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ZANGBOITE, $TiFeSi_2$, A NEW MINERAL SPECIES FROM LUOBUSHA, TIBET, CHINA, AND ITS CRYSTAL STRUCTURE

LI GUOWU[§]

Crystal Structure Laboratory and National Laboratory of Mineral Materials, China University of Geosciences (Beijing), Beijing, 100083, People's Republic of China

FANG QINGSONG

Institute of Geology, Chinese Academy of Geological Sciences, Beijing 100037, People's Republic of China

SHI NICHENG

Crystal Structure Laboratory and National Laboratory of Mineral Materials, China University of Geosciences (Beijing), Beijing 100083, People's Republic of China

BAI WENJI AND YANG JINGSUI

Institute of Geology, Chinese Academy of Geological Sciences, Beijing 100037, People's Republic of China

XIONG MING AND MA ZHESHENG

Crystal Structure Laboratory and National Laboratory of Mineral Materials, China University of Geosciences (Beijing), Beijing 100083, People's Republic of China

RONG HE

Institute of Geology, Chinese Academy of Geological Sciences, Beijing 100037, People's Republic of China

ABSTRACT

We describe the new mineral species *zangboite*, ideally $TiFeSi_2$, found in the podiform chromitites of the Luobusha ophiolite in Tibet, People's Republic of China. The tabular to irregular crystals range from 0.002 to 0.15 mm in diameter and form an intergrowth with native silicon and a Fe–Si phase. Zangboite is steel grey in color. The luster is metallic, it is opaque, and the streak is black. The mineral is brittle; it has a conchoidal fracture and seems devoid of cleavage. The estimated Mohs hardness is 5½, and the calculated density is 5.09 g/cm^3. The ideal composition is Ti 29.95, Fe 34.92, Si 35.13 wt%. Electron-microprobe analyses show traces of Cr, Mn, Zr and Al. The structure of zangboite has been refined by single-crystal X-ray diffraction to R_1 = 3.4%. The mineral is orthorhombic, space group *Pbam*; its unit-cell parameters are a 8.6053(10), b 9.5211(11), c 7.6436(9) Å, V 626.25(13) Å^3, Z = 12. The strongest five lines in the powder pattern [d in Å(hkl)(I/I_0)] are: 2.1291(232)(100), 2.0251(042)(65), 2.2318(312)(50), 1.9155(004)(57), and 3.8358(002)(50). The mineral species and name were approved by the Commission on New Minerals, Nomenclature and Classification (IMA 2007–036).

Keywords: zangboite, new mineral species, $TiFeSi_2$, crystal structure, Luobusha ophiolite, Tibet.

SOMMAIRE

Nous décrivons la nouvelle espèce minérale *zangboïte*, de formule idéale $TiFeSi_2$, provenant de masses podiformes de chromitite dans l'ophiolite de Luobusha au Tibet, République Populaire de Chine. Les cristaux sont tabulaires à irréguliers et vont de 0.002 à 0.15 mm de diamètre et forment une intercroissance avec la silicium natif et une phase Fe–Si. La zangboïte a une couleur gris acier. Son éclat est métallique, et sa rayure, noire. Le minéral est opaque et cassant; il possède une fracture conchoïdale, et semble dépourvu de clivage. Sa dureté sur l'échelle de Mohs est 5½, et la densité calculée est 5.09 g/cm^3. La composition

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[§] *E-mail address*: liguowu@126.com

idéale est Ti 29.95, Fe 34.92, Si 35.13% (poids). Les analyses effectuées avec une microsonde électronique montrent des traces de Cr, Mn, Zr et Al. Nous avons affiné la structure de la zangboïte par diffraction X sur monocristal, jusqu'à un résidu R_1 de 3.4%. Il s'agit d'un minéral orthorhombique, groupe spatial *Pbam*; les paramètres réticulaires sont: *a* 8.6053(10), *b* 9.5211(11), *c* 7.6436(9) Å, *V* 626.25(13) Å^3, Z = 12. Les cinq raies les plus intenses du spectre de diffraction (méthode des poudres) [*d* en Å(*hkl*)(I/I$_0$)] sont: 2.1291(232)(100), 2.0251(042)(65), 2.2318(312)(50), 1.9155(004)(57), et 3.8358(002)(50). La nouvelle espèce et le nom ont reçu l'approbation de la Commission des Nouveaux Minéraux, de Nomenclature et de Classification (IMA 2007–036).

(Traduit par la Rédaction)

Mots-clés: zangboïte, nouvelle espèce minérale, $TiFeSi_2$, structure cristalline, ophiolite de Luobusha, Tibet.

INTRODUCTION

The synthesis of the compounds $MnTiSi_2$ and $TiFeSi_2$ was first reported by Markiv (1966), and the crystal structure of synthetic $TiFeSi_2$ was described by Steinmetz *et al*. (1982). Essene & Fisher (1986) reported the presence of $TiFeSi_2$ crystals intergrown with intermetallic Fe–Si compounds in metallic nuggets in a glassy fulgurite, and a similar occurrence was reported by Wasserman *et al*. (2002). According to Essene & Fisher (1986), reports of highly reduced phases in geological settings should not be rejected *a priori* as requiring impossible geological conditions; they discussed several possibilities to explain the natural occurrence of such phases, including conditions of ultrahigh temperature by oxidation of C and, in the case of fulgurites, by electron flow.

The mineral of composition $TiFeSi_2$ reported here was separated from the heavy-mineral constituents derived from a 1500 kg sample of chromitite collected from orebody 31, in group II of the Luobusha mining district, in Qusum (Qusong) county, Shannan Prefecture, Tibet, China, about 200 km east–southeast of Lhasa (29°5' N, 92°5' E). The new mineral is named *zangboite* after the Yarlong Zangbo River (also known as Brahmaputra), which flows near the locality. The type material has been deposited at the Geological Museum of China in Beijing, and is registered under catalogue number M11651. The mineral species and name were approved by the Commission on New Minerals, Nomenclature and Classification (IMA 2007–036). The present paper deals with the mineralogical description of zangboite; we provide X-ray powder-diffraction data, and present results of a determination and refinement of the structure.

MINERAL-SEPARATION PROCEDURES

Because the minerals were hand-picked from this heavy-mineral separate, the possibility of natural or anthropogenic contamination can be ruled out. The samples were taken directly from the outcrop and carefully cleaned before processing, and the same collection of minerals was recovered twice using completely different laboratories for mineral separation (Fang & Bai 1981). All equipment was dismantled and carefully cleaned before crushing and processing (Bai *et al*. 2000), and a 200-kg sample of granite from the Gangdese batholith was processed first to test for contamination during the separation process. Only quartz, feldspar, garnet, mica, apatite, and zircon were recovered from the granite. Any dark or metallic mineral would have been readily recognized; none was found.

Using the same procedures and equipment with which the granite sample was processed, we found about 70–80 distinct metallic mineral species and alloys in the samples of Luobusha chromitite. These include: native metals and intermetallic compounds, grains of Os–Ir alloy with inclusions of diamond, and metallic carbides. In addition, iron silicides have been identified, for example: native Si, FeSi, $FeSi_2$ (Li *et al*. 2005a), and $Fe_{0.84}Si_2$ (luobusaite, Bai *et al*. 2006). None of these minerals occur in the granite sample, but many of them have been recovered from chromitites of other ophiolites, processed in completely different laboratories (Robinson & Yang 2008). The samples were hand-washed, air-dried, and crushed carefully to avoid any possible anthropogenic contamination. Mineral separation was carried out using gravity, magnetic, and electrical techniques in the Zhengzhou Institute of Multipurpose Utilization of Mineral Resources, Chinese Academy of Geological Sciences. The grains of zangboite were handpicked from separates of various grain-sizes. Selected grains were mounted in epoxy, polished, and analyzed with an electron microprobe. Thus, we are confident that the Luobusha sample is free of contamination. The $TiFeSi_2$ specimens studied are clearly of natural origin.

LOCATION AND GEOLOGY

The new species zangboite was discovered in a chromitite hosted in harzburgite of the Luobusha ophiolite, which is situated in the Indus – Yarlong Zangbo suture zone. The ophiolite extends along Yarlong Zangbo River for about 42 km from east to west and has a width of 1–4 km, with an exposed area of about 70 km^2. It consists mainly of harzburgite, with lesser amounts of dunite, cumulate mafic rocks, pillow lava, and ophiolitic mélange (Fig. 1; Bai *et al*. 2000). Numerous bodies of podiform chromitite are hosted in the mantle-derived rocks, with an aggregate of about 5 million tonnes of

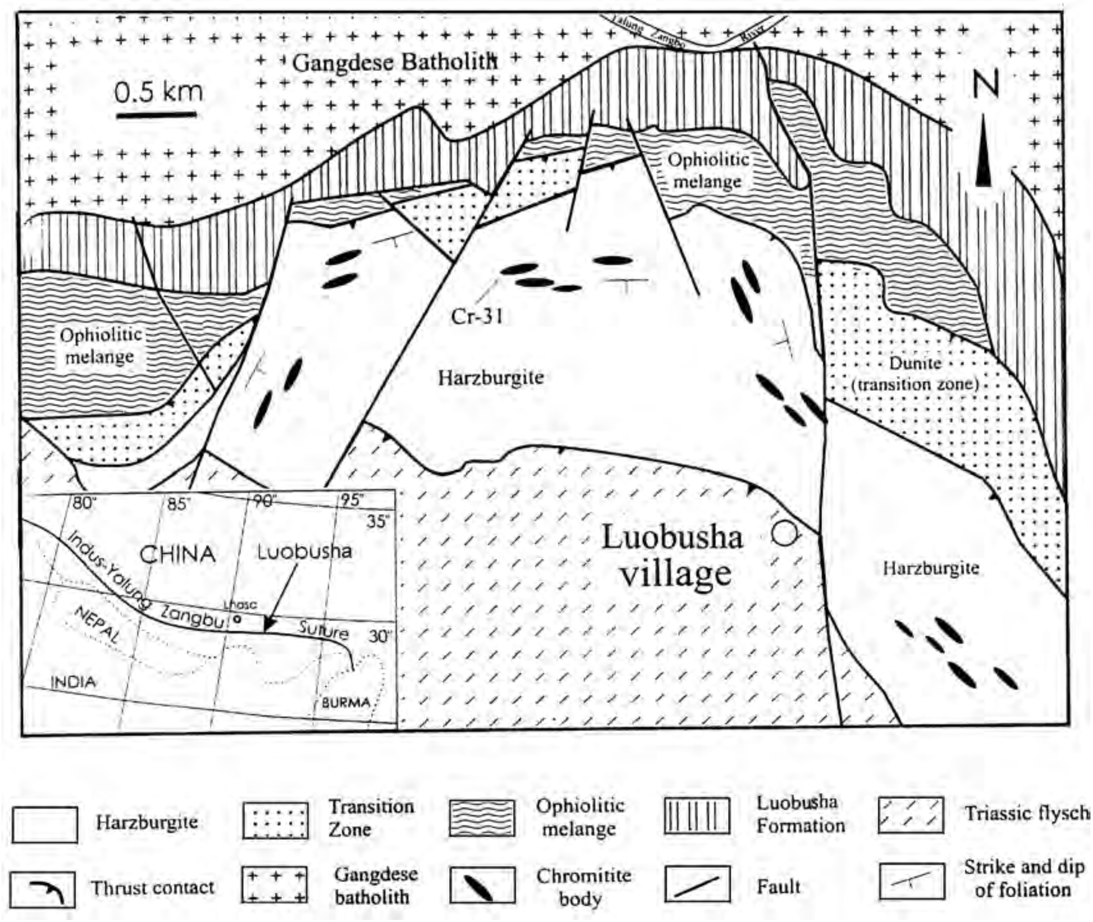

FIG. 1. Location of the Cr–31 and other bodies of podiform chromitite in depleted harzburgite and in the ophiolite at Luobusha (Bai *et al*. 2000).

ore. Chromitite has been mined at Luobusha for over a decade, and a number of seams and pods are exposed in open pits. The age of the ophiolite is uncertain. Zhou *et al*. (2002) obtained a Jurassic age (Sm–Nd isochron of 177 Ma), whereas Robinson *et al*. (2004) concluded that it has a Cretaceous age (126 Ma) on the basis of a SHRIMP analysis of zircon.

APPEARANCE AND PHYSICAL PROPERTIES

Zangboite occurs as grains or tabular crystals generally between 0.002 and 0.15 mm across; some grains measure up to 0.08 × 0.15 mm (Fig. 2A). A small grain was found in a Fe–Si phase as an inclusion with a section through a tablet of about 2 × 11 μm, and native Si forms a rim around grains of zangboite (Fig. 2B). The mineral is steel grey with a black streak, opaque, with a metallic luster. It is non-fluorescent and brittle; the fracture is conchoidal with no observed cleavage. The estimated Mohs hardness is 5½ as tested with a steel needle. The density could not be measured owing to the small grain-size, but the density calculated from the ideal formula and the unit cell is 5.09 g/cm^3. Reflectivity measurements were made in air, using a MPV–3 instrument and WC as a standard. The reflectance values for zangboite are listed in Table 1.

CHEMICAL COMPOSITION

Quantitative chemical analyses were made with an electron microprobe (EPMA–1600 Shimadzu instrument), run at an accelerating voltage of 15 kV, a beam current of 15 nA, and a beam diameter of 1 or 5 μm. Multiple element standards from SW9100 NIST were

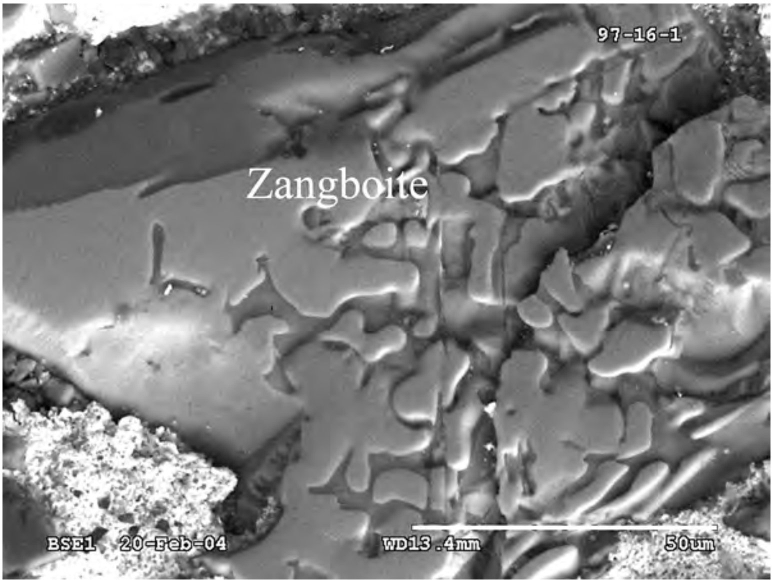

FIG. 2A. Back-scattered electron image showing the morphology of zangboite, 0.08 × 0.15 mm. The tablet-shaped grain contains an intergrown dark Si–Fe–Ca phase.

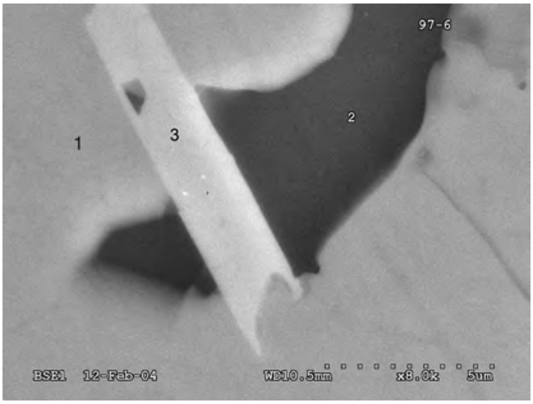

Fig. 2B. Back-scattered electron image of zangboite (3) found as an inclusion in a Fe–Si phase (1), with a section through a tablet about measuring 2 × 11 µm; native Si (2) forms a rim around grains of zangboite. The phase $FeSi_2$ has a composition 49.81% Si, 47.01% Fe, and 3.18%Al, and Si contains 96.78% Si, 2.33% Fe, and 0.89% Ti.

TABLE 1. REFLECTANCE VALUES (R %) FOR ZANGBOITE

R %	λ nm	R %	λ nm	R %	λ nm
26.41	400	36.48	520	42.16	620
27.72	420	36.35	540	41.66	640
32.87	440	37.45	546 (COM)	43.86	650 (COM)
34.87	460	37.75	560	44.69	660
34.90	470 (COM)	41.13	580	45.25	680
34.15	480	42.10	589 (COM)	43.71	700
34.38	500	41.80	600		

used for calibration (Fe, Si, Ti, Cr, Mn, Al and ZrO_2). The results, based on the average result of analyses of three samples, are given in Table 2.

The typical composition is usually close to the ideal formula. However, different grains of zangboite show different trace amounts of Cr, Mn, Zr and Al. Chromium and Mn vary between 0.70 and 1.01 wt% and between 0.62 and 1.01 wt%, respectively; Zr (between 1.49 and 1.53 wt%) was detected in sample 97–8–3, and Al (between 1.59 and 1.61 wt%) measured at two points on grain 97–6. The empirical formula of zangboite is based on the analytically determined average values recalculated to the total of 2 Si atoms per formula unit: $(Ti_{0.99}Zr_{0.01})(Fe_{1.01}Cr_{0.02}Mn_{0.02})(Si_{2.00}Al_{0.03})$. The simplified formula is $TiFeSi_2$, which has the ideal composition Ti 29.95, Fe 34.92, Si 35.13, for a total of 100.00 wt%.

X-RAY POWDER-DIFFRACTION DATA

Because the samples consist of only a small number of grains, the powder-diffraction experiment was done with a small single crystal using single-crystal repeat-rotation diffraction method (Li *et al.* 2005b) with a Bruker SMART APEX CCD area-detector diffractometer and using Mo*K*α radiation (λ = 0.7109 Å). The powder pattern was obtained using GADDS software (Häming 2000). The X-ray powder-diffraction pattern of zangboite is given in Figure 3, and the data are recorded in Table 3. The X-ray powder data have been indexed using unit-cell and space-group parameters obtained from the results of the single-crystal refinement of the structure.

To make a comparison between measured and calculated patterns, a theoretical powder pattern was calculated through PowderCell 2.3 software (Kraus & Nolze 1999) for Debye–Scherrer geometry and Mo*K*α radiation (λ = 0.7109 Å), using unit-cell parameters, space group, atom positions, site occupancies and isotropic displacement factors from the results of the single-crystal refinement of the structure. The results of comparison are shown in Figure 3. The data presented are in good agreement with the calculated and observed values of *d* and I/I_0 patterns.

Determination and Refinement of the Structure

The X-ray single-crystal diffraction experiment was done at the Crystal Structure Laboratory. A suitable single crystal of zangboite (0.05 × 0.08 × 0.15 mm, specimen no. 97–16–1) was carefully selected and glued to a thin glass fiber with a cyanoacrylate adhesive. The single-crystal X-ray-diffraction data were collected on the Bruker SMART APEX CCD diffractometer equipped with a normal focus, 2.4 kW sealed X-ray tube source (Mo*K*α radiation, λ = 0.71073 Å) and operating at 45 kV and 35 mA, with a graphite monochromator. A hemisphere of intensity data was collected at room temperature in 1265 frames with ω scans (frame width of 0.30° and exposure time of 10 s per frame). The refined unit-cell parameters were determined by a least-squares fit of 4492 reflections in the range $5.23° < 2\theta < 67.04°$. A Polarization–Lorentz (PL) correction and absorption corrections based on the symmetry-equivalent reflections were applied using the SADABS software. Pertinent experimental details for the structure determinations are presented in Table 4.

We have determined zangboite to be orthorhombic, space group *Pbam*, *a* 8.6053(10), *b* 9.5211(10), *c* 7.6436(9) Å, *V* 626.25(13) Å^3, *Z* = 12. These results are in excellent agreement with those for the synthetic material: *a* 8.56, *b* 9.53, *c* 7.64 Å (Markiv 1966), and *a* 8.6137(8), *b* 9.534(1), *c* 7.6396(4) Å (Steinmetz *et al.* 1982). The atom coordinates were determined by direct methods and by difference-Fourier maps using SHELXTL PC (Bruker AXS Inc.) procedures, and were refined using full-matrix least-squares. Anisotropic refinement was done using all 1227 ($R_{\text{int}} = 0.0289$) measured independent data and refined to $R[F^2 > 2\sigma(F^2)] = 0.0340$, $wR(F^2) = 0.0730$, $\Delta\rho_{\max}$ (e Å^{-3}) = 0.815; $\Delta\rho_{\min}$ (e Å^{-3}) = –0.998. Tables 5 and 6 give the coordinates and the anisotropic displacement parameters of all atoms. A table of structure factors is available from the Depository of Unpublished Data on the MAC website [document Zangboite CM47_1265].

Figures 4 and 5 show the main features of the structure of zangboite, as seen along [001]. The Fe atoms are located at the center of deformed Si octahedra. Three octahedra sharing faces form a group oriented along the *b* axis, and along the *c* axis, with the groups sharing edges to form chains (Fig. 6). The octahedra share apices between chains through the common tips of the polyhedra to form columns. This structure is based on a framework of octahedra of Si atoms, with the largest atoms, Ti, being located in the holes created between the octahedra.

The various interatomic distances in zangboite are given in Table 7. The Fe–Si distances are 2.274–2.472 Å. These distance agrees with the sum of covalent radii of the Fe and Si, 2.33 Å (R_{Fe} 1.16 Å + R_{Si} 1.17 Å), which suggest that Fe–Si is a covalent bond. However, the Ti–Fe distances are 2.89–3.00 Å, larger than the sum of Ti–Fe covalent radii, 2.48 Å, or the sum of atomic radii, 2.72 Å (atomic radius of Fe 1.27 Å, and of Ti 1.45 Å). As well, the Ti–Si distances are 2.56–2.81 Å, larger than the sum of Ti–Si covalent radii, 2.49 Å, and agree with the sum of atomic radii, 2.79 Å (atomic radius of Si: 1.34 Å). It should be noted that Ti does not interact as strongly with Fe and Si as Fe does with Si. An important structural feature of zangboite is the presence of Si as the packing atoms and of Fe as the filling atoms, to represent coordination polyhedra. The structure is based on a fragment of $FeSi_6$ octahedra forming the basic unit, with Ti atoms filling the holes, representing a new kind of crystal structure for a Fe silicide of Ti. The crystal-chemical formula can be regarded as $TiFeSi_2$. The covalent bonds in structure explain the hardness and brittleness of the mineral, and the Fe–Ti metal bond shows alloy characteristics. As the first natural Ti–Fe silicide, it belongs to the titanium iron silicide zangboite group, and can be classed with the "Native Elements with metallic elements other than the platinum group", based on the New Dana Classification. It can also be classed as a member of the "I/A Metallic and intermetallic compounds, Carbides, Nitrides, Phosphides and Silicides: 1.BB.", in the Strunz Classification System.

Although the synthetic compound $TiFeSi_2$ was reported (Markiv 1966), and the crystal structure of synthetic $TiFeSi_2$ was described (Steinmetz *et al.* 1982), zangboite has a more complex chemical composition. Electron-microprobe analyses show that, in addition to the principal constituents, there are trace amounts of Cr, Mn, Zr and Al in the mineral. The grains are intergrown with Fe–Si phases and native Si. A powder-diffraction pattern of synthetic $TiFeSi_2$ was indexed in the ICDD database as ICDD51–1366. Except for two very weak and high-2θ lines, the observed powder XRD pattern of zangboite is in good agreement with that of synthetic $TiFeSi_2$.

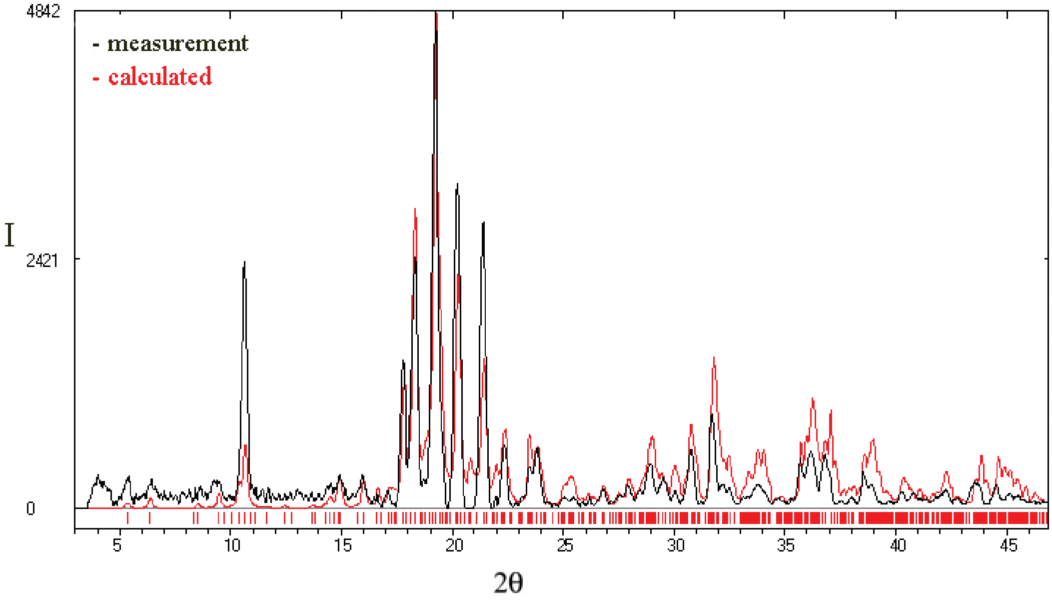

FIG. 3. X-ray powder pattern of zangboite. In red, the calculated pattern, and in black, the measured pattern (Mo*K*α radiation).

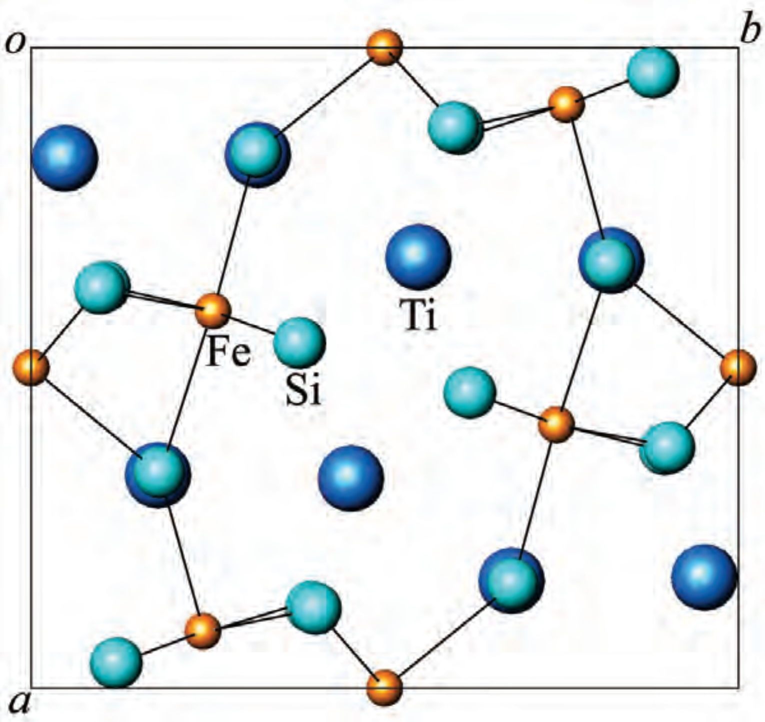

FIG. 4. The unit-cell structure of zangboite, projected along the *c* axis.

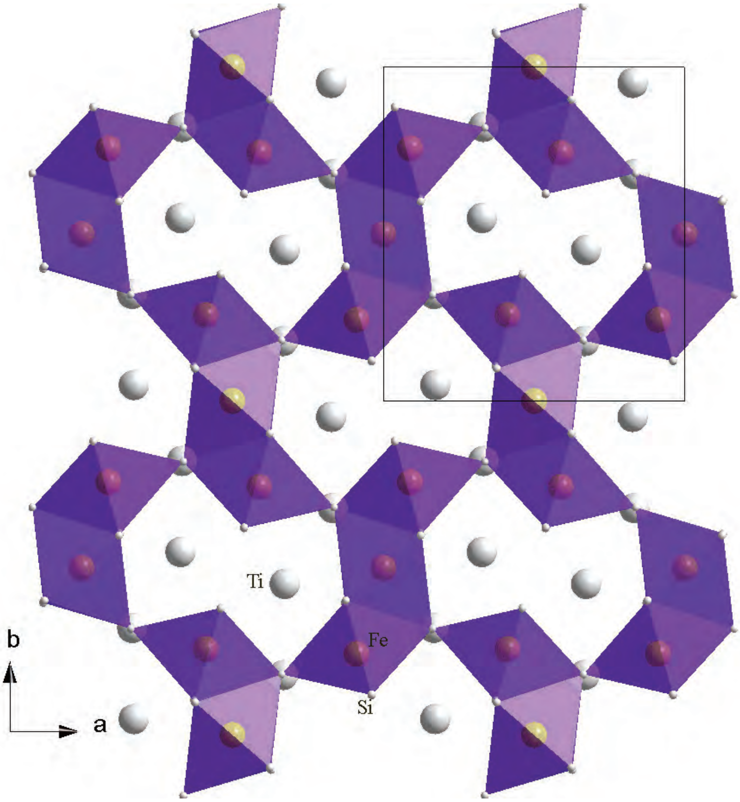

FIG. 5. Three octahedra sharing faces form a group oriented along the *b* axis; octahedra share apices between chains through the common tips of the polyhedra.

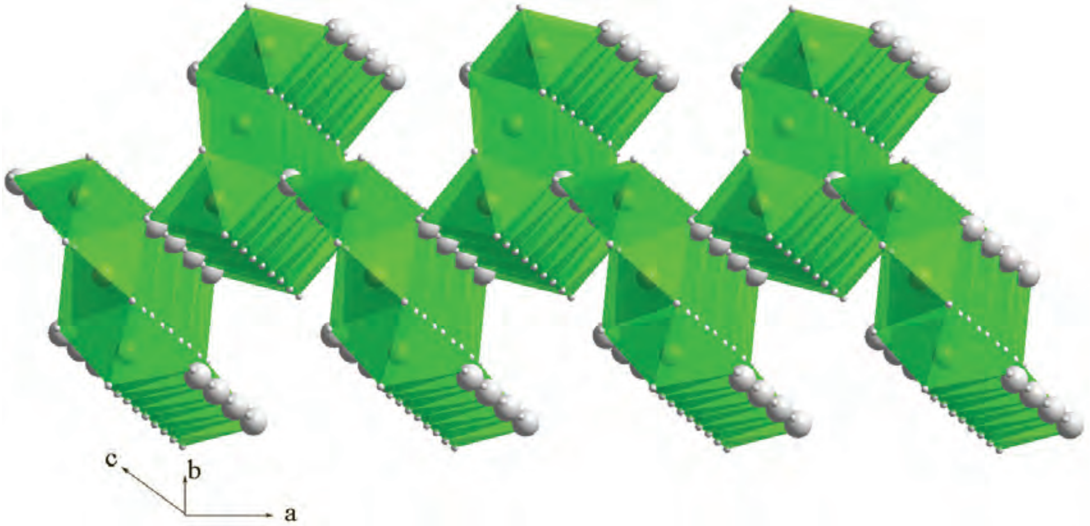

FIG. 6. The chains run parallel to [001] in the crystal structure of zangboite.

Discussion

There have been many reports of native element minerals, intermetallic alloy minerals and inclusions in chromite (Melville 1892, Bird & Weathers 1975, Essene & Fisher 1986, Rudashevsky *et al.* 1987, Melcher *et al.* 1997). Tibetan samples of native metallic elements (Si, Fe, Zn, Pb, Al, Cr, Ni, Os, Ir, Ru, Rh, Pd, Au, Ag, W and Cu), and intermetallic minerals (Fe–Si, Fe–Ti–Si, Ni–Fe–Cr, Ni–C, Fe–C, Cr–C, Ti–C, W–C, Si–C, Fe–Co, Al–Fe–La, W–Co, Fe–Mn, Au–Ag, Ag–Sn Ti–W, Cu–Zn, Ti–N), as well as platinum-group minerals (Ni–Fe–Ir, Rt–Fe, Pt–Fe–Pd, Fe–Ru) (Bai *et al.* 2000, 2003, 2005, 2006, Shi *et al.* 2005, Robinson *et al.* 2004) have already been reported. However, about 70 to 80 of these compounds, including the new minerals

TABLE 2. RESULTS OF ELECTRON-MICROPROBE INVESTIGATIONS OF ZANGBOITE

Sample	97-16-1	97-8-3	97-6
n	5	3	2
Fe wt%	34.31(27)	35.38(64)	34.64(2)
Si	34.14(15)	33.56(6)	36.10(4)
Ti	29.35(14)	27.92(22)	27.67(6)
Cr	1.01(1)	0.75(3)	n.d.
Mn	1.03(1)	0.61(0)	n.d.
Zr	n.d.	1.517(1)	n.d.
Al	n.d.	n.d.	1.60(1)
Total	99.84	99.76	100.01

n: number of analyses made (standard deviations in parentheses).

TABLE 4. STRUCTURE-REFINEMENT INFORMATION FOR ZANGBOITE

Ideal formula of zangboite		$TiFeSi_2$	
Empirical formula		$(Ti_{0.99}Zr_{0.01})(Fe_{1.01}Cr_{0.02}Mn_{0.02})(Si_{2.00}\ Al_{0.03})$	
Formula weight		159.93	
Temperature	291(2) K	Wavelength	0.71073 Å
Crystal system	Orthorhombic	Space group	*Pbam*
Unit-cell dimensions	*a* = 8.6053(10) Å	Volume	626.25(13) Å^3
	b = 9.5211(11) Å	*Z*	12
	c = 7.6436(9) Å	Density (calculated)	5.09 g/cm^3
Absorption coefficient	11.439 mm^{-1}	F(000)	912
Crystal size		0.05 × 0.08 × 0.15 mm	
Theta range for data collection		2.66 to 33.52°	
Index ranges		$-11 \le h \le 13$, $-12 \le k \le 14$, $-11 \le l \le 6$	
Reflections collected		4492	
Independent reflections		1227 [$R_{(int)}$ = 0.0289]	
Absorption correction		Empirical	
Refinement method		Full-matrix least-squares on F^2	
Data / restraints / parameters		1227 / 0 / 63	
Goodness-of-fit on F^2		1.166	
Final R indices [$I > 2\sigma(I)$]		R_1 = 0.0340, wR_2 = 0.0730	
R indices (all data)		R_1 = 0.0449, wR_2 = 0.0767	
Largest diff. peak and hole		0.815 and -0.990 e.Å^{-3}	

TABLE 3. X-RAY POWDER-DIFFRACTION DATA FOR ZANGBOITE

h k l	*d* obs.	*d* calc.	I/I_0	*h k l*	*d* obs.	*d* calc.	I/I_0
0 0 1	7.6383	7.6465	6	4 4 2	1.4713	1.4735	3
1 1 0	6.3510	6.3875	3	1 6 2	1.4481	1.4473	2
2 0 0	4.3162	4.2994	2	3 3 4	1.4230	1.4224	7
0 0 2	3.8358	3.8232	50	6 1 1	1.3937	1.3935	5
1 2 2	2.8321	2.8185	3	5 4 1	1.3712	1.3723	3
2 1 2	2.7379	2.7369	4	4 5 2	1.3383	1.337	12
2 3 0	2.5608	2.5568	5	2 7 0	1.2996	1.2993	20
3 2 0	2.4635	2.4569	3	1 7 2	1.2686	1.2698	2
0 4 0	2.3925	2.3853	4	5 4 3	1.2235	1.2237	2
1 4 0	2.3010	2.2985	30	4 3 5	1.1598	1.1603	10
3 1 2	2.2318	2.2298	50	4 5 4	1.1441	1.1436	8
2 3 2	2.1291	2.1292	100	5 4 4	1.1264	1.1269	10
0 4 2	2.0251	2.0224	65	0 0 7	1.0913	1.0924	2
0 0 4	1.9155	1.9116	57	1 1 7	1.0766	1.0767	6
3 1 3	1.8677	1.8678	2	8 0 1	1.0653	1.0644	3
3 4 0	1.8323	1.8334	13	4 8 1	1.0321	1.0333	3
4 2 2	1.7477	1.7467	6	2 9 1	1.0199	1.0201	2
2 1 4	1.7187	1.7182	10	1 4 7	0.9860	0.9866	3
2 2 4	1.6393	1.6402	2	4 0 7	0.9739	0.9738	2
1 3 4	1.6102	1.6095	2	4 2 7	0.9547	0.9542	4
3 1 4	1.5685	1.5687	2	3 4 7	0.9380	0.9384	6
1 6 1	1.5328	1.5320	4	5 6 5	0.9268	0.928	2

The values of *d* are expressed in Å.

TABLE 5. COORDINATES OF ATOMS IN ZANGBOITE

Atom	Wyckoff symbol	*x*	*y*	*z*
Fe1	4f	0	0.5	0.74258(8)
Fe2	8i	−0.08868(6)	0.24294(4)	0.74824(5)
Ti1	8i	0.32719(7)	0.54777(5)	0.73815(7)
Ti2	4h	0.16749(10)	0.32052(8)	0.5
Si1	4h	0.12725(17)	0.60427(13)	0.5
Si2	4g	0.12376(18)	0.59728(13)	1
Si3	4h	−0.03839(16)	0.11931(12)	0.5
Si4	8i	−0.33705(11)	0.18159(9)	0.84647(11)
Si5	4g	−0.03895(18)	0.12131(13)	1

TABLE 6. ANISOTROPIC DISPLACEMENT PARAMETERS (Å^2) OF ATOMS IN ZANGBOITE

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe1	0.0062(3)	0.0040(2)	0.0060(3)	0.0003(2)	0	0
Fe2	0.0054(2)	0.00509(18)	0.0048(2)	−0.00035(15)	−0.00004(17)	0.00009(14)
Ti1	0.0038(3)	0.0044(2)	0.0065(2)	0.00007(17)	0.0001(2)	−0.00019(16)
Ti2	0.0047(4)	0.0033(3)	0.0057(3)	0.0002(3)	0	0
Si1	0.0059(7)	0.0068(5)	0.0054(5)	0.0006(4)	0	0
Si2	0.0094(7)	0.0085(5)	0.0059(5)	0.0010(5)	0	0
Si3	0.0056(7)	0.0050(5)	0.0057(5)	0.0008(4)	0	0
Si4	0.0054(4)	0.0070(3)	0.0053(3)	−0.0002(3)	0.0001(3)	−0.0001(3)
Si5	0.0143(8)	0.0060(5)	0.0050(5)	0.0018(5)	0	0

luobusaite ($Fe_{0.83}Si_2$) (Bai *et al.* 2006), qusongite (WC) (Fang *et al.* 2009), and yarlongite, $(Cr,Fe,Ni)_{\Sigma 9}C_4$ (Shi *et al.* 2009), have been discovered from this deposit by chemical analysis and X-ray diffraction. These minerals indicate a highly reducing and high-temperature environment of formation.

A mineralogical study of the Luobusha area was proposed in 1981 after the discovery of diamond in the ophiolitic rocks located at Luobusha and Dongqiao in Tibet (Fang *et al.* 1981). An occurrence of diamond as inclusions in Os–Ir alloy and coesite as part of a silicate assemblage rimming a grain of Fe–Ti alloy was also reported by Yang *et al.* (2007) and Dobrzhinetskaya *et al.* (2008). Yamamoto *et al.* (2009) found submicroscopic grains of coesite in the chromite of the Luobusha ophiolite. This occurrence confirmed the presence of UHP minerals in the Luobusha chromitite, requiring a minimum pressure of 2.8–4 GPa. Because the individual coesite "crystals" have an external shape similar to that of stishovite and are polycrystalline, a pseudomorphic replacement, implying a pressure above 9 GPa, was suggested. The explanation proposed for the origin of these minerals is that the UHP minerals were incorporated into the chromitites in the deep upper mantle.

Although zangboite and other intermetallic compounds were collected from a podiform chromitite hosted in ophiolitic harzburgite, they are unlikely to be primary minerals in the sense of having crystallized from the melt that formed the Luobusha chromitites, given the chemical incompatibilities requiring a strongly reducing environment. Thus they are considered to be xenocrysts derived from deep mantle sources, and transported by a plume and incorporated in the ophiolite during seafloor spreading. Note, however, that zangboite was successfully synthesized at low pressure (Markiv *et al.* 1966); also, the synthetic analogue can be produced at the expense of ilmenite ore by reaction with molten Si at ambient pressure (Saito *et al.* 2005). The presence of zangboite thus does not imply a high-pressure environment. Blocks of the mantle containing the exotic minerals were presumably picked up by later boninitic melts from which the chromitites precipitated, transported to a shallow depth and partially digested in the melt, with insoluble residues incorporated into the chromitite (Robinson *et al.* 2004).

TABLE 7. SELECTED BOND-LENGTHS (Å) IN THE STRUCTURE OF ZANGBOITE

Fe1 – Si4	2×	2.363(1)	Ti1 – Si1		2.562(1)
Fe1 – Si1	2×	2.371(1)	Ti1 – Si3^{viii}		2.661(1)
Fe1 – Si2	2×	2.421(1)	Ti1 – Si3i		2.680(1)
Fe1 – Fe2	2×	2.564(0)	Ti1 – Si2		2.700(1)
Fe1 – Ti1	2×	2.852(1)	Ti1 – Si4^{v}		2.708(1)
Fe1 – Ti2	2×	2.904(1)	Ti1 – Si4^{i}		2.730(1)
Fe2 – Si3		2.274(1)	Ti1 – Si5^{ix}		2.796(1)
Fe2 – Si5		2.286(1)	Ti1 – Si5^{i}		2.815(1)
Fe2 – Si4	2×	2.339(1)	Ti2 – Si3^{i}		2.595(2)
Fe2 – Si1^{iii}		2.414(1)	Ti2 – Si3		2.609(2)
Fe2 – Si2^{iv}		2.472(1)	Ti2 – Si1^{iii}		2.635(2)
Fe2 – Ti1	2×	2.862(1)	Ti2 – Si4	2×	2.649(1)
Fe2 – Ti2^{vi}		2.893(1)	Ti2 – Si1^{xii}		2.713(2)
Fe2 – Ti1^{vii}		2.919(1)	Ti2 – Si1		2.724(1)
Fe2 – Ti2		3.001(1)			

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