₂ O ₃	0.04	0.05	0.00–0.11	0.06	
La ₂ O ₃	0.02	0.03	0.00–0.09	0.04							
Ce ₂ O ₃	0.10	0.11	0.03–0.17	0.04		Ce ₂ O ₃	0.94	1.01	0.94–1.14	0.07	
Pr ₂ O ₃	0.04	0.04	0.00–0.17	0.07		Pr ₂ O ₃	0.38	0.41	0.34–0.44	0.04	
Nd ₂ O ₃	0.44	0.46	0.32–0.54	0.06		Nd ₂ O ₃	2.78	2.97	2.83–3.22	0.13	7.31
Sm ₂ O ₃	0.45	0.47	0.27–0.65	0.12		Sm ₂ O ₃	1.43	1.53	1.36–1.72	0.13	
Eu ₂ O ₃	0.36	0.37	0.26–0.44	0.05		Eu ₂ O ₃	0.63	0.67	0.53–0.79	0.08	
Gd ₂ O ₃	1.74	1.82	1.61–2.03	0.14	5.96	Gd ₂ O ₃	0.71	0.76	0.47–0.90	0.15	
Tb ₂ O ₃	0.31	0.32	0.20–0.42	0.07							
Dy ₂ O ₃	0.84	0.87	0.70–1.07	0.09		Dy ₂ O ₃	0.19	0.21	0.15–0.24	0.04	
Ho ₂ O ₃	0.04	0.04	0.00–0.14	0.05							
Er ₂ O ₃	0.31	0.32	0.11–0.44	0.10		Er ₂ O ₃	0.04	0.04	0.00–0.26	0.10	
Tm ₂ O ₃	0.03	0.03	0.00–0.09	0.04							
Yb ₂ O ₃	0.01	0.01	0.00–0.09	0.03							
SiO ₂	2.24	2.33	2.15–2.42	0.07	2.63	SiO ₂	2.59	2.77	2.73–2.84	0.04	2.61
UO ₃	76.13	79.39	77.43–81.40	1.07	75.20	UO ₃	74.69	79.96	78.97–81.10	0.84	74.52
Subtotal	84.20	87.80			84.40	Subtotal	84.44	90.40		84.44	
CO ₂ *	3.90				3.86	CO ₂ **	3.83			3.82	
H ₂ O*	11.90				11.74	H ₂ O**	11.73			11.74	
Total	100.00				100.00	Total	100.00			100.00	

Notes: Norm. = normalisation; S.D. = standard deviation. CO₂* and H₂O* contents calculated based on thermogravimetric analysis and stoichiometry derived from the crystal structure analysis; CO₂** and H₂O** calculated based on the ideal stoichiometry and charge balance; ideal: ideal composition for formulae [Ca_{0.5}Gd_{0.5}(H₂O)₁₈(OH)_{1.5}][Gd(UO₂)₁₂(SiO₃OH)₂(CO₃)₄(OH)₁₀O₂(H₂O)₅] and [Nd(H₂O)₁₈(OH)₂][Nd(UO₂)₁₂(SiO₃OH)₂(CO₃)₄(OH)₁₀O₂(H₂O)₅], respectively.

**Figure 2.** Thermogravimetric curve for lepersonnite-(Gd).

Raman and infrared spectroscopy

The Raman spectroscopic study of lepersonnite-(Nd) was conducted on a Renishaw inVia micro-Raman spectrometer in the range 4000–95 cm⁻¹ at the Department of Physics and Materials Science, University of Luxembourg. Because of the significant fluorescence that appeared using a 532 nm diode laser, the spectrum was finally recorded using a 633 nm laser, which appeared to have the best signal-to-noise ratio (along with lower thermal load to avoid damaging or dehydrating the sample analysed). The final

spectra were recorded with a laser power of ~1 mW through a 50× microscope objective with a numerical aperture N.A. = 0.5. For comparison, the Raman spectrum of lepersonnite-(Gd) was collected in the range 4000–40 cm⁻¹ using a DXR dispersive Raman Spectrometer (Thermo Scientific) mounted on a confocal Olympus microscope at the National Museum, Prague (Czech Republic). The Raman signal was excited by an unpolarised red 633 nm He–Ne gas laser and detected by a CCD detector. The experimental parameters were: 100× objective, 10 s exposure time, 400 exposures, 50 μm pinhole spectrograph aperture and 8 mW laser power level. The spectra were repeatedly acquired from different grains to obtain a representative spectrum with the best signal-to-noise ratio. The eventual thermal damage of the measured point was excluded by visual inspection of the excited surface after measurement, by observation of possible decay of spectral features at the start of excitation and by checking for thermal downshift of Raman lines.

A comparison of both spectra is shown in Fig. 3. In general, the spectra are very similar. The major difference is that the lepersonnite-(Nd) spectrum is much noisier but has a better signal in the range of vibration of (OH)⁻ bonds. For band assignments, we emulate the interpretations of Čejka (1999) for uranyl carbonates and silicates. A broad composite band, consisting of at least three overlapping bands, appearing at ~3500 to 3200 cm⁻¹ is attributed to stretching O–H vibrations of the molecular H₂O and (OH)⁻. The nature of overlapping vibrational bands in this region indicates the presence of multiple independent H-bonds in the structure. Using the empirically derived equation of Libowitzky (1999), the calculated O...O distances of the corresponding hydrogen bonds are

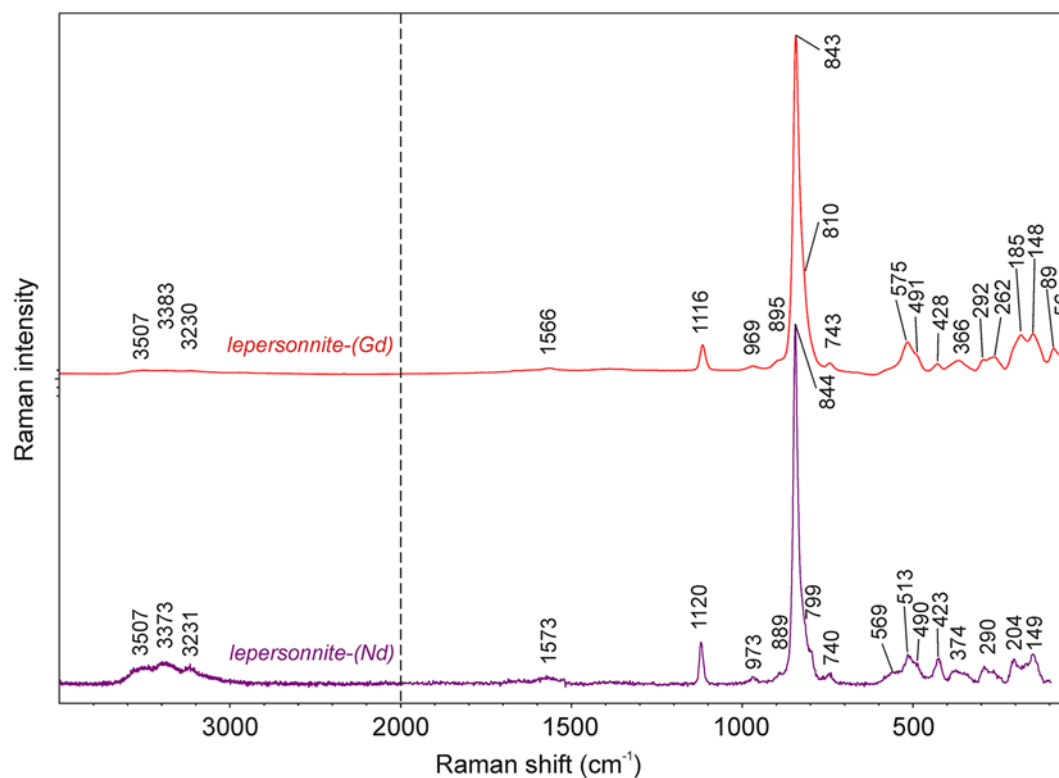


Figure 3. Raman spectra of lepersonnite-(Gd) and lepersonnite-(Nd) (split at 2000 cm^{-1}).

between ~ 3.0 and ~ 2.8 Å. This is in line with the crystal structure model for lepersonnite-(Gd). A weak band located in the spectra of both minerals at around 1570 cm^{-1} is attributed to the ν_2 (δ) (H_2O) of the molecular water. Some authors have speculated that these bands can be assigned, with some uncertainty, to the stretching vibrations of SiO–H (e.g. Frost *et al.*, 2006). The sharp band of medium intensity at 1120 (Nd) and 1116 cm^{-1} (Gd) is attributed to the ν_1 (CO_3) $^{2-}$ symmetric stretching vibrations. No evidence exists for the ν_3 (CO_3) $^{2-}$ antisymmetric stretching vibrations at higher vibration energies. The weak bands at 973 cm^{-1} (Nd) and at 969 cm^{-1} (Gd) are attributed to the ν_3 (SiO_4) $^{4-}$ antisymmetric stretching vibrations. The bands of highest intensity, 844 (Nd) and 843 cm^{-1} (Gd), are assigned to the ν_1 (UO_2) $^{2+}$ symmetric stretching vibrations and very weak shoulders at 889 (Nd) and 895 cm^{-1} (Gd) to the ν_3 (UO_2) $^{2+}$ antisymmetric stretching vibrations. These may overlap with ν_2 (δ) (CO_3) $^{2-}$ bending vibrations. Using the empirical relation of Bartlett and Cooney (1989), we can infer the corresponding U–O_{yl} bond lengths from the wavenumbers mentioned above, 1.77 Å (from ν_1) and 1.79 Å (from ν_3), respectively. These values are in line with most typical U $^{6+}$ ≡O bond lengths in minerals and synthetics (Lussier *et al.*, 2016) and conform to the structure data. Shoulders at ~ 810 (Gd) and 799 cm^{-1} (Nd) may relate to the deformation vibrations of SiO–H bonds. The low-intensity bands at 743 (Nd) and 740 cm^{-1} (Gd) can be related to the librations of H_2O or ν_4 (δ) CO_3^{2-} in-plane bending vibration. A multi-component band, composed of overlapping bands at 569 to 490 cm^{-1} (Nd) and 515 to 491 cm^{-1} (Gd), is related either to (δ) (O–Si–O) or (δ) (Si–O–H) and librations of H_2O (e.g. Colmenero *et al.*, 2019). An isolated composite band centred at 423 (Nd) and 428 cm^{-1} (Gd) is related to the ν_4 (δ) (SiO_4) $^{4-}$. Bands at 374 (Nd) and 366 cm^{-1} (Gd) are probably also assignable to (δ) (Si–O–H)

and librations of H_2O (Colmenero *et al.*, 2019). Composite bands at ~ 290 cm^{-1} (Nd) and 292 to 262 cm^{-1} (Gd) are attributed to ν_2 (δ) (UO_2) $^{2+}$ split doubly-degenerated bending vibrations. Bands of the lowest energies have been attributed to the lattice modes.

The infrared vibrational spectrum of lepersonnite-(Gd) was recorded using the attenuated total reflection (ATR) method with a diamond window on a Nicolet iS5 spectrometer at the National Museum, Prague (Czech Republic). Spectra over the 4000–400 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.4747 cm/s . Spectra were co-added to improve the signal-to-noise ratio. The IR spectrum of lepersonnite-(Gd) is given in Fig. 4. A strong and broad infrared band with components at 3493, 3362 and 3192 cm^{-1} is assigned to the ν O–H stretching vibration of hydrogen-bonded water molecules and OH groups. According to the Libowitzky (1999) correlation function, O–H...O hydrogen-bond lengths vary from approximately 3.0 to 2.8 Å, which are comparable with values inferred from crystal structure data. A medium-strong infrared band at 1626 cm^{-1} is attributed to the ν_2 H_2O bending vibration of water molecules. Strong bands at 1526 and 1373 cm^{-1} are a typical manifestation of the doubly degenerate ν_3 (CO_3) $^{2-}$ antisymmetric stretching vibrations, and a weak band at 1111 cm^{-1} is attributed to the ν_1 (CO_3) $^{2-}$ symmetric stretching vibrations. A strong infrared band at 902 cm^{-1} and shoulder at 836 cm^{-1} are related to ν_3 antisymmetric and ν_1 symmetric stretching vibrations of (UO_2) $^{2+}$. The calculated uranyl U–O bond length (Bartlett and Cooney, 1989) of 1.78 Å is comparable with the structure data. Shoulders at 938 and 812 cm^{-1} may be connected with the ν_3 (SiO_4) $^{4-}$ antisymmetric stretching and ν_2 (δ) (CO_3) $^{2-}$ bending vibrations, respectively. Weak bands at 738 and 693 cm^{-1} are probably related to ν_4 (δ) CO_3^{2-} in-plane bending vibrations; however, some overlap with libration

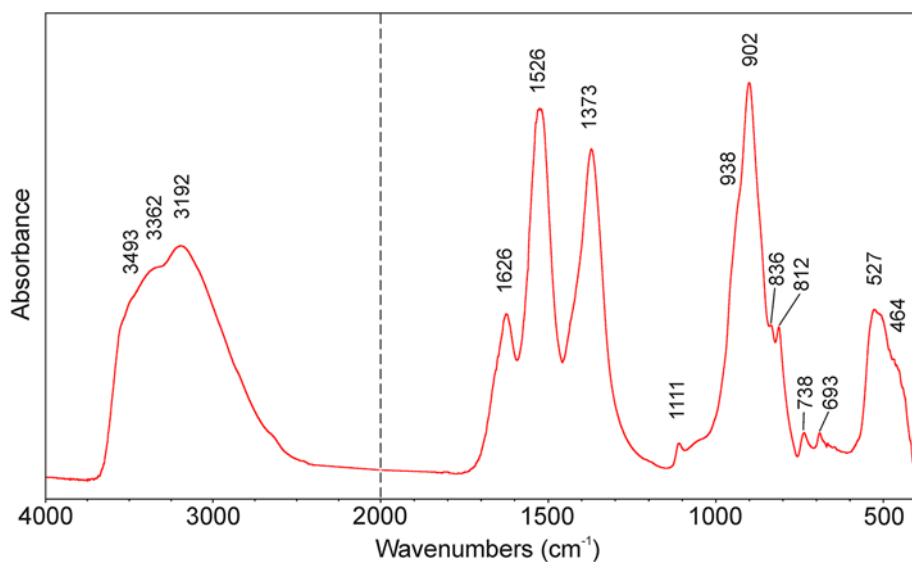


Figure 4. Infrared spectrum of lepersonnite-(Gd) (split at 2000 cm⁻¹).

modes of H₂O groups may be expected. A medium-strong band at 527 cm⁻¹ with a shoulder at 464 cm⁻¹ is attributed to the ν_4 (δ) (SiO₄)⁴⁻ vibrations.

Crystallography and 3D ED data collection

X-ray diffraction on lepersonnite-(Nd)

Powder X-ray diffraction (PXRD) data were recorded using a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer with monochromatised MoK α radiation, at the Mineral Sciences Department, Natural History Museum of Los Angeles County. A Gandolfi-like motion on the ϕ and ω axes was used to randomise the sample. The pattern fits very well to the data given by Deliens and Piret (1982) for lepersonnite-(Gd) from Shinkolobwe (Table 2). Positions and intensities of reflections were found and refined using the PearsonVII profile-shape function with the ZDS program package (Ondruš, 1993) and the unit-cell parameters (Table 3) were refined by the least-squares algorithm implemented by Burnham (1962).

The small size, somewhat poor quality, and intergrown nature (see the discussion section) of lepersonnite-(Nd) crystals made structure determination through X-ray single-crystal diffraction study impossible. The single-crystal X-ray experiment on a Rigaku Synergy DW system at the Rigaku Application Laboratories, Rigaku Europe SE, Germany, with a 1.2 kW rotating Mo-anode and HyPix Arc 150 detector using a 115 × 8 × 1 μ m crystal yielded the following unit-cell parameters based on 3855 observed reflections: $a = 11.7189(7)$ Å, $b = 17.1013(7)$ Å and $c = 38.681(2)$ Å, with $V = 7752(2)$ Å³. The corresponding reciprocal-space reconstructions (UNWARP) obtained from the diffraction data by the CrysAlis software (Rigaku, 2023) are provided in Fig. 5.

X-ray diffraction on lepersonnite-(Gd)

Powder X-ray diffraction data were collected on a Bruker D8 Advance diffractometer at the National Museum, Prague (Czech Republic) with a solid-state 1D LynxEye detector using CuK α

radiation and operating at 40 kV and 40 mA. The powder pattern was collected using Bragg–Brentano geometry in the range 2.5–70°2 θ , in 0.01° steps with a counting time of 20 s per step. Positions and intensities of reflections were found and refined using the PearsonVII profile-shape function with the ZDS program package (Ondruš, 1993). The pattern corresponds very well to published data for lepersonnite-(Gd) (Deliens and Piret, 1982) and measured data for lepersonnite-(Nd) (Table 2). Unit-cell parameters refined from the powder data using Burnham's (1962) program based on the least-squares algorithm are given in Table 3.

The small size, somewhat poor quality, and intergrown nature (see the discussion section) of lepersonnite-(Gd) crystals also made structure determination through X-ray single-crystal diffraction study impossible.

3D ED data collection for lepersonnite-(Gd)

To obtain data for the determination of the crystal structure of lepersonnite-(Gd), three-dimensional electron diffraction (3D ED) was used (Gemmi and Lanza, 2019; Gemmi *et al.*, 2019). For TEM analysis, a powdered portion of the lepersonnite-(Gd) sample was diluted in acetone and deposited on a Cu-grid coated by a thin film of holey amorphous carbon. 3D ED data were collected with a FEI Tecnai G2 20 transmission electron microscope (TEM) (Institute of Physics of the CAS, Prague) (acceleration voltage of 200 kV and LaB₆) equipped with a side-mounted hybrid single-electron detector ASI Cheetah M3, 512 × 512 pixels with high sensitivity and a fast readout. To preserve the hydrated structure of the mineral under the high vacuum in the instrument, the grid was plunged into liquid nitrogen and transferred to the TEM using a Gatan cryo-transfer holder. The PEDT technique (tilt step = 1° and precession semi-angle = 1°) was chosen to reduce the dynamical effects further and to obtain dynamical intensities, using the Nanomegas Digistar precession device (Vincent and Midgley, 1994). Each dataset was collected at 95 K from several single crystals (Fig. 6a,b). To limit the beam-induced damage to the crystals, low illumination settings were used. 3D ED data reduction was performed using the computer program PETS2 (Palatinus *et al.*, 2019;

Table 2. Comparison of new powder X-ray diffraction data (d in Å) for lepersonnite-(Nd), lepersonnite-(Gd) and powder data reported originally by Deliens and Piret (1982) for lepersonnite-(Gd)[#]

h	k	l	Lepersonnite-(Gd)			Lepersonnite-(Gd) [#]		Lepersonnite-(Nd)		
			$I_{\text{rel.}}$	$d_{\text{obs.}}$	$d_{\text{calc.}}$	$I_{\text{rel.}}$	$d_{\text{calc.}}$	$I_{\text{rel.}}$	$d_{\text{obs.}}$	$d_{\text{calc.}}$
0	1	1	0.5	15.275	15.008			6	15.290	14.974
1	0	1	0.5	11.197	11.210	10	11.1	15	11.260	11.232
0	2	0	100.0	8.187	8.137	100	8.15	100	8.160	8.111
0	2	3	1.9	6.918	6.888			3	6.850	6.877
0	0	6	2.0	6.463	6.469	10	6.46	12	6.480	6.485
0	2	5						5	5.620	5.616
1	2	5	1.6	5.079	5.064					
0	2	6			5.064					
1	0	7	0.4	5.005	5.011			10	5.010	5.023
						5	4.93			
2	2	1						10	4.720	4.718
1	2	7						5	4.270	4.271
2	2	2	0.6	4.626	4.616					
0	4	0	7.4	4.066	4.068	15	4.06	10	4.060	4.056
1	2	8	0.6	3.925	3.926					
2	3	2						10	3.900	3.895
0	4	3	2.0	3.879	3.881					
3	1	3	4.9	3.643	3.642	70	3.65	57	3.660	3.648
1	3	8						2	3.460	3.456
1	0	11	1.6	3.373	3.378	5	3.37	4	3.390	3.387
2	4	0	0.8	3.340	3.341					
0	0	12	3.8	3.231	3.234	50	3.21			
3	2	5						33	3.200	3.209
2	1	10	1.3	3.171	3.173					
1	2	11	0.4	3.123	3.120			21	3.110	3.125
3	3	3	0.7	3.086	3.077					
1	5	3	0.7	3.045	3.048					
0	2	12	3.5	3.005	3.006	10	3.00	21	3.010	3.011
3	1	9	1.8	2.849	2.849	40	2.86	22	2.860	2.855
2	3	10						9	2.780	2.781
2	5	4	0.3	2.730	2.730					
3	4	4	0.5	2.706	2.705					
4	0	6	0.4	2.664	2.667			5	2.680	2.672
2	3	11	0.7	2.646	2.640					
3	0	11						3	2.620	2.623
3	3	9	0.4	2.552	2.553	10	2.55	10	2.550	2.556
1	5	9	0.9	2.535	2.536					
4	2	6			2.534					
0	4	12			2.532					
3	5	0	0.4	2.4997	2.4996					
3	1	12						6	2.470	2.467
2	6	0	0.4	2.4568	2.4609					
2	6	6	0.3	2.2959	2.3001			2	2.290	2.296
1	7	3	1.5	2.2389	2.2456	5	2.24	7	2.240	2.239
4	4	6			2.2304					2.231
5	0	7	0.4	2.1545	2.1572			12	2.150	2.162
1	7	6			2.1506					
3	1	15	0.5	2.1370	2.1379	10	2.14			
4	2	12	0.2	2.0972	2.0970					
5	2	7	0.5	2.0806	2.0852			11	2.090	2.089
3	3	15	0.7	2.0053	2.0040			11	2.010	2.007
3	7	0	0.4	2.0008	1.9973					
3	0	17	0.5	1.9690	1.9707					
6	0	0	0.5	1.9517	1.9514			20	1.956	1.955
2	8	0	1.0	1.9232	1.9215					

(Continued)

Table 2. (Continued.)

<i>h</i>	<i>k</i>	<i>l</i>	Lepersonnite-(Gd)			Lepersonnite-(Gd) [#]		Lepersonnite-(Nd)		
			<i>I</i> _{rel.}	<i>d</i> _{obs.}	<i>d</i> _{calc.}	<i>I</i> _{rel.}	<i>d</i> _{calc.}	<i>I</i> _{rel.}	<i>d</i> _{obs.}	<i>d</i> _{calc.}
3	2	17	0.7	1.9149	1.9153					
4	6	6	0.2	1.9030	1.9016			23	1.902	1.901
6	2	0	0.6	1.8981	1.8976					
5	2	11			1.8973					
2	1	20	1.4	1.8283	1.8304	10	1.82	16	1.839	1.835
3	8	2						8	1.795	1.793
3	4	17	0.3	1.7722	1.7736					
5	2	14						10	1.752	1.751
5	5	9	0.3	1.7415	1.7394					
1	9	6	0.3	1.7179	1.7225			5	1.712	1.718
2	1	22						9	1.680	1.684
5	7	3	0.3	1.6352	1.6366					
6	2	12			1.6367			9	1.642	1.640
1	10	2	0.2	1.6073	1.6063					
1	10	2						9	1.606	1.602
1	4	23	0.1	1.5477	1.5451			4	1.549	1.548
5	7	10						4	1.518	1.518
6	7	2	0.1	1.4904	1.4902			4	1.486	1.490

Table 3. Lattice parameters of the different crystals of lepersonnite-(Gd) measured in 3D ED at 95 K. The lattice obtained from powder X-ray diffraction on the same sample and single crystal and powder X-ray data on the lepersonnite-(Nd) are likewise given

	<i>a</i> [Å]	<i>b</i> [Å]	<i>c</i> [Å]	<i>V</i> [Å ³]	<i>a/b</i>	<i>a/c</i>	<i>b/c</i>
Room Temperature, lepersonnite-(Nd)							
SCXRD ¹	11.7189(7)	17.1013(7)	38.681(2)	7752(2)	0.685	0.303	0.442
SCXRD ²	11.765(2)	16.12(1)	38.907(5)	7380(5)	0.730	0.302	0.414
PXRD	11.731(10)	16.223(14)	38.91(3)	7405(8)	0.723	0.301	0.417
Room Temperature, lepersonnite-(Gd)							
PXRD*	11.73(3)	16.23(3)	38.74(9)	7375.24	0.723	0.303	0.419
PXRD	11.709(5)	16.273(7)	38.813(18)	7395(4)	0.720	0.302	0.419
95 K, lepersonnite-(Gd)							
3DED-1**	11.850(7)	16.16(2)	39.506(17)	7563	0.733	0.300	0.409
3DED-2	11.834(1)	15.922(8)	39.164(6)	7379.58	0.766	0.309	0.403
3DED-3	11.848(1)	15.835(5)	39.189(4)	7352.37	0.756	0.305	0.403
3DED-4	11.923(8)	15.7719(1)	39.091(15)	7350.66	0.746	0.304	0.407
3DED-5	11.858(2)	15.889(9)	39.008(7)	7349.66	0.761	0.299	0.394
3DED-6	11.683(5)	15.8937(2)	39.2043(2)	7279.36	0.732	0.298	0.406
3DED-7	11.786(1)	15.4950(4)	39.357(4)	7187.49	0.748	0.302	0.404
3DED-8	11.936(2)	15.575(14)	38.6426(3)	7183.67	0.743	0.302	0.407
<3DED>	11.838	15.822	39.147	7332	0.748	0.302	0.404
	(+/-134)	(+/-333)	(+/-432)	(+/-190)			

Notes: 1 – new crystal, this study; 2 – from the initial experiment (Plášil *et al.*, 2021). PXRD* – Deliens and Piret (1982); 3DED11** was used in the structure characterisation.

Brázda *et al.*, 2022; Khouchen *et al.*, 2023). The structural analysis was performed from the best dataset (3DED-1 in Fig. 6b), which presents the most ordered stacking associated with the highest data coverage, the lowest *Rocking curve width* and the lowest *apparent mosaicity* of the crystal (Fig. 6). For each 3D ED dataset, the data reduction yielded two *hkl*-type files. The first one assumes the kinematical approximation (for structure solution and the so-called kinematical refinement) with $R_{int}(\text{obs/all}) = 0.1979/0.2955$ and 95% coverage for $\sin\theta/\lambda = 0.6\text{\AA}^{-1}$ (Laue class *mmm*). The second *hkl*-type output file is dedicated to the dynamical refinement where all frames of the data set are independently refined. The structure was solved assuming the kinematical approximation using *Superflip* (Palatinus and Chapuis, 2007; Palatinus, 2013) implemented in *Jana2020* (Petříček *et al.*, 2023). The refinement

considering the dynamical theory of diffraction was carried out through *DYNGO* in *Jana2020* (Palatinus *et al.*, 2015a, 2015b).

Structure solution and refinement

From single-crystal ED data obtained at 95 K, the best indexing choice is the orthorhombic unit cell $a = 11.838 \pm 0.134\text{ \AA}$, $b = 15.822 \pm 0.333\text{ \AA}$, $c = 39.147 \pm 0.190\text{ \AA}$ and $V = 7353 \pm 282\text{ \AA}^3$. The individual lattice parameters and the lattice ratio for each measured crystal are provided in Table 3 and Fig. 7, demonstrating significant dispersion across the sample while maintaining the same structure. Most crystals showed strong disorder along the stacking direction [010] and along [100], as evidenced by the single-crystal data obtained from lepersonnite-(Nd), leading to

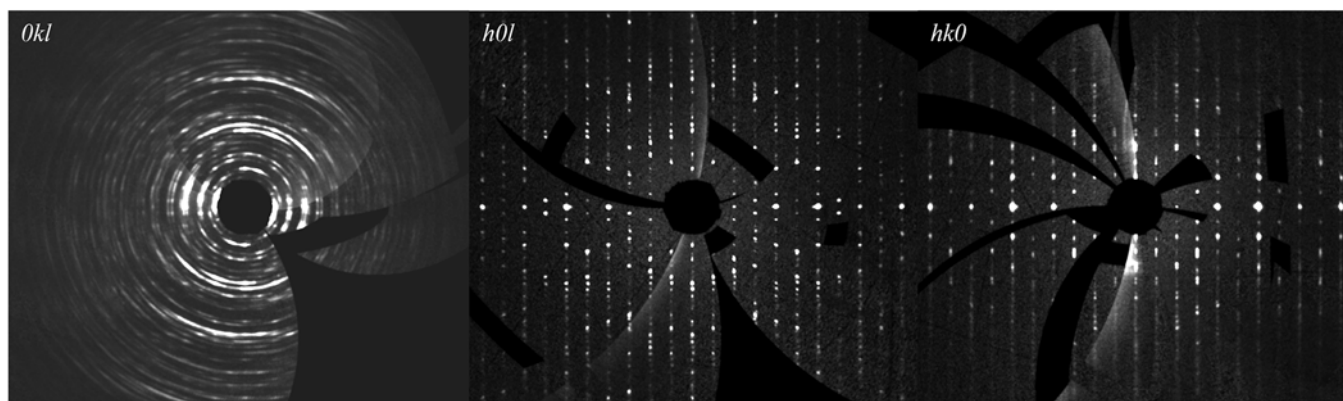


Figure 5. Sections of the reciprocal space for lepersonnite-(Nd) reconstructed from the single-crystal X-ray diffraction data.

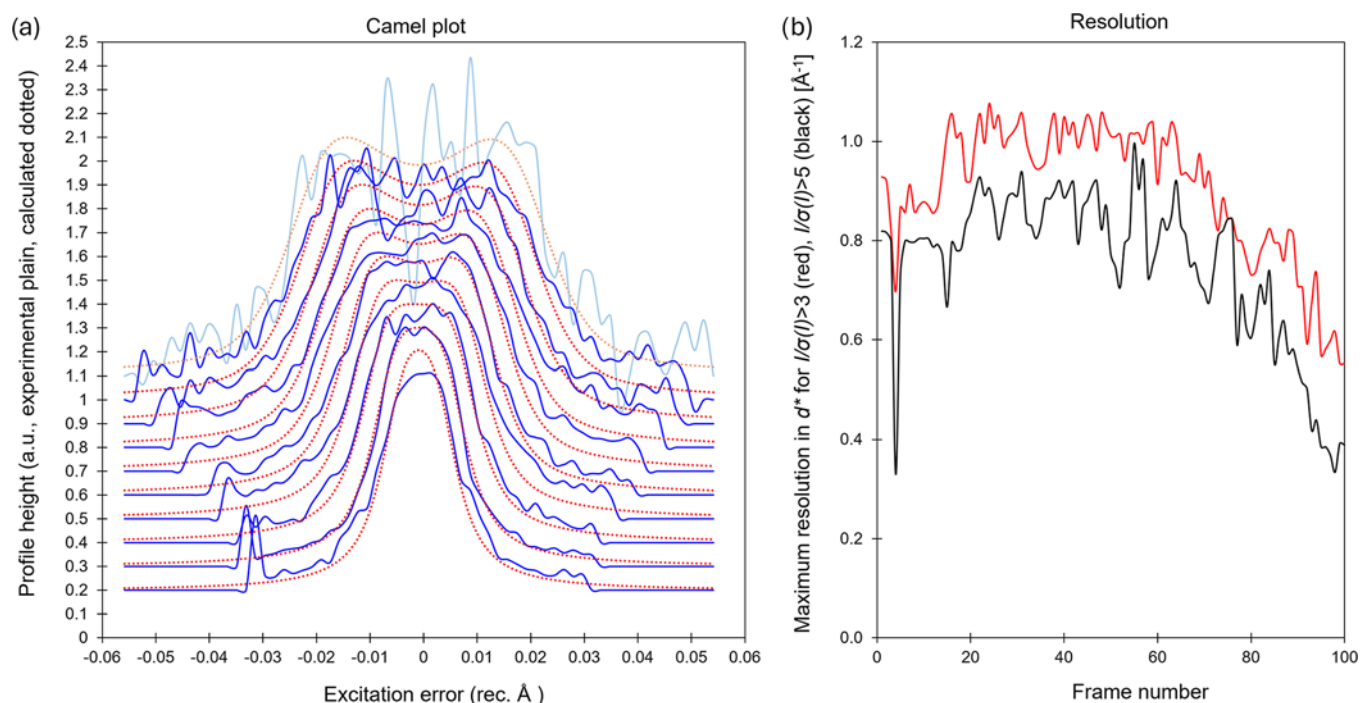


Figure 6. (a) Plots of the rocking-curve profiles (Camel plot) of the experimental 3D ED data at 95 K (3DED-1). The lowest blue curve is the averaged observed rocking curve in the range of 0.2 to 0.3 Å⁻¹, and those subsequent are obtained by steps of 0.1 Å⁻¹. The red curves are calculated from the *Rocking curve width* = 0.00250 Å⁻¹, *apparent mosaicity* = 0.25°, and *precession semi-angle* = 1°. Reflections considered in the Camel plot have $l > 7^* \sigma(l)$. (b) Plot showing the peak of highest resolution in reciprocal space (Å⁻¹) for each frame (red: d^* for $l/\sigma(l) > 3$, black: d^* for $l/\sigma(l) > 5$).

an ambiguous space group determination (compare Figs 5 and 8). The symmetry analysis and structure characterisation relies on the most ordered crystals. Sections through reciprocal space show a possible space group to be $Pmnn$, despite a noisy $0kl$ and above sections ($h+l = 2n$ on $h0l$, $k+l = 2n$ on $hk0$, $h00$: $h = 2n$, $00l$: $l = 2n$, $0k0$ was not visible in our data) (Fig. 8). Only a few 3D ED datasets collected on different single crystals were suitable for structure solution (and kinematical refinement). The 3DED-1 dataset was selected based on good data coverage and on the criteria for refinement using the dynamical theory of diffraction, i.e. reasonable values for *Rocking curve width* = 0.00250 Å⁻¹ and *apparent mosaicity* = 0.25° (Fig. 7). The two values are nevertheless not ideal and were affected by the rather poor crystallinity and stacking disorder. The structure was solved *ab initio* from a data set with 95% completeness up to

a resolution of $\sin(\theta)/\lambda = 0.6$ Å⁻¹. The completeness is limited due to the (010) preferred orientation of the crystals on the grid and the incomplete rotation of the goniometer. The initial model revealed a layered structure with alternating high-density layers connected along the stacking direction [010], mainly through hydrogen bonds with interlayer water molecules. The dense layers are composed of predominantly uranyl cations ($O=U=O$)²⁺ in pentagonal and hexagonal bipyramids, two $SiO_3(OH)$ tetrahedra and one Gd polyhedron. A partially occupied Ca site was found among the water molecules bridging the two dense layers. The water molecules were added during the refinement and are mostly partially occupied. The dynamical refinement converged to $R(\text{obs})/wR(\text{obs}) = 0.1204/0.1088$, $R(\text{all})/wR(\text{all}) = 0.1204/0.1088$ for 3090/50507 observed/all reflections and 247 refined parameters. Few distance restrictions were applied to the

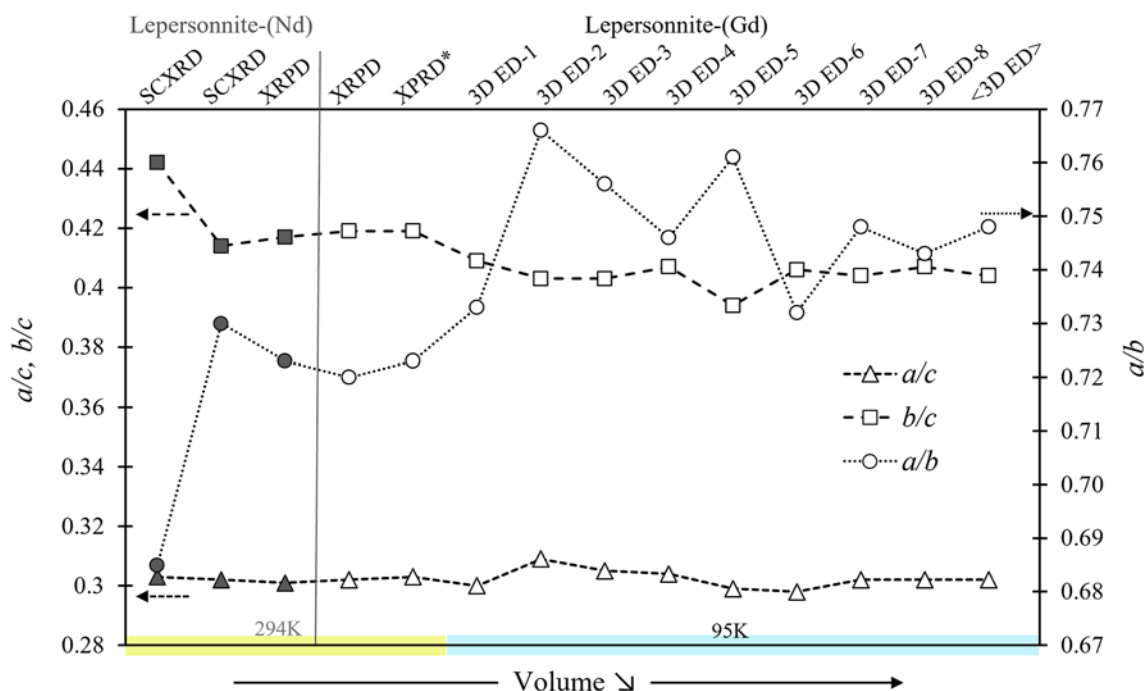


Figure 7. Lattice parameter ratios of lepersonnite-(Nd) (grey) and lepersonnite-(Gd) (white) measured by different X-ray diffraction techniques (single-crystal, powder diffraction, and 3D ED at 294 K or 95 K). Measurements are sorted by decreasing volume (Table 3).

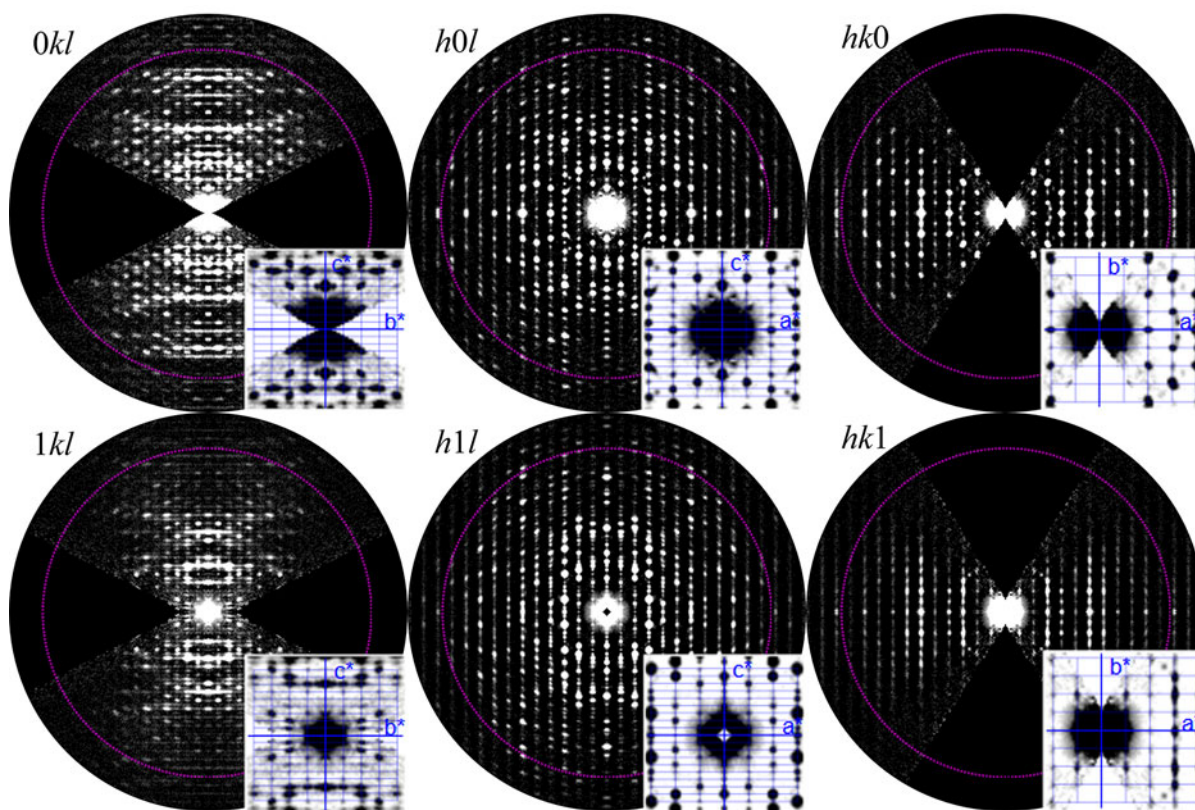


Figure 8. Sections of the reciprocal space reconstructed from 3D ED data collected on a crystal of lepersonnite-(Gd) at 95 K.

model during the refinement to compensate for the inaccuracy brought by the diffuse scattering along $\mathbf{b}$: The $\text{U}-\text{O}_{\text{yl}}$ distances were set at ~ 1.8 (0.004) Å, while the C–O and the O–O distances

of the carbonate groups were maintained at ~ 1.3 (0.005) Å and 2.25 (0.005) Å, respectively. Additionally, a few additional O–O distances were restricted to 2.8 (0.015) Å. For a comparison, the

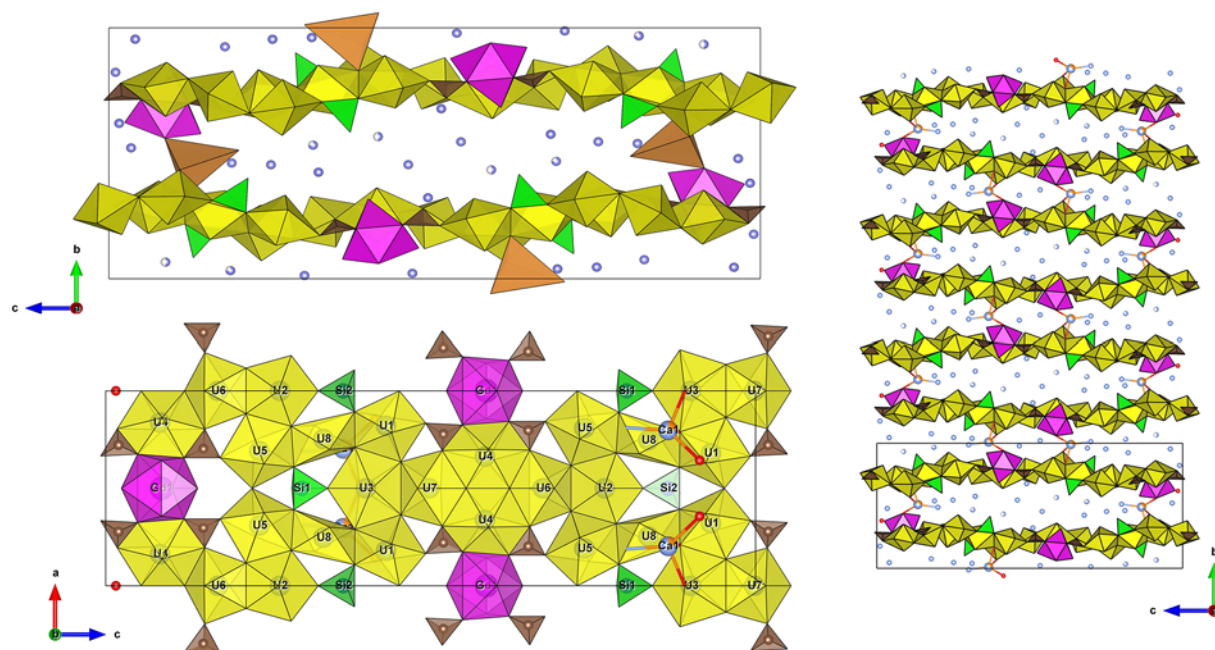


Figure 9. Crystal structure of lepersonnite-(Gd) represented by uranyl coordination polyhedra (UO_7 and UO_8 = yellow), Si-tetrahedra (green), CO_3 groups (dark brown), Gd^{3+} -polyhedra (violet) and Ca^{2+} -polyhedra (orange). Infinite sheets containing uranyl polyhedra (structural units) are stacked perpendicular to b ; the overview of the stacking configuration is given in the last picture (8 individual layers). Structure drawing by Vesta program (Momma and Izumi, 2011).

kinematical refinement gives $R(\text{obs})/wR(\text{obs}) = 0.2956/0.3642$, $R(\text{all})/wR(\text{all}) = 0.4198/0.3790$ and 3454 observed reflections. The R -values decreased significantly when the dynamical theory was applied; however, they remained higher than usual because of the imperfect ordering and the high mosaicity of the crystal, as observed in other layered highly hydrated minerals (Steciuk *et al.*, 2020, 2021, 2024). The formula derived from 3D ED is $\text{Ca}_{0.5}(\text{H}_2\text{O})_{13.25}[\text{Gd}(\text{UO}_2)_{12}(\text{SiO}_3\text{OH})_2(\text{CO}_3)_4(\text{OH})_{10}\text{O}_2(\text{H}_2\text{O})_5]$ ($Z = 4$). Hydroxyl and water molecule oxygen atoms were deduced from the bond-valence analysis. The data quality did not allow localisation of the hydrogen atoms. Further refinement details are given in Table 4, positional parameters are given in Table 5, and the bond-valence analysis was performed using the bond-valence parameters of Gagné and Hawthorne (2015) in Table 6. The crystal structure of lepersonnite-(Gd) is displayed in Fig. 9. The crystallographic information file was deposited in the CCDC database under the deposition number 2417019, and is also available as Supplementary material (see below).

Crystal structure of lepersonnite-(Gd)

The structure of lepersonnite-(Gd) contains eight symmetrically distinct U sites, one Gd, two Si, two C, 41 O sites and 10 O sites in the interlayer belonging to H_2O groups. One of the H_2O groups is bonded to the Ca site. The structure consists of wave-like sheets stacked along $[010]$ (Fig. 9). All U in the structure was found to be in the hexavalent state as the uranyl $(\text{UO}_2)^{2+}$ cation. Six of the eight U atoms are coordinated as pentagonal uranyl bipyramids. One U site is present as a hexagonal bipyramid sharing edges with two carbonate groups, yielding a uranyl bicarbonate complex, $[(\text{UO}_2)\text{O}_2(\text{CO}_3)_2]^{6-}$. Gadolinium is in [8]-coordination with four oxygen sites of the carbonate groups on the equatorial plane (a, c) and four out-of-plane H_2O molecules. Within the

sheet, $(\text{UO}_2)\text{O}_2(\text{CO}_3)_2$, $(\text{UO}_2)\text{O}_5$ and $\text{GdO}_4(\text{H}_2\text{O})_4$ polyhedra are connected through edges, creating some space to host $\text{SiO}_3(\text{OH})$ tetrahedra bonded to uranyl polyhedra *via* three corners. The longer Si–OH bond points towards the interlayer. The sheets are slightly wavy, and their stacking forms an interlayer ranging from ~ 2.7 Å to ~ 5.8 Å thick. The Ca site was identified during the refinement as a mixed O/Ca site in the interlayer, where two neighbouring uranyl sheets (structural units) are at the closest distance. Even though it seems to create a bridge between adjacent layers, the Ca site is only partially occupied. Therefore, most connectivity between layers occurs *via* hydrogen bonds between the two H_2O molecules bonded to Gd^{3+} and the apical oxygen of one uranyl ion of the layer above. The interlayer also hosts water molecules that contribute, to a lesser extent, to the connectivity. The weak bonding between layers explains the disorder observed in most diffraction patterns.

Topology of the structural units and structural complexity of lepersonnite-(Gd)

The sheet anion topology for lepersonnite-(Gd) was generated following the routine described by Burns *et al.* (1996) and is provided in Fig. 10a. It is an intriguing topology comprising combinations of hexagons, pentagons, squares and triangles, and exhibits more complexity than the previously most complex sheet topology found in minerals and synthetic compounds (Gurzhiy *et al.*, 2021), bijvoetite-type sheets (Fig. 10b). This sheet occurs in the minerals bijvoetite-(Y) (Li *et al.*, 2000) and the closely related mineral kamotoite-(Y) (Plášil and Petříček, 2017). The bijvoetite topology is characterised by infinite chains of alternating dimers of edge-sharing uranyl hexagonal and pentagonal bipyramids. The dimers are arranged along the chain's length, while dimers of hexagonal bipyramids are arranged perpendicularly. Each hexag-

Table 4. Summary of 3D ED data collection and refinements for lepersonnite-(Gd)

Crystal data	
Refined structural formula	$\text{Ca}_{0.5}(\text{H}_2\text{O})_{13.25}[\text{Gd}(\text{UO}_2)_{12}(\text{SiO}_3\text{OH})_2(\text{CO}_3)_4(\text{OH})_{10}\text{O}_2(\text{H}_2\text{O})_5]$
System	Orthorhombic
Temperature	95 K
<i>a</i>	11.850(7) Å
<i>b</i>	16.16(2) Å
<i>c</i>	39.506(17) Å
<i>V</i>	7563(12) Å ³
<i>Z</i>	4
Density [g·cm ⁻³] (without H, as refined)	3.7989
Density [g·cm ⁻³] (with H)	3.8419
Space group	<i>Pmnn</i>
Data collection	
TEM	FEI Tecnai G2 20
Measurement method	Precession assisted 3D ED
Radiation (wavelength)	electrons (0.0251 Å)
Precession angle/tilt step/ total α -tilt (°)	1/1/108
Rocking curve width (Å ⁻¹)/mosaicity (°)	0.0025/0.25
Resolution range (θ)	0.04–0.86
Limiting Miller indices	<i>h</i> : –14→14, <i>k</i> : –18→18, <i>l</i> : –46→46
No. of independent reflections (obs/all) – kinematic	3454/6741
<i>R</i> _{int} (obs/all) – kinematic	0.1979/0.2955
Redundancy	4.755
Coverage for $\sin\theta/\lambda = 0.6 \text{ Å}^{-1}$	95%
Kinematical refinement	
No. of reflections (obs/all)	3454/6741
<i>R</i> , <i>wR</i> (obs);	0.2956/0.3642
<i>R</i> , <i>wR</i> (all);	0.4198/0.3790
GOF(obs)/GOF(all)	0.05/0.0377
<i>N</i> refined param.	148
Dynamical refinement	
Reflection selection criteria	0.65
RSg(max)	
Outliers [<i>F</i> _{obs} – <i>F</i> _{calc}] > 10σ(<i>F</i> _{obs})	10
No. of reflections (obs/all)	3090/50507
<i>R</i> , <i>wR</i> (obs);	0.1204/0.1088
<i>R</i> , <i>wR</i> (all);	0.3977/0.1612
GOF(obs)/GOF(all)	0.0218/0.0083
<i>N</i> refined param. all/structural	247/156
Effective thicknesses; variation model	669(5) Å; wedge

onal bipyramid shares two equatorial edges, not participating in the linkage between U polyhedra, with CO₃ groups. These chains are linked into two-dimensional sheets *via* irregular Y³⁺-centred coordination polyhedra through the 6th non-shared equatorial edge from one chain and two O atoms of two carbonate groups from the neighbouring chain. The chains are electroneutral, so neighbouring structural units are linked only by hydrogen bonds provided by H₂O molecules from the coordination sphere of Y/REE atoms and the interlayer H₂O groups. In lepersonnite-(Gd) (Fig. 10a), we can find some similarities to the above-described bijvoetite topology. It is a cluster consisting of two hexagons, two

perpendicularly stacked pentagons, four triangles occupied by Ca and four void triangles (marked in green in Fig. 10). In bijvoetite-(Y) and kamotoite-(Y), those clusters repeat and thus form infinite chains. In lepersonnite-(Gd), each of these clusters is a neighbour with perpendicularly running infinite chains of pentagons (in yellow in Fig. 10a). This chain consists of trimers of edge-sharing pentagons, which in turn share a common edge, thus also producing two oppositely staggered triangles (sharing a vertex). Those triangles are part of the 'rolled-bonbon'-like cluster (red) – consisting of squares and triangles, orientated parallel to the elongation (edge) of the U tetramers (green). The central square of this cluster is occupied in lepersonnite-(Gd) by Gd³⁺, and two smaller adhering squares are voids. Together, each of these subunits forms compact blocks that are separated from each other by an additional infinite chain of vertex-sharing hexagons (occupied by U⁶⁺; atom U8) and triangles (occupied by Si⁴⁺) (in yellow with Si in green) (Fig. 10a). This chain runs parallel to the chain of pentagons and each of the neighbouring large blocks is then shifted relative to each other.

Despite the apparent complexity of the uranyl-anion sheet found in lepersonnite-(Gd), the structure itself is not as complex as one would expect. The structural complexity of lepersonnite-(Gd) was determined as the Shannon information content per atom (*I*_G) and per unit cell (*I*_{G,total}). This approach was developed by Krivovichev (2012, 2013, 2014, 2016, 2017): the complexity of a crystal structure can be quantitatively characterised by the amount of Shannon information, which is measured in bits (binary digits) per atom (bits/atom) and per unit cell (bits/cell), respectively. The amount of Shannon information reflects the diversity and relative proportion of different objects, e.g. the number and relative proportion of different sites in an elementary unit cell of a crystal structure. The information-based structural complexity values were calculated using the software package *TOPOS* (Blatov *et al.*, 2014). The chemical complexity (after Siidra *et al.*, 2014) is estimated by considering the chemical formula as a message, where symbols correspond to different chemical elements. Calculated values for the structural complexity of lepersonnite-(Gd) (without contribution of the H-atoms undetermined by the refinement) are 5.896 bits/atom and 2240.545 bits/cell, reflecting that lepersonnite-(Gd) has a complex structure, at a similar extent to kamotoite-(Y), with 1733.33 bits/cell, or meyerowitzite, 2023.17 bits/cell (Gurzhiy *et al.*, 2021). The chemical complexity, *I*_{chem}, of lepersonnite-(Gd) is 231.88 bits/formula. That makes lepersonnite-(Gd) a particularly chemically complex mineral structure, similar to, e.g. the uranyl-oxide minerals richetite, 225.48 bits/formula (Plášil, 2017) or wölsendorfit, 178.36 bits/formula (Burns, 1999). The furthestmost chemically complex uranyl mineral is uranyl carbonate ewingite, Mg₈Ca₈(UO₂)₂₄(CO₃)₃₀O₄(OH)₁₂(H₂O)₁₃₈ (Olds *et al.*, 2017), with 1024.18 bits/formula.

Discussion

Cell-size variation within lepersonnite-(Gd)

Data collected on lepersonnite-(Gd) show a broad range of lattice parameters for the same sample. The difference cannot be solely due to the different diffraction methods (single-crystal or powder) and temperatures (ambient or low T), as all 3D ED data collected at the same temperature with the same settings also highlight the same discrepancy (3% for *b*, 1.05% for *a* and 1.2% for *c*). Moreover, tools in *PETS2* allow the correction of geometrical and

Table 5. Atom positions, occupational factors (Occ.) and atomic displacement parameters for the lepersonnite-(Gd)

Atom	Wyckoff	Occ.	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq} / <i>U</i> _{iso}
U1	8 <i>h</i>	1	0.17991(15)	0.21327(19)	0.43136(5)	0.0105(5)
U2	4 <i>g</i>	1	½	0.1823(3)	0.76802(7)	0.0136(8)
U3	4 <i>g</i>	1	½	−0.1753(3)	0.59966(7)	0.0167(9)
U4	8 <i>h</i>	1	0.33737(11)	0.25588(17)	0.58368(5)	0.0041(4)
U5	8 <i>h</i>	1	0.19090(13)	0.23151(18)	0.73651(4)	0.0009(4)
U6	4 <i>g</i>	1	½	0.2250(3)	0.67285(8)	0.0202(9)
U7	4 <i>g</i>	1	½	0.2216(3)	0.49787(8)	0.0239(10)
U8	8 <i>h</i>	1	0.2471(3)	−0.2419(4)	0.66504(7)	0.0491(7)
Gd1	4 <i>g</i>	1	0	0.1730(3)	0.58579(12)	0.0174(9)
Si1	4 <i>g</i>	1	½	−0.1896(7)	0.69839(14)	0.0139(5)
Si2	4 <i>g</i>	1	0	0.6804(6)	0.63439(15)	0.0139(5)
C1	8 <i>h</i>	1	0.2218(7)	0.2278(9)	0.51970(17)	0.0139(5)
C2	8 <i>h</i>	1	0.2025(8)	0.2071(10)	0.65030(18)	0.0139(5)
O1u1	8 <i>h</i>	1	0.1292(9)	0.1103(4)	0.4232(3)	0.0139(5)
O2u1	8 <i>h</i>	1	0.2138(9)	0.3198(3)	0.4398(3)	0.0139(5)
O1u2	4 <i>g</i>	1	½	0.0711(4)	0.7660(5)	0.0139(5)
O2u2	4 <i>g</i>	1	½	0.2936(4)	0.7667(3)	0.0139(5)
O1u3	4 <i>g</i>	1	½	−0.0663(4)	0.6089(3)	0.0139(5)
O2u3	4 <i>g</i>	1	½	−0.2842(4)	0.5904(3)	0.0139(5)
O1u4	8 <i>h</i>	1	0.3007(9)	0.3625(3)	0.5889(3)	0.0139(5)
O2u4	8 <i>h</i>	1	0.3622(8)	0.1466(3)	0.5870(4)	0.0139(5)
O1u5	8 <i>h</i>	1	0.2473(10)	0.3334(4)	0.7293(3)	0.0139(5)
O2u5	8 <i>h</i>	1	0.1249(9)	0.1331(4)	0.7434(3)	0.0139(5)
O1u6	4 <i>g</i>	1	½	0.1264(7)	0.6516(4)	0.0139(5)
O2u6	4 <i>g</i>	1	½	0.3280(5)	0.6905(3)	0.0139(5)
O1u7	4 <i>g</i>	1	½	0.3241(5)	0.4799(3)	0.0139(5)
O2u7	4 <i>g</i>	1	½	0.1192(4)	0.5158(3)	0.0139(5)
O1u8	8 <i>h</i>	1	0.2999(10)	−0.3436(5)	0.6552(3)	0.0139(5)
O2u8	8 <i>h</i>	1	0.1777(10)	−0.1489(6)	0.6790(3)	0.0139(5)
O1c1	8 <i>h</i>	1	0.1655(8)	0.2110(10)	0.49236(17)	0.0139(5)
O2c1	8 <i>h</i>	1	0.1753(8)	0.2143(10)	0.54921(17)	0.0139(5)
O3c1	8 <i>h</i>	1	0.3058(7)	0.2799(9)	0.5180(2)	0.0139(5)
O1c2	8 <i>h</i>	1	0.1569(7)	0.1985(7)	0.62046(18)	0.0139(5)
O2c2	8 <i>h</i>	1	0.3040(7)	0.2378(10)	0.6525(2)	0.0139(5)
O3c2	8 <i>h</i>	1	0.1565(8)	0.1717(9)	0.67623(18)	0.0139(5)
O1	4 <i>g</i>	1	0	0.0775(7)	0.6416(3)	0.0139(5)
O2	4 <i>g</i>	1	½	−0.0993(8)	0.7135(3)	0.0139(5)
O3	4 <i>g</i>	1	0	0.2750(10)	0.7255(4)	0.0139(5)
O4	4 <i>g</i>	1	0	0.3184(9)	0.6019(4)	0.0139(5)
O5	4 <i>g</i>	1	0	0.1223(10)	0.5242(4)	0.0139(5)
O6	8 <i>h</i>	1	0.1435(8)	0.0599(7)	0.5858(3)	0.0139(5)
O7	4 <i>g</i>	1	½	−0.1881(9)	0.65869(13)	0.0139(5)
O8	8 <i>h</i>	1	0.3830(5)	0.1595(13)	0.7160(3)	0.0139(5)
O9	8 <i>h</i>	1	0.3642(10)	0.1738(13)	0.4543(3)	0.0139(5)
O10	8 <i>h</i>	1	0.2894(9)	−0.1718(10)	0.6165(3)	0.0139(5)
O11	8 <i>h</i>	1	0.3901(4)	−0.2364(7)	0.71047(16)	0.0139(5)
O12	4 <i>g</i>	1	½	0.2631(8)	0.55459(17)	0.0139(5)
O13	8 <i>h</i>	1	0.3183(9)	0.1845(11)	0.7855(3)	0.0139(5)
O14	8 <i>h</i>	1	0.1081(4)	0.7185(7)	0.61694(17)	0.0139(5)
O15	4 <i>g</i>	1	0	0.5834(6)	0.6295(4)	0.0139(5)
O16	4 <i>g</i>	1	0	0.7050(9)	0.67302(12)	0.0139(5)
O17	4 <i>g</i>	1	0	0.2389(11)	0.4520(4)	0.0139(5)
O18	4 <i>g</i>	1	½	0.2977(9)	0.6215(2)	0.0139(5)
Ca1	8 <i>h</i>	¼	0.2972(7)	−0.0097(9)	0.6343(2)	0.010(2)
Wat1	8 <i>h</i>	¾	0.2972(7)	−0.0097(9)	0.6343(2)	0.010(2)
Wat2	8 <i>h</i>	1	0.3118	0.0124	0.6997	0.008(3)
Wat3	8 <i>h</i>	1	0.3311	−0.0213	0.4659	0.053(6)

(Continued)

Table 5. (Continued.)

Atom	Wyckoff	Occ.	x/a	y/b	z/c	$U_{\text{eq}}/U_{\text{iso}}$
Wat4	4g	1	$\frac{1}{2}$	0.0757	0.1782	0.060(9)
Wat5	4g	$\frac{3}{4}$	0	0.9677	0.1865	0.052(11)
Wat6	8h	$\frac{1}{2}$	0.1526	0.9339	0.0869	0.042(9)
Wat7	8h	1	0.1169	−0.0459	0.7488	0.043(5)
Wat8	4g	1	0	0.6773	0.4898	0.031(6)
Wat9	4g	1	0	0.0455	0.0405	0.038(7)
Wat10	4g	1	0	−0.0389	0.6886	0.022(6)

Table 6. Bond-valence analysis for the lepersonnite-(Gd) structure (values given in valence units)

	U1	U2	U3	U4	U5	U6	U7	U8	Gd1	Ca/Wat1	Si1	Si2	C1	C2	Σ	Attribution
O1u1	1.69(3)														1.69(3)	O ²⁻
O2u1	1.68(3)														1.68(3)	O ²⁻
O1u2		1.69(3)													1.69(3)	O ²⁻
O2u2		1.69(3)													1.69(3)	O ²⁻
O1u3			1.69(3)							0.243(4)					1.93(3)	O ²⁻
O2u3			1.69(3)												1.69(4)	O ²⁻
O1u4				1.72(3)											1.72(3)	O ²⁻
O2u4				1.70(3)											1.70(3)	O ²⁻
O1u5					1.69(3)										1.69(3)	O ²⁻
O2u5					1.71(3)										1.71(3)	O ²⁻
O1u6						1.68(5)									1.68(5)	O ²⁻
O2u6						1.67(4)									1.67(4)	O ²⁻
O1u7							1.68(4)								1.68(4)	O ²⁻
O2u7							1.68(4)								1.68(4)	O ²⁻
O1u8								1.68(4)							1.68(4)	O ²⁻
O2u8								1.68(4)							1.68(4)	O ²⁻
O1c1	0.458(7)												1.28(4)		1.74(4)	O ²⁻
O2c1				0.427(9)					0.225(6)				1.25(4)		1.90(4)	O ²⁻
O3c1				0.279(6)			0.303(6)						1.26(5)		1.84(6)	O ²⁻
O1c2				0.279(6)					0.468(11)					1.26(4)	1.96(4)	O ²⁻
O2c2				0.219(4)		0.411(8)								1.26(5)	1.89(5)	O ²⁻
O3c2					0.308(6)									1.30(5)	1.61(5)	O ²⁻
O1									0.185(6)						0.185(6)	H ₂ O
O2											1.13(5)				1.13(5)	(OH) ⁻
O3					0.929(9)										0.929(9)	(OH) ⁻
O4									0.367(17)						0.367(17)	H ₂ O
O5									0.258(11)						0.258(11)	H ₂ O
O6									0.313(10)	0.092(3)					0.405(11)	H ₂ O
O7			0.536(7)								1.15(2)				1.69(2)	O ²⁻
O8		0.379(10)			0.261(6)	0.435(13)									1.075(17)	(OH) ⁻
O9	0.426(12)		0.266(7)				0.401(12)								1.093(18)	(OH) ⁻
O10	0.485(12)		0.322(7)					0.604(17)		0.137(8)					1.55(2)	(OH) ⁻
O11					0.513(7)			0.408(6)			1.12(3)				2.04(3)	O ²⁻
O12				1.308(8)			0.538(10)								1.846(13)	O ²⁻
O13		0.634(14)			0.330(9)			0.460(14)							1.42(2)	(OH) ⁻
O14	0.513(9)							0.313(5)				1.12(2)			1.95(3)	O ²⁻
O15												1.12(4)			1.12(4)	(OH) ⁻
O16		0.517(7)										1.13(3)			1.64(3)	O ²⁻
O17	1.122(17)														1.122(12)	(OH) ⁻
O18				0.718(7)		0.533(12)									1.251(14)	O ²⁻
Wat2										0.137(8)					0.173(4)	H ₂ O
Wat3															–	H ₂ O
Wat4															–	H ₂ O
Wat5															–	H ₂ O
Wat6															–	H ₂ O
Wat7															–	H ₂ O
Wat8															–	H ₂ O
Wat9															–	H ₂ O
Wat10															–	H ₂ O
Sum	5.82(5)	5.92(5)	5.09(5)	5.59(4)	5.27(5)	5.58(7)	5.31(6)	5.15(6)	2.82(3)	0.609(7)	4.52(7)	4.49(6)	3.78(8)	3.82(8)		

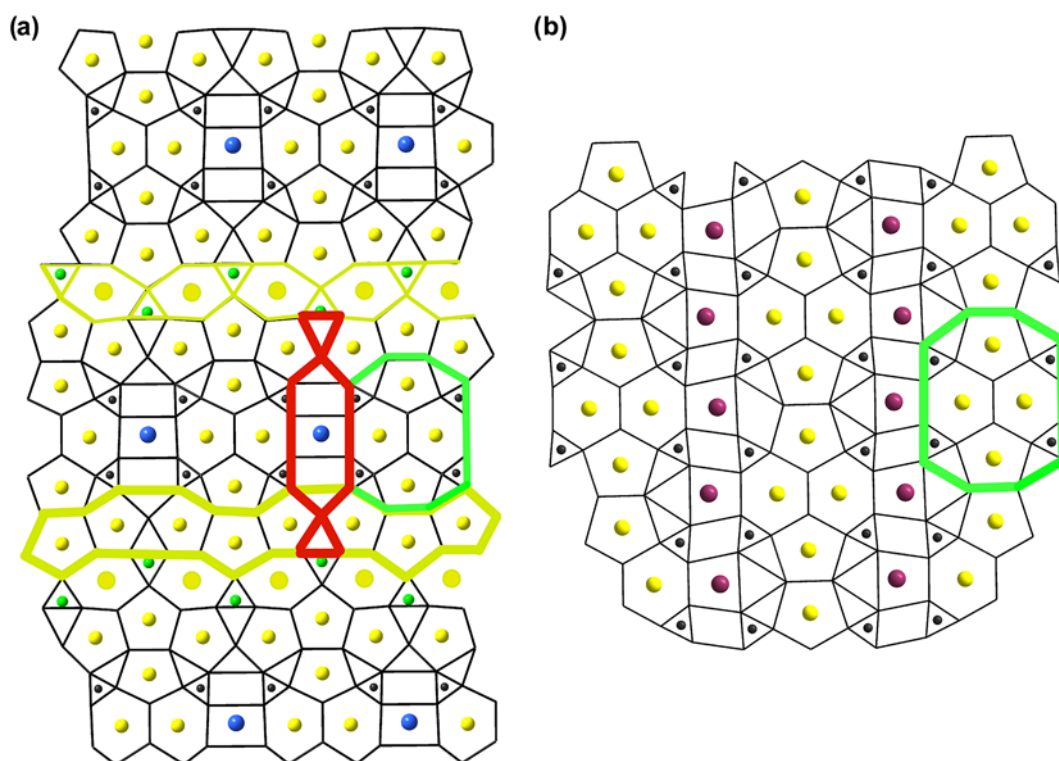


Figure 10. Sheet anion topologies for (a) lepersonnite-(Gd) and (b) bijvoetite-(Y) or kamotoite-(Y). Colour scheme for atoms: U (yellow), Gd (blue), Si (green), C (dark grey) and Y (violet).

optical distortion of 3D ED data (Brázda *et al.*, 2022), allowing accurate lattice parameters. Therefore, the observed discrepancy is a property of the mineral itself, as illustrated by the broad peaks in the powder data. In Fig. 8, a plot displays the lattice ratios for all the reported and measured data for lepersonnite-(Gd) sorted by decreasing lattice volume. Ratios were chosen instead of nominal lattice parameters due to the different diffraction methods and measurement temperatures. The volume strongly affects both ratios b/c and a/b , while a/c remains almost constant in all the reported data (Nd/Gd; room T/95 K). Therefore, the unit-cell volume mainly increases with b , which corresponds to the stacking direction and is affected by the amount of Ca (or other possible cations) and water in the interlayer. The a/c ratio depends only on the topology of the layer: a concomitant increase of a and c would preserve the ratio and could originate from the presence of heavier REE^{3+} at the site with a Wyckoff symmetry 4g (similar to lepersonnite-(Nd)) or in the U sites. The plot in Fig. 8 also indicates that the lepersonnite-(Gd) samples measured in the TEM experienced only slight dehydration (lower b/c) compared to the powder X-ray data collected on the same sample, because of the cryo-plunging method.

Lepersonnite-(Gd) experiences variation at the micro-scale regarding its water content and, probably, Ca levels. However, these changes do not account for the significant disorder seen in the data from single crystals. Like other minerals with sheet structures, cleavage easily occurs when dense layers of heavy atoms covalently bonded alternate thick interlayers connected primarily through strong hydrogen bonds. When the dense layers shift randomly, diffuse reflections along [010] are observed (as seen here) and probably result in other ordered polymorphs with lower symmetry.

Ideal formula of lepersonnite-(Gd)

The original formula assigned to lepersonnite-(Gd) by Deliens and Piret (1982), $CaGd_2(UO_2)_{24}(SiO_4)_4(CO_3)_8(OH)_{24} \cdot 48H_2O$ ($Z = 2$), basically agrees with the results of our recent EPM and TG analyses. Given that no structure data was available during the original description, it was not possible to elucidate the presence of protonated (acid) SiO_3OH groups and the distribution of OH^- and H_2O within the structural units. The sheet $[Gd(UO_2)_{12}(SiO_3OH)_2(CO_3)_4(OH)_{10}O_2(H_2O)_5]$ found in the crystal structure of lepersonnite-(Gd) corresponds well to the results of the EPMA data, only the (SiO_3OH) group is partially substituted by (OH) .

The situation in the interlayer is a bit more complicated due to disorder effects and partial occupancy. The crystal structure data indicate an interlayer content of $Ca_{0.5}(H_2O)_{13.25}$, but microprobe and TG analyses, considering bond valence and charge balance calculations, show $Ca^{*}_{0.39}Gd^{*}_{0.39}(H_2O)_{17.98}(OH)_{0.96}$ (where Ca^* is $Ca+Ba+Sr+Pb+Mn$ and Gd^* is the sum of $REE+Y$). The ideal formula for lepersonnite-(Gd) would therefore be best expressed as $[Ca_{0.5}Gd_{0.5}(H_2O)_{18}(OH)_{1.5}][Gd(UO_2)_{12}(SiO_3OH)_2(CO_3)_4(OH)_{10}O_2(H_2O)_5]$, or as the simplified formula $Ca_{0.5}Gd_{1.5}(UO_2)_{12}(SiO_3OH)_2(CO_3)_4(OH)_{11.5}O_2 \cdot 23H_2O$. Based on our observations, there is no indication that either the site hosting for REE within the sheet or the site hosting for Ca/REE in interlayer shows any preferential occupation by $Gd/Nd/Ca$ or Y .

Implications for the structure of lepersonnite-(Nd)

The current structure determination serves as a reference for defining the formula of the recently described mineral

lepersonnite-(Nd), the Nd-dominant analogue of lepersonnite-(Gd). Nevertheless, essential differences exist between the chemical compositions of the -(Gd) and -(Nd) members. Though lepersonnite-(Gd) contains Ca in all measured chemistries, the -(Nd) analogue does not. Moreover, the content of REE in lepersonnite-(Nd) is higher (2: 12: 2), concerning the REE:U:Si ratio, than in lepersonnite-(Gd) (1.5: 12: 2). Given the fact that the Gd site in the structure of lepersonnite-(Gd) has a Wyckoff symmetry 4g, resulting in one Gd atom per unit cell ($Z = 4$), 'excess' Nd in lepersonnite-(Nd) must occupy an additional site somewhere within the interlayer. As the sheets could not accommodate additional large cations as REE^{3+} , Nd (plus other REE), additional Nd may either occur at the same site that hosts Ca^{2+} in lepersonnite-(Gd), or another O (of H_2O) site in the interlayer. The corresponding Ca site (and several of the O of H_2O groups) have a multiplicity of 8; thus, additional Nd may be distributed ~sub-equitably among these O sites, but a structure analysis is yet required. Though the uranyl-REE-silicate-carbonate sheets are topologically the same, this is probably the most significant difference between the two structures. Thus, the ideal formula of lepersonnite-(Nd) can be expressed as $[Nd(H_2O)_{18}(OH)_2][Nd(UO_2)_{12}(SiO_3OH)_2(CO_3)_4(OH)_{10}O_2(H_2O)_5]$ and the simplified formula $Nd_2(UO_2)_{12}(SiO_3OH)_2(CO_3)_4(OH)_{12}O_{23}H_2O$.

Supplementary material. The supplementary material for this article can be found at <https://doi.org/10.1180/mgm.2025.29>

Acknowledgements. We thank Stephan Wolfsried (Waiblingen, Germany) and Eddy Van Der Meersche (Gent, Belgium) for providing us with the microphotos of the studied minerals. The helpful, thorough comments of Travis Olds, Oleg Siidra, and an anonymous referee are greatly appreciated. We thank Jana Ederová (University of Chemistry and Technology, Prague) for her kind assistance with the TG analyses.

Financial statement. This study was supported by the CzechNanoLab Research Infrastructure supported by MEYS CR (LM2023051) (GS and JP). Additionally, we acknowledge the support by the Ministry of Culture of the Czech Republic (long-term project DKRVO 2024–2028/1.II.b; National Museum, 00023272) for JS and ZD and an OP VVV project (Geobarr CZ.02.1.01/0.0/0.0/16_026/0008459 to RS).

Competing interests. The authors declare none.

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