In this work, we present the synthesis, characterization and surface analysis of two tetraphosphonates [octamethylenediaminetetraakis(methylphosphonates)] hybrids based on calcium (Ca$_2$H$_2$O$_2$Ni$_2$O$_7$) and magnesium (Mg$_2$H$_2$O$_2$Ni$_2$O$_7$·2H$_2$O·0.5(CH$_3$)$_2$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 derivative is a three dimensional framework compound. The BET N$_2$-surface areas were lower than 5 m$^2$/g for both compounds. The BET CO$_2$-surface for the activated Mg-derivative was 160 m$^2$/g. A discussion of the crystal structures and porosities will be reported.


**Keywords:** X-ray Diffraction, hybrids, porosity

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**MS81.P28**


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

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Sr$_x$La$_{1-x}$F$_{2+x}$ crystals are promising materials for optical applications in UV- and IR-bands [1]. Isomorphous doping SrF$_2$ with La enhances its ionic conductivity by 9 orders of magnitude (at T$\approx$ 500 K) in comparison with the pure crystals making it a superionic conductor [2]. Neutron diffraction studies of Sr$_{0.89}$La$_{0.11}$F$_{2.11}$ [3] showed that the interstitial fluorine ions (F$_{\text{int}}$) 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 Sr$_x$La$_{1-x}$F$_{2+x}$ in two 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$_{\text{int}}$ were revealed in all crystals in two positions 32f (w,w,w): F$_{\text{32f}1}$: the ‘cluster type’ (i.e. making up the anionic core of the cluster $\{LaF$_{9}\}$), and the ‘relaxed type’ F$_{\text{32f}2}$ (fig.1). The vacancies V$_{\text{F}}$= (8-F$_{\text{32f}1}$-F$_{\text{32f}2}$) were revealed in the main fluorine position (8c).

In the crystal with x=0.47 a part of ions F$_{\text{int}}$ occupy the position 4b (5/55/5) in the centre of a hollow cube. At higher LaF$_2$ content (x=0.2-0.5) V$_{\text{F}}$/F$_{\text{32f}2}$ is about 1/4 which corresponds to the tetrahedral cluster model [4]. In the crystal Sr$_{0.89}$La$_{0.11}$F$_{2.11}$ (i.e. at lower concentrations) the ratio V$_{\text{F}}$/F$_{\text{32f}2}$ becomes about 1/12 which indicates the change of the defect structure. The excess ions F$_{\text{int}}$ are located beyond the $\{LaF$_{9}\}$ 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 LaF$_2$ 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 Sr$_{0.99}$La$_{0.01}$F$_{2.1}$, with the composition close to the percolation threshold is different from the earlier studied phases Sr$_{1-x}$La$_{x}$F$_{2+x}$, for which it was proposed to describe the defect structure by the percolation model [4]. In the crystal Sr$_{1-x}$La$_{x}$F$_{2+x}$ the ions F$_{\text{int}}$ enter in 4b positions which is followed by substantial deviation of Igr value from the linear dependence in the range x=0.15–0.35.

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**MS81.P27**


**Crystal structures of new heteropolyoxymolybdates 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 polynucleates is due to their great practical importance in the organocatalysis.

Crysals of new heteropolyoxymolybdates [Mn(H$_2$O)${}_6$][CoMo$_4$O$_{13}$OH${}_2$]$_7$H$_2$O ($\text{I}$) (R$^{2}$, a=15.926(1), c=12.363(1)Å, R=0.025) and H$_2$[Mn$_2$Mo$_4$O$_{14}$]·12H$_2$O ($\text{II}_1$) (R$^{2}$, a=15.970(1), c=12.441(1)Å, 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$_{\alpha}$, CCD-detector).

Both structures are based on the Waugh-type polynuclear clusters [MeMo$_4$O$_{13}$], which have D$_5$ symmetry and consist of a central MeO$_6$ octahedron (Me=Co, Mn) sharing edges with nine distorted MoO$_6$ octahedra. The large channels along threefold axis are filled by [Mn(H$_2$O)$_6$]$^{2+}$-groups (I) or statistically distributed H$_2$O-molecules (II).

**Keywords:** molybdates, polyoxometalate structures, inorganic clusters

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**Fig. 1. View, along the c-axis, of the 3D framework for MgC$_{27}$O$_{32}$N$_{32}$H$_{32}$.**