Posters

MS81.P24  
*Acta Cryst.* (2011) A67, C710

Surface modification of hydroxyapatite by grafting alkyl phosphonic dichloride

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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 suspension of calcium hydroxyapatite Ca$_5$(PO$_4$)$_3$(OH) was treated by the different alkyl phosphonates (R-POCl$_2$, R= methyl or octyl) in organic solvent using a molar ratio x=2 or 4, x= n(organic)/ napatite. 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 phosphonate groups appear 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 theapatite (=CaOH and =POH) and alkyl phosphonic dichloride. AFM proved that the texture surface was changed and roughness decreased. The number of phosphate 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

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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$_2$$_1$_1$_2$$_0$_1), Pbca and cotunnite-type (Pmna) structures in order to obtain the anisotropy of sound wave phase velocities and have calculated the thermodynamic mixing properties of HfO$_2$-ZrO$_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 acoustic 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  

Crystal structures and ultramicroporosity in Mg & Ca tetraphosphate hydrates

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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.
In this work, we present the synthesis, characterization and surface analysis of two tetraphosphonates [octamethylenediaminetetraakis(methylene phosphonates)] hybrids based on calcium (Ca₆C₁₂H₉O₉N₉P₈·3H₂O) and magnesium (Mg₆C₁₂H₉O₉N₉P₈·2H₂O·0.5(C₆H₇NCHO)₈). prepared at RT and hydrothermally. The crystal structures of both derivates have been solved by ab initio x-ray powder diffraction methods. The calcium sample present a two dimensional framework meanwhile the magnesium derivate is a three dimensional compound. The BET N₂-surface were lower than 5 m²/g for both compounds. The BET CO₂-surface for the activated Mg-derivative was 160 m²/g. A discussion of the crystal structures and porosities will be reported.


Keywords: molybdates, polyoxometalate structures, inorganic compositions with a unique structure and diverse properties. The interest in the synthesis and structure investigation of the polymolybdates is due to their great practical importance in the organocatalysis. Isomorphous doping Sr₉La₄F₁₃₋ₓ gives only in the case of x=0.47 the ions Fₓ⁻ enter in 4b positions which is followed by substantial deviation of Igσ value from the linear dependence in the range x=0.15–0.35.

MS81.P28

Defect structure and ionic conductivity of Sr₉La₄F₁₃₋ₓ (x= 0.1-0.5)

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Sr₉La₄F₁₃₋ₓ crystals are promising materials for optical applications in UV- and IR-bands [1]. Isomorphous doping SrFₓ with La enlarges its ionic conductivity by 9 orders of magnitude (at T= 500 K) in comparison with the pure crystals making it a superionic conductor [2]. Neutron diffraction studies of Sr₉,xLaₓ₋₁F₁₃ [3] showed that the interstitial fluorine ions (Fₓ⁻) are present only in the 32j-position of the fluorite structure (sp.gr. Fm3m). The tetrahedral cluster was proposed [4] to set the additional interstitial ions in the lattice. We report the evolution of the defect structure in the system Sr₉La₄F₁₃₋ₓ in a wide concentration range (x=0.1-0.5) determined by x-ray single crystal method and its relation to the conductivity measurements taken from [5]. The same crystals were used.

The crystals were grown from the melt by the Bridgman method and were used 'as grown' with the compositions x= 0.11; 0.20; 0.32; 0.37; and 0.47. The ions Fₓ⁻ were revealed in all crystals in two positions 32j (w;w;w;w; w; F₃2f) the ‘cluster type’ (i.e. making up the anionic core of the cluster [LaF₃2]), and the ‘relaxed type’ F₁6c (fig.1). The vacancies Vₓ= (8-Fₓ₋ₓ/F₃2f) were revealed in the main fluorine position (8c).

In the crystal with x= 0.47 a part of ions Fₓ⁻ occupy the position 4b (5/5/5) in the centre of a hollow cube. At higher LaFₓ content (x=0.2-0.5) Vₓ/F₁6c is about 1/4 which corresponds to the tetrahedral cluster model [4]. In the crystal Sr₉La₄F₁₃₋ₓ (i.e. at lower concentrations) the ratio Vₓ/F₁6c becomes about 1/12 which indicates the change of the defect structure. The excess ions Fₓ⁻ are located beyond the [LaF₃2] clusters.

We think these ions produce the initial conductivity rise but this nevertheless does not result in a superionic state. Fig. 1 presents two concentration dependences at T=500 K: (1) taken from [5] and (2) taken from [2]. The crystal becomes superionic (the conductivity activation energy is about 0.6 eV) at LaFₓ concentrations higher than the percolation threshold (8–12 mol. %), after which the tetrahedral clusters make up a 3D network. It is shown, that the defect structure of Sr₉,xLaₓ₋₁F₁₃₋ₓ with the composition close to the percolation threshold is different from the earlier studied phases M₉,RₓF₁₃₋ₓ (M = Ca, Sr, Ba), for which it was proposed to describe the defect structure by the tetrahedral cluster model. For crystals with x = 0.47 the ions Fₓ⁻ enter in 4b positions which is followed by substantial deviation of Igσ value from the linear dependence in the range x=0.15–0.35.