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Synthesis and structure of a new layered potassium sodiostannate

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A new layered $K_{0.72}Na_{0.24}Sn_{0.76}O_2$ has been obtained and its structure has been refined using powder XRD profile analysis.

Layered structures with high ionic conduction are of interest due to their potential applications such as solid electrolytes and electrode materials for concentration sensors in gas and liquid media. Very high potassium ionic conduction was found in complex oxides with the β-$RbScO_2$ structure.

Previously,[1] we described the potassium lithiostannate $K_{0.72}Li_{0.24}Sn_{0.76}O_2$ with this structure type and a conduction of 0.23 S m^{-1} at 500 K. Lithium and tin ions occupy oxygen octahedra at random and form brucite-like layers. Potassium cations are distributed over two types of trigonal prisms between them. One half of these prisms has adjacent edges with six tin/lithium octahedra from two nearest brucite-like layers, and the other half shares trigonal faces with two octahedra. The former (electrostatically preferable) were represented as main prisms, and the latter, as additional ones[1] (Figure S1, Online Supplementary Materials).

In this work, we used a solid-state two-stage technique for the synthesis of potassium sodiostannate. The starting materials of analytical grade were tin dioxide, sodium hydroxide and potassium hydroxide.

Potassium stannates[2] are convenient precursors for potassium metallostannates. However, they are irreproducible with a solid-state procedure.[1] Therefore, we used potassium hydroxide and developed a new technique for the synthesis of metallostannates. As solid alkalis are extremely hydroscopic, there is no way to grind them with other substances. Moreover, water vapor produced by decomposition of alkali can form pores, and disturbs the interaction. Therefore, at the first stage the powders of non-alkali compounds were ground together; the granules of alkalis were put on the surface. Then, the substances were heated at 500–600 °C for 30 min; the alkalis were melted down and impregnated powders. At the second stage, these fused substances were repeatedly ground, pressed into a pellet and heated again at higher temperatures.

Sodium stannate Na_2SnO_3 was synthesized with second heating at 900 °C for 1.5 h. Potassium sodiostannate was obtained from tin oxide, sodium stannate and potassium hydroxide. At the second stage, the pellet was heated at 1000 °C for 2.5 h in air. In the latter synthesis, we had to take a 150% excess of potassium hydroxide because it reacts with atmospheric carbon dioxide at the synthesis temperature.

We investigated a set of compositions with the general formula $K_xNa_{x/3}Sn_{1-x/3}O_2$ (x = 0.58, 0.62, 0.72 and 0.82). In this way, we obtained only one pure single-phase sample with the formula $K_{0.72}Na_{0.24}Sn_{0.76}O_2$. On the other hand, for remainder compounds obtained layered phase had different lattice constants and some impurities. The samples of $K_{0.72}Na_{0.24}Sn_{0.76}O_2$ are hygroscopic; therefore, this substance should be stored in a dry desiccator with alkali. Scanning rate for fitted profile was 1 deg min^{-1}.

As a starting model for structural analysis,[†] we used the atomic coordinates of isostructural potassium indiostannate $K_{0.72}In_{0.24}Sn_{0.76}O_2$[3] and potassium lithiostannate $K_{0.72}Li_{0.24}Sn_{0.76}O_2$[1] with two sorts of interlayer prisms, but without a shift of interlayer potassium from the center of these prisms. The space group for the new potassium sodiostannate is *P*6$_3$/*mmc*. It was previously proposed[4] for the isostructural compounds and used later.[1,5,6]

To fit the structure, we applied the JANA2006 package. The structure was refined with a damping factor of 0.1. Thirty six (36) terms of Chebyshev polynomials were used to describe the background. The Berar and Baldinozzi method for asymmetry correction and pseudo-Voigt profile function were applied. We also took into account the preferred orientation with respect to the 001 axis according to March and Dollase.[‡]

During the refinement, it was revealed that interlayer potassium ions are shifted from the centers of the prisms. The potassium ions in main prisms are shifted along the x and y axes. In additional prisms, some potassium ions are shifted along the x and y axes, and the other part, along the z axis (Figure 1).

It is related, apparently, to the effect of framework tin and sodium ions. The distance from the center of additional prisms to the framework cation is smaller than in the case of main prisms; therefore, its influence is stronger. As the part of tin positions

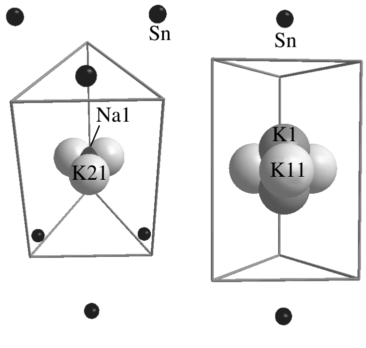

Figure 1 Splitted potassium positions. Grey spheres represent interlayer potassium (sodium) ions, black – tin/sodium from framework. On the left – tripled potassium positions in the main prisms K21 (light grey) and sodium position Na1 (dark grey); on the right – tripled potassium positions K11 (light grey) and doubled potassium positions K1 (medium grey) in the additional prisms.

[†] The XRD scans were recorded using an ARL'Xtra diffractometer with monochromatic CuKα radiation.

[‡] Details of Rietveld refinement for $K_{0.72}Na_{0.24}Sn_{0.76}O_2$. Space group *P*6$_3$/*mmc* (194); lattice constants: a = 3.19509(15) Å, c = 13.7956(10) Å; cell volume, 121.965(12) Å^3; formula weight, 155.9; wavelength, 1.5406 Å; 2θ range, 6–100°; step width, 0.02°; agreement factors (%): R(obs) = 3.30, R_w(obs) = 3.39, R(all) = 3.35, R_w(all) = 3.41, χ^2 = 1.19, R_p = 7.39, R_{wp} = = 10.13.

in the brucite-like layers is occupied by sodium, there are four environments for the interlayer ion (in the second coordination sphere): Sn/Sn, Na/Na, Na/Sn and Sn/Na (first ion above, second – below the prism). In the two latter versions, the coordination environment for the interlayer ion is not isotropic and this ion has to shift from the center of the prism along the z axis. In the case of potassium lithiostannate, we found that potassium ions are shifted to lithium because lithium and tin ions have similar radii, but lithium has a smaller charge. In the case of potassium sodiostannate, there is no way to make such simple conclusion. Interlayer ion can be shifted to the sodium ion due to its lesser charge or to tin due to its smaller radius.

If the interlayer cation is shifted from the center of the prism along z axis, its distance to other interlayer cation (non-shifted along z axis) from the neighbor prism is increased, and its influence is, accordingly, decreased.

Cations from the additional prisms with an isotropic coordination environment (first two variants) and cations from the main prisms are not shifted along the z axes. However, due to this the repulsion effect of the neighbor interlayer cations increases. Therefore, this part of cations is shifted along x and y axes towards unoccupied prisms.

Little part of sodium ions from the rigid part moved to main prisms with potassium ions with generating cationic vacancies.

During the refinement, we did not fix site occupancies, and, as a result, we get the following formula of potassium sodiostannate: $K_{0.78}Na_{0.221}Sn_{0.755}O_2$.

Refinement results show that $Sn(Na)O_6$ octahedra are flattened along the 001 translation. This distortion reduces the Born repulsion between large interlayer K cations (see Figure S1). However, the degree of framework octahedra flattening in $K_{0.72}Na_{0.24}Sn_{0.76}O_2$ is smaller than that in $K_{0.72}Li_{0.24}Sn_{0.76}O_2$.[1] Apparently, the larger radius of sodium compared to lithium leads to increase in a parameter of unit cell. Thus, the edges of octahedra are raised and, consequently, the edges of neighbor prisms also increase. Therefore, the distance between potassium ions in these prisms is extended and the repulsion decreases. Moreover, partial location of sodium ions between the layers in $K_{0.72}Na_{0.24}Sn_{0.76}O_2$ also reduces repulsion due to smaller sodium ion radius compared to potassium ion.

New potassium sodiostannate is extremely unusual. The most of sodium ions in $K_{0.72}Na_{0.24}Sn_{0.76}O_2$ are disordered with tin (+4) in rigid part, and only a small part of sodium ions is located with potassium between the layers. Thus, sodium oxide in this compound introduces acid properties more than alkali ones.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2015.07.025.

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