

[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.

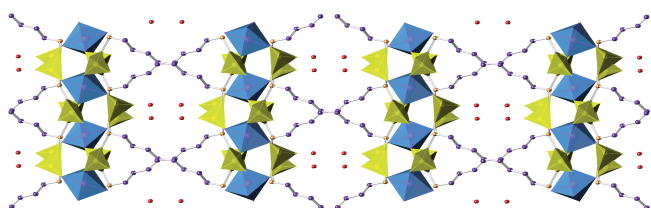


Fig. 1. View, along the c-axis, of the 3D framework for $\text{MgC}_{12}\text{H}_{30}\text{O}_{12}\text{N}_2\text{P}_4 \cdot 2\text{H}_2\text{O} \cdot 0.5[(\text{CH}_3)_2\text{NCHO}]$

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Keywords: X-ray_Diffraction, hybrids, porosity

MS81.P27

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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 $\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$ ($x=0.1-0.5$)

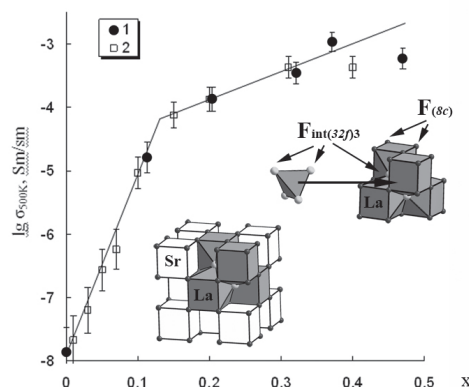
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$\text{Sr}_{1-x}\text{La}_x\text{F}_{2+x}$ crystals are promising materials for optical applications in UV- and IR-bands [1]. Isomorphous doping SrF_2 with La enlarges its ionic conductivity by 9 orders of magnitude (at $T=500 \text{ K}$) in comparison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



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Poster Sessions

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Keywords: fluoride, structure, conductivity

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New oxide-ion conductors with La₂Mo₂O₉ structure

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The lanthanum molybdate La₂Mo₂O₉ (LM) attracts attention as perspective oxide-ion conductor with the conductivity 0.06 S/cm at 800°C [1]. The molybdates of such composition with other rare earths, with the exception of praseodymium Pr [2], don't exist under usual synthesis conditions; however there are tungstates with La, Pr, Nd, Sm, Eu, Gd [3]. LM has a phase transition of the order-disorder type at the temperature close to 580°C and two phases: low-temperature monoclinic α - phase and high-temperature cubic β -phase. La₂W₂O₉ (LW) has similar phase transition, but at the temperature of 1070°C [4, 5]. X-ray investigations showed that cubic LW β -phase corresponds to cubic LM β -phase [5]. The monoclinic Nd₂W₂O₉ (NW) and Pr₂W₂O₉ (PW) also have high-temperature transitions at 1255°C and 1200°C, respectively [6 - 9]. We can assume that the structure of high temperature NW and PW phases may be similar to that of LM and they may have oxide-ion conductivity.

With the aim of search of novel oxide-ion conductors with the LM structure compositions in the La₂Mo₂O₉ - Nd₂W₂O₉ - "Nd₂Mo₂O₉" (LM - NW - "NM") and La₂Mo₂O₉ - Pr₂W₂O₉ - Pr₂Mo₂O₉ (LM - PW - PM) systems were examined.

All specimens were prepared by solid state synthesis. The expansive field of the compounds with the LM-structure was discovered in the above systems. It should be noted, that in both systems the compounds with LM structure and full substitution of La for other lanthanide (Pr, Nd) are formed. Pure PM decomposes at 700 - 900°C with arising of Pr₂Mo₃O₁₂ and recombines into itself at higher temperatures (above 1000°C). An addition of 10% W or La in PM-based solid solutions leads to disappearance of this instability. Pure "NM" is a mix of Nd₂Mo₃O₁₂ and Nd₄Mo₈O₄₅. The compounds with the LM-type structure are formed in pseudo binary "NM" - NW system even at small amount of W (3 - 7%).

In the case of LM - NW - "NM" system the $\alpha \rightarrow \beta$ phase transition, which was observed in pure LM, is suppressed with addition of Nd or W and cubic phase was stabilized at room temperature in all synthesized compounds. The pure PM is monoclinic at room temperature and undergoes the $\alpha \rightarrow \beta$ phase transition at 520 - 540°C. However, mutual substitution La and Pr leads to disappearance of this transition and stabilization of cubic phase at 50 - 60% Pr. The cubic phase is also stabilizes at room temperature on addition of W similar to Nd contained system.

All synthesized compounds with LM structure show high anionic conductivity like LM (10⁻¹ - 10⁻² S/cm at 800°C). An addition of Nd and W leads to little decreasing of conductivity value. The conductivity of NW compound was no better than 10⁻⁴ S/cm at 800°C.

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Keywords: LAMOX, phase diagrams, oxide-ion conductivity

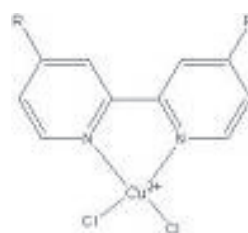
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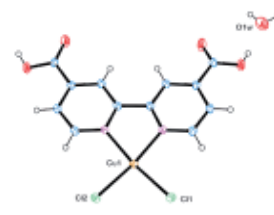
Structural and DNA binding studies of bipyridine-copper complexes

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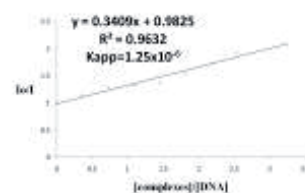
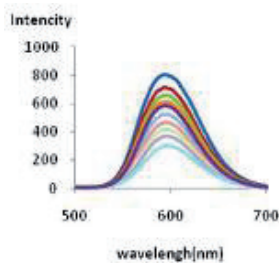
In the present, cancer is the leading cause of death. Transition metal complexes, for example cisplatin, carboplatin and oxaliplatin are an effective anticancer chemotherapy, but they have side effects and easily excreted. Therefore, substituted bipyridine-copper complexes have been developed as potential antitumor agent owing to copper metal can inhibit the cancer cell cycle. In this work, the series of substituted-bipyridine copper complexes have been intensively studied as DNA-binding anticancer agents in order to investigate the effect of substituents on the cytotoxic activity.



R = -H, -NH₂, -CH₃, -COOH, -OCH₃



Cu(COOH-bipy)Cl₂•H₂O



Emission spectra of bpy-copper complexes, Arrow show the intensity changing upon increasing bipyridine-copper concentration in displacement ethidium bromide bound to DNA and A Stern-Volmer quenching plot of the increasing amount of complexes to determine Kapp

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Keywords: bipyridine-copper complexes, structural and DNA-binding study, anticancer