MS81.P24

**Acta Cryst.** (2011) A67, C710

**Surface modification of hydroxyapatite by grafting alkyl phosphonic dichloride**

Hassen Agougui, Abdallah Aissa, Mongi Debbabi, Laboratoire de Physico-Chimie des Matériaux, Faculté des Sciences de Monastir, Monastir, Tunisia.

E-mail: Hassenagougui@yahoo.fr

The inorganic-organic hybrids have interesting applications resulting from the combination of some characteristic properties of the inorganic substrate (mechanical and chemical properties, exchange capacity, bioreactivity, optical properties...) with those of the organic grafting (polymerizability, superficial tension...). Such modified materials are used in catalysis, chromatography, biomedical domain... A treatment of calcium hydroxyapatite Ca$_3$(PO$_4$)$_2$(OH) was performed by the different alkylphosphonates (R-POCl$_2$, R= methyl or octyl) in organic solvent using a molar ratio x=2 or 4, x=n(organic)/n(apatite). The surface of the modified CaHAp was characterized using X-ray diffraction, IR and $^{31}$P MAS-NMR spectroscopies, chemical analysis and Atomic Force Microscopy (AFM). No remarkable change in XRD patterns was observed after grafting. FTIR results indicated that new vibration modes related to phosphonic groups appeared essentially at 2930, 1315, 945, 764 and 514 cm$^{-1}$. The $^{31}$P MAS-NMR spectra of treated hydroxyapatite show new signals due to the formation of organic–inorganic bonds in the surface between the superficial hydroxyl groups of the apatite (=CaOH and =POH) and alkyl phosphonic dichloride. AFM proved that the texture surface was changed and roughness decreased. The number of phosphonate groups grafted, in the modified materials, was calculated from chemical analysis results.

**Keywords:** apatite, functional, AFM

MS81.P25

**Acta Cryst.** (2011) A67, C710

**An ab initio study of ZrO$_2$-H$_2$O, solid solution with cotunnite structure**

Alexandra M. Goryaeva,$^1$ Victor L. Vinograd,$^3$ Bjorn Winkler,$^2$ Nikolay N. Eremin,$^1$ Vadim S. Urusov,$^1$ $^1$Department of Crystallography and Crystal Chemistry, Moscow State University, Moscow (Russia). $^2$Institute of Energy and Climate Research (IEF-6), Forschungszentrum Jülich, Jülich (Germany). $^3$Institute of Geosciences, University of Frankfurt, Frankfurt a.M. (Germany).

E-mail: a.goryaeva@mail.ru

Previous experimental and theoretical studies [1], [2], [3], [4] suggested that cotunnite-type zirconia and hafnia, as well as their solid solutions, could be candidates for superhard materials due to their high bulk moduli. Another possible application of cotunnite-type ZrO$_2$ and HfO$_2$ as waveguide materials is discussed here. An investigation of these questions requires knowledge of the elastic stiffness tensor as a function of chemical composition. According to the results of ab initio calculations [2, 4 and this study] the elastic stiffness coefficients of the H$_2$O polymorphs are significantly larger than those of the corresponding ZrO$_2$ polymorphs, while the volumes of the ZrO$_2$ polymorphs are consistently smaller. It is not obvious whether the contraction of the HfO$_2$ structure due to the incorporation of a smaller, but more compressible cation causes an increase in the bulk modulus, or how the incorporation of the larger, but less compressible Hf cation changes the elastic stiffness properties of ZrO$_2$.

We have computed the elastic stiffness tensors of ZrO$_2$ and HfO$_2$ polymorphs with baddeleyite-type (P$\bar{2}$$_1$)$_2$, Pbca and cotunnite-type (P$\bar{2}$$_1$) structures in order to obtain the anisotropy of sound wave phase velocities and have calculated the thermodynamic mixing properties of H$_2$O-ZrO$_2$ solid solutions with the cotunnite structure. The calculations were based on density functional theory within the generalized gradient approximation (GGA) with PBE and PBEsol functionals [5, 6]. The calculations were carried out with the program CASTEP [7] using high-performance computers at the University of Frankfurt and at the Moscow State University.

The anisotropic sound wave phase velocities were determined using the Christoffel tensor [8]. Despite the lower stiffness, the calculated speeds of sound wave propagation are generally higher for ZrO$_2$ polymorphs because of their lower density. Cotunnite-type ZrO$_2$ has rather high longitudinal acoustic wave velocities (about 8 km/s) which are not strongly dependent on direction and thus could be considered for applications as a solid acoustical waveguide material.

The solid solution is characterized by unusual negative enthalpy and volume of mixing. The ordering energies corresponding to the reaction ZrZr + HfHf = 2ZrHf were calculated for 9 interatomic distances within a 2x2x1 supercell. These energies are very small (< 1 kJ/mol). This suggests that any intermediate ordered compound can be used as a probe for the elastic stiffness of the solid solution at intermediate compositions. The calculations of elastic stiffness tensors of ordered compounds within the HfO$_2$-ZrO$_2$ binary are currently underway.

**Keywords:** solid_solution, elastic_property

MS81.P26

**Acta Cryst.** (2011) A67, C710-C711

**Crystal structures and ultramicroporosity in Mg & Ca tetraphosphonate hybrids**

Rosario M. Pérez Colodrero,$^1$ Aurelio Cabeza Díaz,$^2$ Jordi Rius,$^3$ Pascual Olivera-Pastor,$^4$ Konstantinos D Demadis,$^1$ Didier Villemin,$^4$ Miguel Angel Garcia Aranda,$^5$ Departamento de Química Inorgánica, Universidad de Málaga, Málaga (Spain). $^1$Institucions de Ciencies de Materials de Barcelona, Bellaterra, Catalunya (Spain). $^2$Crystal Engineering, Growth & Design Laboratory, Department of Chemistry, University of Crete, Heraklion, Crete (Greece). $^3$UMR CNRS 6597, INSTM, Université de Caen, Caen (France).

E-mail: colodrero@uma.es

The chemistry of hybrid organic-inorganic materials has experimented, during the past decade, an exponential growth due to the high number of possible applications in many fields such as gas storage, catalysis, and ion exchange [1]. The phosphonate-based metal organic framework is today under investigation, and it is a common opinion that the best results are forthcoming. This is mainly due to the fact that generally the phosphonic acids have a higher flexibility degree, with respect to the carboxylic ligands, leading to a major structural variability and therefore to a lower control in their design.