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## **Revision 2**

# 2 Wenlanzhangite–(Y) from the Yushui deposit, South China: a potential proxy for

## 3 tracing the redox state of ore formation

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#### ABSTRACT

24 Mineral phases in which vanadium (V) and heavy-rare-earth elements (HREEs) coexist are rarely documented. Here, we report a new V-HREE-bearing silicate mineral species, wenlanzhangite-(Y), 25 which is a vanadiferous derivate of jingwenite-(Y) [Y<sub>2</sub>Al<sub>2</sub>V<sup>4+</sup><sub>2</sub>(SiO<sub>4</sub>)<sub>2</sub>O<sub>4</sub>(OH)<sub>4</sub>] coexisting with 26 jingwenite-(Y) in bedded/massive ores at Yushui, South China. Wenlanzhangite-(Y) forms as a dark 27 brown, 70-100 µm-thick rim on a core domain of jingwenite-(Y), which occurs as 100-200 µm 28 columnar crystals. The colour, streak, lustre, and hardness (Mohs) are dark brown, yellow grey, 29 vitreous, and ~4, respectively. Compared to jingwenite-(Y), wenlanzhangite-(Y) has higher 30 31 vanadium and lower aluminium contents. Calculated on the basis of 8 cations, the empirical formula 32 is  $(Y_{1,26}Dy_{0,17}Er_{0,11}Gd_{0,09}Yb_{0,09}Nd_{0,09}Sm_{0,06}Sc_{0,04}Ho_{0,03}Ce_{0,02}Tb_{0,02}Tm_{0,02}Pr_{0,01})_{\Sigma 2,00}(V^{3+}_{1,46}Al_{0,54})_{\Sigma 2,00}V^{4+}_{1,46}Nd_{0,03}Ce_{0,02}Tb_{0,02}Tm_{0,02}Pr_{0,01})_{\Sigma 2,00}(V^{3+}_{1,46}Al_{0,54})_{\Sigma 2,00}V^{4+}_{1,46}Nd_{0,03}Ce_{0,02}Tm_{0,02}Pr_{0,01})_{\Sigma 2,00}(V^{3+}_{1,46}Al_{0,54})_{\Sigma 2,00}V^{4+}_{1,46}Nd_{0,03}Ce_{0,02}Tm_{0,02}Pr_{0,01})_{\Sigma 2,00}(V^{3+}_{1,46}Al_{0,54})_{\Sigma 2,00}V^{4+}_{1,46}Nd_{0,03}Ce_{0,02}Tm_{0,02}Pr_{0,01})_{\Sigma 2,00}(V^{3+}_{1,46}Al_{0,54})_{\Sigma 2,00}V^{4+}_{1,46}Nd_{0,03}Ce_{0,02}Tm_{0,02}Pr_{0,01})_{\Sigma 2,00}(V^{3+}_{1,46}Al_{0,54})_{\Sigma 2,00}V^{4+}_{1,46}Nd_{0,03}Ce_{0,02}Tm_{0,02}Pr_{0,01})_{\Sigma 2,00}(V^{3+}_{1,46}Al_{0,54})_{\Sigma 2,00}V^{4+}_{1,46}Nd_{0,03}Ce_{0,02}Pr_{0,01})_{\Sigma 2,00}(V^{3+}_{1,46}Al_{0,54})_{\Sigma 2,00}V^{4+}_{1,46}Nd_{0,03}Ce_{0,02}Pr_{0,01})_{\Sigma 2,00}(V^{3+}_{1,46}Al_{0,03})_{\Sigma 2,00}V^{4+}_{1,46}Nd_{0,03}Ce_{0,02}Pr_{0,01})_{\Sigma 2,00}(V^{3+}_{1,46}Al_{0,03})_{\Sigma 2,00}V^{4+}_{1,46}Nd_{0,03}Ce_{0,02}Pr_{0,01})_{\Sigma 2,00}(V^{3+}_{1,46}Al_{0,03})_{\Sigma 2,00}V^{4+}_{1,46}Nd_{0,03}Ce_{0,02}Pr_{0,01})_{\Sigma 2,00}(V^{3+}_{1,46}Al_{0,03})_{\Sigma 2,00}V^{4+}_{1,46}Nd_{0,03}$ 33  $_{2}(SiO_{4})_{2}O_{4}(OH)_{4}$ , which can be simplified to the ideal formula  $Y_{2}V_{2}^{3+}V_{2}^{4+}(SiO_{4})_{2}O_{4}(OH)_{4}$ . 34 Wenlanzhangite–(Y) is triclinic, with space group P-1(#2), Z = 2, and unit–cell parameters a =35 5.9632(7) Å, b = 9.599(1) Å, c = 9.9170(9) Å,  $\alpha = 90.033(8)^{\circ}$ ,  $\beta = 98.595(2)^{\circ}$ ,  $\gamma = 90.003(9)^{\circ}$ , and V 36 = 561.28(10)  $Å^3$ . Wenlanzhangite-(Y) is approved by the International Mineralogical Association 37 Commission on New Minerals, Nomenclature and Classification (IMA2022-142). The structure of 38 wenlanzhangite-(Y) is composed of a-axis-oriented chains of  $[VO_6]$  octahedra consisting of edge-39 sharing octahedra linked by insular [SiO<sub>4</sub>] tetrahedra, leaving open channels occupied by rare earth 40 elements. Observed compositional variation and crystal structure demonstrate that V<sup>3+</sup> can substitute 41 for  $Al^{3+}$  in jingwenite-(Y), forming wenlanzhangite-(Y). The occurrence of wenlanzhangite-(Y) 42 indicates a relatively more reducing hydrothermal environment causing reduction of V<sup>5+</sup> in oxidized 43 fluids to  $V^{3+}$  and thus represents a useful proxy for tracing the redox state of ore formation. 44

## 45 *Keywords*: New mineral; Wenlanzhangite–(Y); Heavy rare earth elements; Yushui Cu deposit

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#### **INTRODUCTION**

Recent studies have reported the first account of significant HREE (and associated U) mineralization within a sediment-hosted Cu deposit, the Yushui deposit, South China (Liu et al. 2023). It is well known that sandstone-hosted uranium deposits can host economic concentrations of V (e.g., Colorado Plateau, USA) (Dahlkamp 2010), and form at an oxidation-reduction interface (Northrop et al. 1990; Shawe 2011). Vanadium, as V<sup>3+</sup>, V<sup>4+</sup>, V<sup>5+</sup>, or a combination thereof, can occur as oxide phases or is combined with redox-sensitive elements (Weeks et al. 1959). In practice, V–HREEbearing mineral phases are rarely documented.

A new V–HREE–bearing silicate mineral, jingwenite–(Y)  $[Y_2Al_2V^{4+}_2(SiO_4)_2O_4(OH)_4]$ , has been 54 discovered and is an abundant phase in the Yushui deposit (Liu et al. 2023). Here we describe a 55 jingwenite–(Y) from Yushui, 56 vanadiferous derivate of wenlanzhangite–(Y), ideally  $Y_2V^{3+}_2V^{4+}_2(SiO_4)_2O_4(OH)_4$ . Wenlanzhangite-(Y) has been approved by the International 57 Mineralogical Association Commission on New Minerals, Nomenclature and Classification 58 (IMA2022-142). It is named in honor of Professor Wenlan Zhang (born in 1957), a famous expert in 59 electron probe microbeam analysis at the School of Earth Sciences and Engineering, Nanjing 60 61 University, China. She has published more than 80 papers that contribute to improvements and capabilities of electron probe analysis technology in China. Type material is deposited in the 62 mineralogical collections of the Geological Museum of China, catalogue number GMCTM 2202. 63

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#### **GEOLOGICAL BACKGROUND**

The Yushui deposit, located in the southwestern domain of the southeastern coastal belt, South China (Fig. 1a), is a small yet high–grade Cu deposit with significant HREE enrichment, and minor enrichment in U, Co, and V (Liu et al. 2023). Mineralization is concealed beneath Late–Jurassic volcanic cover and is hosted at the unconformity between Upper Carboniferous dark grey dolostone/limestone with organic– and apatite–rich beds and a >300 m–thick sequence of Lower Carboniferous red sandstone (Figs. 1, 2a, and 2b) characterized by an abundance of heavy minerals

including clastic xenotime-(Y), rutile, zircon, and hematite. There are three types of Cu ore: I) 71 bedded/massive; II) disseminated; and III) vein-type (Fig. 2c-g). HREE-bearing minerals occur 72 mainly in bedded/massive ore (orebody  $V_1$ ). Based on mineral assemblages, orebody  $V_1$  can be split 73 into: I) a lower chalcopyrite-rich part; and II) an upper galena-rich part. The lower part is 74 characterized by chalcopyrite, and abundant HREE-V- and V-Sc-bearing minerals including 75 nolanite, thortveitite, roscoelite, xenotime-(Y), jingwenite-(Y) (Liu et al. 2023), hingganite-(Y), 76 bastnäsite-(Y) and an unknown V-HREE-Sc-bearing silicate mineral phase. Minor components 77 include bornite, barite, sphalerite, galena, uraninite, and quartz. The upper part of the orebody 78 underlies the dolostone, and is dominated by galena, sphalerite, bornite, chalcopyrite, and hematite, 79 and minor anhydrite, calcite, and apatite. Wenlanzhangite-(Y) occurs in the lower part of the 80 81 bedded/massive orebody, and associated minerals are chalcopyrite, bornite, nolanite, thortveitite, 82 jingwenite-(Y), and roscoelite (Fig. 3a). Wenlanzhangite-(Y) is observed as a dark brown, 70-100 um-thick rim on a core domain of jingwenite-(Y) or 100 um-thick core on jingwenite-(Y), which 83 84 occurs as 100–200 µm columnar crystals (Fig. 3b–d). The crystals display regular oscillatory compositional zoning on back-scattered electron images (Fig. 3b). 85

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#### ANALYTICAL METHODS

#### 87 **Reflectance measurements**

88 Reflectance values for wenlanzhangite-(Y) were measured in air using a CRAIC 20/30PV Pro 89 microspectrophotometer at Westlake University, Hangzhou, China. The reference material is 89 aluminum metal (R= 85-90 %) (SPFS) with MgF<sub>2</sub> coating. Reflectance values were obtained from 91 five spots in a single wenlanzhangite-(Y) grain, with  $\times$  50 objective and 16  $\times$  16 µm aperture size.

#### 92 Chemical composition analysis

93 Quantitative major-element analysis was performed at Xi'an Center of Mineral Resources Survey,

94 China, using a Shimadzu EPMA-1720HT electron microprobe. All measurements were performed

95	using an accelerating voltage of 15 kV and a beam current of 50 nA. The beam size was 20 $\mu$ m for
96	the standards and 5 µm for wenlanzhangite-(Y). Crystals used were PET (Y, Sc and Si), LIF (Ce, Pr,
97	Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb and V), and RAP (Al). The $K\alpha$ line was chosen for analysis of
98	Si, Al, V, and Sc; the $L\alpha$ line for Ce, Pr, Sm, Nd, Tb, Gd, Dy, Er, Yb, and Y; and the $L\beta$ line for Ho
99	and Tm. Count times on peaks were 10 s and background intensities were measured on both sides of
100	the peak for half of the peak time. The standards were CeP <sub>5</sub> O <sub>14</sub> for Ce, PrP <sub>5</sub> O <sub>14</sub> for Pr, NdP <sub>5</sub> O <sub>14</sub> for
101	Nd, SmP <sub>5</sub> O <sub>14</sub> for Sm, GdP <sub>5</sub> O <sub>14</sub> for Gd, Tb <sub>3</sub> Ga <sub>5</sub> O <sub>12</sub> for Tb, DyP <sub>5</sub> O <sub>14</sub> for Dy, HoP <sub>5</sub> O <sub>14</sub> for Ho, ErP <sub>5</sub> O <sub>14</sub>
102	for Er, TmP <sub>5</sub> O <sub>14</sub> for Tm, YbP <sub>5</sub> O <sub>14</sub> for Yb, Y <sub>2</sub> SiO <sub>5</sub> for Y and Si, kyanite for Al, YVO <sub>4</sub> for V and pure
103	Sc for Sc. Element mapping was carried out using a JEOL JXA-8230 electron microprobe at the
104	State Key Laboratory of Continental Dynamics, Northwest University (China), with an accelerating
105	voltage of 15 kV, beam current of 50 nA and beam diameter of 2 $\mu$ m.
106	In-situ trace element analysis was undertaken at the State Key Laboratory of Continental
107	Dynamics, Northwest University (China). An Agilent 7900 ICP-MS coupled with RESOlution M-50

108 193–nm ArF Excimer Laser Ablation system was used to analyze mineral chemical compositions on 109 polished thin sections. He and Ar were mixed via a T–connector before entering the ICP. 110 International standard reference materials NIST SRM 610, NIST SRM 612, and BCR–2G were used 111 as external standards for calculations (Bao et al. 2016). The concentration of Si obtained by EPMA 112 was used as the internal standard for trace element content calculations. Data processing was 113 performed using ICPMSDataCal (Liu et al. 2008).

#### 114 **Crystal structure analysis**

A transparent single crystal  $(0.02 \times 0.015 \times 0.01 \text{ mm})$  was cut from the polished section on a doublefocused ion beam platform (TESCAN GAIA 3). This crystal was used for the subsequent X–ray diffraction study. X–ray powder and single–crystal diffraction were carried out at the Science Research Institute, China University of Geosciences, China, with a Rigaku Oxford diffraction XtaLAB PRO–007HF single crystal diffractometer equipped with a rotating anode microfocus X–ray

source (50 kV, 24 mA; MoK $\alpha$ ,  $\lambda$  = 0.71073 Å) and a hybrid pixel array detector. The crystal structure 120 determination and refinement process of wenlanzhangite-(Y) were performed using OLEX2-1.3 121 (Dolomanov et al. 2009). The structure model was solved with the SHELXT using intrinsic phasing 122 123 and refined by SHELXL with least square (Sheldrick 2015a, b). Since the crystal cell parameters obtained by X-ray single crystal diffraction were close to a monoclinic cell and different from those 124 125 of jingwenite-(Y), selected-area electron diffraction (SAED) analyses for wenlanzhangite-(Y) were undertaken to confirm the single crystal data. Experiments were performed using a JEM-2100 (HR) 126 Transmission Electron Microscope equipped with a double-tilt holder, a Gatan digital camera, and an 127 INCA Energy TEM100 energy-dispersive spectroscopy instrument at the Institute of Mineral 128 129 Resources, Chinese Academy of Geological Sciences, Beijing, operated at 200 kV. A TEM foil of 130 about 50 nm thickness was prepared on a FIB-SEM platform (TESCAN GAIA 3) at the analytical 131 laboratory of the Beijing Research Institute of Uranium Geology. Images of the foil and its location in polished section before cutting are shown in Fig. 3b. Results were successfully indexed with P-1 132 133 model and the calculated parameters are listed below.

#### 134 **Raman spectroscopy analysis**

Raman spectra of wenlanzhangite-(Y) were collected from a randomly oriented grain using a 135 Renishaw Invia confocal Raman spectrometer equipped with 50× objective at the State Key 136 Laboratory of Continental Dynamics, Northwest University, Xi'an, China. Raman spectra were 137 138 collected with an invia laser Raman spectrometer (Renishaw, UK) at 24 °C. The excitation 139 wavelength is 514.5 nm (semiconductor laser), and the output power of the laser was set at 100 mW with a Renishaw edge filter. The 50X objective on a Leica DM LM microscope was used, and a 140 grating with 1800 grooves/mm was selected. The spectral resolution (apparatus function) was ~3.0 141  $cm^{-1}$  determined by an emission spectrum from a neon lamp at ~918.6 cm<sup>-1</sup>. 142

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#### RESULTS

## 144 Optical, morphological, and physical properties of wenlanzhangite–(Y)

145	Wenlanzhangite-(Y) is translucent to transparent. Reflectance data are given in Table 1 and Figure 4.
146	The refractive index n of wenlanzhangite-(Y) is 2.17, which is calculated by N=Kd+1 (K values
147	from Mandarino 1981). The dispersion is medium with r $<$ v, and the pleochroism is with X = brown,
148	Y = dark brown, $Z = brown black$ . The a: b: c ratio from single-crystal X-ray diffraction data is
149	0.601: 0.968: 1. The colour, streak, lustre, and hardness (Mohs) are dark brown, yellow grey, vitreous,
150	and ~4, respectively. The cleavage is good and parallel to $\{110\}$ . The calculated density is 4.54 g/cm <sup>3</sup>
151	based on the empirical formula and unit cell volume determined from single crystal XRD data.

#### 152 Chemical composition

- 153 Wenlanzhangite-(Y) displays narrow ranges of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, Dy<sub>2</sub>O<sub>3</sub>, Er<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>, Yb<sub>2</sub>O<sub>3</sub>,
- 154  $Nd_2O_3$ , and  $Sm_2O_3$  contents, ranging from 16.07 to 16.63 wt%, 3.38 to 4.18 wt%, 18.55 to 19.59
- 155 wt%, 3.93 to 4.46 wt%, 2.42 to 3.11 wt%, 1.88 to 2.34 wt%, 2.18 to 2.74 wt%, 1.86 to 2.27 wt%, and 156 1.16-1.48 wt%, respectively. Sc<sub>2</sub>O<sub>3</sub>, Ho<sub>2</sub>O<sub>3</sub>, Ce<sub>2</sub>O<sub>3</sub>, Tb<sub>2</sub>O<sub>3</sub>, Tm<sub>2</sub>O<sub>3</sub> and Pr<sub>2</sub>O<sub>3</sub> contents are low with
- 157 0.15-0.66 wt%, 0.54-1.11 wt%, 0.26-0.50 wt%, 0.45-0.67 wt%, 0.38-0.80 wt%, and 0.08-0.28
- 158 wt%, respectively (Table 2). The average empirical formula, calculated on the basis of 8 cations per

is

- 159 formula unit (apfu),
- $160 \qquad (Y_{1.26}Dy_{0.17}Er_{0.11}Gd_{0.09}Yb_{0.09}Nd_{0.09}Sm_{0.06}Sc_{0.04}Ho_{0.03}Ce_{0.02}Tb_{0.02}Tm_{0.02}Pr_{0.01})_{\Sigma 2.00}(V^{3+}_{1.46}Al_{0.54})_{\Sigma 2.00}V^{4+}_{1.46}N^{3+}_{0.54})_{\Sigma 2.00}V^{4+}_{1.46}N^{3+}_{0.54}N^{3+}_{0.5}N^{3+}_{0.5}N^{3+}_{0.5}N^{3+}_{0.5}N^{3+}_{0.5}N$
- $_{2}(SiO_{4})_{2}O_{4}(OH)_{4}$ . The type and amount of OH were determined from bond–valence calculations of O
- atoms in the crystal structure, and the Raman spectrum of wenlanzhangite–(Y) (Fig. 5). As for total
- 163 REE and HREE contents, wenlanzhangite–(Y) has  $\sum \text{REE}$  concentrations of 2.50–2.98×10<sup>5</sup> ppm,
- 164 with Y/Ho ratios (16–19, mean= 18), and Eu/Eu\* (0.21–0.32, mean= 0.26) ratios (Fig. 6; Table S1).

#### 165 Crystal structure

166 Unit-cell parameters obtained from the single-crystal and selected-area electron using TEM 167 diffraction (Fig. 7) data are: a = 5.9632(7) Å, b = 9.599(1) Å, c = 9.9170(9) Å,  $\alpha = 90.033(8)^{\circ}$ ,  $\beta =$ 168 98.595(2)°,  $\gamma = 90.003(9)^{\circ}$ , and V = 561.28(10) Å<sup>3</sup>, and a = 5.948(1) Å, b = 9.616(1) Å, c = 9.916(1)169 Å,  $\alpha = 90.00(1)^{\circ}$ ,  $\beta = 98.35(1)^{\circ}$ ,  $\gamma = 90.00(1)^{\circ}$ , and V = 561.14(3) Å<sup>3</sup>, respectively. The X-ray

powder diffraction data are shown in Table S2. The initial crystal structure determination was 170 performed using OLEX2-1.3 (Dolomanov et al. 2009), and the refined structure model was solved 171 172 with the SHELXT2014/5 directly and subsequently by SHELXL2016/6 with least square refinement (Sheldrick 2015a, b). Although the single-crystal XRD data indicate two possible crystal structures, 173 174 P-1 and I2/a, the TEM results indicated that the SAED can only be indexed by a P-1 structure and not I2/a. The structure was therefore solved in space group P-1 (#2). Crystallographic data and 175 176 refinement statistics are given in Table 3. The occupancies of atoms are refined toward minimum  $R_1$ 177 and show good agreement with the measured chemical composition. For simplicity, only Y and Dy are considered in the refinement for rare earth elements (REE), since they are the first two major 178 elements according to microprobe analyses. The final atomic coordinates and displacement 179 180 parameters are listed in Table 4, and selected bond lengths in Table 5. The bond-valence sums of 181 atoms are presented in Table S3.

182 The structure of wenlanzhangite-(Y) is composed of a-axis-oriented chains of edge-sharing  $[VO_6]$  octahedra linked by insular  $[SiO_4]$  tetrahedra, leaving open channels occupied by rare earth 183 184 elements (Fig. 8). The octahedra could be divided into two types according to geometry. Type one  $([V1O_6] \text{ and } [V2O_6])$  are strongly distorted octahedra (DO) with respect to the major difference 185 between the shortest V–O distance ( $\approx 1.7$  Å) and the longest V–O distance ( $\approx 2.4$  Å). Type two 186 187 ([V3O<sub>6</sub>], [V4O<sub>6</sub>] and [V5O<sub>6</sub>]) are closer to regular octahedra (RO). Two different octahedra are distributed in different chains, respectively. Like the structure of jingwenite-(Y) (Liu et al. 2023), the 188 two types are dominated by  $V^{4+}$  in  $[V1O_6]$  and  $[V2O_6]$ , and by  $V^{3+}$  in  $[V3O_6]$ ,  $[V4O_6]$  and  $[V5O_6]$ 189 190 for wenlanzhangite-(Y). The [SiO<sub>4</sub>] tetrahedra share corners with two separate chains of RO and 191 share corners with two neighboring octahedra in the same chains of DO. Rare earth elements are 8coordinated and occupy open channels along the b-axis. Bond valence calculations show that 192 193 hydrogen atoms are attached with four oxygen atoms (O13, O14, O15, O16), leading to the ideal crystal chemical formula  $Y_2V^{3+}_2V^{4+}_2(SiO_4)_2O_4(OH)_4$ . The atomic occupancies for each site are 194

195 described below:

(1) V1 and V2 sites: These two sites are 6-coordinated. The bond valence calculations of 196 jingwenite–(Y) (Liu et al. 2023) have indicated that a similar site is dominated by  $V^{4+}$ . This situation 197 is consistent in wenlanzhangite-(Y). But, during the structure refinement of wenlanzhangite-(Y), 198 slightly weaker scatterers of X-rays than V are noticed at both sites, indicating that some 199 heterovalent Al<sup>3+</sup> can co-occupy the V1 and V2 sites. This is also confirmed by broadband 200 viscoelastic spectroscopy. The edge-sharing chains of  $[V^{4+}O_6]$  octahedra also occur in synthetic VO<sub>2</sub> 201 (C2/m) (Marezio et al. 1972) and VO<sub>2</sub> (P2<sub>1</sub>/c) (Longo and Kierkegaard 1970), in which V–O bond 202 lengths vary from 1.73 Å to 2.13 Å. 203

204 (2) V3, V4 and V5 sites: These three sites are 6–coordinated.  $V^{3+}$  and  $Al^{3+}$  are mixed in V5 205 sites and structure refinement result shows they are all dominated by  $V^{3+}$ .

(3) Si sites: there are two distinct Si positions, all tetrahedrally coordinated by oxygen anions.
 The average Si–O distances are 1.654 and 1.650 Å, which is longer than the normally observed range
 in silicates.

(4) **REE sites:** Y1 and Y2 sites are 8–coordinated and dominated by  $Y^{3+}$ . Dy3 and Dy4 sites are dominated by  $\Box$ , because they only possess 7.34 and 7.28 e<sup>-</sup>. They are recognized as trace amounts of Dy<sup>3+</sup> rather than Y<sup>3+</sup> due to the average bond length of Dy3–O being longer than either Y1–O or Y2–O. The small amounts of additional rare earths balance the valence state that is insufficient due to the substitution of Al<sup>3+</sup> for tetravalent elements (e.g., V<sup>4+</sup>).

Therefore, the crystal structure of wenlanzhangite–(Y) is sufficiently close to that of jingwenite–(Y) (Liu et al. 2023) that it should be classified within the same group of jingwenite–(Y)with a Dana classification number 52.4.10.2.

## 217 Raman spectrum

218 The Raman spectrum of wenlanzhangite–(Y) shows the bands of O–H stretching vibrations at 3572

219 cm<sup>-1</sup>, the bands of Si–O stretching vibrations at 829, 893, and 951 cm<sup>-1</sup>, and the bands of Al–O, V–O,

and Y–O vibrations in the range of 100–600  $\text{cm}^{-1}$  (Liu et al. 2023).

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## DISCUSSION

In contrast to jingwenite-(Y) with 21.65 wt% VO<sub>2</sub>, 4.04 wt% V<sub>2</sub>O<sub>3</sub>, and 10.85 wt% Al<sub>2</sub>O<sub>3</sub>, 222 wenlanzhangite-(Y) displays similar VO<sub>2</sub> (22.05–22.60 wt%) but higher V<sub>2</sub>O<sub>3</sub> (14.07–15.42 wt%) 223 and lower Al<sub>2</sub>O<sub>3</sub> (3.38–4.18 wt%) contents. Moreover, the crystal system, space group, and unit cell 224 225 of wenlanzhangite-(Y) are all distinct from those of jingwenite-(Y) (Table 6) (Fig. 8). The structure of jingwenite-(Y) is composed of *b*-axis-oriented chains of octahedra consisting of edge-sharing Al 226 (V, Fe)–O octahedra and V (Ti)–O octahedra linked by insular Si–O tetrahedra (Liu et al. 2023). In 227 the chains of Al-O octahedra, two alternative cation sites, All and Al2, share edges O4-O4 and O7-228 O7. Both sites are dominated by Al but with the incorporation of  $Fe^{3+}$  and  $V^{3+}$ , more in Al2 than in 229 All. On this basis, V mainly occurs as  $V^{4+}$  in jingwenite–(Y), while  $V^{3+}$  can substitute for  $Al^{3+}$  and 230  $Fe^{3+}$ . Both  $V^{3+}$  and  $V^{4+}$  are dominant cations in wenlanzhangite–(Y) with less  $Al^{3+}$  and  $Fe^{3+}$ . The 231 differences in space group and unit cell are the results of the splitting of V sites. Given the measured 232 variation in calculated  $V^{3+}/(V^{3+}+AI)$ , there is likely a solid-solution series extending from 233 endmember,  $Y_2Al_2V_2^{4+}(SiO_4)_2O_4(OH)_4$ , toward another endmember,  $Y_2V_2^{3+}V_2^{4+}(SiO_4)_2O_4(OH)_4$ . 234 Compositions across this solid solution are present in the zoned crystal shown in Fig. 3b, in which 235  $V^{3+}/(V^{3+}+Al+Fe^{3+})$ , ranges from 0.19 in jingwenite–(Y) up to 0.76 (equivalent to 1.53 a.p.f.u.  $V^{3+}$ ) in 236 wenlanzhangite-(Y) (Fig. 6b) (Tables 4 and S1). The observed intracrystal zoning is likely an 237 expression of an evolutionary process involving changes in the composition of hydrothermal fluid 238 239 and/or fluid parameters over time. Moreover, the structure of a V-enriched analogue of jingwenite-(Y),  $Y_2AIV^{3+}V^{4+}_2(SiO_4)_2O_4(OH)_4$ , has been determined in which the two nearly regular octahedra 240 sites are dominated by  $Al^{3+}$  and  $V^{3+}$ , respectively. 241

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# IMPLICATIONS

In general, V can be dissolved and transported in oxidized fluids as  $V^{5+}$ . In turn,  $V^{4+}$  and  $V^{3+}$  are

insoluble in hydrothermal fluids and preferentially partition into mineral phases (Fischer 1973; 244 Huang et al. 2015b). Thus, like HREE and U, V is also likely leached and transported as  $V^{5+}$  by 245 oxidized fluids, and then reduced to insoluble  $V^{4+}$  or  $V^{3+}$  upon contact with organic– and apatite–rich 246 beds in the overlying dolostone/limestone, precipitating and partitioned into jingwenite-(Y). The 247 presence of wenlanzhangite-(Y) as rims on normal jingwenite-(Y) indicates an evolution to a 248 relatively more reduced hydrothermal environment causing conversion, in which  $V^{5+}$  is reduced to 249  $V^{4+}$  and additional  $V^{3+}$ . This interpretation is also suggested by the higher Eu/Eu\* ratios in 250 wenlanzhangite-(Y) (Fig. 6c), as well as by the negative correlation between measured  $Fe^{3+}$  and 251 calculated V<sup>3+</sup>. Dissolution of Fe–Mn–rich particles or oxyhydroxides can lead to fractionation of Y 252 and Ho due to the higher marine particle-reactivity of Ho compared to Y (Bau et al. 1996). Fe-Mn 253 oxyhydroxides facilitate dissolution under anoxic conditions, yielding low Y/Ho ratios (<28) in 254 hydrothermal systems (Planavsky et al. 2010). Therefore, the lower Y/Ho ratios in wenlanzhangite-255 (Y) (Fig. 6c) can be interpreted as a response to greater volumes of Fe-Mn-rich oxyhydroxides in 256 257 dolostone/limestone and red sandstone dissolved in relatively reduced ore-forming fluids during fluid-rock reaction. All these observations suggest that wenlanzhangite-(Y) and jingwenite-(Y) have 258 259 great potential as proxies for tracing the redox state of ore-formation. Temperature and pressure 260 conditions of wenlanzhangite-(Y) formation are estimated to be 110-287 °C and 50 MPa, respectively, based on fluid-inclusion studies (Liu 1997; Jiang et al. 2016). 261

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## **FIGURE CAPTIONS**

- Fig 1. (a) Geological map of the Yushui deposit (after Huang et al., 2015a). (b) Geological cross
  section of the exploration line a–b (from Chen et al., 2021).
- Fig 2. (a) Stratigraphic column of the Yushui deposit. (b) Photograph of drillcore of red sandstone;
- 333 (c)–(e) Photographs of bedded orebody. (f) Photomicrograph of disseminated ore in red sandstone. (g)
- 334 Photograph of vein–style orebody in red sandstone. Bn–bornite; Cc–chalcocite; Ccp–chalcopyrite.
- **Fig 3**. Photomicrographs showing the occurrence and mineral association of wenlanzhangite–(Y) and
- 336 jingwenite-(Y) (Jw-Y). (a). Wenlanzhangite-(Y) (Wlz-Y) as a dark brown, 100 µm-thick core on
- 337 jingwenite–(Y) with bornite (Bn), roscoelite (Rcl), and thortveitite (Tv). (b) Back–scattered electron
- image of euhedral jingwenite-(Y) and wenlanzhangite-(Y) crystals with bornite, in reflected light,
- 339 parallel nicols. (c) and (d). EPMA element (Al and V) maps of the marked box shown in (b). Note
- 340 grain-scale compositional zoning in (b) reflecting variation from typical jingwenite–(Y), 341  $Y_2Al_2V^{4+}_2(SiO_4)_2O_4(OH)_4$ , to wenlanzhangite–(Y).
- Fig 4. Reflectance data for wenlanzhangite–(Y) in air. The reflectance values (R%) are plotted versus
  wavelength in nm.
- **Fig 5**. Raman spectra for wenlanzhangite–(Y).
- Fig 6. (a). Chondrite–normalized rare earth element (REE) fractionation patterns for jingwenite–(Y)
- and wenlanzhangite–(Y). (b). Y/(REE+Y+Sc) vs.  $V^{3+}/(V^{3+}+Al+Fe^{3+})$  ratio plot. (c). Eu/Eu\* vs. Y/Ho
- ratio plots for jingwenite–(Y) and wanlanzhangite–(Y).
- **Fig 7**. SAED patterns of wenlanzhangite–(Y) from 4 different zone axes.
- Fig 8. Crystal structure of wenlanzhangite-(Y) (a) and jingwenite-(Y) (b), plotted with VESTA
  (Momma and Izumi, 2011).
- 351

352	TABLE CAPTIONS
353	Table 1. Reflectance data for wenlanzhangite–(Y).
354	Table 2. Major-element data for wenlanzhangite-(Y) compared with jingwenite-(Y) (wt.%).
355	Table 3. Information on crystal and structural refinement for wenlanzhangite–(Y).
356	Table 4. Site, Wyckoff position (W.p.), site occupancy (s.o.), fractional atomic coordinates, and
357	equivalent isotropic (and anisotropic) displacement parameters (Å <sup>2</sup> ) for wenlanzhangite–(Y).
358	Table 5. Selected bond lengths (Å) for wenlanzhangite–(Y).
359	<b>Table 6.</b> Comparison between wenlanzhangite–(Y) and jingwenite–(Y).
360	SUPPLEMENTARY TABLE CAPTIONS
361	Table S1 REE contents in jingwenite–(Y) and wenlanzhangite–(Y) as determined by LA–ICP–MS.
362	Table S2. X-ray powder diffraction data (d in Å, I in %) for wenlanzhangite-(Y).
363	Table S3. Calculated bond valences (v.u.) for atoms in wenlanzhangite-(Y).
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Fig. 1 revision 2



ne sto ime omite/ 01 D



Fig. 2 revision 2





![](_page_20_Figure_0.jpeg)

![](_page_21_Figure_0.jpeg)

![](_page_22_Figure_0.jpeg)

1.0 (a) (apfu) (3.0 (apfu)) (+Sc) (apfu) 4T 0.6 V/REE+V 0.4 0.2 0.4 Yb 0.0  $0.2 0.4 0.6 0.8 V^{3+}/(V^{3+}+Al+Fe^{3+})$  (apfu) 0.2 0.0 Lu Fig. 6 revision 2

![](_page_22_Figure_2.jpeg)

![](_page_23_Picture_0.jpeg)

**(b)** Zone Axis: [111]  $X = 8.0^{\circ}$  $Y = 26.0^{\circ}$ Tx:8.0 Ty:26.0 Tx:7.7 Ty:2.3  $5 \, 1/nm$ **(d)** Zone Axis: [012]  $X = -9.5^{\circ}$  $Y = 0.4^{\circ}$ 111 Tx:-9.5 Ty:0.4 tx:7.5 ty:-20.4 <u>5 1/nm</u> Fig. 7 revision 2

![](_page_24_Figure_0.jpeg)

Fig. 8 revision 2

λ (nm)	R <sub>max</sub> (%)	R <sub>min</sub> (%)
400	11.7	11.5
420	12.2	12.0
440	12.5	12.4
460	12.6	12.5
470	12.7	12.5
480	12.8	12.6
500	12.8	12.6
520	12.8	12.7
540	12.9	12.8
546	12.9	12.8
560	13.0	12.8
580	13.0	12.8
589	13.0	12.9
600	12.9	12.8
620	12.9	12.7
640	13.0	12.7
650	13.0	12.7
660	13.0	12.7
680	13.0	12.7
700	13.2	12.7

 Table 1. Reflectance data for wenlanzhangite–(Y).

Constituent	Jw-Y	Wlz-Y-1	-2	-3	-4	-5	-6	-7	-8	-9	-10	Mean (Wlz-Y)
SiO <sub>2</sub>	16.45	16.48	16.25	16.24	16.10	16.07	16.61	16.63	16.38	16.50	16.55	16.38
$Al_2O_3$	10.85	3.53	3.71	3.38	3.67	3.45	4.18	3.96	3.80	3.89	3.69	3.73
$VO_2^*$	21.65	22.25	22.40	22.28	22.10	22.05	22.55	22.60	22.49	22.49	22.40	22.36
V <sub>2</sub> O <sub>3</sub> *	4.04	14.96	15.17	15.42	14.81	14.90	14.07	14.49	15.04	14.27	14.51	14.76
Fe <sub>2</sub> O <sub>3</sub>	0.89	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<>	<mdl< td=""></mdl<>
TiO <sub>2</sub>	1.83	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<>	<mdl< td=""></mdl<>
$Sc_2O_3$	<mdl< td=""><td>0.34</td><td>0.20</td><td>0.19</td><td>0.21</td><td>0.15</td><td>0.66</td><td>0.62</td><td>0.21</td><td>0.65</td><td>0.46</td><td>0.37</td></mdl<>	0.34	0.20	0.19	0.21	0.15	0.66	0.62	0.21	0.65	0.46	0.37
$Y_2O_3$	24.67	18.55	19.12	19.13	19.04	18.92	19.30	19.55	19.45	19.59	19.26	19.19
$Ce_2O_3$	<mdl< td=""><td>0.50</td><td>0.33</td><td>0.39</td><td>0.26</td><td>0.42</td><td>0.33</td><td>0.38</td><td>0.35</td><td>0.31</td><td>0.36</td><td>0.36</td></mdl<>	0.50	0.33	0.39	0.26	0.42	0.33	0.38	0.35	0.31	0.36	0.36
$Pr_2O_3$	<mdl< td=""><td>0.14</td><td>0.17</td><td>0.08</td><td>0.20</td><td>0.19</td><td>0.13</td><td>0.23</td><td>0.12</td><td>0.28</td><td>0.19</td><td>0.17</td></mdl<>	0.14	0.17	0.08	0.20	0.19	0.13	0.23	0.12	0.28	0.19	0.17
$Nd_2O_3$	0.03	2.19	1.97	1.91	1.98	2.08	1.86	2.11	2.10	2.00	2.27	2.05
$Sm_2O_3$	0.1	1.38	1.27	1.21	1.26	1.16	1.40	1.51	1.26	1.41	1.48	1.33
$Gd_2O_3$	0.69	2.20	1.96	1.96	1.95	1.93	2.22	2.27	1.88	2.34	2.25	2.09
$Tb_2O_3$	0.32	0.45	0.59	0.51	0.59	0.67	0.58	0.49	0.63	0.49	0.57	0.56
$Dy_2O_3$	3.25	4.35	4.29	4.40	4.07	4.25	4.12	3.97	4.46	3.93	4.17	4.20
Ho <sub>2</sub> O <sub>3</sub>	0.83	0.61	0.71	0.67	0.85	1.11	0.68	0.54	0.54	0.83	0.67	0.72
$Er_2O_3$	3.55	2.80	3.08	3.03	3.02	3.11	2.61	2.42	3.03	2.60	2.55	2.83
$Tm_2O_3$	0.6	0.80	0.61	0.71	0.56	0.50	0.78	0.66	0.38	0.71	0.71	0.64
$Yb_2O_3$	3.99	2.24	2.74	2.70	2.60	2.55	2.34	2.18	2.60	2.20	2.22	2.44
$Lu_2O_3$	2.4	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td><mdl< td=""></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""></mdl<></td></mdl<>	<mdl< td=""></mdl<>
H <sub>2</sub> O*	4.65	4.83	4.87	4.84	4.80	4.79	4.90	4.91	4.89	4.89	4.87	4.86
Total	101.23	98.58	99.43	99.04	98.05	98.32	99.33	99.51	99.59	99.37	99.19	99.04
	apfu				C	Calculated on b	asis of 8 catio	ns				
Sc	-	0.04	0.02	0.02	0.02	0.02	0.07	0.07	0.02	0.07	0.05	0.04
Y	1.54	1.22	1.25	1.26	1.27	1.26	1.26	1.27	1.27	1.28	1.26	1.26
Ce	-	0.02	0.01	0.02	0.01	0.02	0.01	0.02	0.02	0.01	0.02	0.02
Pr	-	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Nd	0.00	0.10	0.09	0.08	0.09	0.09	0.08	0.09	0.09	0.09	0.10	0.09
Sm	0.00	0.06	0.05	0.05	0.05	0.05	0.06	0.06	0.05	0.06	0.06	0.06
Gd	0.02	0.09	0.08	0.08	0.08	0.08	0.09	0.09	0.08	0.10	0.09	0.09
Tb	0.02	0.02	0.02	0.02	0.02	0.03	0.02	0.02	0.03	0.02	0.02	0.02
Dy	0.12	0.17	0.17	0.18	0.16	0.17	0.16	0.16	0.18	0.16	0.17	0.17

**Table 2.** Major-element data for wenlanzhangite–(Y) compared with jingwenite–(Y) (wt.%). Number of point analyses = 10.

Но	0.04	0.02	0.03	0.03	0.03	0.04	0.03	0.02	0.02	0.03	0.03	0.03
Er	0.14	0.11	0.12	0.12	0.12	0.12	0.10	0.09	0.12	0.10	0.10	0.11
Tm	0.02	0.03	0.02	0.03	0.02	0.02	0.03	0.03	0.01	0.03	0.03	0.02
Yb	0.14	0.08	0.10	0.10	0.10	0.10	0.09	0.08	0.10	0.08	0.08	0.09
Lu	0.08	-	-	-	-	-	-	-	-	-	-	-
Total (Sc,Y,REE)	2.13	1.98	1.99	1.99	1.99	2.01	2.01	2.01	1.99	2.04	2.02	2.00
Al	1.5	0.52	0.54	0.49	0.54	0.51	0.60	0.57	0.55	0.56	0.54	0.54
$V^{3+}$	0.38	1.49	1.50	1.53	1.48	1.50	1.38	1.42	1.48	1.40	1.43	1.46
Fe	0.08	-	-	-	-	-	-	-	-	-	-	-
Total (Al,V,Fe) <sup>3+</sup>	1.96	2.01	2.04	2.02	2.02	2.00	1.98	1.99	2.03	1.97	1.97	2.00
$V^{4+}$	1.84	2	2	2	2	2	2	2	2	2	2	2.00
Ti	0.16	-	-	-	-	-	-	-	-	-	-	-
Total (V,Ti) <sup>4+</sup>	2	2	2	2	2	2	2	2	2	2	2	2.00
Si	2	2.02	1.98	1.98	1.98	1.98	2.01	2.00	1.98	2.00	2.01	2.00
V <sup>3+</sup> /(V+Fe+Al) <sup>3+</sup>	0.19	0.74	0.74	0.76	0.73	0.75	0.70	0.71	0.73	0.71	0.73	0.73
Y/(REE+Y+Sc)	0.72	0.62	0.63	0.63	0.63	0.63	0.63	0.63	0.64	0.63	0.63	0.63

\*The VO<sub>2</sub> and V<sub>2</sub>O<sub>3</sub> contents were calculated based on the basis that  $V^{4+}$  is ideally 2 apfu.

\*\*The  $H_2O$  content was calculated on the basis of stoichiometry (i.e., OH = 4 apfu).

<mdl means below the minimum detection limit. Data for jingwenite-(Y) (Jw-Y) from Liu et al. (2023).

Crystal data	
Ideal chemical formula	Y <sub>2</sub> V <sup>3+</sup> <sub>2</sub> V <sup>4+</sup> <sub>2</sub> (SiO <sub>4</sub> ) <sub>2</sub> O <sub>4</sub> (OH) <sub>4</sub>
Crystal size/mm	$0.02\times0.01\times0.005$
Crystal system	Triclinic
Space group	<i>P</i> -1 (#2)
	a = 5.9632(7) Å
	b = 9.5990(10) Å
Unit cell dimensions	c = 9.9170(9)  A
	$\alpha = 90.033(8)^{\circ}$
	p = 98.393(9) $y = 90.003(9)^{\circ}$
Volume	561 28(10)Å <sup>3</sup>
Z	2
Density (calculated)	$4.54 \text{ g/cm}^3$
Data collection and refinemen	t
Instrument	Rigaku-Oxford diffraction XtaLAB PRO-007
Radiation, wavelength, temper	rature MoKα, 0.71073, 293(2) K
2θ range (°)	5.938 to 58.414
$\mu / mm^{-1}$	14.448
<i>F</i> (000)	676
Total reflections	6438
Unique ref (all)	2583
Unique ref [ $I \ge 2\sigma(I)$ ]	1998
R <sub>int</sub>	0.0494
$R_{\sigma}$	0.0587
Range of <i>h</i> , <i>k</i> , <i>l</i>	$-8 \le h \le 8; -12 \le k \le 13; -12 \le l \le 13$
$R_{1,} w R_2 [I \ge 2\sigma(I)]$	$R_1 = 0.0736, wR_2 = 0.1813$
$R_{1,} w R_{2}$ [all data]	$R_1 = 0.0944, wR_2 = 0.1949$
Goodness-of-fit	1.090
No. of parameters, restraints	244, 19
Max./min. residual peak (e Å <sup>-</sup>	<sup>3</sup> ) 5.51/-2.90

**Table 3**. Information on crystal and structural refinement for wenlanzhangite-(Y).

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$								
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Sites	W.p.	x	У	Z	S	.0.	$U_{ m eq}$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Y1	2 <i>i</i>	0.56987(12)	0.49227(8)	0.31186(8)	0.70(2)Y+	0.312(15)Dy	0.0127(3)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Y2	2 <i>i</i>	-0.16344(13)	-0.00777(9)	0.31188(8)	0.74(2)Y+	0.273(15)Dy	0.0135(3)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Dy3	2 <i>i</i>	0.092(4)	0.492(2)	0.312(2)	0.02	21(3)	0.009(9)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Dy4	2 <i>i</i>	0.678(4)	0.004(3)	0.690(3)	0.02	26(4)	0.028(9)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	V1	2 <i>i</i>	0.3986(3)	0.2206(2)	0.4849(2)	0.84(3)V	+0.16(3)Al	0.0145(7)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	V2	2 <i>i</i>	0.9063(3)	0.2786(2)	0.5143(2)	0.82(3)V	+0.18(3)Al	0.0145(8)
V41a1010.93(4)V+0.07(4)Al0.0110(9)V51d0.5010.52(3)V+0.48(4)Al0.0134(12)Si12i0.0503(5)0.2859(3)0.2177(3)10.0144(8)Si22i0.6914(5)0.2111(3)0.7817(3)10.0135(8)Ol2i0.4475(12)0.1776(8)0.6845(8)10.0135(17)O32i0.0317(13)0.1216(8)0.1701(8)10.0145(16)O42i0.6976(13)0.3761(8)0.8303(9)10.0194(18)O52i0.8992(12)0.1828(8)0.6919(8)10.0157(17)O72i0.7286(12)0.1098(9)0.9162(8)10.0163(17)O82i0.0206(12)0.3882(8)0.0814(8)10.0155(17)O92i0.1051(12)0.1231(9)0.4738(9)10.0191(18)O102i1.1332(14)0.3827(9)0.5582(9)10.0220(19)O112i0.648(14)0.1151(9)0.4396(9)10.0157(17)O122i0.6048(14)0.1151(9)0.4396(9)10.0152(17)O152i0.5490(13)0.1142(9)1.1570(9)10.0217(18)O132i-0.4808(12)0.3955(8)0.0056(8)10.0152(17)O152i0.5490(13)0.1142(9)1.1570(9)10.0212(19)O162i-0.2182(12)0.6092(9)0.1566(9)1	V3	2 <i>i</i>	-0.2457(3)	0.4960(2)	-0.0029(2)	0.83(3)V	+0.17(3)Al	0.0154(8)
V51d0.5010.52(3)V+0.48(4)A10.0134(12)Si12i0.0503(5)0.2859(3)0.2177(3)10.0144(8)Si22i0.6914(5)0.2111(3)0.7817(3)10.0135(8)O12i0.4475(12)0.1776(8)0.6845(8)10.0135(16)O22i-0.1465(11)0.3203(8)0.3151(8)10.0153(17)O32i0.0317(13)0.1216(8)0.1701(8)10.0145(16)O42i0.6976(13)0.3761(8)0.8303(9)10.0194(18)O52i0.8992(12)0.1828(8)0.6919(8)10.0139(16)O62i0.3007(11)0.3136(8)0.3097(8)10.0157(17)O72i0.7286(12)0.1098(9)0.9162(8)10.0155(17)O82i0.0206(12)0.3882(8)0.0814(8)10.0155(17)O92i0.1051(12)0.1231(9)0.4738(9)10.0160(17)O122i0.6172(13)0.3729(8)0.5260(8)10.0160(17)O122i0.6048(14)0.1151(9)0.4396(9)10.0217(18)O132i-0.4808(12)0.3955(8)0.0855(8)10.0152(17)O142i0.2327(12)0.1065(9)0.9144(8)10.0152(17)O152i0.5490(13)0.1142(9)1.1570(9)10.0212(19)O162i-0.2182(12)0.6092(9)0.1566(9)	V4	1 <i>a</i>	1	0	1	0.93(4)V	+0.07(4)Al	0.0110(9)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	V5	1d	0.5	0	1	0.52(3)V	+0.48(4)Al	0.0134(12)
Si22i0.6914(5)0.2111(3)0.7817(3)10.0135(8)O12i0.4475(12)0.1776(8)0.6845(8)10.0136(16)O22i-0.1465(11)0.3203(8)0.3151(8)10.0153(17)O32i0.0317(13)0.1216(8)0.1701(8)10.0145(16)O42i0.6976(13)0.3761(8)0.8303(9)10.0194(18)O52i0.8992(12)0.1828(8)0.6919(8)10.0137(17)O72i0.7286(12)0.1098(9)0.9162(8)10.0163(17)O72i0.0206(12)0.3882(8)0.0814(8)10.0155(17)O92i0.1051(12)0.1231(9)0.4738(9)10.0191(18)O102i1.1332(14)0.3827(9)0.5582(9)10.0220(19)O112i0.6172(13)0.3729(8)0.5260(8)10.0157(17)O122i0.6048(14)0.1151(9)0.4396(9)10.0217(18)O132i-0.4808(12)0.3955(8)0.855(8)10.0152(17)O142i0.2327(12)0.1065(9)0.9144(8)10.0152(17)O152i0.5490(13)0.1142(9)1.1570(9)10.0212(19)O162i-0.2182(12)0.6092(9)0.1566(9)10.0185(18)Y10.0129(5)0.023(5)0.0056(4)-0.0012(3)0.0037(3)-0.0011(17)Y20.0139(15)0.0216(6)0.0	Si1	2 <i>i</i>	0.0503(5)	0.2859(3)	0.2177(3)		1	0.0144(8)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Si2	2 <i>i</i>	0.6914(5)	0.2111(3)	0.7817(3)		1	0.0135(8)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	01	2 <i>i</i>	0.4475(12)	0.1776(8)	0.6845(8)		1	0.0136(16)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	02	2 <i>i</i>	-0.1465(11)	0.3203(8)	0.3151(8)		1	0.0153(17)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	03	2 <i>i</i>	0.0317(13)	0.1216(8)	0.1701(8)		1	0.0145(16)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	04	2 <i>i</i>	0.6976(13)	0.3761(8)	0.8303(9)		1	0.0194(18)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	05	2 <i>i</i>	0.8992(12)	0.1828(8)	0.6919(8)		1	0.0139(16)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	06	2 <i>i</i>	0.3007(11)	0.3136(8)	0.3097(8)		1	0.0157(17)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	07	2 <i>i</i>	0.7286(12)	0.1098(9)	0.9162(8)		1	0.0163(17)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	08	2 <i>i</i>	0.0206(12)	0.3882(8)	0.0814(8)		1	0.0155(17)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	09	2 <i>i</i>	0.1051(12)	0.1231(9)	0.4738(9)		1	0.0191(18)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	O10	2 <i>i</i>	1.1332(14)	0.3827(9)	0.5582(9)		1	0.0220(19)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	011	2 <i>i</i>	0.6172(13)	0.3729(8)	0.5260(8)		1	0.0160(17)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	012	2 <i>i</i>	0.6048(14)	0.1151(9)	0.4396(9)		1	0.0217(18)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	013	2 <i>i</i>	-0.4808(12)	0.3955(8)	0.0855(8)		1	0.0157(17)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	014	2 <i>i</i>	0.2327(12)	0.1065(9)	0.9144(8)		1	0.0152(17)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	015	2 <i>i</i>	0.5490(13)	0.1142(9)	1.1570(9)		1	0.0212(19)
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	016	2 <i>i</i>	-0.2182(12)	0.6092(9)	0.1566(9)		1	0.0185(18)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	lites	$U^{11}$	$U^{22}$	$^2$ $U$	<sub>7</sub> 33	$U^{23}$	$U^{13}$	$U^{12}$
Y2 $0.0139(5)$ $0.0216(6)$ $0.0067(5)$ $-0.0009(3)$ $0.0069(3)$ $-0.0014(6)$ V1 $0.0137(11)$ $0.0251(14)$ $0.0053(10)$ $0.0018(8)$ $0.0033(7)$ $-0.0057(6)$ V2 $0.0142(11)$ $0.0251(14)$ $0.0059(11)$ $0.0031(8)$ $0.0069(7)$ $0.0062(8)$ V3 $0.0118(12)$ $0.0276(16)$ $0.0077(13)$ $-0.0001(10)$ $0.0049(8)$ $-0.0020(6)$ V4 $0.0111(14)$ $0.0174(17)$ $0.0056(14)$ $0.0001(10)$ $0.0046(9)$ $0.0001(10)$ V5 $0.0121(18)$ $0.019(2)$ $0.0106(19)$ $0.0021(14)$ $0.0061(12)$ $0.0005(11)$ Si1 $0.0125(15)$ $0.0213(17)$ $0.0106(15)$ $-0.0026(12)$ $0.0055(11)$ $-0.0016(16)$ Si2 $0.0139(15)$ $0.0213(17)$ $0.0063(14)$ $0.0004(12)$ $0.0050(11)$ $0.0000(11)$ O1 $0.015(3)$ $0.021(4)$ $0.006(3)$ $-0.002(3)$ $0.007(3)$ $-0.004(3)$ O2 $0.007(3)$ $0.028(5)$ $0.011(4)$ $0.004(3)$ $0.006(3)$ $-0.001(3)$ O3 $0.026(4)$ $0.014(4)$ $0.005(4)$ $0.002(3)$ $0.006(3)$ $-0.001(3)$	Y1	0.0129	0(5) $0.0202$	3(5) 0.00	56(4) -0	0.0012(3)	0.0037(3)	-0.0011(3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Y2	0.0139	0(5) 0.0210	5(6) 0.00	67(5) -0	.0009(3)	0.0069(3)	-0.0014(3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	V1	0.0137	(11) 0.0251	(14) 0.005	<b>3</b> (10) 0	.0018(8)	0.0033(7)	-0.0057(8
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	V2	0.0142	(11) 0.0251	(14) 0.005	<b>59(11)</b> 0.	.0031(8)	0.0069(7)	0.0062(8
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	V3	0.0118	(12) 0.0276	(16) 0.007	-0.	.0001(10)	0.0049(8)	-0.0020(8
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	V4	0.0111	(14) 0.0174	(17) 0.005	6(14) 0.	0001(10)	0.0046(9)	0.0001(1
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	V5	0.0121	(18) 0.019	(2) 0.010	06(19) 0.0	0021(14)	0.0061(12)	0.0005(12
Si20.0139(15)0.0213(17)0.0063(14)0.0004(12)0.0050(11)0.0000(1O10.015(3)0.021(4)0.006(3)-0.002(3)0.007(3)-0.004(3)O20.007(3)0.028(5)0.011(4)0.004(3)0.006(3)0.001(3)O30.026(4)0.014(4)0.005(4)0.002(3)0.006(3)-0.001(3)	Sil	0.0125	(15) 0.0213	(17) 0.010	06(15) -0.	.0026(12)	0.0055(11)	-0.0016(1
O10.015(3)0.021(4)0.006(3)-0.002(3)0.007(3)-0.004(3)O20.007(3)0.028(5)0.011(4)0.004(3)0.006(3)0.001(3)O30.026(4)0.014(4)0.005(4)0.002(3)0.006(3)-0.001(3)	Si2	0.0139	(15) 0.0213	(17) 0.006	53(14) 0.	0004(12)	0.0050(11)	0.0000(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	01	0.015	(3) 0.021	(4) 0.00	)6(3) -(	0.002(3)	0.007(3)	-0.004(3
$O_3 = 0.026(4) = 0.014(4) = 0.005(4) = 0.002(3) = 0.006(3) = -0.001(3)$	02	0.007	(3) 0.028	(5) 0.01	1(4) 0	).004(3)	0.006(3)	0.001(3)
	03	0.026	(4) 0.014	(4) 0.00	05(4) 0	).002(3)	0.006(3)	-0.001(3

**Table 4.** Site, Wyckoff position (*W.p.*), site occupancy (s.o.), fractional atomic coordinates and equivalent isotropic (and anisotropic) displacement parameters ( $Å^2$ ) for wenlanzhangite-(Y).

O4	0.026(4)	0.017(4)	0.015(4)	0.003(3)	0.004(3)	0.005(3)
O5	0.020(4)	0.018(4)	0.006(3)	-0.003(3)	0.007(3)	-0.001(3)
O6	0.009(3)	0.029(5)	0.009(4)	0.000(3)	0.004(3)	0.002(3)
07	0.017(4)	0.027(5)	0.006(4)	-0.001(3)	0.004(3)	0.000(3)
08	0.012(3)	0.021(4)	0.015(4)	-0.002(3)	0.006(3)	-0.001(3)
09	0.019(4)	0.021(4)	0.018(4)	0.008(4)	0.005(3)	0.000(3)
O10	0.028(4)	0.026(5)	0.011(4)	0.003(3)	0.000(3)	-0.004(3)
011	0.025(4)	0.017(4)	0.007(4)	0.001(3)	0.006(3)	0.001(3)
O12	0.027(4)	0.027(5)	0.013(4)	-0.001(3)	0.011(3)	0.002(3)
013	0.013(3)	0.019(4)	0.016(4)	-0.003(3)	0.004(3)	-0.001(3)
O14	0.012(3)	0.028(5)	0.007(4)	-0.001(3)	0.006(3)	0.002(3)
015	0.019(4)	0.034(5)	0.011(4)	-0.007(4)	0.003(3)	-0.005(3)
O16	0.017(4)	0.029(5)	0.012(4)	-0.008(3)	0.010(3)	0.001(3)

Y1 Dy1–O2 <sup>1</sup>	2.360(7)	Y2 Dy2–O1 <sup>4</sup>	2.355(7)	Dy3–O2	2.18(2)
Y1 Dy1–O4 <sup>2</sup>	2.336(8)	Y2 Dy2–O3	2.316(7)	$Dy3-O4^2$	2.39(2)
Y1 Dy1–O6	2.347(8)	Y2 Dy2–O5 <sup>5</sup>	2.308(7)	Dy3–O6	2.12(2)
Y1 Dy1–O10 <sup>3</sup>	2.357(8)	Y2 Dy2–O9 <sup>4</sup>	2.376(8)	Dy3–O8	2.47(2)
Y1 Dy1–O11 <sup>2</sup>	2.457(8)	Y2 Dy2-O9	2.439(8)	$Dy3-O10^2$	2.33(2)
Y1 Dy1-O11	2.392(8)	Y2 Dy2–O12 <sup>6</sup>	2.330(8)	Dy3–O10 <sup>6</sup>	2.63(2)
Y1 Dy1–O13 <sup>1</sup>	2.406(8)	Y2 Dy2–O14 <sup>4</sup>	2.413(8)	Dy3–O11 <sup>2</sup>	2.54(2)
Y1 Dy1–O16 <sup>1</sup>	2.411(8)	Y2 Dy2–O15 <sup>7</sup>	2.426(9)	Dy3016	2.49(2)
<y1 dy1-o></y1 dy1-o>	2.383	<y2 dy2–o></y2 dy2–o>	2.370	<dy3–o></dy3–o>	2.39
Dy4–O1	2.15(2)	V1 Al1-O1	2.001(8)	$V2 A12-O2^1$	1.994(8)
$Dy4-O3^5$	2.38(3)	V1 A11-O6	1.963(8)	V2 A12-O5	1.993(8)
Dy4–O5	2.16(3)	V1 A11-O9	1.973(8)	$V2 A12-O9^1$	1.984(8)
Dy4–O7	2.44(3)	V1 A11–O10 <sup>6</sup>	2.407(9)	V2 Al2-O10	1.686(9)
Dy4–O9 <sup>5</sup>	2.53(3)	V1 A11-O11	1.961(8)	V2 Al2-O11	1.966(8)
Dy4-012	2.67(3)	V1 A11-O12	1.704(9)	V2 A12-O12	2.418(9)
$Dy4-O12^{5}$	2.27(3)	<v1 al1-o></v1 al1-o>	2.002	<v2 al2–o></v2 al2–o>	2.007
Dy4–O15 <sup>8</sup>	2.46(3)				
<dy4–o></dy4–o>	2.38				
7		5		0	
V3 Al3–O4′	2.001(9)	V4 Al4–O3 <sup>5</sup>	2.036(8)	V5 A15–O7 <sup>8</sup>	2.000(8)
V3 A13–O8	1.974(8)	V4 A14–O3	2.036(8)	V5 A15–O7	2.000(8)
V3 Al3–O89	1.989(8)	V4 Al4–O7	2.005(7)	V5 A15–O14 <sup>8</sup>	1.976(7)
V3 Al3-O13	2.009(8)	V4 Al4–O7 <sup>12</sup>	2.005(7)	V5 A15–O14	1.976(7)
V3 Al3–O13 <sup>10</sup>	2.004(7)	V4 Al4–O14 <sup>8</sup>	2.011(8)	V5 A15–O15	1.890(8)
V3 Al3-O16	1.906(8)	$V4 Al4-O14^1$	2.011(8)	V5 A15–O15 <sup>8</sup>	1.890(8)
<v3 al3–o></v3 al3–o>	1.981	<v4 al4–o></v4 al4–o>	2.017	<v5 al5-o></v5 al5-o>	1.955
0.1 0.2	1 ((1(0))	C'A 01	1 (50(0)		
Si1-02	1.661(8)	S12-01	1.652(8)		
S11-03	1.645(8)	S12–O4	1.654(9)		
S11-06	1.651(8)	S12-05	1.653(8)		
S11-O8	1.659(9)	S12-07	1.639(8)		
<si1-0></si1-0>	1.654	<si2–o></si2–o>	1.650		

**Table 5.** Selected bond lengths (Å) for wenlanzhangite-(Y).

Symmetry codes: (i)1+X,+Y,+Z; (ii) 1-X,1-Y,1-Z; (iii) 2-X,1-Y,1-Z; (iv) -X,-Y,1-Z; (v) 1-X,-Y,1-Z; (vi)-1+X,+Y,+Z; (vii)-1+X,+Y,+Z; (vii) 1-X,-Y,2-Z; (ix) -X,1-Y,-Z; (x) -1-X,1-Y,-Z; (xi) 1+X,+Y,1+Z; (xii) 2-X,-Y,2-Z

	Jingwenite-(Y)	Wenlanzhangite-(Y)
Ideal Formula	$Y_2Al_2V_{2}^{4+}(SiO_4)O_4(OH)_4$	$Y_2V_2^{3+}V_2^{4+}(SiO_4)_2O_4(OH)_4$
Ζ	4	2
Crystal System	Monoclinic	Triclinic
Space Group	<i>I</i> 2/ <i>a</i> (#15)	<i>P</i> -1 (#2)
$V^{3+}/(V^{3+}+Al+Fe^{3+})$	0.19	0.58-0.72 (mean = $0.67$ )
		a = 5.9632(7)Å
	a = 9.4821(2)Å	b = 9.599(1)  Å
	b = 5.8781(1) Å	c = 9.9170(9) Å
Unit-cell parameters	c = 19.3987(4) Å	$\alpha = 90.033(8)^{\circ}$
	$\beta = 90.165(2)^{\circ}$	$\beta = 98.595(9)^{\circ}$
	V=1081.21(4) Å <sup>3</sup>	$\gamma = 90.003(9)^{\circ}$
		$V = 561.28(10) \text{ Å}^3$
Reference	Liu et al. (2023)	This study

Table 6. Comparison between wenlanzhangite-(Y) and jingwenite-(Y)