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Characterization of fibrous minerals by Raman Spectroscopy

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The study of the fibrous minerals has been until now carried out by techniques (X-Ray, SEM, TEM, AEM) for which careful preparation of the samples, with also risks of creating artefacts, is necessary. In this work we applied Raman spectroscopy which needs no samples preparation for the characterization of fibrous minerals [1-3], in particular fluoro-edenite, carlosturanite and the fibrous variety of antigorite. Until now these mineral phases are not still considered by the law "asbestos" but being fibrous, their toxicity on human health is actually under study. All the samples were previously characterized by using the classic X-Ray, SEM, TEM methods in order to be sure of the mineralogical characteristic of the fibres. After, a μ-Raman study has been performed on single bundles of fibres placed with different orientation with respect to the laser incident beam. The μ-Raman used is a spectrometer HR800 LabRam Jobin Yvon equipped with a CCD air-cooled detector, an Olympus BX41 microscope, a television camera and a 20 mW HeNe laser working at 632.8 nm. In order to compensate for noise, the spectra were registered using 10 cycles of 60 scans each, resolution 1 cm^{-1}. The correct calibration of the instrument was verified by measuring the Stokes and anti-Stokes bands and checking before every run the position of Si band at ± 520.6 cm^{-1}. During this work it was be possible to identify the vibrational modes of the different groups constituting the crystalline structure. In particular, the vibrational frequencies of the SiO_4 and AlO_4 groups lye at characteristic values for each mineral phase considered. The value experimentally observed are discussed in function of the crystalline structure and of the vibrational frequencies calculated for fluoro-edenite. In fact on this last phase the theoretical vibrational spectrum has been recently calculated by Causà, Orlando by using the program CRYSTAL [3], an ab initio Hartree-Fock and Density Functional set of programs for periodic systems in three, two and one dimensions.

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Organic/inorganic hybrid materials containing benzyldimethyl-n-alkylammonium haloplumbates with n = 2-4

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The relationship between sorption properties and the behaviour of benzyldimethyl-n-alkylammonium cations in the crystalline phases containing polimeric chains built of -$[PbBr_3]$- mers have been studied for alkyl of various lengths [1]. Halometallates(II) represent interesting systems for designing low-dimensional architecture with useful electronic, thermal, electrical, magnetic and other properties. Haloplumbates(II) form a particular class of these materials because the flexibility of Pb(II) coordination sphere and non-stereospecific nature of the halide anions. Organic/inorganic hybrid materials containing benzyldimethyl-n-alkylammonium haloplumbates(II) combine behaviour typical for organic molecular crystals, especially hydrophobic properties provided by the alkyl chains with those associated to inorganic solids.
The crystal structures of three derivatives with n = 2-4 were determined by X-ray diffraction showing one-dimensional linear $[PbBr_3]_n$ strands similar to those found in the structures of long (n = 9, 10) chain benzyldimethyl-n-alkylammonium bromoplumbates(II) reported previously [2]. The modification of the lengths of alkyl substituent influences the packing properties and type of interactions: in the case of propyl and buthyl derivatives a pseudo-hexagonal packing is observed whereas the benzyldimethyletylammonium bromoplumbate shows layerd architecture like that in the crystals of long (n = 9, 10) chain benzyldimetyl-n-alkylammonium bromo-plumbates(II). In all of the structures an ability to form weak hydrogen bond systems of C-H...π and C-H...X (X = halogene atom) type is observed.

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