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LIUDONGSHENGITE, $Zn_4Cr_2(OH)_{12}(CO_3)\cdot 3H_2O$, A NEW MINERAL OF THE HYDROTALCITE SUPERGROUP, FROM THE 79 MINE, GILA COUNTY, ARIZONA, USA

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ABSTRACT

A new mineral species, liudongshengite, ideally $Zn_4Cr_2(OH)_{12}(CO_3)\cdot 3H_2O$, has been found in the 79 mine, Gila County, Arizona, USA. It occurs as micaceous aggregates or hexagonal platy crystals (up to 0.10 × 0.10 × 0.01 mm). The mineral is pinkish and transparent with white streak and vitreous luster. It is brittle and has a Mohs hardness of $\sim$1.5, with perfect cleavage on (001). No twinning or parting is observed macroscopically. The measured and calculated densities are 2.95 (3) and 3.00 g/cm^3, respectively. Optically, liudongshengite is uniaxial (–), with $\omega = 1.720$ (8), $\varepsilon = 1.660$ (7) (white light). An electron microprobe analysis, combined with the carbon content measured using an elemental combustion system equipped with mass spectrometry, yielded the empirical formula $(Zn_{3.25}Mg_{0.17}Cr_{2.58})_{\Sigma 6.00}(OH)_{12}(CO_3)_{1.29}\cdot 3H_2O$, based on $(M^{2+} + M^{3+}) = 6$ *apfu*, where M^{2+} and M^{3+} are divalent and trivalent cations, respectively.

Liudongshengite belongs to the quintinite group within the hydrotalcite supergroup and is the Cr-analogue of zaccagnaite-3*R*, $Zn_4Al_2(OH)_{12}(CO_3)\cdot 3H_2O$. It is trigonal, with space group $R\bar{3}m$ and unit-cell parameters $a = 3.1111(4)$, $c = 22.682(3)$ Å, and $V = 190.12(4)$ Å^3. The crystal structure of liudongshengite is composed of positively charged brucite-like layers, $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}$, alternating with negatively charged layers of $(CO_3)^{2-}\cdot 3H_2O$. Compared to other minerals in the quintinite group, liudongshengite is remarkably enriched in M^{3+}, with an M^{2+}:M^{3+} ratio of 1.33:1. Like zaccagnaite-3*R* and many other hydrotalcite-type minerals, liudongshengite may also possess polytypes, as a series of synthetic hydrotalcite-type compounds with a general chemical formula $[Zn_4Cr_2(OH)_{12}]X_2\cdot 4H_2O$, where $X = Cl^-$, NO_3^-, or ½ SO_4^{2-}, but with unit-cell parameters different from those for liudongshengite, have been reported previously.

Keywords: liudongshengite, hydrotalcite, crystal structure, X-ray diffraction, Raman spectra.

INTRODUCTION

A new mineral species of the hydrotalcite supergroup, liudongshengite, ideally $Zn_4Cr_2(OH)_{12}(CO_3)\cdot 3H_2O$, has been found in the 79 mine, Gila County, Arizona, USA. It is named in honor of the late Prof. Liu Dongsheng (1917–2008), a distinguished Chinese geologist and archaeologist. Professor Liu was a Research Fellow at the Institute of Vertebrate Paleontology and Paleoanthropology and then at the Institute of Geology and Geophysics, Chinese Academy of Sciences. He had a total of 278 publications,

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including eight books. In particular, four of his books on loess [*Chinese Loess Accumulation* (1965), *Compositions and Structures of Loess* (1966), *Loess in China* (1980), and *Loess, Environment, and Global Change* (1991)] have become the foundation for loess research in China. Professor Liu was elected as an academician of the Chinese Academy of Sciences in 1980 and as a member of the Third World Academy of Sciences in 1991. In 2002, he was the recipient of the Tyler Prize for Environmental Achievement. In 2003, Prof. Liu received the Chinese Preeminent Science and Technology Award. The new mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA 2019-044). The cotype samples have been deposited at the University of Arizona Mineral Museum (Catalogue # 22043) and the RRUFF Project (deposition # R180016) (http://rruff.info).

The hydrotalcite supergroup of minerals (Mills *et al.* 2012) includes 44 members to date. They are a type of clay mineral that is often called anionic clays or layered double hydroxides (LDHs). These minerals have attracted considerable attention recently because of their significant industrial applications, especially in catalysis (Othman *et al.* 2009), water treatments (Douglas *et al.* 2010, Hövelmann *et al.* 2018 and references therein), and human health (del Hoyo 2007).

Hydrotalcite-type minerals may have one of the following two general chemical formulas: (1) $M^{2+}_{6-x}M^{3+}_{2+x}(OH)_{16}A{\cdot}4H_2O$ or (2) $M^{2+}_{4-x}M^{3+}_{2+x}(OH)_{12}A{\cdot}3H_2O$, where M^{2+} and M^{3+} are divalent (*e.g.*, Mg, Fe, Mn, Ni, Zn, Cu) and trivalent (*e.g.*, Al, Fe, Cr, Ga) cations, respectively, and A is typically monovalent or divalent anions (*e.g.*, CO_3^{2-}, SO_4^{2-}, Cl^-, OH^-). Their structures are composed of positively charged brucite-like layers, $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}$, alternating with negatively charged layers of $A{\cdot}nH_2O$. Polytypism in hydrotalcite-group minerals is common, and they usually exhibit one of two polytypic modifications, trigonal (3R-6R) and hexagonal (1H-2H-3H) (Bookin & Drits 1993, Mills *et al.* 2012), with monoclinic (1M) polytypes being rare (Martini 1980, Krivovichev *et al.* 2010). This paper describes the physical and chemical properties of liudongshengite and the determination of its crystal structure by means of single-crystal X-ray diffraction analysis.

SAMPLE DESCRIPTION AND EXPERIMENTAL METHODS

Occurrence

Liudongshengite was found in the 79 mine (33° 3′ 50″ N and 110° 48′ 54″ W), Chilito, Hayden area, Banner District, Dripping Spring Mountains, Gila County, Arizona, USA. The 79 mine was a lead-zinc mine originally exploited for rich oxidized ores and which extended several hundred feet below the surface (Kiersch 1949). An excellent examination of the geology and paragenesis of the mine was reported by Keith (1972). Later mining focused on the deeper sulfide ores. Liudongshengite occurs on the 4th level of the mine in an area rich in cerussite and wulfenite. It was found in a narrow, highly oxidized quartz-sulfide vein along a steeply dipping fault where the original sulfide minerals have been almost entirely replaced by secondary minerals. The mineral occurs on cerussite occupying voids left by altered galena crystals. Other minerals commonly found in these voids include malachite, rosasite, hemimorphite, chrysocolla, mimetite, wulfenite, and fornacite. Scheelite, stolzite, galena, and rarely linarite and kuksite also occur in the quartz vein.

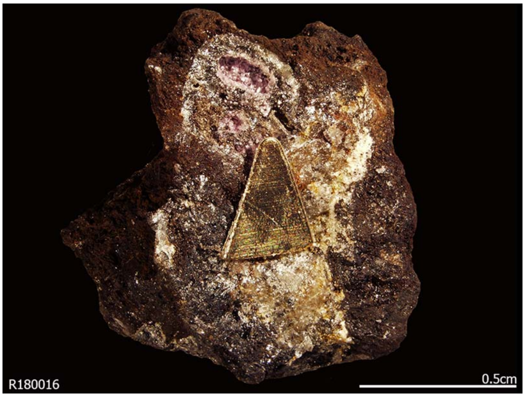

FIG. 1. The specimen on which liudongshengite was found.

Physical and chemical properties and Raman spectra

Liudongshengite occurs as micaceous aggregates or hexagonal platy crystals (up to 0.10 × 0.10 × 0.01 mm) (Figs. 1 and 2). No twinning or parting is observed

FIG. 2. A microscopic view of pinkish, hexagonal, platy liudongshengite crystals.

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TABLE 1. CHEMICAL DATA (IN wt.%) FOR LIUDONGSHENGITE

Constituent	Mean	Range	Stand. Dev. (s)	Reference Material
ZnO	38.78	38.07–39.27	0.46	ZnO
Cr_2O_3	28.72	27.96–29.45	0.33	Chromite ($FeCr_2O_4$)
MgO	1.02	0.90–1.18	0.10	Olivine (Fo92)
CO_2	8.33			Converted and adjusted from the measured C content
H_2O	23.78			Added in ideal value
Total	100.63	100.00–100.98	0.55	

Notes: (a) The C content of 2.31(2) wt.% was obtained from an elemental combustion system equipped with mass spectrometry. This value is very close to that of 2.26 wt.% adjusted for charge balance in the chemical formula calculation (see the text). Due to the limited amount of the sample, the δ^{13}C‰ value could not be measured accurately.

(b) The H_2O content was added to the ideal value (total 9 H_2O).

(c) Trace amounts of Si and S were detected by WDS, but they are below the limits of the reliable measurements ($<3\sigma$) by the electron microprobe analysis.

macroscopically. The mineral is pinkish and transparent with white streak and vitreous luster. It is brittle and has a Mohs hardness of ~1.5, with perfect cleavage on {0001}. The measured (by flotation in heavy-liquids) and calculated densities are 2.95(3) and 3.00 g/cm^3, respectively. Optically, liudongshengite is uniaxial (–), with $\omega = 1.720(8)$, $\varepsilon = 1.660(7)$ (white light). Pleochroism is weak, with O = pale pink and E = colorless. The calculated compatibility index based on the empirical formula is –0.0326 (excellent) (Mandarino 1981). Liudongshengite is insoluble in water or hydrochloric acid.

The chemical composition was determined using a Cameca SX-100 electron microprobe (WDS mode, 15 kV, 6 nA, and a beam diameter of 5 μm). The standards used for the probe analysis are given in Table 1, along with the determined compositions (eight analysis points). The C content was measured with an elemental combustion system equipped with mass spectrometry. The resultant chemical formula is $(Zn_{3.25}Mg_{0.17}Cr_{2.58})_{\Sigma 6.00}(OH)_{12}(CO_3)_{1.29}\cdot 3H_2O$, which is calculated on the basis of $(M^{2+} + M^{3+}) = 6$ *pfu* (M^{2+} = divalent cations and M^{3+} = trivalent cations) with the following assumptions for the hydrotalcite-type minerals (Lozano *et al*. 2012, Mills *et al*. 2012): (1) The number of H_2O present between the octahedral layers is half that of ($M^{2+} + M^{3+}$). (2) There are two OH^- groups for each ($M^{2+} + M^{3+}$) cation and 0.5 $(CO_3)^{2-}$ for each trivalent (M^{3+}) cation for charge balance. Therefore, the final amount of $(CO_3)^{2-}$ was adjusted to be 1.29 *pfu*, which corresponds to a C content of 2.26 wt.%, as compared to the measured value of 2.31 wt.%. The simplified formula is $(Zn^{2+},Mg^{2+},Cr^{3+})_6(OH)_{12}(CO_3)\cdot 3H_2O$ and the ideal one is $Zn^{2+}{}_4Cr^{3+}{}_2(OH)_{12}(CO_3)\cdot 3H_2O$, which requires ZnO 47.62, Cr_2O_3 22.23, CO_2 6.44, and H_2O 23.71 (wt.%).

TABLE 2. POWDER X-RAY DIFFRACTION DATA FOR LIUDONGSHENGITE

I%	$d_{(\text{meas.})}$	$d_{(\text{calc.})}$	$d_{(\text{diff.})}$	$h\ k\ l$
46.2	7.5300	7.5468	–0.0168	0 0 3
63.9	3.7710	3.7734	–0.0024	0 0 6
19.1	2.6770	2.6751	0.0019	0 1 $\bar{1}$
100.0	2.6200	2.6208	–0.0008	0 1 2
14.3	2.4290	2.4325	–0.0035	0 1 $\bar{4}$
82.6	2.3140	2.3152	–0.0012	0 1 5
11.5	2.0710	2.0700	0.0010	0 1 $\bar{7}$
48.0	1.9520	1.9513	0.0007	0 1 8
17.7	1.7300	1.7332	–0.0032	0 1 $\overline{10}$
7.5	1.6360	1.6355	0.0005	0 1 11
42.1	1.5550	1.5554	–0.0004	1 1 0
31.7	1.5230	1.5234	–0.0004	1 1 3
15.7	1.4390	1.4380	0.0010	1 1 6
5.8	1.3870	1.3865	0.0005	0 1 14

The Raman spectrum of liudongshengite was collected from a randomly oriented crystal with a Thermo Almega microRaman system, using a solid-state laser with a frequency of 532 nm at the full power of 150 mW and a thermoelectrically cooled CCD detector. The laser is partially polarized with 4 cm^{-1} resolution and a spot size of 1 μm.

X-ray crystallography

The powder X-ray diffraction data for liudongshengite were collected using a Rigaku D/Max 2500 diffractometer equipped with Cu$K\alpha$ radiation at 45 kV and 250 mA. Listed in Table 2 are the measured powder X-ray diffraction data, along with those calculated from the determined structure using the program XPOW (Downs *et al*. 1993). The unit-cell parameters obtained from the powder X-ray diffraction

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TABLE 3. COMPARISON OF MINERALOGICAL DATA FOR LIUDONGSHENGITE, ZACCAGNAITE-3R, AND STICHTITE

	Liudongshengite	Zaccagnaite-3R	Stichtite
Ideal chemical formula	$Zn_4Cr_2(OH)_{12}(CO_3)\cdot3H_2O$	$Zn_4Al_2(OH)_{12}(CO_3)\cdot3H_2O$	$Mg_6Cr_2(OH)_{16}(CO_3)\cdot4H_2O$
Space group	$R\bar{3}m$	$R\bar{3}m$	$R\bar{3}m$
a (Å)	3.1111(4)	3.06616(1)	3.09575(3)
c (Å)	22.682(3)	22.6164(1)	23.5069(6)
V (Å^3)	190.12(4)	184.139(1)	195.099(6)
Z	3/6 (or 0.5)	3/6 (or 0.5)	3/8
ρ_{cal} (g/cm^3)	2.997	2.82	
Measured A^{2+}/B^{3+} ratio	1.33	1.61.6	
2θ range for data collection	≤65.67		
No. of reflections collected	557		
No. of independent reflections	120		
No. of reflections with $I > 2\sigma(I)$	119		
No. of parameters refined	19		
R(int)	0.020		
Final R_1, wR_2 factors [$I > 2\sigma(I)$]	0.034, 0.081	$R_p = 0.052$, $R_{wp} = 0.070$	$R_p = 0.016$, $R_{wp} = 0.020$
Goodness-of-fit	1.209	1.209	3.74
Data measured by	Single-crystal X-ray	Powder X-ray	Powder X-ray
Reference	This work	Lozano *et al.* (2012)	Mills *et al.* (2011)

data are $a = 3.1107(10)$, $c = 22.640(11)$ Å, and $V = 189.73(11)$ Å^3.

Single-crystal X-ray diffraction data for liudongshengite were collected from a hexagonal platy crystal (0.06 × 0.06 × 0.01 mm) using a Bruker X8 APEX2 CCD X-ray diffractometer equipped with graphite-monochromatized Mo$K\alpha$ radiation with frame widths of 0.5° in ω and 60 s counting time per frame. All reflections were indexed on the basis of a hexagonal unit cell (Table 3). The intensity data were corrected for X-ray absorption using the Bruker program SADABS. The systematic absences of reflections suggested the possible space groups $R32$, $R3m$, or $R\bar{3}m$. The crystal structure was solved and refined using SHELX2018 (Sheldrick 2015a, b) based on the space group $R\bar{3}m$, because it yielded better refinement statistics in terms of bond lengths and angles, atomic displacement parameters, and R factors. During the structure refinements, the crystal chemistry was constrained to that in the empirical formula $(Zn_{3.25}Mg_{0.17}Cr_{2.58})_{\Sigma6.00}(OH)_{12}(CO_3)_{1.29}\cdot3H_2O$. Moreover, H_2O was treated as a unit that occupies the same atomic site as the O atoms in the $[CO_3]^{2-}$ molecule, as previously reported for many other minerals in the hydrotalcite supergroup (*e.g.*, Mills *et al.* 2011, 2016, Lozano *et al.* 2012). Final coordinates and displacement parameters of atoms in liudongshengite are listed in Table 4 and selected bond distances in Table 5.

CRYSTAL STRUCTURE DESCRIPTION AND DISCUSSION

Liudongshengite belongs to the quintinite group within the hydrotalcite supergroup and is the Cr-analogue of zaccagnaite-3*R*, $Zn_4Al_2(OH)_{12}(CO_3)\cdot3H_2O$ (Lozano *et al.* 2012) (Table 3). Its structure consists of positively charged brucite-like layers, $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2]^{x+}$, alternating with negatively charged layers of $A\cdot nH_2O$ (Fig. 3). According to Mills *et al.* (2012), liudongshengite possesses a $3R_1$ layer stacking sequence. For minerals in the hydro-

TABLE 4. ATOMIC FRACTIONAL COORDINATES AND DISPLACEMENT PARAMETERS (Å^2) FOR LIUDONGSHENGITE

Atom	x	y	z	U_{iso}	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
M	0	0	0	0.0154(4)	0.0093(4)	0.0093(4)	0.0276(6)	0	0	0.0046(2)
O1	0	0	0.3779(2)	0.0202(8)	0.0200(12)	0.0200(12)	0.0204(14)	0	0	0.0100(6)
H	0	0	0.411(4)	0.07(4)						
C	0.333	0.667	0.502(5)	0.07(3)						
O2	0.188(3)	0.892(3)	0.5006(12)	0.044(4)						

Site occupancies are M = (0.542 Zn + 0.430 Cr + 0.028 Mg); C = 0.1075 C; O2 = 0.1908 O (= 0.1075 O + 0.0833 H_2O).

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TABLE 5. SELECTED BOND DISTANCES (Å) IN LIUDONGSHENGITE, ZACCAGNAITE-3R, AND STICHTITE

	Liudongshengite	Zaccagnaite-3R	Stichtite
A^{2+}/B^{3+}–O1	2.0611(18)	2.030(1)	2.0123(8)
O1–H	0.74(9)	1.13(5)	0.903
C–O2	1.213(19); 1.588(6)	1.165(7)	1.121(4); 1.5644(6)
Reference	This work	Lozano *et al.* (2012)	Mills *et al.* (2011)

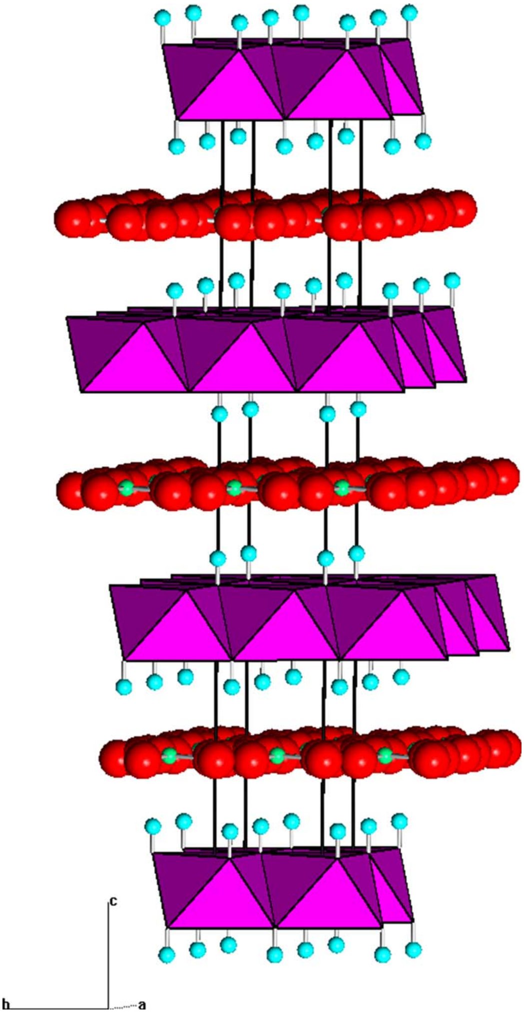

FIG. 3. Crystal structure of liudongshengite. The purple octahedra, large red, small green, and small light blue spheres represent Zn/Cr$(OH)_6$, O/H_2O, C, and H, respectively.

talcite supergroup, the ratio of M^{2+}:M^{3+} can deviate significantly from the ideal value of 3:1 for minerals with the chemical formula $M^{2+}_{6-x}M^{3+}_{2+x}(OH)_{16}A\cdot 4H_2O$ or 2:1 for those with the chemical formula $M^{2+}_{4-x}M^{3+}_{2+x}(OH)_{12}A\cdot 3H_2O$. Lozano *et al.* (2012) noted that zaccagnaite-3*R* is markedly enriched in M^{3+}, with an unusual M^{2+}:M^{3+} ratio of 1.6:1. Compared to zaccagnaite-3*R*, liudongshengite contains even more M^{3+} cation, yielding an M^{2+}:M^{3+} ratio of 1.33:1.

Raman spectroscopy has been widely used to investigate crystal structures and chemical variations of hydrotalcite-type materials, such as hydrotalcite, $Mg_6Al_2(CO_3)(OH)_{16}\cdot 4H_2O$ (Kloprogge *et al.* 2002, Frost *et al.* 2003); stichtite, $Mg_6Cr_2(CO_3)(OH)_{16}\cdot 4H_2O$ (Frost & Erickson 2004, Mills *et al.* 2011, Theiss *et al.* 2013); and quintinite, $Mg_4Al_2(OH)_{12}(CO_3)\cdot 3H_2O$ (Theiss *et al.* 2015). The Raman spectrum of liudongshengite is displayed in Figure 4, along with that of stichtite from the RRUFF Project (http://rruff.info/R060675) for comparison. Based on previous Raman spectroscopic studies on minerals of the hydrotalcite group (*e.g.*, Kloprogge *et al.* 2002, Frost *et al.* 2003, Frost & Erickson 2004, Mills *et al.* 2011, Theiss *et al.* 2013, 2015), we made the following tentative assignments of major Raman bands for liudongshengite: A strong, asymmetric band at 3480 cm^{-1} and a very weak, broad band at 2918 cm^{-1} are attributed to the O–H stretching vibrations in OH and H_2O groups. Theiss *et al.* (2015) observed three overlapping bands (3485, 3334, and 3078 cm^{-1}) between 2900 and 3500 cm^{-1} for quintinite. Thus, the strong asymmetric band at 3480 cm^{-1} for liudongshengite is likely to result from the overlap of two bands. The sharp band at 1059 cm^{-1} and the weak, broad band at 1390 cm^{-1} are due to the C–O symmetric (ν_1) and asymmetric (ν_3) stretching vibrations, respectively, within the CO_3^{2-} groups. These two bands are typical of hydrotalcite-type minerals containing carbonates, although their relative positions and intensities may vary. Interestingly, two bands due to the ν_1 vibrations are observed for both stichtite and quintinite (Frost & Erickson 2004, Mills *et al.* 2011, Theiss *et al.* 2015), indicating that D_{3h} site symmetry for the ideal CO_3 group in these two minerals is not maintained and, instead, that the site symmetry has been lowered to C_{2v} or C_s.

According to Theiss *et al.* (2015), the weak bands between 990 and 830 cm^{-1} may be assigned to the H_2O librational modes. The most intense band at 537 cm^{-1}

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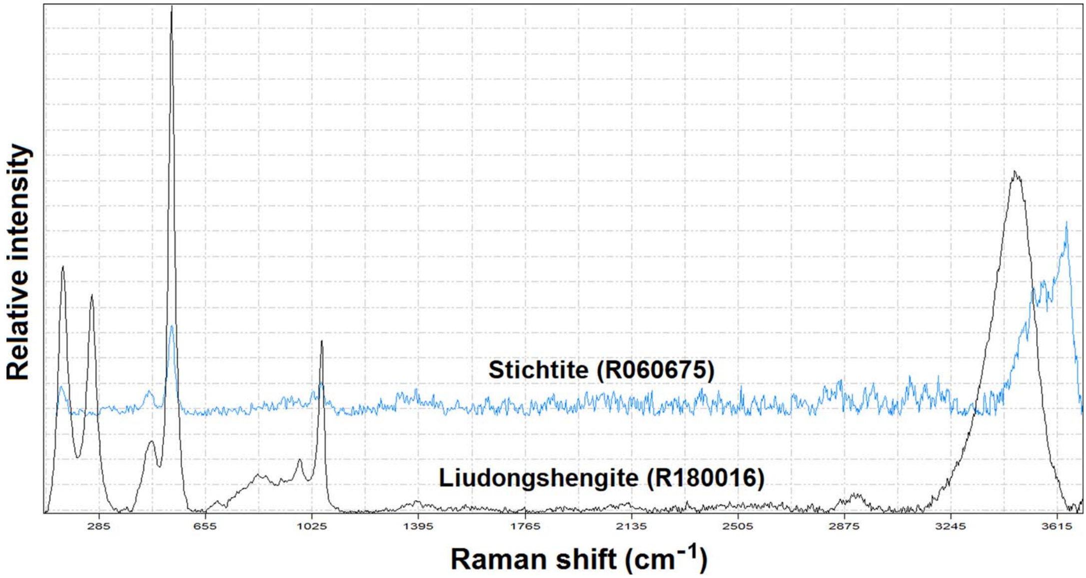

FIG. 4. Raman spectrum of liudongshengite, with that of stichtite for comparison.

and the very weak, broad band at 696 cm^{-1} can been assigned to the to O–C–O symmetric (ν_2) and asymmetric (ν_4) bending modes within the CO_3 groups. The ν_2 band was observed at 539 cm^{-1} for stichtite (Frost & Erickson 2004) and 559 cm^{-1} for quintinite (Theiss *et al*. 2015). The relatively weak band at 466 cm^{-1} may originate from the *M*–O (*M* = Zn/Cr) stretching vibrations. The bands below 400 cm^{-1} may be ascribed to the lattice and O–*M*–O bending vibrations.

The hydrotalcite-type minerals are notable for a wide range of polytypism, with trigonal and hexagonal forms being dominant (*e.g.*, Bookin & Drits 1993, Bookin *et al*. 1993a, b, Evans & Slade 2006, Mills *et al*. 2012, Zhitova *et al*. 2018). For example, zaccagnaite possesses two polytypes, $R\bar{3}m$ and $P6_3/mmc$ (Merlino & Orlandi 2001, Lozano *et al*. 2012), and so does stichtite (Mills *et al*. 2011). Interestingly, Boehm *et al*. (1977) synthesized a series of gray- or pink-violet hydrotalcite-type compounds with a general chemical formula of $[Zn_4Cr_2(OH)_{12}]X_2{\cdot}4H_2O$, where $X = Cl^-$, NO_3^-, or ½ SO_4^{2-}. However, their powder X-ray diffraction data revealed that those compounds have *a* = 5.36 Å, rather than 3.11 Å (as in liudongshengite), suggesting that liudongshengite may also possess some polytypes, as other hydrotalcite-type minerals do.

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