S1–24

Crystal Structure Determined of Micron "Jixianite" and Redefinition of a New Mineral "Hydroelsmoreite"

Li Guowu [1, 2*], *Xue Yuan* [1], *Yang Guangming*[2]
[1] Scientific research institute crystal structure laboratory, China University of Geosciences (Beijing) Beijing, China, 100083;
[2] State Key Laboratory of geological process and mineral resources, China University of Geosciences, Beijing & Wuhan, China
Email: liguowu@cugb. edu. cn

Summary

"Jixianite" is a new mineral that was found in Nanhe tungsten deposit in Jixian County, Hebei, China, in 1979. It is an oxide containing W, Pb components, and was approved as a new mineral by the IMA–CNMNC at that time. However, because of its fine crystallization, its crystal structure was not obtained. According to the powder diffraction data, the diffraction characteristics was similar to that of pyrochloresuper group minerals, so it was classified as a pyrochlore group mineral containing W and Pb. In 2010, based on the proposed new scheme of nomenclature for the pyrochloresuper group, approved by the IMA –CNMNC, "jixianite" was listed as a discredited mineral. Recently we've got the typical material specimens. A 1.2kw high power microfocus rotating anode X–ray source (Mo Kα) and a hybrid pixel array detector single crystal diffractometer (XtaLAB PRO–007HF) were used for the structure investigation, and the single crystal diffraction data were obtained with a small crystal which is less than 10 micron. The crystal structure research results (R=0.02) show that the mineral was a cubic system, the lattice parameters a=10.342 1(5)Å, space group F*d*–3*m*, Z=8, and the crystal structure belongs to the pyrochlore–type structure. W is [6]–coordinated (site *16c*), located at the center of octahedron, with a W–O bond length of 1.941Å. Pb as a large cation is [8]–coordinated (site 16d), distributed in the channel, and the Pb–O bond length is 2.239Å.Some H_2O occupies the site of Pb while the others occupies the Y site (site*8b*). So "jixianite" is still a pyrochloresupe rgroup mineral. The ideal end member formula is $(H_2O, Pb)_2(W, Fe)_2O_6(H_2O)$ by the crystal structure and composition analysis. It belongs to the elsmoreite group mineral of pyrochloresuper group, and this new mineral can be renamed as "hydroelsmoreite".

Keywords: Jixianite; Crystal Structure; Hydroelsmoreite

1. Introduction

In 1979, a new oxide mineral containing Pb, W was found in Yanhe tungsten deposit of Jixian County, Hebei Province, China, which was named "Jixianite" according to the place of discovery (Liu, 1979). It was approved as a new mineral by IMA–CNMNC at that time, but its crystal structure could not be obtained because of its small crystal size. According to the powder crystal diffraction data, the diffraction characteristics are similar to those of the pyrochlore group minerals, so they are classified as the W–bearing pyrochlore group minerals. However, Atencio et.al. (2010) presented a new scheme of nomenclature for the pyrochloresuper group (Atencio, *et.al*, 2010), and the "jixianite" was listed as a discredited mineral. Mr. Liu Jianchang, who is the original discoverer of "jixianite", provided the prototype mineral specimens. In this paper, Rigaku oxford diffraction XtaLAB PRO–007HF single crystal diffractometer with a rotating anode microfocus X–ray source (1.2kW Mo*Kα* λ = 0.710 73Å) and hybrid pixel array detector, has been used to studied crystal structure. The mineral has been studied in mineralogy and the new mineral has been redetermined. According to the present classification scheme, the proposed name is "hydroelsmoreite", which needs the formal approval by IMA–CNMNC to be effective.

2. Crystal sturcutre

Samples for determine Crystal structures are about 10 microns of crystals isolated from aggregates, wrapped in vaseline and stuck in the Kepler model. The single crystal diffraction data was performed on the Rigaku oxford diffraction XtaLAB PRO–007HF single crystal diffractometer. The test conditions were as: 50kV, 24mA microfocus X source (Mo*Kα* *λ*=0.710 73Å), hybrid pixel array detector, the exposure time is 100s per frame. The global data of $-14<h<13$, $-14<k<14$, $-14<l<14$ were obtained. The structure was determined by direct method using shelxs. The structure was refined by shelxl, and finally *R* 0. 02. The results show that the mineral was a cubic system, the lattice parameters a=10.3421(5) Å, space group Fd–3m, *Z*=8, and the crystal structure belongs to the pyrochlore–type structure (Fig. 1). W is [6]–coordinated (site *16c*), located at the center of octahedron, with a W–O bond length of 1.941Å. Pb as a large cation is [8]–coordinated (site 16d), distributed in the channel, and the Pb–O bond length is 2.239Å. It is found that the occupancy of Pb is relatively low (the occupation is only 0.3) in the structural refinement, and the electron probe analysis results also show that the apfu of Pb is low, which is not enough to be the dominant component. Some of the H_2O occupy the crystal chemical position of Pb, and the other of H_2O occupies the *Y* site (*8b*).

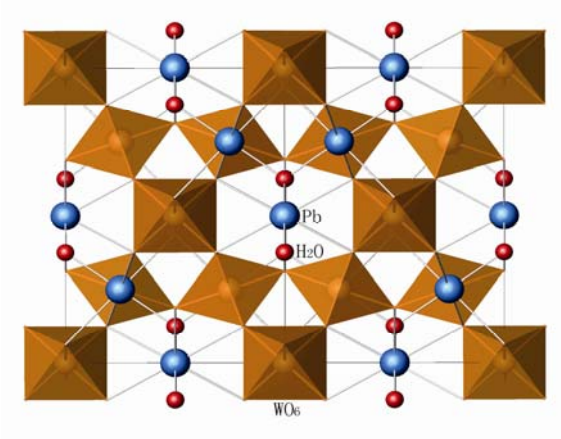

Figure 1. Crystal structure of "jixianite" viewed along the [110]

3. Redefinition of a new mineral "hydroelsmoreite"

By the crystal structure of the mineral "jixianite" proves that the mineral is still a new mineral of the pyrochloresuper group. The general chemical formula of the pyrochloresuper group is $A_{2-x}B_2O_6Y$, in which the *B* site cation is W, and it is elsmoreite group. However, in order to confirm the classification and naming of the new mineral, it is necessary to determine the dominant component at *A*site and the form of water.

Chemical analysis results are as shown in table 1, in which the PbO 19.77–24.49%, average 22.7%, calculate Pb*apfu* is 0.58. Obviously Pb is not the dominant component. The infrared spectrum analysis shows that 3 530cm^{-1} is H_2O–stretching vibrations, and 1 644cm^{-1} is H_2O – bending vibrations. H_2O is located at both *Y* site and *A* site. Base on B = 2 calculate the molecular formula as follows:

$((H_2O)_{1.11}Pb_{0.58}Ce^{3+}_{0.06}Sr_{0.05}Na_{0.05}Ca_{0.04}\sum_{0.11})_{\sum 2.00}(W_{1.48}Fe^{3+}_{0.49}Al_{0.02}Zr_{0.01})_{\sum 2.00}O_6(H_2O)$, simplified formula is $(H_2O, Pb)_2(W, Fe)_2O_6(H_2O)$

Table 1. Chemical components by the electron probe analysis

Constituent	Wt %	Range	Deviation
MgO	0.01	0–0.03	0.01
Na_2O	0.27	0.05–0.38	0.09
WO_3	59.82	52.72–63.23	3.22
PbO	22.70	19.77–27.49	2.23
SrO	0.95	0.88–1.08	0.06
Al_2O_3	0.20	0–0.75	0.30
FeO	6.75	4.53–11.11	2.25
K_2O	0.04	0–0.11	0.03
MnO	0.04	0–0.11	0.04
CaO	0.43	0.1–0.62	0.16
Ta_2O_5	0.09	0–0.4	0.13
ZrO_2	0.27	0.09–0.39	0.08
Ce_2O_3	1.67	1.18–2.08	0.29
Nb_2O_5	0.09	0–0.18	0.07
Total	93.34	92.11–94.5	0.79
H_2O	6.66	5.5–7.89	0.79

4. Discussion and Conclusion

(i) The chemical composition analysis results are different from that of the 1979, in that the wet chemical result PbO in 1979 is 38.72%. But the PbO measured by the electron probe analysis is on low, with the average value of 20 points being 25.59% (two grains). It is obvious that the main element Pb at *A* sites for the *apfu* value is not dominant and can only be replaced by H_2O!

(ii) The "single mineral" sample of this microsize mineral aggregate is at least 200mg for the wet quantitative analysis. It seems that the purity of the sample is difficult to guarantee. It has been tested by using powder diffraction and electron probe analysis, wulfenite ($PbMoO_4$) and stolzite ($PbWO_4$) are found to be very similar to this mineral under binocular microscope, so the mixing of these minerals leads to the chemical composition that Pb is too high in the "Jixianite".

(iii) The IR results showed that the form of water was H_2O, which was verified by structure determination. According to the results of single crystal diffraction and electron probe analysis, the mineral is determined to be *A* site H_2O >Pb, and H_2O is dominant. According to the pyrochloresuper group classification scheme, the original "jixianite" was renamed as "hydroelsmoreite". At present, checklist has been prepared and submitted to IMA–CNMNC for proposal.

(iv) The water form in the mineral is a neutral H_2O, and in theory W_2O_6 is valence equilibrium. In order for Pb^{+2} to enter the structure, Fe^{+3} must replace W^{+6}. The substitution relation is $(H_2O)_{1.5x-1}Pb_{3-1.5x}(W_xFe^{+3}_{2-x})O_6H_2O$, when x>1.43, the (H_2O) >Pb, the mineral is "hydroelsmoreite". When x<1.43, the (H_2O)<Pb, mineral is "hydroplumelsmoreite". The results of electron probe examination show that most of the minerals are "hydroelsmoreite". Only a few particles are "hydroplumelsmoreite".

Acknowledgment

We are grateful to Liu Jianchang for providing typical material specimens and to Ge Xiangkun for composition analysis. This work was financially supported by the National Natural Science Foundation of China (41672043).

Refferences

1. Liu Jianchang, Jixianite, 1979. Pb(W, Fe^{3+})$_2$(O, OH), A new tungsten mineral, *Acta Geologica Sinica* , 1, 45–50.

2. Atencio, D., Andrade, M.B., Christy, A.G., Giere´, R., & Kartashov, P.M. 2010. The pyrochloresuper group of minerals: nomenclature. *Canadian Mineralogist* 48, 673–698.