

[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.

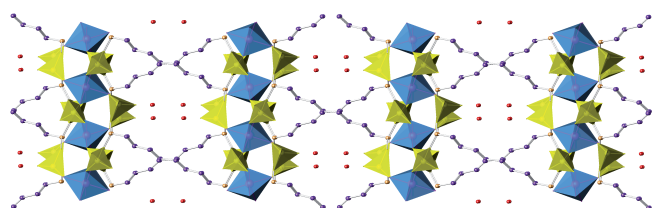


Fig. 1. View, along the c-axis, of the 3D framework for $\text{MgC}_{12}\text{H}_{30}\text{O}_{12}\text{N}_2\text{P}_4 \cdot 2\text{H}_2\text{O} \cdot 0.5[(\text{CH}_3)_2\text{NCHO}]$

[1] F. Constantino, T. Bataille, N. Audebrand, E. Le Fur, C. Sangregorio, *Crystal Growth & Design* **2007**, *7*, 1881-1888 [2] F. Constantino, A. Ienco, P.L. Gentili, F. Presciutti, *Crystal Growth & Design* **2010**, *10*, 4831-4838. [3] N. Stock, A. Stoll, T. Bein, *Microporous & Mesoporous Materials* **2004**, *69*, 65-69.

Keywords: X-ray_Diffraction, hybrids, porosity

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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

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

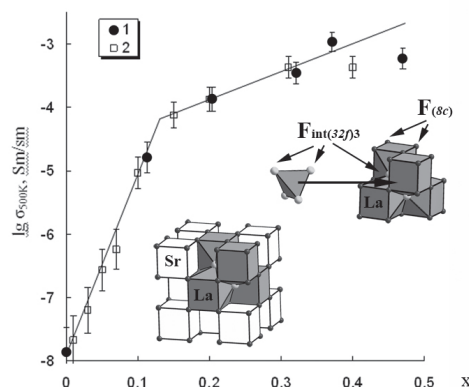
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$\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$ crystals are promising materials for optical applications in UV- and IR-bands [1]. Isomorphous doping SrF_2 with La enlarges its ionic conductivity by 9 orders of magnitude (at $T=500 \text{ K}$) in comparison 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 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 $x=0.15-0.35$.



[1] B.P. Sobolev, D.N. Karimov, *et al. Cryst. Rep.* **2009**, *54*(1), 122. [2] A.K. Ivanov-Shits, N.I. Sorokin, *et al. Fiz. Tverd. Tela.* **1983**, *25*(6), 1748. [3] L.A. Muradyan, B.A. Maximov, *et al. Kristallografiya.* **1986**, *31*(2), 248. [4] L.A.