

Reexamination of yedlinitite, $\text{Pb}_6(\text{Cl},\text{OH})_6\text{Cr}^{3+}(\text{OH},\text{O})_8$, using single-crystal X-ray diffraction and Raman spectroscopy, and redetermination of the chemical formula

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The crystal structure of yedlinitite was determined by Wood et al. (1974) and refined to $R = 14\%$. They suggested several possible chemical compositions and the IMA adopted $\text{Pb}_6\text{Cl}_6\text{Cr}(\text{O},\text{OH},11_2\text{O})_8$. Wood et al. (1974) suggest that the Cr valence should be 6+ based on their short Cr–O bond length (1.82(10)Å). They state that yedlinitite is the first recognized mineral containing 6-coordinated Cr^{6+} . Due to the rarity of Cr^{6+} , its toxicity, and the high R-factor in the previous study, we undertook a reinvestigation of yedlinitite with single-crystal X-ray diffraction and Raman spectroscopy. Using 5310 X-ray diffraction intensity data collected on a Bruker X8 Apex CCD diffractometer, the crystal structure of yedlinitite has been refined to $R_1 = 1.5\%$ with 37 variables and 824 independent reflections. The space group is R-3; $a = 12.8762(2)$ Å and $c = 9.8367(3)$ Å.

Our refinement indicates that Cr is bonded to six OH groups with bond lengths of 1.973(3)Å, consistent with Cr^{3+} in 6-coordination with O^{2-} or OH, as observed in chromite and chlorite ($\text{Cr}^{3+}-\text{O}^{2-} = 1.995$ Å and $\text{Cr}^{3+}-\text{OH} = 2.008$ Å) (cf. Lenaz et al. 2004; Bailey 1986). Difference Fourier maps reveal the locations of H bonded to O^{2-} atoms in the structure. H atoms were not located in the previous study, and have rarely been found in structures with heavy atoms such as Pb. The refinement also indicates that O, OH, or H_2O substitutes for Cl in about 11% of the sites.

If Cr^{3+} is coordinated to six OH in an octahedral arrangement, then O–H...O groups are oriented subparallel to the c-axis of the crystal with an average O–O separation of ~2.9Å. Therefore we collected polarized Raman spectra, which shows a broad O–H...O stretching peak centered at 3515 cm^{-1} , consistent with an O–O distance of ~2.9Å (Nakamoto et al., 1955). The mode only appears when the laser polarization is subparallel to the c-axis of the crystal, indicating that OH is subparallel to this axis. This observation supports our conclusion that Cr is coordinated to OH.

To test our conclusions, bond valence calculations (Brown, 1981) were undertaken. These verify the valence of Cr^{3+} and show significant underbonding of both O1 and O2 sites. The underbonding can be explained by the presence of OH in both sites, with occupancies of ~0.75 and ~0.25, respectively. This study indicates that the formula of our yedlinitite is $\text{Pb}_6(\text{Cl}_{0.887}\text{OH}_{0.113})_6\text{Cr}^{3+}(\text{OH}_{0.63}\text{O}_{0.38})_8$.

P08-13

Site distribution and structural state of Th in fluorapatite determined by single crystal XRD and EXAFS

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Thorium in apatite has been used extensively in geochronologic and petrogenetic studies for decades. Because of its high affinity for Th and other radionuclides and its thermal annealing behavior, there is also great interest in apatite as a solid nuclear-waste form and an engineered contaminant barrier. Fundamental to our understanding of thorium retention and release by apatite are crystal chemical parameters such as site occupancy and structural distortions created by this substituent. Despite the interest in Th in apatite, the basic crystal chemistry of its substitution in the structure is still unknown. There are two cation sites in the apatite structure that can accommodate Th. The Ca1 site has a coordination shell of nine oxygens, and six nearest neighbor oxygens and fluorine surround the Ca2 site. We present the first direct evidence of the site of incorporation and the response of the structure to Th. Single crystal X-ray diffraction data were used to refine the structure and site occupancies of a synthetic fluorapatite with approximately 2 wt% Th in the structure. Extended X-ray absorption fine structure (EXAFS) was used to probe the local structure of Th within the synthetic sample and a natural fluorapatite from Mineville, NY with a Th concentration of approximately 2000 ppm.

Structure refinements of three separate crystals of the synthetic Th doped fluorapatite ($R = 0.0167\text{--}0.02167$), including site occupancies, indicate that Th partitions almost exclusively into the Ca2 site. EXAFS results also indicate that Th substitutes into the Ca2 site and yield Th specific bond distances not obtainable from XRD data. Discrimination of the site of Th occupation

P08-14

Crystal chemistry of the new asbestiform fluoro-edenite amphiboles of volcanic origin from Biancavilla (Sicily, Italy)

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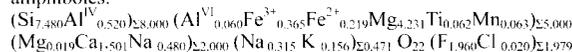
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Natural fluoro-edenite, $[\text{NaCa}_2\text{Mg}_5(\text{Si}_7\text{Al})\text{O}_{22}\text{F}_2]$, a new end-member of the Ca-amphibole group, belonging to the edenite→fluoro-edenite series, was found as both prismatic and asbestiform morphologies in the altered lavic products of the Monte Calvario locality, Biancavilla (Mt. Etna, Sicily, Italy). Environmental studies of the area allowed recognizing the fluoro-edenite asbestiform variety as the cause of the health disease in the local population. Crystal chemistry of the prismatic variety was first described by Gianfagna and Oberti (2001), whereas the asbestiform variety has never been studied so far.

Present work reports original crystal chemical data on these asbestiform amphiboles. Chemical investigations on the fibres from Biancavilla were performed through specific methodologies: SEM-EDS standardized microanalyses, and Mössbauer spectroscopy. The specific procedures adopted for material preparation are also reported. Prismatic fluoro-edenite was utilised as chemical reference standard for fibre microanalysis. Mössbauer investigation in the region from -10 to 10 mm/s showed no evidence of magnetic sextets due to Fe oxides or hydroxides. On these bases, both the sharp and the wide components were considered when quantifying the actual Fe^{3+} content, which turned out to be 67.2% of Fe_{tot} .

Combining Mössbauer $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios with microchemical data, the following averaged chemical formula was obtained for the asbestiform fluoro-edenite amphiboles:



Powder diffraction data were collected on a fully automated parallel-beam Siemens D5005 diffractometer, and were evaluated by the Rietveld method using the GSAS crystallographic suite of programs. Cell parameters, positional parameters for all the atoms, and site scattering for O3, M1, M2, M3, M4, A, and Am were refined. In agreement with cation site partition based on both XRPD and Mössbauer data, Fe^{3+} was assigned to M2 and M3 sites and all Fe^{2+} was assigned to M2 site. In particular, Fe^{2+} content of each M2 site is far larger (0.090 apfu) than the analogous content of M3 (0.039 apfu).

The results of this multi-analytical approach to the crystal chemistry of the asbestiform fluoro-edenite amphiboles, in addition to mineralogical interest, is also highly relevant for environmental and health aspects. In fact, detailed chemical and structural characterization of fibres revealed to be extremely useful to understand the reactivity mechanisms between mineral fibres and biological environment.

P08-15

Architecture and physical properties of Cyndrite $\text{Fe}_{1\pm m}\text{Sn}_{4\pm n}\text{Pb}_{3\pm y}\text{Sb}_{2\pm z}\text{S}_{14}$

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For to find novel semiconducting materials promising application in micro- and nano-technology, we focused on cyndrite $\text{FeSn}_4\text{Pb}_3\text{Sb}_2\text{S}_{14}$, due to its narrow band gap, magnetic properties and the possibility to design the morphology. Natural cyndrite appears as lamellae and as cylinders. Its crystal structure is incommensurately modulated. Its band gap energy (E_g) cyndrite was found to be 0.65eV [1]. Paramagnetic behaviour and ferromagnetic effects were observed for $T < 30\text{ K}$ [2], which correlate to cylinder size and Fe(II)-content. For the first time, synthetic crystals of cyndrite, lamellae, cylinders, tubes and scrolls around glass rods, have been produced by CVT from 660° to 630°C with iodine as transporting agent. Depending on the chemical composition of the educt we influenced the morphology of the cyndrites. At excesses of Pb leads cylindrical shaped crystals occurred, while cylindrical cyndrites appear for (Pb+Fe)/(Sn+Sb)-ratios larger than 0.64±0.02. For ratios less than that value the growth of lamellar individuals are favoured. The crystal structure (SG P1) is formed by alternating T-slabs (pseudo-tetragonal, PbS-type) and H-slabs (pseudohexagonal, SnS_2 -type) with a misfit between them. According to Makovicky [3] subcells can be defined: T-slabs are characterized by $a_0=11.73$ Å, $b_0=5.79$ Å, $c_0=5.81$ Å, $\alpha=90^\circ$, $\beta=92.38^\circ$, $\gamma=93.87^\circ$ and H-slabs show $a_0=23.42$ Å, $b_0=3.67$ Å, $c_0=6.32$ Å, $\alpha=90^\circ$, $\beta=92.58^\circ$ and $\gamma=90.85^\circ$. In both cases there is a long-range incommensurability along the b-axis. Smaller mismatches along the c-direction are accommodated by a semicommutate modulation of wavelength $6c_0^{\text{H}}$ or $6.5c_0^{\text{T}}$. For cylindrical cylinders the c-direction lies parallel to the "rolling-axis", whereas the curvature follows the b-direction. The a-axis lies perpendicular to both slabs and to the cylinder. For natural cyndrite ($\varnothing > 1\text{ mm}$) the curvature is realized by intergrowth of wedge-shaped segments, inside of which the (100) layers are relaxed. Within the relatively sharp interfaces between adjacent wedge-shaped segments, they are appreciably bent or interrupted. TEM studies revealed a tilt angle of about 14° between adjacent segments. Superstructure models for the (001)-plane indicate an interfacial plane (120). Due to the above mentioned tilt angle, the (120) plane acts as symmetry plane and, therefore, the wedge-shaped segments are in twin-orientation. In contrast to natural cyndrites, the (100) planes inside the segments of synthetic cylinders ($\varnothing < 20\ \mu\text{m}$) are elastically strained. They are continuously bent without a well-distinct interface between adjacent segments. The platelets and lamellae do not show any segmentation. U-I-measurements of natural and synthetic cyndrite cylinders confirm the semiconducting behaviour. Hall-measurements of a synthetic lamella of $\text{Fe}_{0.7}\text{Sn}_{4.2}\text{Pb}_{3.5}\text{Sb}_{1.5}\text{S}_{14}$ revealed n-type conductivity and an electrical resistance of 0.5 Ω·m. Optical measurements of E_g ranged from 0.65eV for natural cyndrite cylinders to 1.15eV for synthetic platelets with degreasing (Pb+Fe)/(Sn+Sb)-ratio from 0.71 to 0.53.

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