

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].

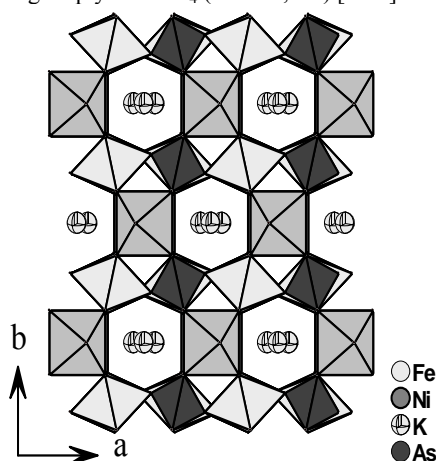


Fig. 1. A view of the $K_{1.250}Ni_{0.875}Fe_2(AsO_4)_3$ structure along the c direction showing the tunnels where reside the sodium cations.

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

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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