

STRUCTURE OF INORGANIC COMPOUNDS

Determination of the Crystal Structure of Khanneshite by the Rietveld method

Yu. V. Belovitskaya*, I. V. Pekov*, E. R. Gobechiya*, Yu. K. Kabalov*, and J. Schneider**

* Department of Geology, Moscow State University,
Vorob'evy gory, Moscow, 119899 Russia
e-mail: mineral@geol.msu.ru

** Institute for Crystallography and Applied Mineralogy, Ludwig Maximilian University,
Theresienstrasse 41, D-80333 Munich, Germany

Institut für Kristallographie und Angewandte Mineralogie, Universität München

Received October 4, 1999; in final form, February 22, 2001

Abstract—The crystal structure of khanneshite ($\text{Na}_{2.75}\text{Ca}_{0.23}\text{Ba}_{1.08}\text{Sr}_{0.63}\text{Ca}_{0.46}\text{Ce}_{0.46}\text{La}_{0.18}\text{Nd}_{0.15}\text{Pr}_{0.04}\text{Pr}_{0.04}\text{CO}_3)_5$ found in carbonatites from the Khibiny massif (the Kola Peninsula) was solved by the Rietveld method. The X-ray diffraction data were collected on a focusing STOE-STADIP diffractometer equipped with a bent $\text{Ge}(111)$ primary-beam monochromator ($\lambda\text{MoK}\alpha_1$ radiation, $2.00^\circ < 2\theta < 54.98^\circ$, 311 reflections). All the calculations were performed within the sp. gr. $P6_3mc$; $a = 10.5790(1) \text{ \AA}$, $c = 6.5446(1) \text{ \AA}$, $V = 634.31(1) \text{ \AA}^3$, $R_p = 2.38$, $R_{wp} = 3.26$, $R_B = 1.42$, $R_F = 1.79$. The atoms of the cations were refined with anisotropic thermal parameters. © 2002 MAIK "Nauka/Interperiodica".

INTRODUCTION

Khanneshite ($\text{Na, Ca}_3(\text{Ba, Sr, TR, Ca})_3(\text{CO}_3)_5$) belongs to the burbankite structural family including hexagonal and monoclinic pseudohexagonal carbonates of the general formula $A_{3-4}B_{2-3}(\text{CO}_3)_5$, where $A = \text{Na, Ca, or } \square$ and $B = \text{Sr, Ba, TR, or Ca}$.

Khanneshite, the Ba-dominant member of the family, is the most rare of all the burbankite-like minerals. This mineral was discovered in the Khanneshin carbonate complex (Afghanistan) in 1982. After the first publication, a number of questions remained open, because the original material analyzed by the wet method was substantially contaminated with other carbonates and barite. Based on the X-ray diffraction powder pattern, the authors discovered Khanneshite assumed that the new mineral is structurally similar to burbankite ($\text{Na,Ca}_3(\text{Sr,Ca,TR,Ba})_3(\text{CO}_3)_5$, determined its unit-cell parameters, and interpreted them within the hexagonal system ($a = 10.65 \text{ \AA}$, $c = 6.58 \text{ \AA}$) [1].

We revised the structure data based on the results of local X-ray spectral analysis of a holotypic specimen of khanneshite from Khanneshin. On the one hand, our investigation confirmed the existence of the Ba-dominant chemical analogue of burbankite and, on the other hand, demonstrated that the substance under study occurred as thin concretions of this phase with barium-rich burbankite, mckelveyite, and barite [2]. This material was unsuitable for precision X-ray diffraction study. Hence, the structure type of khanneshite remained unknown. We found this mineral also in carbonatites from the Khibiny alkaline massif (the Kola

Peninsula). The latter specimens appeared to be homogeneous [2]. However, all the attempts to study several seemingly single-crystal (according to the optical characteristics) grains of khanneshite from the Khibiny massif by the Laue method have failed: the Laue patterns taken from these grains had no reflections at all. At the same time, the X-ray diffraction powder patterns of the mineral had high quality, and their reflections were adequately indexed within a hexagonal unit cell of the burbankite type. In this connection, we used the Rietveld method for determining the structure of this mineral.

EXPERIMENTAL

Khanneshite from the Khibiny massif was discovered in the only fragment of a core sample from a well on the shore of the Tul'ilukht gulf located in the east part of the massif [2]. The mineral was found in the

Table 1. Chemical composition (wt %) of khanneshite

Na_2O	11.86	Ce_2O_3	10.46
CaO	5.37	Pr_2O_3	1.01
SrO	9.04	Nd_2O_3	3.60
BaO	22.99	CO_2	(30.59)
La_2O_3	4.07	Total	98.99

Note: The CO_2 concentration was calculated from the stoichiometry.

Table 2. Unit-cell parameters and characteristics of the refinement of the khanneshite structure by the Rietveld method

a , Å	10.5790(1)	R_p	2.38
c , Å	6.5446(1)	R_{wp}	3.26
cla	0.6186	R_{exp}	5.34
V , Å ³	634.31(1)	R_B	1.42
Sp. gr.	$P6_3mc$	R_F	1.79
2θ range, deg	2.00–54.98	s^*	1.55
Number of reflections	311	DWD**	0.74
Number of parameters to be refined	54	σ_x^{***}	1.814

* $s = R_{wp}/R_{exp}$, where R_{exp} is the expected R_{wp} value.

** DWD is the Durbin–Watson statistics [9].

*** The multiplier in the calculations of standard deviations [10].

form of irregularly shaped grains up to 2 mm in diameter and the bright carrot-red aggregates of such grains located in a zonal carbonate vein. Khanneshite occurs in association with magnetite, calcite, and dawsonite.

The chemical composition of khanneshite (Table 1) was determined by X-ray spectral analysis (a Camebax microbeam instrument; analyst I.M. Kulikova, Institute of Mineralogy, Geochemistry, and Crystal Chemistry of Rare Elements).

X-ray diffraction study was performed with the use of homogeneous khanneshite grains. The X-ray spectrum of a powdered sample was measured on a focusing STOE-STADIP diffractometer equipped with a bent Ge(111) primary-beam monochromator ($\lambda\text{MoK}\alpha_1$ radiation, $2.00^\circ < 2\theta < 54.98^\circ$, 311 reflections). All the calculations were performed with the use of the WYRIET program (version 3.3) [3] within the sp. gr. $P6_3mc$. The atomic coordinates reported in [4] were used as the starting model. The ionic scattering curves were used. The peak profiles were approximated by the Pearson-VII function with 6FWHM. The asymmetry was refined at $2\theta < 40^\circ$. The refinement was made with the gradual addition of parameters to be refined with the continuous automatic modeling of the background until the attainment of stable R factors. The isotropic refinement converged to the R_{wp} factor of 3.40%.

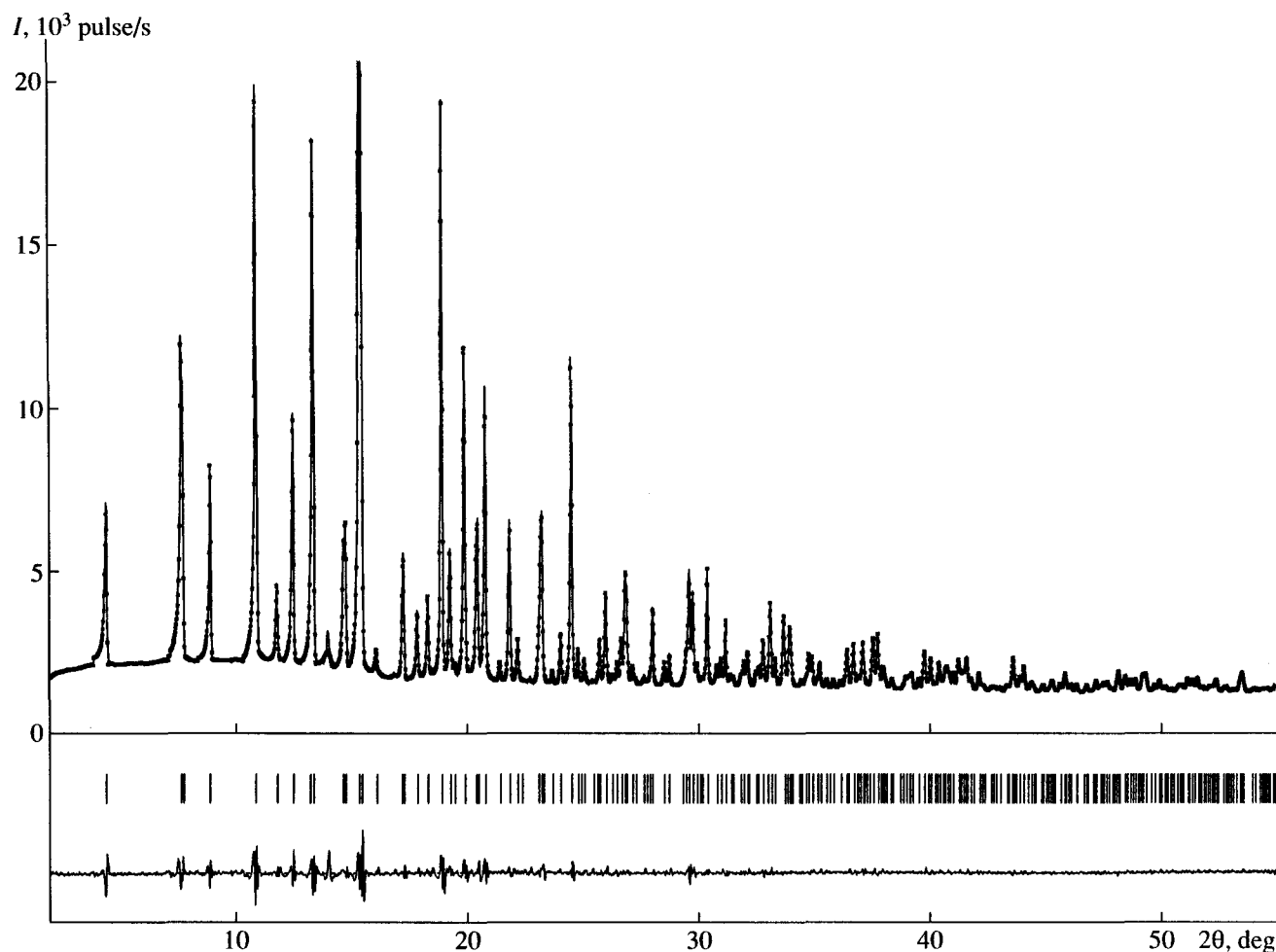
**Fig. 1.** Experimental (solid line) and calculated (dots) X-ray diffraction spectra of khanneshite.

Table 3. Coordinates, thermal parameters ($\text{\AA}^2$), and position occupancies in the khanneshite structure

Atom	Characteristic	Value	Atom	Characteristic	Value
A	<i>x</i>	0.5246(5)	C(3)	<i>x</i>	1/3
	<i>y</i>	0.4754(5)		<i>y</i>	2/3
	<i>z</i>	0.308(2)		<i>z</i>	0.50(2)
	B_j	1.1(2)	O(1)	B_j	3(1)
	<i>q</i> (Na)	2.57(4)		<i>x</i>	0.379(1)
	<i>q</i> (Ca)	0.43(4)		<i>y</i>	0.085(1)
B	<i>x</i>	0.8403(2)	O(2)	<i>z</i>	0.629(2)
	<i>y</i>	0.1597(2)		B_j	1.6(3)
	<i>z</i>	0		<i>x</i>	0.928(1)
	B_j	0.85(3)	O(3)	<i>y</i>	0.072(1)
	<i>q</i> (Sr)	0.63(1)		<i>z</i>	0.344(3)
	<i>q</i> (TR + Ba)	1.90(1)		B_j	3.7(6)
C(1)	<i>q</i> (Ca)	0.46(1)	O(4)	<i>x</i>	0.405(1)
	<i>x</i>	0.799(1)		<i>y</i>	0.595(1)
	<i>y</i>	0.201(1)		<i>z</i>	0.486(8)
	<i>z</i>	0.541(6)		B_j	1.9(4)
C(2)	B_j	1.4(8)		<i>x</i>	0.774(1)
	<i>x</i>	0		<i>y</i>	0.226(1)
	<i>y</i>	0		<i>z</i>	0.359(3)
	<i>z</i>	0.838(9)		B_j	2.4(5)
	B_j	1(1)			

Note: The calculations for TR and Ba atoms were made with the use of the *f*-curve for Ba.

Some selected characteristics of X-ray data collection and the results of the refinement of the khanneshite structure with anisotropic (the A and B cations) and isotropic (the oxygen and carbon atoms) thermal parameters are given in Table 2. The experimental (solid line) and the calculated (dots) X-ray spectra of khanneshite are shown in Fig. 1. The unindexed reflection ($2\theta = 14.00^\circ$, $d = 2.91 \text{ \AA}$, $I = 4$ arb. units) apparently belongs to a mineral-impurity (probably, clinopyroxene). The atomic coordinates, the isotropic thermal parameters, and the occupancies of the positions in the khanneshite structure are listed in Table 3.

RESULTS AND DISCUSSION

Similar to the burbankite structure [5], the crystal structure of khanneshite contains two independent cationic positions corresponding to the eight-vertex

A-polyhedron (Na and Ca) and the ten-vertex B-polyhedron (Ba, Sr, TR, and Ca), and three types of triangular carbonate groups (C(1), C(2), and C(3)) having different orientations (Fig. 2). The average distances in the polyhedra are as follows: A–O, 2.50 $\text{\AA}$; B–O, 2.71 $\text{\AA}$; C(1)–O, 1.27 $\text{\AA}$; C(2)–O, 1.32 $\text{\AA}$; and C(3)–O, 1.31 $\text{\AA}$. The A and B positions are statistically occupied by the corresponding cations.

The unit-cell parameters of khanneshite are larger than those of burbankite ($a = 10.48\text{--}10.53 \text{ \AA}$, $c = 6.48\text{--}6.53 \text{ \AA}$ [4, 5]) due to the incorporation of large barium cations. This also explains the fact that the average interatomic distance in the ten-vertex B-polyhedron in khanneshite (2.71 $\text{\AA}$) is the largest one of all the analogous distances in the structures of other known representatives of the burbankite family: burbankite (2.68–2.70 $\text{\AA}$) [4, 5, 6], calcioburbankite (2.67 $\text{\AA}$) (our data), remondite-(Ce) (2.63 $\text{\AA}$) [7], and petersenite-(Ce)

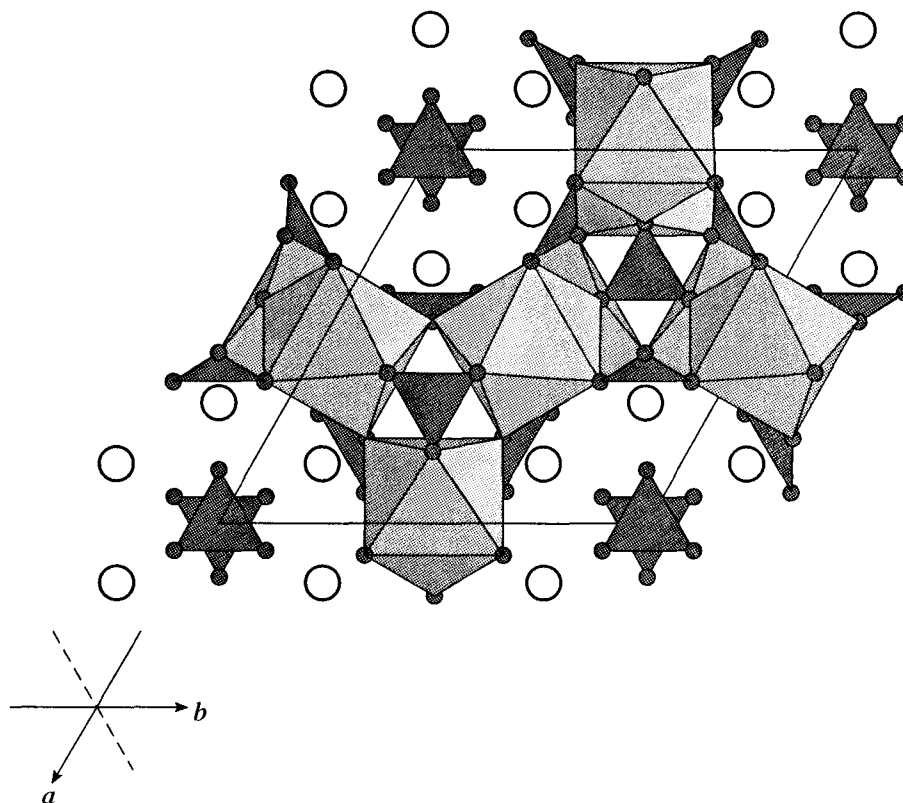


Fig. 2. The khanneshite structure projected onto the *ab* plane; the eight-vertex *A*-polyhedra are indicated by shaded circles, the centers of the ten-vertex *B*-polyhedra are indicated by empty circles, and the CO_3^{-2} triangular anions are indicated by solid circles.

(2.59 Å) [8]. In the transition from burbankite to khanneshite, the physical properties also change because of the replacement of Sr by the heavier Ba cation. The density and the refractive indices in this series increase regularly.

CONCLUSIONS

Khanneshite and burbankite form a continuous series of compositions [2]. Moreover, these two minerals are isostructural ($P6_3mc$). Thus, contrary to the replacement of Sr by *TR*, the incorporation into the structure of larger Ba ions instead of Sr does not change the structural type. Indeed, the burbankite-like mineral remondite $\text{Na}_3(\text{TR}, \text{Sr}, \text{Ca}, \text{Na})_3(\text{CO}_3)_5$, having a similar structural motif, is characterized by the monoclinic symmetry ($P2_1$) [7]. However, on the whole, the burbankite structural type is unfavorable for barium-rich compositions. This is evidenced by the fact that khanneshite occurs very rarely in nature against the background of the rather often occurrence of burbankite forming commercially important deposits.

REFERENCES

1. G. K. Eremenko and V. A. Vel'ko, *Zap. Vseross. Mineral. O–va.* **111** (1), 321 (1982).
2. I. V. Pekov, N. V. Chukanov, and Yu. V. Belovitskaya, *Zap. Vseross. Mineral. O–va.* **127** (2), 92 (1998).
3. J. Schneider, in *Profile Refinement on IBM-PC's: IUCr International Workshop on the Rietveld Method*, Petten, 1989, p. 71.
4. H. Effenberger, F. Kluger, H. Paulus, and E. R. Wolfel, *Neues Jahrb. Mineral., Monatsh.* **4**, 161 (1985).
5. A. A. Voronkov and N. G. Shumyatskaya, *Kristallografiya* **13**, 246 (1968) [*Sov. Phys. Crystallogr.* **13**, 192 (1968)].
6. Yu. V. Belovitskaya, I. V. Pekov, and Yu. K. Kabalov, *Kristallografiya* **45**, 32 (2000) [*Crystallogr. Rep.* **45**, 26 (2000)].
7. P. D. Ginderow, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **45**, 185 (1989).
8. J. D. Grice, J. van Velthuisen, and R. A. Gault, *Can. Mineral.* **32**, 405 (1994).
9. R. Hill and H. Flack, *J. Appl. Crystallogr.* **20**, 356 (1987).
10. J.-F. Berar and P. Lelann, *J. Appl. Crystallogr.* **24**, 1 (1991).

Translated by T. Safonova