

CRYSTAL STRUCTURE OF $Tl_6Ag_{2.2}Cu_{6.8}As_9S_{21}$ E. Makovicky¹ T. Balic-Zunic¹ L. Karanovic² D. Poleti² D. Topa³¹University of Copenhagen Geological Institute Oester Voldgade 10 COPENHAGEN 1350 DENMARK ²University of Belgrade ³University of Salzburg

The crystal structure of a new complex sulfosalt from Binntal, Switzerland, $Tl_6Ag_{2.2}Cu_{6.8}As_9S_{21}$, was determined by a combination of direct methods and difference Fourier syntheses. The 5303 reflections [$I > 2\sigma(I)$] used were collected on a Bruker-AXS four-circle diffractometer equipped with a 1000 K area detector. Empirical absorption correction was used; the resulting R1 value is 0.057 (0.11 for all reflections). Triclinic unit cell ($P-1$) has $a = 12.138$, $b = 12.196$, $c = 15.944$ Å, $\alpha = 78.54^\circ$, $\beta = 84.72^\circ$ and $\gamma = 60.47^\circ$, $Z = 2$. Crystal structure is composed of a layer (A) of pure Tl coordination polyhedra with complex coordinations, CN = 7 to 9. Layer symmetry is $P-1$. This layer is sandwiched by (B) layers composed of AsS_3 coordination pyramids, CuS_3 triangles and AgS_4 tetrahedra. The AsS_3 pyramids are oriented away from the A layer, resulting in an idealized layer group $P3$. The C slabs contain fragments of As_2S_4 columns, 2 paired AsS_3 pyramids high, arranged cyclically around hexagonal channels with Tl-Tl pairs (3.14 Å apart) and trigonal channels occupied by single Tl atoms (CN = 6). The B-C-B slabs have layer symmetry $P-3$. They are staggered by a vector of approximately $[1/3 a - 1/3 b]$ and inverted on the A interlayers. Thus, they give rise to potential stacking polytypes. In the structure determined, polytypy appears to be limited by non-equivalent occupancy of ideally identical Cu/Ag sites in the B layers.

Keywords: THALLIUM SULFOSALT, PSEUDOSYMMETRY, POLYTYPE

3T-TRIOCTAHEDRAL-MICAS, COEXISTING-POLYTYPES, CATION-ORDERINGF. Scordari¹ E. Schingaro G. Ventruiti A. Rinaldi

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Chemical and crystallographic investigations allowed to ascertain that coexistence of at least three polytypes in the same single crystal affect the structure of phlogopite samples belonging to the same volcanoclastic level Mt. Vulture lower pyroclastic deposits. Two single crystals have been analysed in the present work. The first one, labelled LC7-270, is a perfectly ordered 1M polytype, with main crystal data $a = 5.346(1)$, $b = 9.257(3)$, $c = 10.312(3)$ Å, $\beta = 99.92(2)^\circ$, space group $C2/m$, $R = 3.77$, $R_w = 4.09\%$. The second one, labelled LC7G, exhibits coexistence of 1M and 3T and 6-layers polytypes in different proportions. The structural features of the 1M polytype have been reported in a previous work (Schingaro et al., 2001 Eur. J. Mineral., 13, 1057-1069), where this sample was described as affected by structural disorder and its structure refined in space group $C2$ instead of $C2/m$. In the present work an interpretation of that disorder is given in terms of occurrence of coexisting polytype components in the same crystal, with 3T as major component. Relevant crystal data for the 3T polytype are: $a = b = 5.325(1)$, $c = 30.267(3)$ Å, space group $P3_112$, $R = 11.36$, $R_w = 10.67\%$. The occurrence of the 6-layers polytype was deduced by the analysis of the electron density residuals revealed in the 3T structure. Evidence of tetrahedral cation ordering is proved and the way it is related to the formation of different polytype in the same single crystal, particularly 1M and 3T, is discussed.

Keywords: 3T-TRIOCTAHEDRAL-MICAS COEXISTING-POLYTYPES CATION-ORDERING

CRYSTAL-CHEMICAL FEATURES OF FOUR NEW MEMBERS OF LABUNTISOVITE GROUP

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Crystal structure of four members of labuntsovite group from the pegmatites and hydrothermalites of alkaline Kola peninsula massifs were studied using X-ray single-crystal diffraction. Minerals of labuntsovite group are of interest because of ion-exchange properties. The crystal structure of these minerals is characterized by a framework consisting of chains of (Ti,Nb)O-octahedra, linked by tetrahedral four-membered rings $[SiO_4]$, to form a three dimensional framework containing cavities, which are occupied by H_2O and extra-framework cations. There are three extraframework cation sites - A, B, C. In monoclinic members ($a = 14.3$, $b = 13.8$, $c = 7.8$ Å, $\beta = 116.8^\circ$), the chains of (Ti,Nb)O-octahedra can be linked additionally by DO - octahedra, where D is usually a bivalent cation like Mn. The first studied mineral, Cm , has the following formula

$[(Na_{0.7}Ca_{0.7})(Sr_{0.7}Nb_{0.3})][(H_2O)_2K_1]\{[Ba_{0.2}] [Zn_{1.64}(Mn,Fe)_{0.18}(H_2O)_{3.64}]\}$
 $[Ti_{5.68}Nb_{2.32}(O_{5.18} OH_{2.82})][Si_4O_{12}]_4 * 3.3H_2O$, ($Z=1$), (here and further, the composition of A, B, C and D - sites is shown in brackets correspondingly). The distinctive feature of this mineral is split of A site into two sites which are occupied by (Na, Ca) and (Sr, Na) and presence of cation vacancies in B site. The second mineral, Cm has the formula $[Na_{2.4}K_{1.6}][K_{2.2}(H_2O)_{0.8}]\{[K_{0.72}Ba_{0.48}][Fe_{0.66}Mg_{0.44}(H_2O)_{2.2}]\}[Ti_{4.8}Nb_{3.2}(OH_{5.27}O_{2.73})][Si_4O_{12}]_4 * 2.92H_2O$, ($Z=1$). This mineral is also characterized by the A site split into two position occupied by Na and K correspondingly and presence of cation vacancies in B and C sites. The third studied mineral,

Cm , $[Na_{1.96}][K_{2.6}H_3O_{1.36}]\{[Ba_{1.51}K_{0.9}][Mn_{0.3}Zn_{0.2}(H_2O)_1]\}$
 $[Ti_{6.56}Nb_{1.44}(O_{4.22}OH_{3.78})][Si_4O_{12}]_4 * 8H_2O$, ($Z=1$),
 is similar to minerals of vuoriyarvite subgroup due to the small occupancy of D-octahedra. The last one, $C2/m$, $[Na_{3.5}][K_4]\{[Ba_{1.5}][Mn,Fe]_{0.9}(H_2O)_{1.8}\}$
 $[Ti_{7.8}Nb_{0.2}(O,OH)_8][Si_4O_{12}]_4 * 5.4H_2O$, ($Z=1$) contains cation vacancies dominating in D and present in C sites.

Keywords: CRYSTAL STRUCTURE MINERAL LABUNTISOVITE

LOCATION OF BOTH CALCIUM AND SODIUM CATIONS IN DEHYDRATED 5A ZEOLITES AN ANOMALOUS DIFFRACTION STUDYC. Pichon¹ H. Paoli¹ T. Bataille² M. Gailhanou³ B. Rebours¹ J. Lynch¹¹Institut Francais Du Petrole (Ifp) Division Physique Et Analyse 1 Et 4,

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The distribution of charge compensating cations in dehydrated 5A zeolites was studied by anomalous diffraction. The influence of temperature (between 495 and 640K) and of exchange rate (49 and 83% in monovalent cationic equivalent) is followed. The data were recorded on synchrotron beamline H10 (LURE, Orsay - France) near to and far from the K-absorption edge of calcium (4000, 4038, 4043 and 8800eV). A Paar XRK600 diffraction cell was used for the dehydration of the zeolitic samples and the recording of data at temperature. X-ray diffraction patterns were refined by the Rietveld method. Anomalous diffraction with the contrast method allows precise location of both calcium and sodium cations in the zeolitic framework. For an exchange rate of Ca^{2+} of 83% (Na_2Ca_5A), both calcium and sodium cations were located near type I cationic site (at the centre of a hexagonal ring between the sodalite cage and the α -cage). The variation of the temperature (between 495 and 640 K) had no influence on the distribution of cations near this site. Calcium cations were found in majority inside the sodalite cage whereas sodium cations were located in the α -cage. For an exchange rate of 49% (Na_6Ca_3A), calcium cations were all located on site I in the α -cage whereas sodium cations were located on sites I in the sodalite cage of the zeolite. At 605 K a similar calcium and sodium cation distribution near type I cationic site was found. At lower temperature (495 K), an inversion in the cationic distribution between sodium and calcium was noticed.

Keywords: ANOMALOUS DIFFRACTION ZEOLITES