CRYSTAL STRUCTURE OF THE FIRST COPPER-SILVER ARSENIDE, KUTINAITE ($Cu_{14}Ag_6As_7$)

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The crystal structure of kutinaite was determined from powder data on a synthetic sample obtained from pure elements at 623 K. The data were collected on a Guinier diffractometer and reflection intensitites extracted by profile-fitting assuming a cubic P lattice. The structure was solved by direct methods and then refined by Rietveld method to Rp = 13.4% and RB = 1.8%. The cubic structure has a = 11.78079(2) Å and space group $Pm3m$, Z=4. Apart from partially ordered Cu vacancies, the atomic arrangement is practically consistent with Fm3m symmetry, and it is suggested that it is the true symmetry of the high-temperature modification which is supposed to host dynamically disordered vacancies. Cu atoms in partially occupied positions (24/32 per unit cell) are tetrahedrally coordinated by As, while the atoms in fully occupied positions have trigonal planar As coordinations. Ag forms octahedral Ag_6 clusters (Ag-Ag bonds = 2.95-3.05 Å) in octahedral cavities of the Cu-As framework. In the latter, alternativelly, supertetrahedra and cuboctahedra of As-coordinated Cu clusters can be delineated. 1/7 of As atoms are hexahedrally coordinated by Cu atoms, while 6/7 are in somewhat distorted icosahedral coordinaitons by 8 Cu and 4 Ag atoms. A multitude of metal-metal (Cu-Cu, Ag-Ag, and Ag-Cu) and metal-semimetal contacts allows an alternative description of kutinaite as a complex alloy with predominantly icosahedral mutually interpenetrating coordinations.

Keywords: CRYSTAL STRUCTURE KUTINAITE COPPER-SILVER ARSENIDE

INFLUENCE OF FLUORINE CONTENT ON THE COMPOSITION OF Al-RICH SYNTHETIC PHLOGOPITE INVESTIGATED BY SOLID STATE NMR

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The influence of fluorine content on the formation and stability of Al-rich phlogopite has been investigated using solid state NMR spectroscopy. Samples with varying OH/F-ratios and nominal gel compositions of $K(Mg_{3-x}Al_x)[Al_{1+x}Si_{3-x}O_{10}]$ $(OH)_y(F)_{2-y}$ (0.0 < x < 0.8 and 0.5 < y < 1.8) were studied using ^{29}Si, ^{1}H, ^{19}F, ^{27}Al MAS, MQMAS, and {$^{1}H/^{19}F$} ^{27}Al 2D CPMAS (HETCOR) MAS NMR spectroscopies. The ^{29}Si MAS NMR spectra show up to four resonances which can be assigned as Q3(n Al) signals with n = 0 - 3. The experimental Si/[4]Al ratios of hydroxyl-rich compositions indicate an increased Al-content in the tetrahedral sheets suggesting a stabilizing effect on the formation of Al-rich phlogopite. Comparison of the ^{1}H and ^{19}F MAS NMR spectra for different Al- and F-contents reveals a non-statistical distribution of F- and OH-groups at the crystallographic sites in the octahedral sheets where F prefers sites coordinated by three Mg and OH prefers sites with Al and two Mg in the next-nearest coordination sphere. The ^{27}Al quadrupolar parameters for the [4]Al site in phlogopite remain nearly unchanged with increasing F-content whereas for the [6]Al site, there is a clear increase of the asymmetry parameter with increasing F-content. The {^{1}H} ^{27}Al 2D CPMAS (HETCOR) NMR spectrum shows that magnetization is only transferred to the octahedral Al- sites from hydroxyl- groups in Mg_2AlOH sites. The {^{19}F} ^{27}Al 2D CPMAS (HETCOR) NMR spectra are dominated by the resonance from the Mg_3F-complex in phlogopite. Resonances from Mg_2AlF- complexes are not observed.

Keywords: MICAS SOLID STATE NMR SPECTROSCOPY FLUORINE

MIXED COMPLEXES IN THE STRUCTURES OF Zr-PHOSPHATES AND SILICATES

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The compounds with mixed complexes formed by TO_4 tetrahedra (T=P,Si) and MO_6 octahedra (M=Zr,Ti) often exhibit tehnologically important alkali-ion mobility or ion exchange properties. The crystal structures of one synthetic Zr-phosphate $Fe_{0.3}Zr_2(PO_4)_3$(I) and two rare Zr-silicates (hilairite $Na_2ZrSi_3O_9 x 3H_2O$(II) and Zr-rich seidozerite $Mn_{0.425}Ti_{0.575}Zr_{0.925}[Si_2O_7]OF$(III)) were recently studied by x-ray diffraction. The crystal structure of I was solved using Rietveld method in sp. gr. $P2_1/n$, Rwp=3.21%, the crystal structure of II and III were investigated from x-ray single crystal diffraction: II - $R32$, Rhkl=4.65%, III - $P2/c$,Rhkl=5.3%. The 3-dimensional mixed framework in I is of S type ($Sc_2WO_4)_3$): it is built from ZrO_6 octahedra and PO_4 tetrahedra linked together by corner sharing. The F^{3+} ion has an irregular 4-fold coordination. The structure is characterized by the positional disorder and non-stoichiometry that lead to the following structural formula of I: $Fe_{0.46}Zr_2P_{2.9}O_{12}$. Topologically different mixed framework formed by Zr-octahedra and silicate tetrahedral $[Si_3O_9]$ chains was revealed in the structure of hilairite. The results obtained exhibit two new peculiarities in this structure: i)c-parameter is 2 times smaller as compared with previous works (7.975 vs 15.855 Å), ii) a new site statistically occupied by Na atoms and H_2O molecules was localized inside the mixed framework. The structural study of Zr-rich seidozerite allowed considering a lage group of bafertisite-like minerals as the member of a mero-plesiotype series. In fact, the heterophyllosilicate HOH layer which in first approximation represents the common module in this series (merotypism), may modify this kind of structures in different members (plesiotypism).

Keywords: CRYSTAL STRUCTURE, ZR-COMPOUNDS

QUARTZ TWINS WITH INCLINED AXES

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McLaren [1] showed that many quartz twins with inclined axes can be understood in terms of the coincidence site lattice (CSL) model with multiplicity values S<26 and axial ratio approximating the experimental value c/a=1.10000±5 to within ±1.64%. An exception is the Friedel twin, which he interpreted as S=72 with a c/a value deviating more strongly from 1.1. McLaren used graphical methods to find the CSL approximations. The methods developed by Grimmer [2] make it possible to systematically determine all CSL misorientations with c/a in a given interval and S less than a given value. Comparison with [1] generally confirms McLarens results but leads to some corrections and alternative interpretations. We have also calculated the CSL misorientations for the exact axial ratio c/a=1.1. for this axial ratio the lowest specific S-value is 110 and corresponds to the Friedel twin. Also the other twins considered by McLaren can be explained as CSL misorientations for this axial ratio with S-values that are among the lowest that exist for c/a=1.1. This new interpretation has several advantages: 1) It explains also the occurrence of Friedel twins and why these have been observed only in quartz that existed as α-quartz since the time of its formation. 2) The theoretical value of the angle describing the misorientation of the two crystals coincides precisely with the literature value for the corresponding twin law. The higher probability of neighbouring grains in CSL misorientations with low values of S was clearly demonstrated in a number of experimental situations, e.g. [3, 4]. In naturally grown quartz, misorientations are favoured that correspond even to large values of S. We attribute this fact to the slow and mechanically unconstrained hydrothermal growth, where even shallow energy minima as a function of the misorientation lead to observably higher frequencies of occurrence.

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