Order-disorder high-temperature phase transition in kogarkoite, $Na_3(SO_4)F$
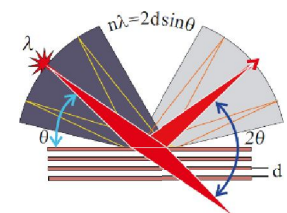
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Introduction

Kogarkoite, Na_3SO_4F, from alkaline rocks of the Lovozero alkaline massif, Kola peninsula, Russia was first described by L.N. Kogarko (1961). Later it was found in hot-springs deposits at Mt. Princeton, Colorado, and named in honor of L.N. Kogarko [1]. Synthetic analogue of kogarkoite was first reported by de Marignac (1859).
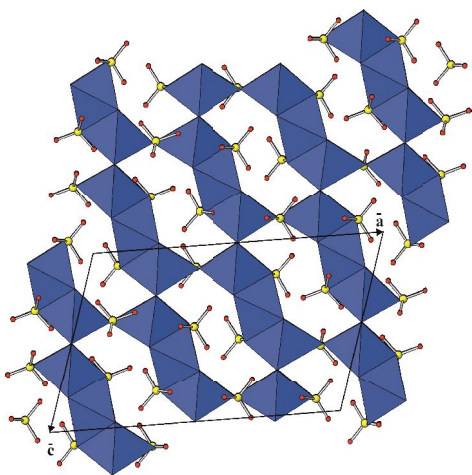

Figure 1. Room-temperature modification of kogarkoite. Projection on plane (010).

The crystal structure of synthetic kogarkoite was studied by single crystal X-Ray diffraction analysis by means of a Bruker Kappa Apex Duo diffractometer equipped with a CCD detector at room temperature and at 150 °C using low-temperature Oxford Cobra Plus system. The room-temperature crystal structure is monoclinic, $P2_1/m$, $a = 18.065(3)$, $b = 6.958(1)$, $c = 11.446(1)$ Å, $\beta = 107.711(1)°$.
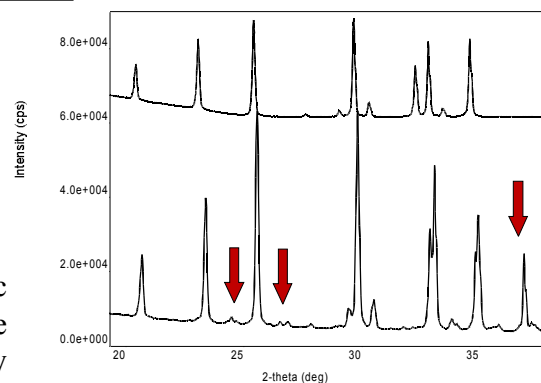

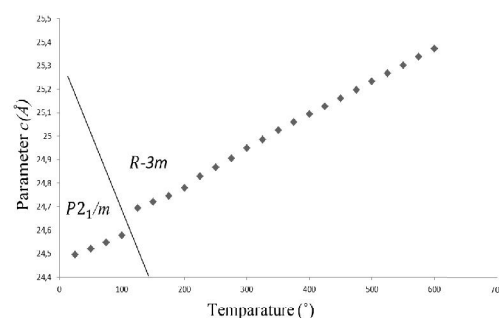Figure 4. The diffraction pattern of kogarkoite under heating in vacuum for room temperature and for 300° C.

Figure 5. Temperature dependence of the trigonal lattice parameter c of kogarkoite.

Results

The structure is based upon face-sharing $[FNa_6]$ octahedra, which form triplets further linked into a three-dimensional framework by sharing corners. The SO_4 tetrahedra are located in the framework cavities (Figure 1) [2]. The high-temperature modification of kogarkoite is trigonal, R-$3m$, $a = 6.94(1)$, $c = 24.58(4)$ Å. The structure of high-temperature modification has the same framework of fluorine-centered octahedra (Figure 2). However, in contrast to the room-temperature modification, SO_4 tetrahedra in the framework cavities are disordered with different orientations of tetrahedra observed at the same time (Figure 3).
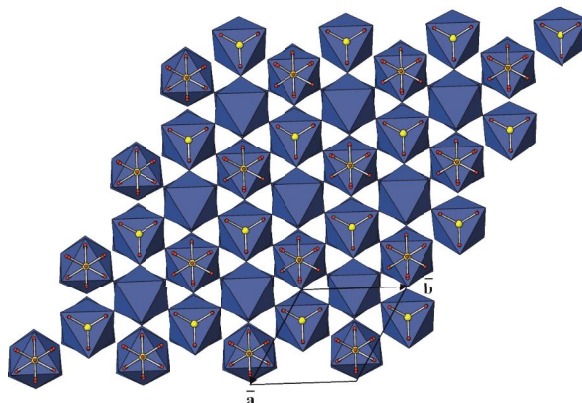

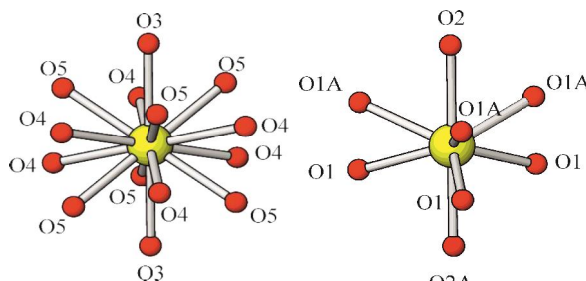Figure 2. High-temperature modification of kogarkoite. Projection on plane (001).

Figure 3. The disodered sulfur tetrahedra in the structure of high-modification of kogarkoite.

Methods

In our study, synthetic crystals of kogarkoite were prepared by evaporation from aqueous solutions of sodium sulfate and sodium fluoride at 25 °C. Thermal behavior of synthetic kogarkoite was studied by high-temperature X-ray powder diffraction method using a Rigaku Ultima IV ($CuK\alpha_{1+2}$ radiation, 40 kV/30 mA, Bragg-Brentano geometry, PSD D-Tex Ultra) diffractometer with a high-temperature attachment in the temperature range of 25-700 °C with the 30-40 degree steps. Thin powder sample was deposited on a Pt sample holder (20x12x2 mm^3) from an ethanol suspension. The unit cell parameters were calculated using the program package Topas 4.2 (Bruker). It was observed that the diffraction pattern of kogarkoite changed dramatically in between 100 and 125 °C that was assigned to the monoclinic-to-trigonal phase transition (Figure 4,5).

Conclusions

Therefore, the $P2_1/m \rightarrow R$-$3m$ phase transition in kogarkoite is associated with the disorder of sulfate tetrahedra in the cavities of the antiperovskite-type framework formed by face- and corner-sharing FNa_6 octahedra.

[1] A. Pabst, W.N. Sharp, *Amer. Mineral.* **58** (1973) 116.

[2] S.V. Krivovichev, *Z. Kristallogr.* **228** (2008) 109.