

On the crystal structure and low-temperature behaviour of davyne: A single-crystal X-ray and neutron diffraction study



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ABSTRACT

The crystal structure of a natural davyne $[(\text{Na}_{3.98}\text{K}_{1.79}\text{Ca}_{1.89}\text{Mg}_{0.02}\text{Fe}_{0.01})_{\Sigma 7.69}(\text{Al}_{5.99}\text{Si}_{6.01}\text{O}_{24})(\text{SO}_4)_{0.65}\text{Cl}_{1.96}]$, $a = 12.7908(5)$ Å, $c = 5.3469(2)$ Å and $V = 757.59(6)$ Å³, space group $P6_3$, its thermoelastic behaviour and low-temperature induced structural evolution have been investigated by single-crystal neutron diffraction and *in situ* single-crystal X-ray diffraction within the range $110 \leq T$ (K) ≤ 293 . X-ray and neutron structure refinements provided a better picture of the disordered configuration of the SO_4 -groups and of the cation sites into the $[0001]$ -channel. No evidence of phase transition or change of the thermoelastic behavior have been observed within the T -range investigated. The volume thermal expansion coefficient is $\alpha_V = 4.2(4) \cdot 10^{-5} \text{ K}^{-1}$, and the axial thermal coefficients are $\alpha_a = 1.4(1) \cdot 10^{-5} \text{ K}^{-1}$ and $\alpha_c = 1.6(1) \cdot 10^{-5} \text{ K}^{-1}$. A series of structure refinements based on X-ray intensity data collected between 293 and 110 K showed that the structural evolution of davyne is driven by the rotation of the rigid TO_4 framework tetrahedra. The main deformation mechanisms of framework and extraframework population, in response to the applied temperature, are described. A comparison between the low-temperature structure evolution of the isotypic davyne, balliranoite and cancrinite is carried out.

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1. Introduction

The cancrinite group comprises more than ten mineralogical species [1,2] and a very large amount of synthetic compounds [e.g., 1–4 and references therein] all sharing the [CAN]-topology of the framework. This very large variety is due to the remarkable flexibility of the [CAN]-framework type, which is built by single six-membered rings (S6Rs) of tetrahedra stacked according to an $\cdots\text{ABAB}\cdots$ sequence. This stacking gives rise to columns of base-sharing ($\text{S6R} \perp [0001]$) cages, the so-called *can* units (or undecahedral/cancrinite cages), which surround large channels (around the 6_3 axis, with 5.9 Å free diameter, [5]) parallel to $[0001]$ and bound by twelve-membered rings of tetrahedra (12R) (Fig. 1). Channel and cage voids are linked by ditrigonal S6R windows ($\text{S6R} \angle [0001]$) (Fig. 2). Each column of cages, centered on a 3-fold axis, can also be viewed as built by three symmetry-related double zigzag chains of tetrahedra (*dzc* unit, [5]) (Fig. 2), whose extension along $[0001]$ controls the symmetry and thermo-elastic properties of the cancrinite-group compounds [6]. Among the mineralogical species, two distinct subgroups can be identified according to the content of the *can* units columns: (1) the cancrinite-subgroup, showing $-\text{Na}-\text{H}_2\text{O}-\text{Na}-\text{H}_2\text{O}$ chains and (2) the davyne subgroup,

with $-\text{Ca}-\text{Cl}-\text{Ca}-\text{Cl}-$ chains (Fig. 3). The 12R-channels can be stuffed with a large variety of cations (e.g., Na^+ , K^+ , Ca^{2+}), closer to the walls, and anions (e.g., CO_3^{2-} , SO_4^{2-} , Cl^- , PO_4^{3-} , $\text{C}_2\text{O}_4^{2-}$) in the center (Fig. 4) [1,2]. In the davyne subgroup, two cationic sites can be found [6–8]: an “external” site (*i.e.*, closer to the wall) occupied by Na^+ and an “internal” site partially occupied by K^+ and Na^+ (or Ca^{2+} in balliranoite, [9,10]) (Fig. 4).

Two minerals belonging to the davyne subgroup can only with difficulty be distinguished: microsommite and davyne *sensu stricto*. Microsommite and davyne share similar chemical compositions, with ideal chemical formulas $[\text{Na}_4\text{K}_2(\text{SO}_4)][\text{Ca}_2\text{Cl}_2][\text{Si}_6\text{Al}_6\text{O}_{24}]$ and $[(\text{Na},\text{K})_6(\text{SO}_4,\text{Cl})][\text{Ca}_2\text{Cl}_2][\text{Si}_6\text{Al}_6\text{O}_{24}]$, respectively. However, their structures are different. Metrically, $a_{\text{mic}} = \sqrt{3}a_{\text{dav}}$, and $c_{\text{mic}} = c_{\text{dav}}$. Hence, microsommite can be identified by the occurrence of superstructure reflections with $h - k \neq 3n$. This superstructure is due to the long-range ordering of the extraframework content within adjacent channels, as already investigated by Bonaccorsi et al. [8]. This long-range order arises from geometrical constraints limiting the number of SO_4 groups to one per unit-cell translation (*i.e.*, 1/2 occupancy of the S site on the 6_3 axis, $2a$ position). The SO_4^{2-} group can coexist with an “external” Na site at the same z coordinate, but it is mutually exclusive with the “internal” K site. If the maximum content of one SO_4^{2-} per formula unit is reached, the channel must be internally ordered, giving rise to a sequence made of clusters of $[\text{Na}_3(\text{SO}_4)]$ at z , followed by clusters of $[(\text{K},\text{Na})_3]$ at

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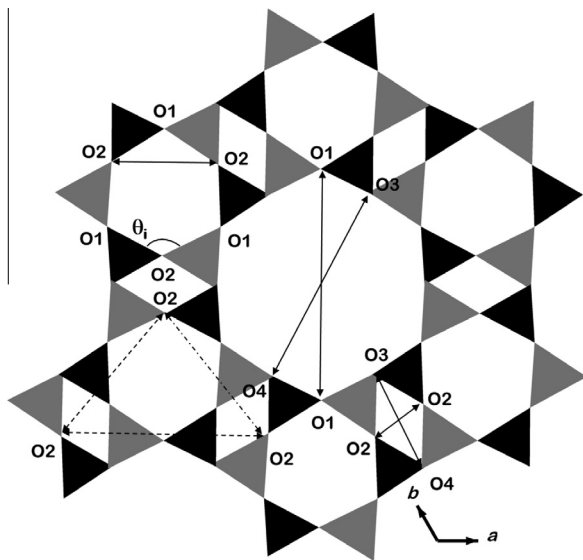


Fig. 1. The [CAN]-framework viewed down [0001]. The 12mR channel is centred on the 6_3 axis and its symmetry-independent diameters are shown. The channel is surrounded by six columns of *can* units, of which, in this projection, are shown the $S6R_{\perp}[0001]$ bases and the $S4R$. The diameters O1–O1_{12R} and O2–O2_{54R} represent the projections onto the (0001) plane.

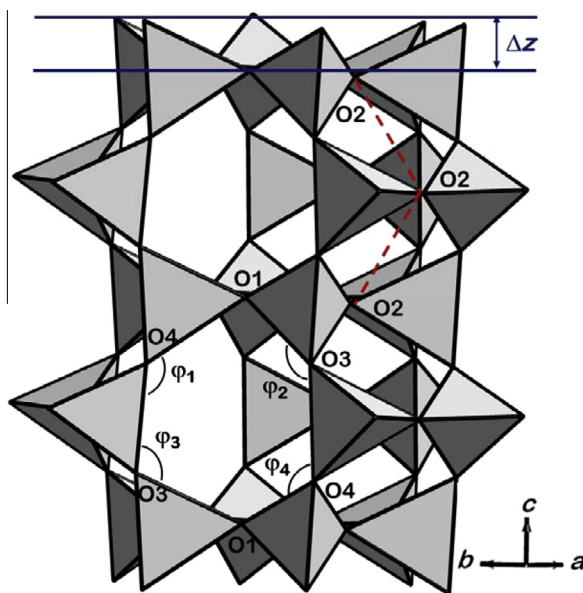


Fig. 2. A column of base-sharing *can* units.

$z + 0.5$, or *viceversa*, since the two possible sequences, arbitrarily defined – and + [8], are energetically equivalent. In microsommite at room- T , Bonaccorsi et al. [8] reported that the order between adjacent channels can be described using a triangular lattice, where two nodes (*i.e.*, channels) are ordered with – and + sequences, respectively, and the third is disordered (*i.e.*, it can show both – or + sequences). This ordering gives rise to the microsommite supercell, keeping the $P6_3$ space group also shown by davyne; the “disordered” channel is centred on the 6_3 axis and the ordered ones on the 3-fold axes. In davyne, the ordering of the channel population is prevented by the insertion of Cl^- according to the $SO_4^{2-} \leftrightarrow 2Cl^-$ substitution. Microsommite can also be seen as the SO_4^{2-} end-member of the subgroup, being quadridavyne [11], with a different kind of superstructure, the Cl^- end-member and davyne

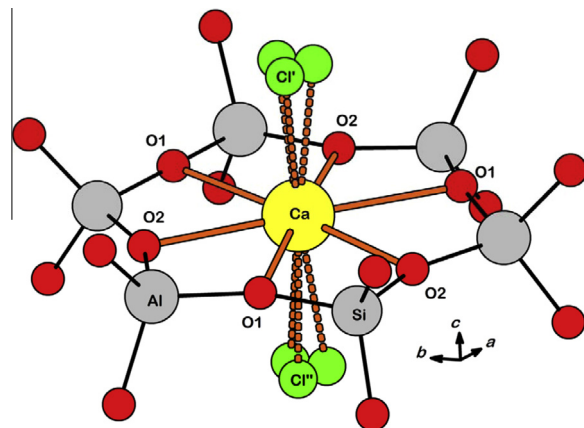


Fig. 3. The Ca coordination environment within the *can* unit. Dashed lines represent the mutually exclusive Ca–Cl bonds.

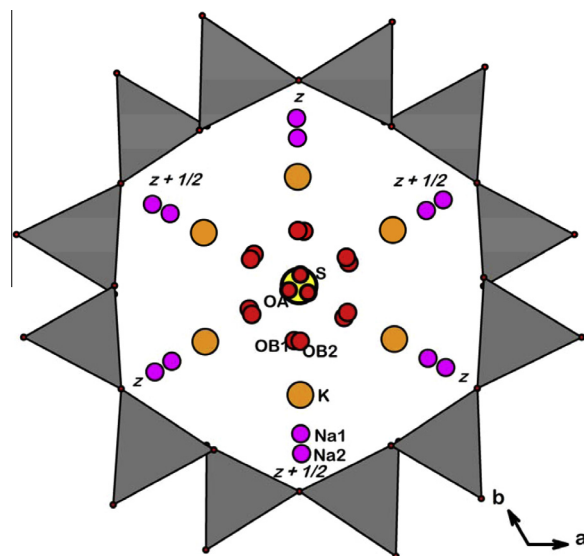


Fig. 4. The channel population viewed down [0001].

the intermediate one. The recently IMA-approved balliranoite [12] is the (CO_3^{2-}) -rich term.

The high-temperature elastic behavior of davyne-group minerals has been studied by Bonaccorsi et al. [6], who reported a T -induced $P6_3$ -to- $P6_3/m$ displacive phase transition in both microsommite and davyne. Above the transition temperature, a very low thermal expansion along the c -axis was observed. Later, Bonaccorsi et al. [8] showed how microsommite undergoes a T -induced phase transition to davyne-type structure, through a continuous decrease of order. In addition, Bonaccorsi et al. [8] reported a Monte Carlo simulation of the low-temperature evolution of the long-range order, with an expected low- T phase transition to the space group $P3$.

The aim of this study is the experimental characterization of the low- T ($T \leq 293$ K) elastic behavior and structure evolution of davyne by means of *in situ* single-crystal X-ray diffraction. For a better description of the crystal structure of the natural davyne used in this study, a single-crystal neutron diffraction investigation (at room- T) has also been performed. Neutron diffraction data are a good probe to describe order–disorder processes when a site population is represented by elements of neighbouring atomic number (as the non-linear dependence of neutron scattering for different

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