Experimental Report

30/09/2013

Proposal: **5-11-403** **Council:** 10/2012

Title: New insight into the crystal structure of davyne (Na,Ca,K)8(Si,Al)12O24(SO4,Cl)3

This proposal is a new proposal

Researh Area: Other...

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Samples: (Na,Ca,K)8(Si,Al)12O24(SO4,Cl)3

Instrument	Req. Days	All. Days	From	To
D9	5	4	11/03/2013	15/03/2013

Abstract:

Davyne, [ideally (Na,Ca,K)8(Si,Al)12O24(SO4,Cl)3, space group P63 or P63/m, a~12.8 and c~5.36 Å] is a member of the so-called “cancrinite group” of minerals. Its crystal structure is built from layers of six-membered rings of Si/Al-tetrahedra with open-cavities in which the extra-framework content (cations, anions and minor H2O) lies. Despite the structure model of davyne previously reported being consistent, at least for the tetrahedral framework, the X-ray experiments left several open questions about the tetrahedral Si/Al-ordering and the extra-framework population: 1) a different configuration of the SO4 groups and of the -Ca-Cl- chains is reported in the previous studies, 2) Na and K have been modeled as ordered in two mutually exclusive sites (only 0.9 Å apart), 3) the main Cl site shows an uncommon vibrational parameters with a pronounced anisotropy (U11~0.1 Å2). The aim of the present study is a reinvestigation of the crystal structure of a natural H2O-bearing davyne (3 wt% H2O) at ambient conditions by means of single-crystal neutron diffraction, in order to define: 1) A reliable description of the Si/Al-ordering at the tetrahedral sites, and so the actual symmetry

New insight into the crystal structure of davyne $(Na,Ca,K)_8(Si,Al)_{12}O_{24}(SO_4,Cl)_3$

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The crystal chemistry and crystal structure of a natural davyne [ideally $(Na,Ca,K)_8(Si,Al)_{12}O_{24}(SO_4,Cl)_3$, $a \sim 12.8$ Å, $c \sim 5.3$ Å, space group $P6_3$,], along with its thermoelastic behaviour and low-T 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.

A large crystal of davyne (0.7 cm^3) from Mt. Vesuvius, Naples, Italy, free of defect under polarized microscope, was selected for this multi-methodological study. The crystal was cut in three fragments in order to perform the chemical analysis, the low-T X-ray diffraction and the room-T neutron diffraction experiments. Electron microprobe analysis in wavelength dispersive mode was performed using a JEOL 8200 microprobe. The average chemical formula, based on 20 point analyses and calculated on the basis of (Si + Al) = 12 a.p.f.u., is the following: $(Na_{3.98}K_{1.79}Ca_{1.89}Mg_{0.02}Fe_{0.01})_{\Sigma 7.69}(Al_{5.99}Si_{6.01}O_{24})(SO_4)_{0.65}Cl_{1.96}$. A further fragment of the original crystal (0.22 x 0.18 x 0.13 mm^3) was used in order to investigate the low-T behavior of davyne by *in situ* single-crystal X-ray diffraction. Six intensity data collections have been performed at 293 (room-T), 250, 220, 180, 140 and 110 K using an Oxford Diffraction Gemini Ultra diffractometer, equipped with a Ruby CCD detector. *In situ* low-T conditions were generated by cooling the crystal with a nitrogen gas flux using an Oxford Cryosystems 700 Plus device. A combination of ω scans, with 1° step and 10 s exposure time per frame, was chosen to maximize the redundancy and data coverage. The reflection conditions confirmed the space group $P6_3$ within the T-range investigated. Intensity data at any T were integrated and corrected for Lorentz-polarization effects and absorption of the crystal. Neutron intensity data were collected at 293 K on the high resolution four-circle diffractometer D9 at ILL, using a wavelength of 0.8242(1) Å obtained using the (220) reflection of a new diamond monochromator working in transmission geometry. The wavelength was calibrated using a germanium single crystal. D9 is equipped with a small two- dimensional area detector, which allowed optimal separation of the peaks from the background. A total number of 2366 reflections were collected up to $2\theta_{max} = 75.54°$, giving 1351 unique reflections. For all data, background corrections and Lorentz corrections were applied. After corrections, the discrepancy factors among the symmetry related reflections was $R_{int} = 0.0305$ (Laue class $6/m$). Least-squares matching of the observed and calculated centroids of the 482 strongest reflections gave a metrically hexagonal unit cell with: $a = b = 12.7615(7)$ Å and $c = 5.3416(3)$ Å , with a primitive lattice. The reflection conditions agreed with the space group $P6_3$.

The high-quality X-ray and neutron structure refinements of this study provided a better picture of the site distribution, bonding configuration and ordering of framework and extra-framework population in davyne structure. The refinements confirm the perfectly ordered Si/Al-distribution in the tetrahedral framework. The cages are occupied by chains of alternated Ca^{2+} and Cl^{-} almost equally spaced. In the channel, the "internal" *K* site is located far from the oxygen walls, likely in order to fit the longer *K-O* bonds. The broad distribution of electron and nuclear density closer to the channel walls has been modelled with two Na sites (*i.e.*, *Na*1 and *Na*2). The K^{+} cation is coordinated with 5 framework oxygen atoms and up to two *OA* apical oxygen (if adjacent upward and downwad SO_4 tetrahedra occur), whereas the Na^{+} cations are coordinated by 4-5 framework oxygen and one *OB* basal oxygen of the sulphate tetrahedron at the same height.

Further details pertaining to the experimental protocols and structure refinement are in Gatta *et al.* (2013).

References

Gatta G.D., Lotti P., Nénert G., Kahlenberg V. (2013) On the crystal structure and low-temperature behaviour of davyne: A single-crystal X-ray and neutron diffraction study. *Microporous and Mesoporous Materials* (under review).

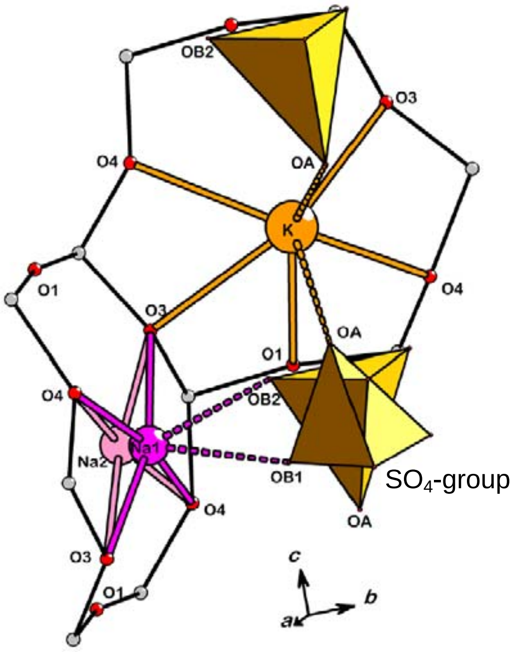

Fig. 1. Bonding configuration of the channel population in davyne structure. Dashed lines represent the mutually exclusive bonds.