MS81.P28

**Acta Cryst.** (2011) A67, C711-712

Defect structure and ionic conductivity of Sr$_x$La$_{1-x}$F$_{3+2x}$ (x = 0.1-0.5)

E.A. Sulyanova, D.N. Karimov, B.P. Sobolev, N.I. Sorokin, Shubnikov Institute of Crystallography, Russian Academy of Sciences, Moscow, (Russia).
E-mail: rahelen@ns.crys.ras.ru

Sr$_x$La$_{1-x}$F$_{3+2x}$ 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 = 500 K) in comparison with the pure crystals making it a superionic conductor [2]. Neutron diffraction studies of Sr$_{0.90}$La$_{0.1}$F$_{3+2}$ [3] showed that the interstitial fluorine ions (F$_{int}$) are present only in the 32j-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$_{3+2x}$ in the 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 32j (V$_{rel}$- the 'cluster type' (i.e. making up the anionic core of the cluster [LaF$_{3x}$]), and the 'relaxed type' F$_{rel}$ (fig.1)). The vacancies V$_F$=(8-F$_{rel}$) 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 (5/8) in the centre of a hollow cube. At higher LaF$_2$ content (x=0.2-0.5) V$_F$ is about 1/4 which corresponds to the tetrahedral cluster model [4]. In the crystal Sr$_x$La$_{1-x}$F$_{3+2x}$ (i.e. at lower concentrations) the ratio V$_F$ approaches becomes about 1/12 which indicates the change of the defect structure. The excess ions F$_{int}$ are located beyond the [LaF$_{3x}$] 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$_{0.90}$La$_{0.10}$F$_{3+2}$ with the composition close to the percolation threshold is different from the earlier studied phases M$_x$R$_{1-x}$F$_{3+2x}$ (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 F$_{int}$ enter in 4b positions which is followed by substantial deviation of lg value from the linear dependence in the range x=0.15–0.35.

---

**MS81.P27**

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

Crystal structures of new heteropolyoxometalates with waugh-type polyanion.

E-mail: anir@ns.crys.ras.ru

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 polyanion is due to their great practical importance in the organocatalysis.

Crysatls of new heteropolyoxometalates [Mn(H$_3$O)$_2$]$_2$[CoMo$_6$O$_{19}$(OH)$_7$H$_2$O] (I) (R32, a=15.9261(1), c=12.3631(1) Å, R=0.025) and [H$_2$MnMo$_6$O$_{19}$]·12H$_2$O (II) (R32, a=15.9701(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 (I) 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 polymeric clusters [MeMo$_6$O$_{19}$], which have D$_3h$ 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$_3$O)$_2$]$_2$-groups (I) or statistically distributed H$_2$O-molecules (II).

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

---

**References**

MS81.P29

New oxide-ion conductors with La$_n$Mo$_x$O$_{3x}$ structure
Elena Kharitonova, Valentina Voronkova, Ekaterina Orlova, Daria Kolesnikova, Faculty of Physics, M.V. Lomonosov Moscow State University (Russia). E-mail: harit@polyu.phys.msu.ru

The lanthanum molybdate La$_n$Mo$_x$O$_{3x}$ (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. La$_n$W$_x$O$_{3x}$ (LM) 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 Nd$_n$W$_x$O$_{3x}$ (NW) and Pr$_n$W$_x$O$_{3x}$ (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 La$_n$Mo$_x$O$_{3x}$ - Nd$_n$W$_x$O$_{3x}$ - "Nd,Mn,Mo" (LM - NW - "NM") and La$_n$Mo$_x$O$_{3x}$ - Pr$_n$W$_x$O$_{3x}$ - Pr$_n$Mo$_x$O$_{3x}$ (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 Pr$_n$Mo$_x$O$_{3x}$ 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 Nd$_n$Mo$_x$O$_{3x}$ and Nd$_n$Mo$_x$O$_{3x}$. 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 α → β 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 α → β 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 stabilized 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$^{-2}$ - 10$^{-3}$ 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$^{-3}$ S/cm at 800°C.

This work is supported by RFBR (11-03-00243-a).


MS81.P30

Structural and DNA binding studies of bipyridine-copper complexes
Aphiwat Kaewthong, Mongkol Sukwattanasinitt and Nongnui Muangsin, Department of Chemistry, Faculty of Science, Chulalongkorn University, Pathumwan, Bangkok, 10330, (Thailand). E-mail: aphiwat_golf@hotmail.com

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 excrated. 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.

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


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