

MS43 P01

Crystal Structure of a new mixed potassium nickel iron arsenate Ridha Ben Smail, Ahmed Driss, Laboratoire de Matériaux et Cristallographie, Faculté des Sciences de Tunis, 2092 El Manar II Tunis, Tunisia.
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The new mixed potassium nickel iron arsenate, $K_{1.250}Ni_{0.875}Fe_2(AsO_4)_3$, has been synthesized by a flux method in air at 800 °C. Single crystal X-ray diffraction shows that it is isostructural to $Na_{1.28}Ni_{0.86}Fe_2(PO_4)_3$ (S.G. Ibmm) [1]; the lattice parameters are $a=6.737(2)$, $b=10.773(3)$, $c=13.574(3)$ Å and $Z=4$.

The crystal structure was solved and refined against F^2 using the SHELX-97 [2,3] computer programs included in the WingX software package [4]. Refinement including all atomic coordinates and anisotropic thermal parameters converged at $R1 = 0.028$ and $wR2 = 0.087$. The structural model is validated by the two structural tools bond valence sums BVS [5,6] and Charge distribution analysis CD [7, 8].

The three-dimensional structure is found to be closely related to that of the well known α -CrPO₄ structural type [8]. It is composed of -O-As-O-Ni-O- chains combined with Fe₂As₂O₁₄ units which are formed by edge-sharing of tetrahedra and octahedra. The potassium ions are located in tunnels parallel to c direction (Fig. 1).

The main feature of the title compound, compared to $NaV_3(PO_4)_3$ [9], is the presence of a new interstitial site, partially occupied by the potassium cations. Counterpart sites being empty in MPO₄ (M = Cr, Rh) [8-11].

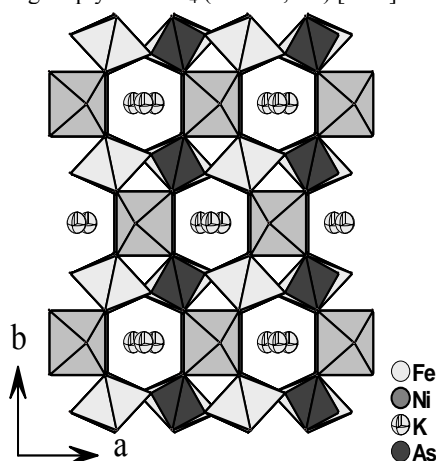


Fig. 1. A view of the $K_{1.250}Ni_{0.875}Fe_2(AsO_4)_3$ structure along the c direction showing the tunnels where reside the sodium cations.

The compound under investigation, to our knowledge, is the first iron arsenate with the α -CrPO₄ structure.

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MS43 P02

Structure validation and monovalent ion conduction pathways simulation in $Na_3Co_2AsO_4As_2O_7$ and $K_2CoP_2O_7$ A. Guesmi^a, N. Ouerfelli^a, D. Mazza^b and A. Driss^a ^a Laboratoire de Matériaux et Cristallographie, Faculté des Sciences, El Manar, 2092 Tunis, Tunisia. ^b Dipartimento di Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy.

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The two structural validation tools, although with different formulations, Bond valence sum BVS [1,2] and Charge distribution analysis CD [3,4] are always chosen to validate the structural models. The CD analysis which is the most recent development of the classical theory of bond strength is mainly chosen because of the insights into the structural details (average weighted distances, effective coordination numbers ECoN) that it gives at the same time. The BVS and CD show that the two structures are well refined and yield adequate valences (V) / charges (Q) for all atoms with minor deviations from expected values.

The BVS can also be applied to model ion conduction pathways in the crystal bulk. The ionic moving species in the framework are usually alkali metal cations but might be also transition-metals, lanthanides and anions as well (like O²⁻, F⁻). The BVS was successfully employed to model lithium ion conduction in $La_{2/3-x}Li_xTiO_3$ [5], sodium in Nasicon conductors [6] and in $Na_2M_2(BO_3)_2O$ (M=Al, Ga) and $Na_{2-2x}Ca_xGa_2(BO_3)_2O$ ($x=0.25, 0.50$) [7] and thallium in $TlFe_{0.22}Al_{0.78}As_2O_7$ [8].

Starting from crystallographic positions, as determined by X-ray diffraction analysis, Bond Valence Sum $\phi(x,y,z)$ is calculated in an iterative procedure for a grid of points normal to a given direction. Soft Bond Valence parameters R_0 and B, and cutoff distance, are taken from [2]. The procedure allows to identify a pathway of points with lowest Bond Valence Sum $\phi(x,y,z)$ which correspond to lowest energy of mobile ions in the lattice. The valence sum for the mobile cation can be plotted versus the distance (d) travelled along, thus obtaining a plot of $\phi(d)$ versus d(Å). Saddle points of the $\phi(d)$ function correspond to potential barriers encountered by the ion along its trajectory.

The ionic conductivity of the arsenate $Na_3Co_2AsO_4As_2O_7$ (monoclinic, S.G: C2/m, $a=10,484$ Å, $b=16,309$ Å, $c=6,531$ Å and $\beta=120,40^\circ$) should be weak: although the crystal structure shows tunnels, many

bottlenecks are encountered ($V_{\text{max}} \approx 1.7\text{-}2$) by the sodium for several migration directions. The structure of $\text{K}_2\text{CoP}_2\text{O}_7$ [9] (tetragonal, S.G.: $P4_2/mnm$, $a=7.926 \text{ \AA}$, $c=11.350 \text{ \AA}$) consists of $[\text{CoP}_2\text{O}_7]_{\infty}$ layers with alkali metal cations lying between the layers. The cation motion seems to be bidimensional in the (001) planes with V_{max} less than 1.30 along [110]. The possible motion through adjacent layers (c axis) seems subsequently difficult. These suggestions are to be confirmed by electrical measurements.

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MS43 P03

Full formula of Molybdenum(V) phosphates out of empiric bond strength evaluation André Leclaire *CRISMAT-ENSICAEN, CNRS-UMR6508, University of Caen, France.* E-mail: andre.leclaire@ensicaen.fr

Keywords: Bond strength calculations, Molybdenum phosphates, Molybdenum(V).

Generally the X-ray structures of crystals obtained from hydrothermal synthesis or out of an aqueous solution don't allow distinguishing between an oxygen atom or a hydroxyl group or a water molecule bonded to transition elements, due to the great difficulty to find hydrogen atoms on the Fourier and Difference Synthesis maps. Donnay and Allmann [1] gave a procedure based on the sum of electrostatic valences received by the oxygen atoms. They gave also equations for determining the electrostatic valences given by a central ion to the surrounding oxygen atoms. Latter a more convenient empirical expression was reported: $v_{ij} = \exp[(R_{ij} - d_{ij})/0.37]$ where R_{ij} tabulate by Brese and O'Keeffe [2] is characteristic of a cation and d_{ij} the cation oxygen distances. We synthesized and studied a huge number of **pentavalent molybdenum** phosphates and mixed-valence phosphates containing Mo^{5+} but only the R_{ij} value for Mo^{6+} was tabulated. So in a first time we compute the **R_{ij} constant for Mo^{5+} of 1.879 with 86 Mo(V)O_6 octahedra.** This values works very well and latter Zocchi [3] found a $R_{ij}=1.8788$ which associated to $B=0.3046$ works for all oxidation states from +3 to +6.

During the studies of compounds containing **$\text{Mo}^{5+}_{12}\text{M}^{2+}_8\text{P}_8\text{O}_{62}\text{H}_x$ clusters**, the R_{ij} value of 1.879 lead to valences ranging from 4.63 to 5.05 with a mean value of 4.85 for Mo^{5+} whereas valences ranging from 4.60 to 5.27 with a mean value of 4.84 were obtained for phosphorus with the $R_{ij} = 1.604$ reported by Brese and O'Keeffe [2]. In order to improve the valence calculations, new R_{ij} values were computed from 328 PO_4 tetrahedra for phosphorus and from 42 Mo^{5+}O_6 octahedra sharing only

edges in Mo_6 rings. So **R_{ij} values of 1.890 and 1.615 were obtained for Mo^{5+} and P respectively.** With these values the electrostatic bond valence sums are centered on 4.99 for both polyhedra with valences ranging from 4.77 to 5.20 for Mo^{5+} and from 4.73 to 5.40 for P in the compounds exhibiting $\text{Mo}_{12}\text{MP}_8\text{O}_{62}\text{H}_x$. The most amazing result deduced from the bond valence sum calculations was that **three oxygen atoms of the Mo_6O_{24} rings are hydroxyl groups** (lack of 0.9 v.u.) so the ring consist of six edge sharing MoO_5OH octahedral leading to the formulation $\text{Mo}_6\text{O}_{21}(\text{OH})_3$. on the other hand the valence sums received by the phosphorus tetrahedral show that they belong to the PO_4 , or PO_3OH , or $\text{PO}_2(\text{OH})_2$ species according to the other cations in the structure. So the cluster will be $[\text{Mo}_{12}\text{M}^{2+}\text{O}^{24}(\text{OH})_6(\text{PO}_4)_x(\text{PO}_3\text{OH})_y(\text{PO}_2(\text{OH})_2)_{8-x-y}]$. One observes also on some oxygen atoms lacks of 0.30 or 0.65 v.u. pointing out that those oxygen atoms receive hydrogen bonds.

In conclusion the use of experimental bond valence sums allowed to establish the real formulation of the clusters containing pentavalent molybdenum obtained by hydrothermal synthesis and also to set up the hydrogen bonds network.

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MS43 P04

The crystal structure of caesium disulfate at 120 and 273 K. Kenny Stahl^a, Rolf W. Berg^a, K. Michael Eriksen^a, Rasmus Fehrmann^a. ^a*Chemistry Department, Technical University of Denmark, Lyngby, Denmark.* E-mail: kenny@kemi.dtu.dk

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The crystal structures of $\text{Cs}_2\text{S}_2\text{O}_7$ have been determined at 120 and 273 K from $\text{MoK}\alpha$ data: T=120 K, P-1, Z=20, $a=14.941(2)$, $b=16.036(2)$, $c=19.300(2) \text{ \AA}$, $\alpha=85.025(2)$, $\beta=67.630(2)$, $\gamma=74.968(2)^\circ$; T=273 K, P-1, Z=10, $a=7.5229(5)$, $b=15.959(1)$, $c=17.973(1) \text{ \AA}$, $\alpha=90.207(1)$, $\beta=90.418(1)$, $\gamma=102.206(2)^\circ$. Their crystal structures represent a novel structure type, entirely different from the dichromate type structures of other alkali disulfates [1]: 8/10 of the caesium ions form a "tube" surrounding 2/10 of the disulfates (Fig. 1), while the remaining disulfates enclose the remaining caesium ions in a sandwich structure.