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Keywords: framework, expansion, cyanide

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 $\text{Ca}_{10}(\text{PO}_4)(\text{OH})_2$ was treated by the different alkylphosphonates (R-POCl_2 , R= methyl or octyl) in organic solvent using a molar ratio $x=2$ or 4 , $x=n(\text{organic})/n(\text{apatite})$. 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 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 the apatite ($\equiv\text{CaOH}$ and $\equiv\text{POH}$) 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 - HfO_2 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 HfO_2 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 ($P2_1c$), $Pbca$ and cotunnite-type ($Pnma$) 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 $\text{ZrZr} + \text{HfHf} = 2\text{ZrHf}$ were calculated for 9 interatomic distances within a $2 \times 2 \times 1$ 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.

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Keywords: solid_solution, elastic_property

MS81.P26

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

Crystal structures and ultramicroporosity in Mg & Ca tetrakisphosphate hybrids

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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 are 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

[2]. Whereas a vast number of inorganic–organic hybrid materials with mono- and diphosphonates have been described, little is known about tri- and other polyphosphonate compounds [3].

In this work, we present the synthesis, characterization and surface analysis of two tetraphosphonates [octamethylenediaminetetrakis-(methylenephosphonates)] hybrids based on calcium ($\text{CaC}_{12}\text{H}_{30}\text{O}_{12}\text{N}_2\text{P}_4 \cdot 3\text{H}_2\text{O}$), and magnesium ($\text{MgC}_{12}\text{H}_{30}\text{O}_{12}\text{N}_2\text{P}_4 \cdot 2\text{H}_2\text{O} \cdot 0.5[(\text{CH}_3)_2\text{NCHO}]$), prepared at RT and hydrothermally. The crystal structures of both derivatives 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 framework compound. The BET N_2 -surface areas were lower than $5 \text{ m}^2\text{g}^{-1}$ for both compounds. The BET CO_2 -surface for the activated Mg-derivative was $160 \text{ m}^2\text{g}^{-1}$. A discussion of the crystal structures and porosities will be reported.

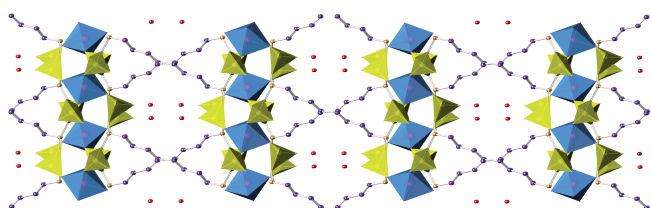


Fig. 1. View, along the c-axis, of the 3D framework for $\text{MgC}_{12}\text{H}_{30}\text{O}_{12}\text{N}_2\text{P}_4 \cdot 2\text{H}_2\text{O} \cdot 0.5[(\text{CH}_3)_2\text{NCHO}]$

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Keywords: X-ray_Diffraction, hybrids, porosity

MS81.P27

Acta Cryst. (2011) A67, C711

Crystal structures of new heteropolymolybdates with waugh-type polyanion.

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Heteropoly compounds are coordination compounds of complex 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.

Crystals of new heteropolymolybdates $[\text{Mn}(\text{H}_2\text{O})_4][\text{CoMo}_9\text{O}_{27}(\text{OH})_3] \cdot 7\text{H}_2\text{O}$ (I) (*R*32, $a=15.926(1)$, $c=12.363(1)\text{\AA}$, $R=0.025$) and $\text{H}_6[\text{MnMo}_9\text{O}_{32}] \cdot 12\text{H}_2\text{O}$ (II) (*R*32, $a=15.970(1)$, $c=12.441(1)\text{\AA}$, $R=0.023$) were prepared from a solution of ammonium salt of the conforming heteropoly acid with Mn-acetate (1) and by evaporation under caustic potash (2). Crystal structures were determined by single crystal x-ray diffraction (Xcalibur S, Mo-K α , CCD-detector).

Both structures are based on the Waugh-type polymetallic clusters $[\text{MeMo}_9\text{O}_{32}]$, which have D_3 symmetry and consist of a central MeO_6 octahedron ($\text{Me}=\text{Co}$, Mn) sharing edges with nine distorted MoO_6 octahedra. The large channels along threefold axis are filled by $[\text{Mn}(\text{H}_2\text{O})_4]$ -groups (I) or statistically distributed H_2O - molecules (II).

Keywords: molybdates, polyoxometalate structures, inorganic clusters

MS81.P28

Acta Cryst. (2011) A67, C711-C712

Defect structure and ionic conductivity of $\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$ ($x=0.1-0.5$)

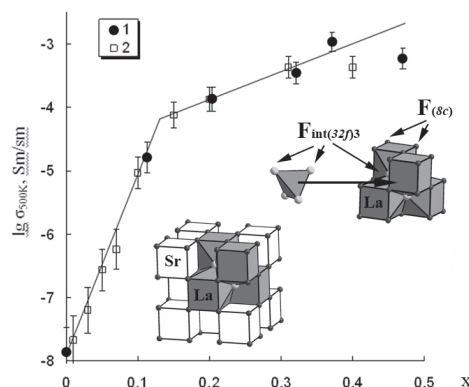
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$\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$ crystals are promising materials for optical applications in UV- and IR-bands [1]. Isomorphous doping SrF_2 with La enlarges its ionic conductivity by 9 orders of magnitude (at $T=500 \text{ K}$) in comparison with the pure crystals making it a superionic conductor [2]. Neutron diffraction studies of $\text{Sr}_{0.69}\text{La}_{0.31}\text{F}_{2.31}$ [3] showed that the interstitial fluorine ions (F_{int}) are present only in the $32f$ -position of 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 $\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$ 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 F_{int} were revealed in all crystals in two positions $32f(w,w,w)$: $\text{F}_{\text{int}(32f3)}$ – the 'cluster type' (i.e. making up the anionic core of the cluster $\{\text{La}_4\text{F}_{26}\}$), and the 'relaxed type' $\text{F}_{\text{int}(32f1)}$ (fig.1). The vacancies $\text{V}_{\text{F}}=(8-\text{F}_{(8c)}-\text{F}_{\text{int}(32f1)})$ were revealed in the main fluorine position ($8c$).

In the crystal with $x=0.47$ a part of ions F_{int} occupy the position $4b$ ($1/2, 1/2, 1/2$) in the centre of a hollow cube. At higher LaF_3 content ($x=0.2-0.5$) $\text{V}_{\text{F}}/\text{F}_{\text{int}(32f3)}$ is about $1/4$ which corresponds to the tetrahedral cluster model [4]. In the crystal $\text{Sr}_{0.89}\text{La}_{0.11}\text{F}_{2.11}$ (i.e. at lower concentrations) the ratio $\text{V}_{\text{F}}/\text{F}_{\text{int}(32f3)}$ becomes about $1/12$ which indicates the change of the defect structure. The excess ions F_{int} are located beyond the $\{\text{La}_4\text{F}_{26}\}$ 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 $T=500 \text{ K}$: (1) taken from [5] and (2) taken from [2]. The crystal becomes superionic (the conductivity activation energy is about 0.6 eV) at LaF_3 concentrations higher than the percolation threshold ($8-12 \text{ mol. \%}$), after which the tetrahedral clusters make up a 3D network. It is shown, that the defect structure of $\text{Sr}_{0.89}\text{La}_{0.11}\text{F}_{2.11}$ with the composition close to the percolation threshold is different from the earlier studied phases $\text{M}_{1-x}\text{R}_x\text{F}_{2+x}$ ($M=\text{Ca}$, 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 F_{int} enter in $4b$ positions which is followed by substantial deviation of $\lg\sigma$ value from the linear dependence in the range $x=0.15-0.35$.



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