

## STRUCTURE OF INORGANIC COMPOUNDS

# Crystal Structure of Jinshajiangite from the Norra Kärr Complex (Sweden)

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**Abstract**—The structure of the mineral jinshajiangite from the Norra Kärr alkaline complex (Sweden) was determined by single-crystal X-ray diffraction and refined to  $R = 6.7\%$ . The monoclinic unit-cell parameters are  $a = 5.350(2)$  Å,  $b = 6.909(6)$  Å,  $c = 20.96(1)$  Å,  $\beta = 99.83(4)^\circ$ , sp. gr.  $P2/m$ . This mineral is an Fe-rich analogue of surkhobite and perraultite, but it crystallizes in a different space group, and the unit-cell parameters  $a$  and  $b$  are two times smaller than those of these two minerals. The framework of jinshajiangite from Norra Kärr contains narrow and wide channels, which are occupied by Ca, Na, Ba, and K atoms in an ordered fashion.

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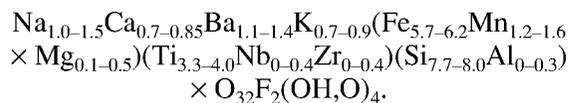
## STRUCTURE OF INORGANIC COMPOUNDS

The first characterization of the mineral jinshajiangite was carried out on a specimen found in China [1] as titanosilicate with the simplified formula  $\text{Na}_2\text{KCaBa}(\text{Fe}^{2+}, \text{Mn})_8\text{Ti}_4\text{Si}_8\text{O}_{32}(\text{O}, \text{Fe})_6$  ( $\text{Fe}^{2+} : \text{Mn} = 1.46$ ) and the unit-cell parameters  $a = 10.732$  Å,  $b = 13.847$  Å,  $c = 20.817$  Å,  $\beta = 95.3^\circ$  determined from X-ray powder diffraction data. The possible space groups are  $C2/m$ ,  $C2$ , or  $Cm$ . More recently, Mn-rich analogues of jinshajiangite, the minerals perraultite  $\text{Na}_2\text{KBaMn}_8\text{Ti}_4\text{Si}_8\text{O}_{32}(\text{OH}, \text{F}, \text{O})_6$  [2, 3] and surkhobite  $\text{NaCaKBa}(\text{Mn}, \text{Fe})_8\text{Ti}_4\text{Si}_8\text{O}_{32}(\text{F}, \text{OH}, \text{O})_6$  [4, 5], were discovered and structurally characterized. Originally, surkhobite was considered as an  $\text{Fe}^{2+}$ -rich mineral. However, subsequent studies by Mössbauer spectroscopy [6] showed that the Mn content in surkhobite invariably dominates over the  $\text{Fe}^{2+}$  content. Perraultite and surkhobite crystallize in sp. gr.  $C2$  and have unit-cell parameters similar to those determined for jinshajiangite from the X-ray powder diffraction pattern.

The second discovery of jinshajiangite was made in nepheline syenite deposits of the Norra Kärr alkaline complex (Sweden) [7]. The mineral is late magmatic in origin and occurs in association with magnesio-arfvedsonite, aegirine, fluoroapatite, and rosenbuschite. The X-ray diffraction pattern, physical properties, and the chemical composition of jinshajiangite from Sweden are similar to those of the specimen found in China, but the specimen from Sweden is characterized by a higher iron content. The unit-cell parameters determined from the X-ray powder diffraction data are  $a = 10.696$  Å,  $b =$

$13.800$  Å,  $c = 20.705$  Å,  $\beta = 94.96^\circ$ , whereas the single-crystal X-ray diffraction data correspond to  $a = 5.350(2)$  Å,  $b = 6.909(6)$  Å,  $c = 20.96(1)$  Å,  $\beta = 99.83(4)^\circ$ , sp. gr.  $P2/m$ . In spite of the fact that the unit cell of the mineral from Norra Kärr is four times smaller in volume, the lack of structural data for the Chinese specimen allows us to arbitrarily assign both minerals to jinshajiangite.

According to the results of electron-probe X-ray microanalysis and taking into account the inhomogeneity (zoning) of the crystals, the empirical formula of jinshajiangite from Norra Kärr can be written as



The X-ray diffraction data were collected from a multidomain crystal on an Oxford Diffraction X-calibur S diffractometer equipped with a CCD area detector ( $\omega$ -scanning technique,  $\text{MoK}_\alpha$  radiation, graphite monochromator) in the full sphere of reciprocal space. The main characteristics of the crystal and the X-ray data-collection and refinement statistics are given in Table 1. The structure was solved by direct methods followed by the use of the phase-correction procedure implemented in the AREN crystallographic program package [8] and then refined to  $R = 15\%$ . All atoms of the structure were located in subsequent electron density maps. In the refinement with the use of mixed scattering curves and anisotropic–isotropic displacement parameters, the  $R$  factor converged to 6.7%. The absorption correction was applied using the DIFABS

**Table 1.** Characteristics of the crystal and the X-ray diffraction-data collection and refinement statistics

Characteristics	Parameters
Unit-cell parameters, Å	$a = 5.350(2)$ $b = 6.909(6)$ $c = 20.96(1)$ $\beta = 99.83(4)$
Volume, Å <sup>3</sup>	$V = 763$
Space group	$P2/m$
Radiation $\lambda$ , Å <sup>-1</sup>	MoK $\alpha$ ; 0.7106
$D_x$ , g/cm <sup>3</sup>	4.2
Crystal dimensions, mm	0.15 × 0.1 × 0.03
Diffractionmeter	X-calibur S, CCD detector
Data-collection range	$-5 < h < 5$ ; $-7 < k < 8$ ; $-31 < l < 23$
$\sin \theta / \lambda$	$< 0.75$
Total number of reflections	2446 $F > 2\sigma(F)$
Number of independent reflections	668 $F > 2\sigma(F)$
Merging $R$ factor	4.7%
$R$ factor after refinement	6.7%
Program for refinement	AREN [8]
Program for absorption correction	DIFABS [9]

program [9]. The absorption could not be adequately taken into account ( $\mu = 80$ ) because of imperfection of the crystal and its flattened shape. This resulted in the high  $R$  factor, distortions of some atomic displacement ellipsoids, and the unequal distances in the Si tetrahedra.

The final atomic coordinates and their isotropic thermal parameters are listed in Table 2. The compositions of the sites and characteristics of the coordination polyhedra are given in Table 3.

The structure of jinshajiangite from Sweden, like the structures of other related minerals derived from the bafertisite structure type, consists of three-layer slabs or heteropolyhedral  $H-O-H$  layers [1] ( $O$  is an octahedron and  $H$  are mixed layers composed of tetrahedra and octahedra). The  $O$  octahedra containing Fe, Mn, and Mg atoms form the central planar layer, whereas the peripheral layers consist of Ti octahedra and Si tetrahedra.

The family of Ba-containing titanosilicate micas includes minerals characterized by different distributions of Ba, Na, Sr, Ca, and K atoms located either between the slabs or in the channels. In minerals consisting of isolated slabs, such as bafertisite, Ba-lamprophyllite, and K-baritolamprophyllite, Ba, Sr, and K atoms are distributed in a disordered manner in the common space between the slabs. The most complex

**Table 2.** Atomic coordinates and isotropic thermal parameters

Atom	$x/a$	$y/b$	$z/c$	$B_{\text{iso}}$ , Å <sup>2</sup>
Si(1)	0.5809(9)	0.2246(6)	0.1182(1)	1.4(1)
Si(2)	0.424(1)	0.292(1)	0.3792(1)	1.3(1)
Ti(1)	0.924(1)	0	0.3966(2)	1.4(2)
Ti(2)	0.0609(8)	0.5	0.1013(1)	2.0(1)
Fe(1)	0.0010(5)	0.2542(5)	0.2491(1)	1.4(1)
Fe(2)	0.5053(8)	0.5	0.2463(1)	1.1(1)
Fe(3)	0.5126(6)	0	0.2570(1)	1.0(1)
Ba	0	0.5	0.5	1.8(1)
K	0	0	0	2.3(1)
Ca	0.5	0.5	0	2.5(2)
Na	0.5	0	0.5	3.8(5)
F	0.131(3)	0.5	0.1878(4)	1.8(4)
O(1)	0.633(2)	0.260(1)	0.2004(3)	0.5(4)
O(2)	0.143(3)	0	0.2053(7)	2.1(6)
O(3)	0.5	0.5	0.5	3.2(6)
O(4)	0.884(3)	0.5	0.2900(6)	1.2(5)
O(5)	0.368(2)	0.284(1)	0.3052(4)	1.3(3)
O(6)	0.862(3)	0	0.312(1)	2.3(6)
O(7)	0.319(2)	0.262(2)	0.0829(4)	1.6(4)
O(8)	0	0.5	0	1.4(5)
O(9)	0.806(2)	0.299(3)	0.0879(4)	1.1(3)
O(10)	0.488(5)	0	0.1023(5)	2.5(6)
O(11)	0.317(3)	0.5	0.4032(8)	1.7(6)
O(12)	0.688(3)	0.154(3)	0.4091(6)	4.9(4)
O(13)	0.241(4)	0.160(6)	0.415(1)	5.3(3)
O(14)	0	0	0.5	5.9(7)
O(15)	0.5	0	0	5.6(6)

ordering is observed in titanosilicate micas consisting of linked  $H-O-H$  slabs, such as perraultite and surkhobite (as well as in jinshajiangite), where Ba, K, Na, and Ca atoms occupy their own sites in the channels, resulting in the doubling of all three unit-cell parameters.

In the structure of jinshajiangite from Sweden (Fig. 1), there are two types of mutually perpendicular channels. Calcium atoms in jinshajiangite, like those in the structure of surkhobite (Fig. 2), prevail in the site in the narrow channel, whereas Na atoms completely occupy the site in another channel. Large Ba atoms fill one wide channel with the involvement of a minor amount of K atoms, whereas K atoms dominate in another channel with the involvement of Ba.

The crystal-chemical formula of the mineral jinshajiangite ( $Z = 1$ ) can be written as

**Table 3.** Characteristics of the coordination polyhedra

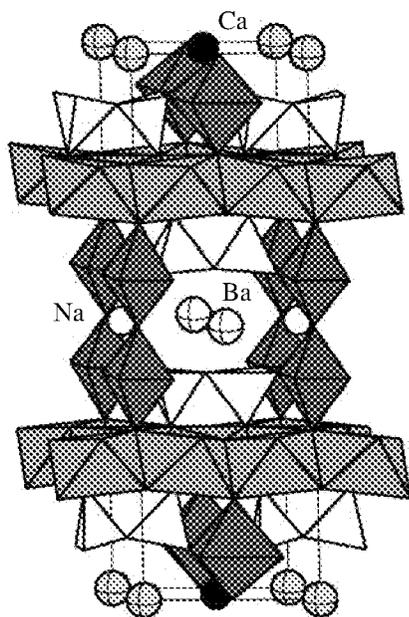
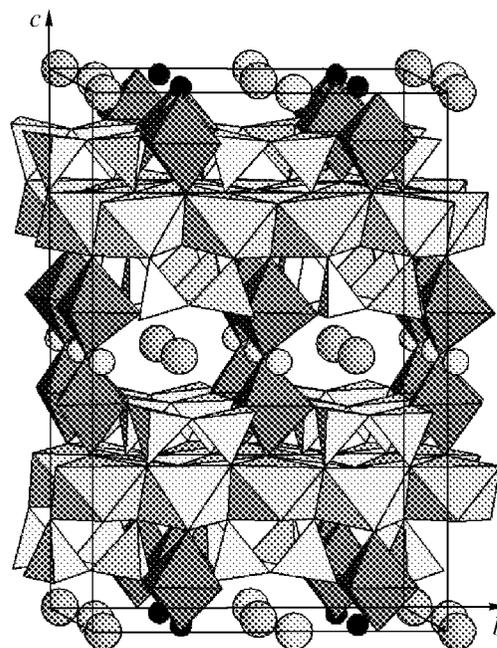
Site	Composition	Coordination number	Cation–anion distances, Å		
			minimum	maximum	average
Ba	0.8Ba + 0.2K	12	2.67(1)	3.34(3)	3.14
K	0.6K + 0.4Ba	12	2.67(1)	3.08(1)	2.93
Ca	0.76Ca + 0.24Ba	10	2.64(1)	2.68(1)	2.66
Na	1Na	10	2.34(2)	2.67(1)	2.48
Fe(1)	4(Fe, Mn)	6	2.04(1)	2.38(1)	2.18
Fe(2)	1.5Fe + 0.5Mg	6	2.07(1)	2.16(1)	2.11
Fe(3)	2(Fe, Mn)	6	2.01(1)	2.39(1)	2.24
Ti(1)	2Ti	6	1.70(1)	2.14(1)	1.88
Ti(2)	1.6Ti + 0.2Nb + 0.2Zr	6	1.78(1)	2.21(1)	2.02
Si(1)	4Si	4	1.49(1)	1.71(1)	1.59
Si(2)	4Si	4	1.53(1)	1.73(1)	1.63

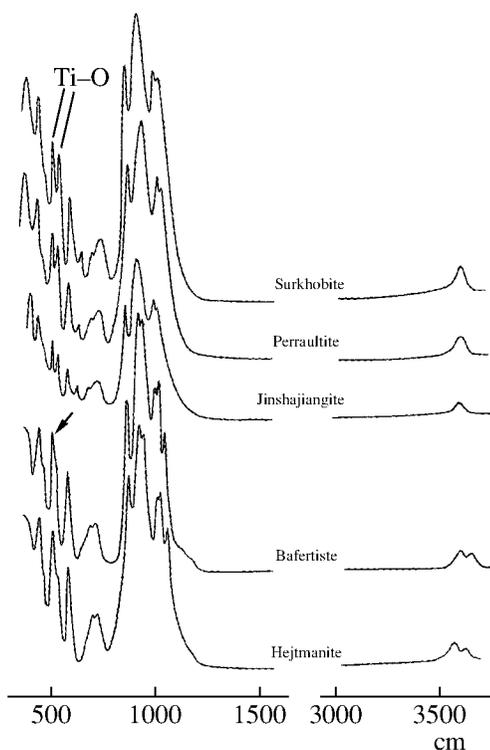
follows:  $[\text{Ba}_{1.44}\text{Na}_1\text{K}_{0.8}\text{Ca}_{0.76}]_{\Sigma 4}[\text{Si}_2\text{O}_7]_4 \times [\text{Ti}_2][\text{Ti}_{1.6}\text{Nb}_{0.2}\text{Zr}_{0.2}][\text{Fe}_6\text{Mn}_{1.5}\text{Mg}_{0.5}]\text{O}_2(\text{OH})_8\text{F}_2$ . The  $\text{O}^{2-}$  and  $\text{OH}(\text{F})$  anions were distinguished on the basis of the bond-valence balance.

The charge-balanced idealized formula can be represented as follows:  $\text{BaKNaCaTi}_4\text{Fe}_6^{2+}\text{Mn}_2 \times [\text{Si}_2\text{O}_7]_4\text{O}_2(\text{OH})_8\text{F}_2$ .

Chinese jinshajiangite was not structurally characterized. However, on the basis of the chemical compo-

sition, the unit-cell parameters, and most of the physical properties, Ferraris et al. [10] showed that this mineral is very likely to belong to the same structure type as perraultite. The fact that this mineral belongs to the perraultite-surkhobite–jinshajiangite family is evident also from the IR spectra (Fig. 3). The arrows in Fig. 3 indicate the Ti–O stretching bands strongly split owing to resonance interactions in the minerals, in which the titanium octahedra from the adjacent layers share vertices (surkhobite, perraultite, and jinshajiangite). In min-

**Fig. 1.** Structure of jinshajiangite from Norra Kärr.**Fig. 2.** Structure of surkhobite. The Ba cations are represented by large closed circles; K, by large open circles; Na, by small open circles; Ca, by small closed circles.



**Fig. 3.** IR spectra of minerals of the bafertisite–perraultite family.

erals in which the Ti octahedra from the adjacent layers are isolated from each other (bafertisite and hejtmanite), the resonance interactions between Ti–O stretching vibrations are substantially weakened, the splitting is virtually absent, and the additional band appears as a shoulder.

The doubling of the  $c$  parameter in minerals belonging to the perraultite structure type is due primarily to the mutual shift of the  $H-O-H$  slabs. As a result, the perraultite structure type is composed of two types of independent three-layer slabs instead of one type of slabs observed in bafertisite. The doubling of the  $a$  and  $b$  parameters is attributed to both the shifts of the cations located in the interlayer space and their positional

ordering involving the distribution of Fe, Mn, and Na cations in the  $O$  layer.

However, the unit-cell volume of the mineral jinshajiangite from Sweden is four times smaller than the volumes of perraultite and surkhobite (and, conceivably, of Chinese jinshajiangite), and the symmetry of the new mineral is lower ( $P2/m$  instead of  $C2$ ). Because of a high Ca content, this mineral is more similar to surkhobite than to perraultite. However, since  $Mn < Fe^{2+}$  in jinshajiangite from Sweden, it can be considered as an iron-rich variety or a polymorph of jinshajiangite, whose unit-cell parameters  $a$  and  $b$  are two times smaller.

#### ACKNOWLEDGMENTS

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