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Zhangpeishanite, BaFCl, a new mineral in fluorite from Bayan Obo, Inner Mongolia, China

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Abstract: Zhangpeishanite, ideally BaFCl, occurs as inclusions up to 100 μm across in fluorite from Bayan Obo, Inner Mongolia, China. It is associated with barite, hematite and norsethite in fluorite. Zhangpeishanite occurs as transparent, colourless crystals with a white streak and vitreous luster. It is tetragonal, $P4/nmm$, a = 4.3951(8), c = 7.223(2) Å, V = 139.52(7) Å^3, Z = 2. The five strongest lines in the powder XRD pattern are [d(Å), I/I_0, hkl]: (3.75, 100, 101), (3.11, 94, 110), (2.36, 82, 112), (2.79, 67, 012) and (1.898, 49, 211). The mean of twelve electron-microprobe analyses is (wt.%); Ba 70.90, F 9.88, Cl 18.85, and leads to the empirical formula $Ba_{0.99}F_{0.99}Cl_{1.02}$ on the basis of 3 apfu. Zhangpeishanite is a member of the matlockite group (Struntz–Nickel grouping 3DC.25), the Ba-dominant analogue of matlockite and rorisite. The calculated density of zhangpeishanite is 4.54 g/cm^3. Zhangpeishanite is non-fluorescent. The hardness is 2½ on Mohs' scale (measured on a synthetic equivalent). The optical data obtained from the synthetic equivalent are: uniaxial (−), ω = 1.656(2), ε = 1.652(2) (589 nm).

Key-words: zhangpeishanite, new mineral, Bayan Obo, matlockite group, barium fluoride chloride.

Introduction

Fine inclusions were recognized in a specimen of deep purple fluorite from Bayan Obo, Inner Mongolia, China – the world's largest resource of rare-earth elements (Zhang *et al*., 1994). The inclusions form as bands within fluorite and show higher refractive indexes relative to that mineral. The inclusions are all Ba minerals – barite [$BaSO_4$], norsethite [$BaMg(CO_3)_2$] and a new species of barium fluoride chloride, the subject of this paper. This mineral and name were approved by the IMA Commission on New Minerals, Nomenclature and Classification in February 2007 (IMA 2006-045). The name is for Prof. Zhang, Peishan (born in 1925), mineralogist, in recognition of his contributions to the mineralogy of Bayan Obo. The type material is housed in the mineralogical collections of the National Museum of Nature and Science, Tokyo, Japan under the registered number NSM-MF14696 and at the Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, China (registration number KDX013).

Geological background and occurrence

Bayan Obo is a world-class Nb–REE–Fe deposit located in Inner Mongolia, China (109°57′E, 41°46′N). The majority of Nb–REE–Fe deposit is hosted by the 'H8' dolomite marble unit, along with units of sandstones and slates which belong to the Proterozoic Bayan Obo Group (Fig. 1).

The deposit extends approximately 18 km in an east–west direction and has a variable width of between 0.5 and 5 km. The East and Main orebodies are the two major Nb–REE–Fe orebodies amongst several smaller ones. Nearly 200 mineral species have so far been identified from the Bayan Obo deposit (*e.g.* Zhang & Tao, 1986).

Zhangpeishanite occurs as inclusions in dark purple fluorite up to 100 μm across (Fig. 2–4) in fluorite-type ore found in the transition zone between the dolomite and slate (Fig. 1) at the south orebody, East-Mine, Bayan Obo. Associated minerals are norsethite, barite and hematite within fluorite.

Appearance, physical and optical properties

Zhangpeishanite inclusions occur up to 100 μm, but are typically much smaller (~ 50 μm; Fig. 3 and 4). Owing to the minute grain size, some of the physical and optical properties could not be directly measured. Instead, a synthetic BaFCl crystal, which was grown in flux by Kurobori *et al*. (1999) according to the methods described by Somaiah & Hari Babu (1976), was used to determine these properties. Zhangpeishanite occurs as transparent, colourless crystals

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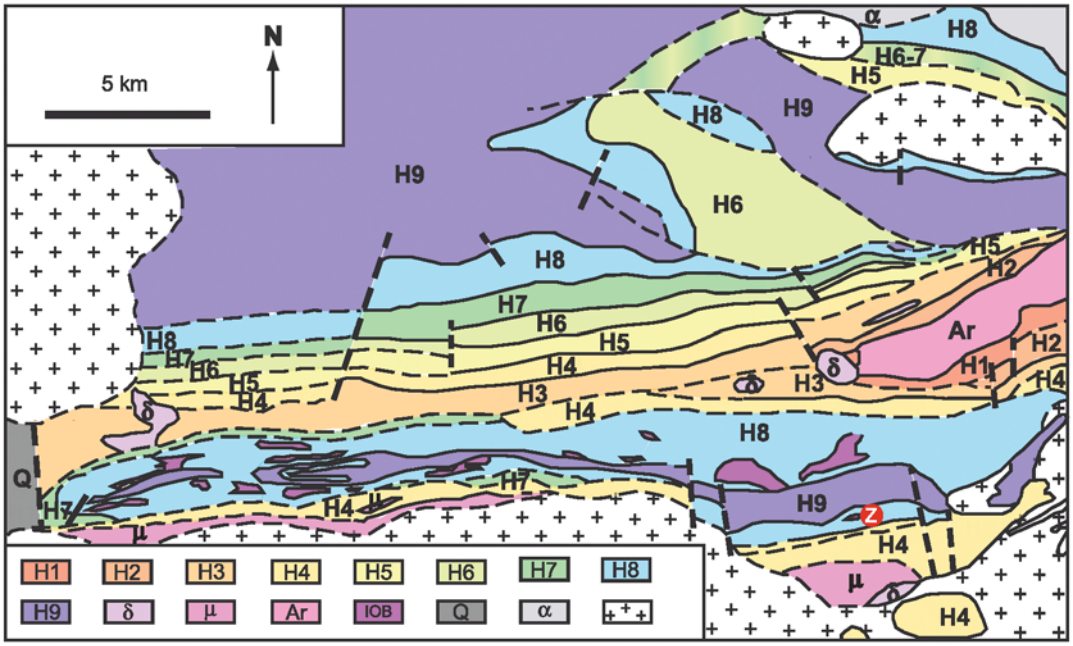

Fig. 1. A regional geological sketch map of the Bayan Obo Nb–REE–Fe ore deposits (after Zhang *et al*., 1995), with the indication of the position of type locality of zhangpeishanite. Z: The position of type locality of zhangpeishanite; H1: conglomerate and quartz-sandstone; H2: light-coloured quartzite with slate; H3: lime slate; H4: dark-coloured quartzite with slate; H5: dark-coloured slate with quartz-sandstone; H6: light-coloured quartzite with marl; H7: siliceous limestones with quartz-sandstone; H8: dolomite and limestones; H9: slate with quartzite; δ: gabbro and gabbrodiabase; μ: migmatite; Ar: schist and gneiss; IOB: iron orebody; Q: Quaternary alluvial deposits; α: andesite-tuff; +: Hercynian granite.

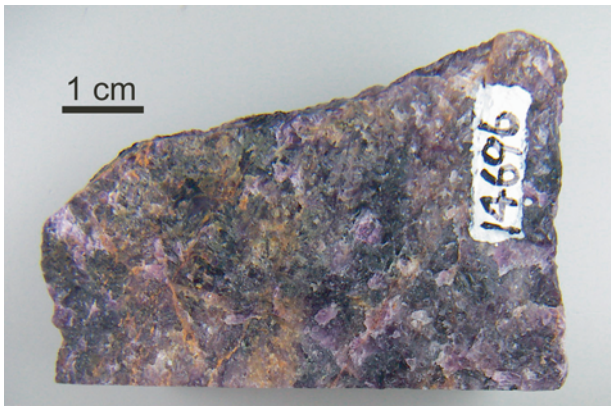

Fig. 2. Photograph of the type specimen of zhangpeishanite in a massive, dark-purplish-coloured, fluorite rock.

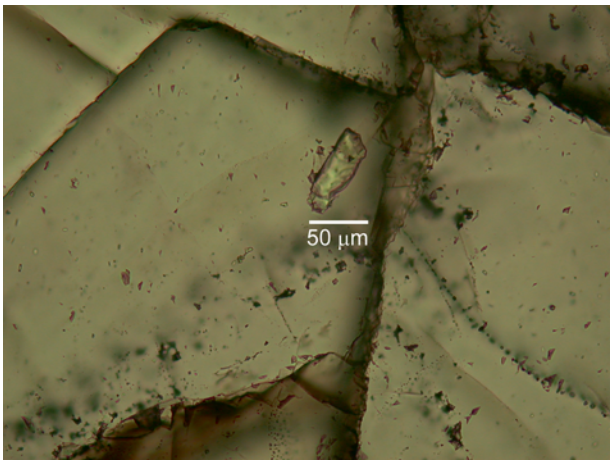

Fig. 3. Photomicrograph of a zhangpeishanite grain in fluorite matrix in thin section (transmitted, plane polarized light).

with a white streak and vitreous luster. It is non-fluorescent under short or long wave UV light. The hardness is 2½ on Mohs' scale (measured on a synthetic sample). Tenacity and fracture could not be determined. Synthetic BaFCl shows perfect cleavage on {001}. The density of zhangpeishanite could not be measured because of small grain size, however the calculated density is 4.54 g/cm^3 on the basis of the empirical formula and unit cell. The optical data from synthetic BaFCl are; uniaxial (−), $\omega = 1.656(2)$ and $\varepsilon = 1.652(2)$ (589 nm). The forms and twinning could not be observed due to the grain size of zhangpeishanite.

Chemical composition

Thin sections of zhangpeishanite were prepared from the type specimen using oil, as the mineral is soluble in water. Chemical analyses of zhangpeishanite (12 analyses on 6 grains) and synthetic BaFCl were carried out by means of an electron microprobe (JEOL JXA-8800M, WDS mode, 15 kV, 20 nA, 2 μm beam diameter). The analytical results are given in Table 1. The empirical formula for zhangpeishanite (based on 3 apfu) is $Ba_{0.99}F_{0.99}Cl_{1.02}$ and is within the

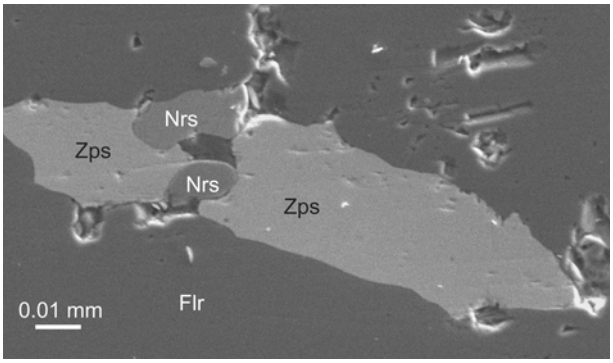

Fig. 4. Back-scattered electron image of zhangpeishanite. Abbreviations: Zps = zhangpeishanite, Flr = fluorite, Nrs = norsethite.

analytical error of the ideal formula. The simplified formula is BaFCl, which requires: Ba 71.61, F 9.91, Cl 18.48, total 100 wt.%. The electron-microprobe analysis for the synthetic BaFCl leads to the empirical formula $Ba_{1.00}F_{0.99}Cl_{1.01}$.

Crystallography

Single-crystal X-ray studies could not be carried out due to the small crystal size of zhangpeishanite. Powder X-ray diffraction (PXRD) data were obtained using a 114.6 mm diameter Gandolfi camera with Ni-filtered Cu$K\alpha$ radiation. A fragment consisting of zhangpeishanite with small amount of fluorite was hand picked from the thin section used for the chemical analysis under a binocular microscope. The data were recorded on an imaging plate (IP) and processed with a Fuji BAS-2500 bio-image analyzer using a computer program written by Nakamuta (1999). The unit-cell parameters were refined from the PXRD data and calibrated with the fluorite as an internal standard, using the computer program of Toraya (1993). The lattice parameters of the fluorite were first refined from IP-Gandolfi diffraction data with an internal quartz-standard (reference material NIST SRM #1878a). The PXRD data of zhangpeishanite are given in Table 2 with those of the synthetic BaFCl for comparison. Zhangpeishanite is tetragonal, with space group *P*4/*nmm* and unit-cell parameters $a = 4.3951(8)$, $c = 7.223(2)$ Å, $V = 139.52(7)$ Å^3, $Z = 2$. The *c*:*a* ratio calculated from the unit-cell parameters is 1.6434:1.

Table 2. PXRD data of zhangpeishanite and its synthetic equivalent.

	Zhangpeishanite				BaFCl*	
hkl	I/I_0	$d_{meas.}$ (Å)	$d_{calc.}$ (Å)	$I_{calc.}$**	I/I_0	*d*(Å)
001	10	7.21	7.22	15	13	7.15
101	**100**	**3.75**	**3.75**	**100**	**100**	**3.73**
002	29	3.61	3.61	25	45	3.59
110	**94**	**3.11**	**3.11**	**72**	**68**	**3.09**
012	**67**	**2.79**	**2.79**	**55**	**65**	**2.78**
112	**82**	**2.36**	**2.36**	**59**	**97**	**2.35**
200	**32**	**2.20**	**2.20**	**41**	**25**	**2.19**
103	31	2.11	2.11	21	37	2.10
211	**49**	**1.898**	**1.897**	**29**	**61**	**1.889**
202	14	1.877	1.877	15	36	1.871
212	**34**	**1.726**	**1.726**	**22**	**52**	**1.719**
104	**39**	**1.670**	**1.670**	**17**	**59**	**1.664**
220	11	1.553	1.554	12	14	1.548
213	19	1.522	1.523	13	35	1.518
222	7	1.428	1.427	6	17	1.423
310	18	1.389	1.390	10	19	1.385
214	30	1.330	1.330	15	43	1.327
115	13	1.310	1.310	5	22	1.306
312	18	1.297	1.297	13	33	1.293
205	15	1.207	1.207	6	35	1.200
321	16	1.202	1.202	5		
106	6	1.161	1.161	3	18	1.159
323	9	1.088	1.088	4		
225	12	1.058	1.058	4		
411	5	1.055	1.055	4		
330	3	1.036	1.036	2		
007	2	1.033	1.032	1		
216	14	1.027	1.027	4		
412	6	1.022	1.022	3		
324	13	1.010	1.010	6		
315	10	1.002	1.002	5		
420	6	0.983	0.983	5		
117	11	0.980	0.979	4		

*Data of the synthetic equivalent.
**Relative intensities calculated with atomic positional data of BaFCl given by Sauvage (1974).

Discussion

Zhangpeishanite is a member of the matlockite group (3DC.25: Strunz & Nickel, 2001) and is the Ba-analogue of matlockite (PbFCl) and rorisite (CaFCl; Chesnokov *et al*., 1990). The crystal structure of synthetic BaFCl was determined by Nicklaus & Fischer (1972) and later refined by Sauvage (1974). The crystal structure of zhangpeishanite can be described as a stacking or a packing of layers with a sequence of F–Ba–Cl–Cl–Ba–F along the *c* axis. The two adjacent Cl layers are weakly connected, causing cleavage on (001) (Sauvage, 1974). Zhangpeishanite and rorisite as well as the synthetic compounds BaFBr, BaFI and SrFCl can be activated by the doping of a divalent lanthanide, *e.g.*, $BaFCl:Eu^{2+}$, to show photostimulative luminescence, and are used as the base material for IPs, two-dimensional

Table 1. Chemical composition (electron-microprobe data) of zhangpeishanite and synthetic BaFCl.

Constituent	Zhangpeishanite			Synthetic BaFCl	Probe standard
	Wt.%	Range	Stand. dev.	Wt.%	
Ba	70.90	69.25–72.56	1.01	71.00	BaF_2
F	9.88	9.66–10.30	0.18	9.73	CaF_2
Cl	18.85	18.58–19.16	0.18	18.68	NaCl
Total	99.63			99.41	

X-ray detectors, or as *in situ* pressure gauges for high-pressure and high-temperature experiments with a diamond-anvil cell (*e.g.* Kurobori *et al.*, 1999).

The chemical analysis of zhangpeishanite shows remarkable stoichiometry which is within the analytical error of the ideal formula, and there was no detectable Ca, Sr or Br. Although zhangpeishanite (BaFCl) and rorisite (CaFCl) are isostructural with each other, they show no isomorphous substitution between Ca and Ba. This is likely due to the significant difference in the ionic radii. Neither Ba nor Cl was detected in the associated fluorite, indicating perfect partitioning of Ba and Ca into zhangpeishanite and fluorite.

The BaFCl shows anisotropic compression under high pressure (Beck *et al*., 1983; Shen *et al*., 1994; Kalpana *et al*., 1997; Decremps *et al*., 1999) and has a structural phase transition at *ca*. 21 GPa (Shen *et al*., 1994; Decremps *et al*., 1999). The refined lattice parameters of zhangpeishanite of $a = 4.3951(8)$, $c = 7.223(2)$ Å, $V = 139.52(7)$ Å^3, are comparable to those of synthetic BaFCl crystals in the literature (*e.g.* $a = 4.3939(6)$, $c = 7.2248(9)$ Å, Sauvage, 1974). No physical compression was indicated for the specimen of zhangpeishanite studied.

Zhang & Tao (1986) described that some samples of fluorite from Bayan Obo contain elevated concentrations of Sr, Ba, Mn, Fe, Ti, Al, Si, REE and Be. Among our specimens of fluorite from Bayan Obo, both Y-bearing and Y-free fluorites were discovered with the electron microprobe. Zhang & Tao (1986) reported that there are commonly small inclusions of rare-earth minerals in fluorite. The rare-earth minerals bastnäsite-(Ce), huanghoite-(Ce), monazite-(Ce) and aeschynite-(Ce), as well as barite, norsethite and apatite were encountered in both the Y-bearing and Y-free fluorites examined in this study. However, no inclusions of rare-earth minerals were observed in the fluorite specimen that is hosting zhangpeishanite and is Y-free.

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References

Beck, H.P., Limmer, A., Denner, W., Schulz, H. (1983): Influence of high hydrostatic pressure on the crystal structure of BaFCl in the pressure range up to 6.5 GPa. *Acta Cryst.*, **B39**, 401-404.

Chesnokov, B.V., Nishanbaev, T.P., Bazhenova, L.F. (1990): Rorisite CaFCl – a new mineral. *Zap. Vses. Mineral. Obshch.*, **119**, 73-76 (in Russian).

Decremps, F., Fischer, M., Polian, A., Itié, J.P. (1999): Ionic layered PbFCl-type compounds under high pressure. *Phys. Rev. B*, **59**, 4011-4022.

Kalpana, G., Palanivel, B., Shameem Banu, I.B., Rajagopalan, M. (1997): Structural and electronic properties of alkaline-earth fluorohalides under pressure. *Phys. Rev. B*, **56**, 3532-3535.

Kurobori, T., Kozake, S., Hirose, Y., Ohmi, M., Haruna, M., Kimura, T., Inabe, K., Somaiah, K. (1999): Determination of the optical constants of photostimulable BaFCl:Eu^{2+} and KCl:Eu^{2+} crystals. *Jpn. J. Appl. Phys.*, **38**, 901-904.

Nakamuta, Y. (1999): Precise analysis of a very small mineral by an X-ray diffraction method. *J. Mineral. Soc. Japan*, **28**, 117-121 (in Japanese with English abstract).

Nicklaus, E. & Fischer, F. (1972): A modified Kyropoulos method for growing BaFCl single crystal. *J. Crystal Growth*, **12**, 337-338.

Sauvage, M. (1974): Refinement of the structure of SrFCl and BaFCl. *Acta Cryst.*, **B30**, 2786-2787.

Shen, Y.R., Englisch, U., Chudinovskikh, L., Porsch, F., Haberkorn, R., Beck, H.P., Holzapfel, W.B. (1994): A structural study on the PbFCl-type compounds *M*FCl (*M* = Ba, Sr and Ca) and BaFBr under pressure. *J. Phys.: Condens. Matter*, **6**, 3197-3206.

Somaiah, K. & Hari Babu, V. (1976): Etch pit and dislocations in BaFCl, BaFBr, SrFCl and SrFBr crystals. *Indian J. Pure Appl. Phys.*, **14**, 702-704.

Strunz, H. & Nickel, E.H. (2001): Strunz mineralogical tables. Chemical-structural mineral classification system, ninth ed., E. Schweizerbart'sche Verlagsbuchhandlung (Nägele u. Obermiller) Stuttgart, 176-177.

Toraya, H. (1993): The determination of unit-cell parameters from Bragg reflection data using a standard reference material but without a calibration curve. *J. Appl. Cryst.*, **26**, 583-590.

Zhang, P. & Tao, K. (1986): Bayan Obo mineralogy. Science Press, Beijing, China, 208 p (in Chinese with an English comprehensive synopsis).

Zhang, Z., Tang, S., Wang, J., Yuan, Z., Bai, G. (1994): New data for ore-forming age of the Bayan Obo REE ore deposit, Inner Mongolia. *Acta Geosci. Sin.*, **30**, 85-94 (in Chinese).

Zhang, P., Yang, Z., Tao, K., Yang, X. (1995): Mineralogy and geology of rare earths in China. Science Press, Beijing, China, 209 p.

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