Co-cation Conduction of the \((\text{Na}_{1-x}\text{K}_x)_{3.8}\text{M}_{0.1}\text{P}_2\text{O}_7\) (M = Ca, Sr, Cd) Solid Solutions

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Abstract—Samples of systems \((\text{Na}_{1-x}\text{K}_x)_{3.8}\text{M}_{0.1}\text{P}_2\text{O}_7\) (M = Ca, Sr, Cd; 0 ≤ x ≤ 1) are synthesized. It is established that solid solutions with the structure of \(\gamma\text{-K}_4\text{P}_2\text{O}_7\) form in these systems. At room temperature, the solutions exist at x ≥ 0.7. In the calcium-containing system, they form a continuous series at temperatures exceeding ~500°C. The co-cation character of conduction of the solutions is confirmed by measured transport numbers. The concentration dependences of the electroconductivity and its activation energy point to a polyalkali effect, which decreases with an increase in the M\(^{2+}\) ion radius. Partial conductivities of sodium and potassium cations in the \((\text{Na}_{1-x}\text{K}_x)_{3.8}\text{Ca}_{0.1}\text{P}_2\text{O}_7\) system are calculated and their dependences on the balance between alkali cations in the solid solution are discussed.

A study of the ranges of the existence and electric properties of solid solutions in the \((\text{Na}_{1-x}\text{K}_x)_{4}\text{P}_2\text{O}_7\) system [1] revealed the presence of a polyalkali effect (PAE), which means that the dependences of the specific electroconductivity and its activation energy on the sodium and potassium ratio contains extremums. As shown earlier by the example of monocation solid electrolytes based on \(\text{A}_4\text{P}_2\text{O}_7\) [2, 3], a partial substitution of Na\(^{+}\) and K\(^{+}\) cations by divalent ions results in an abrupt increase in their electric characteristics. Therefore, it was of interest to study corresponding solid electrolytes containing two alkali cations.

In the present paper, we synthesized and studied solid solutions in the systems \((\text{Na}_{1-x}\text{K}_x)_{3.8}\text{M}_{0.1}\text{P}_2\text{O}_7\) (M = Ca, Sr, Cd, Ba). The modifying additives and their concentrations were chosen on the basis of studying systems \(\text{Na}_{4-2x}\text{M}_x\text{P}_2\text{O}_7\) [2] and \(\text{K}_{4-2x}\text{M}_x\text{P}_2\text{O}_7\) [3]. The initial compounds were sodium and potassium carbonates of reagent grade, \(\text{NH}_4\text{HEPO}_4\) of analytical grade, and one of the following components: \(\text{CaCO}_3\), \(\text{SrCO}_3\), \(\text{CdO}\) of analytical grade, or \(\text{BaCO}_3\) of ultra-high purity grade.

The initial reactants, with the exception of \(\text{NH}_4\text{H}_2\text{PO}_4\), were dried at ~500°C, mixed in the required amounts by a joint grinding in a jasper mortar, and sintered in aluminum crucibles first at 250–450°C (to completely remove volatile components) and then, depending on the modifying cation, at 700–800°C for 20–30 h, with an intermediate homogenization of the reaction mass every 5–6 h. The procedures used for preparing the samples and performing the X-ray diffractometry and derivatography (DTA) analyses are given in [4]. The electroconductivity was measured using an R5083 ac bridge with gold electrodes at a frequency of 100 kHz, as the preliminary experiments showed that the electroconductivity values measured at this frequency in the studied temperature range practically coincide with the values obtained by extrapolating the admittance complex plane plots to the active conductivity axis.

The maximum temperature range of conductivity measurements was 300–700°C. In some cases, however, it was narrowed due to a low electroconductivity or a low mp of samples. The transport numbers for each sort of alkali cations were determined at 600°C by the modified method of Tubandt [5]. Partial conductivities were calculated with the equation

\[ \sigma_{\text{Na}^+\text{(K}^+) = t_{\text{Na}^+\text{(K}^+)}\sigma}, \]

where \(\sigma_{\text{Na}^+\text{(K}^+)\) and \(t_{\text{Na}^+\text{(K}^+\) are, respectively, the partial specific electroconductivity and the transport number of sodium (potassium) cations, and \(\sigma\) is the overall specific electroconductivity.

RESULTS AND DISCUSSION

According to X-ray diffractometry, at room temperature, the \((\text{Na}_{1-x}\text{K}_x)_{3.8}\text{Ca}_{0.1}\text{P}_2\text{O}_7\) samples with 0.7 ≤ x ≤ 1.0 have the structure of \(\gamma\text{-K}_4\text{P}_2\text{O}_7\). The phase content of samples with 0.1 ≤ x ≤ 0.6 at room temperature could not be interpreted by the JCPDS (Joint Committee on Powder Diffraction Standards) data. One of the coexisting phases in this range of component ratios may be the \(3\text{Na}_4\text{P}_2\text{O}_7 \cdot 2\text{K}_4\text{P}_2\text{O}_7\) compound [6] whose diffractograms are absent in the literature. In the \((\text{Na}_{1-x}\text{K}_x)_{3.8}\text{Sr}_{0.1}\text{P}_2\text{O}_7\) and \((\text{Na}_{1-x}\text{K}_x)_{3.8}\text{Cd}_{0.1}\text{P}_2\text{O}_7\) systems, single-phase regions of solid \(\gamma\)-solutions are situated in the range 0.7 ≤ x ≤ 0.9 at room temperature. In a similar barium-containing system, solid solutions probably form in a rather narrow content range: samples with
Fig. 1. Heating DTA curves for \((\text{Na}_1-\text{xK}_x)_3\text{sCa}_0.1\text{P}_2\text{O}_7\) at \(x\) of (1) 0.2, (2) 0.4, (3) 0.6, and (4) 0.7.

\(x \leq 0.9\) were not single-phase; hence, no electroconductivity measurements were performed in the \((\text{Na}_1-\text{xK}_x)_3\text{s}\text{Ba}_0.1\text{P}_2\text{O}_7\) system.

The DTA curves for samples containing calcium at \(0.7 \leq x \leq 0.9\) display no heat effects up to the melting (Fig. 1, curve 4). Similar curves for samples with \(x < 0.7\) have peaks at 470–490°C (Fig. 1, curves 1–3). According to [6, 7], at high temperatures, \(\text{Na}_3\text{P}_2\text{O}_7\) and \(\text{K}_4\text{P}_2\text{O}_7\) form a continuous series of solid solutions. The data on the phase content of the \(\text{Na}_4\text{P}_2\text{O}_7\text{-K}_4\text{P}_2\text{O}_7\text{-M}_2\text{P}_2\text{O}_7\) systems are absent in the literature. We performed thermal and X-ray diffractometry analyses of the \((\text{Na}_{0.8}\text{K}_{0.2})_3\text{s}\text{Ca}_0.1\text{P}_2\text{O}_7\) sample at \(-550°C\), which is somewhat higher than the polymorphous conversion temperature, but lower than \(\text{mp} (490\) and 855°C, respectively, according to DTA data, Fig. 1, curve 1). The obtained diffractogram is presented in Fig. 2, along with that for a \((\text{Na}_1-\text{xK}_x)_4\text{P}_2\text{O}_7\) sample with the \(\gamma\)-\(\text{K}_4\text{P}_2\text{O}_7\) structure. As seen, both diffractograms are practically identical. This suggests that a continuous series of solid solutions with the \(\gamma\)-\(\text{K}_4\text{P}_2\text{O}_7\) structure forms in the \((\text{Na}_1-\text{xK}_x)_3\text{s}\text{Ca}_0.1\text{P}_2\text{O}_7\) system above \(-500°C\). At room temperature, solid \(\gamma\)-solutions are stable at \(x > 0.65\). The DTA curves for systems containing Sr and Cd with \(0.1 \leq x \leq 0.6\) display peaks at 440–460°C. Hence, one can expect the generation of wide ranges of \(\gamma\)-solid solutions at high temperatures in these systems as well. However, the temperature range of their existence is probably much narrower than in the system with calcium, because according to preliminary data, the melting in systems containing Sr and Cd starts at considerably lower temperatures than in the \((\text{Na}_1-\text{xK}_x)_3\text{s}\text{Ca}_0.1\text{P}_2\text{O}_7\) system. Therefore, in systems containing Sr and Cd, we limited our studies to the investigation of electric properties of samples with \(0.7 \leq x \leq 1\), while in a Ca-containing system we studied the range of \(x\) from 0 to 1.

As seen from the \(\log \sigma\) vs. \(1/T\) dependences presented in Fig. 3, those for solid electrolytes with \(0.7 \leq x \leq 1.0\) are linear in the entire studied range of temperatures (curves 6–9), while the curves for the Ca-containing samples with \(0.1 \leq x \leq 0.6\) have each an inflection near 500°C and an increase in the activation energy at low temperatures. We attribute the inflection to the appearance of a second phase with a low conductivity at low temperatures.

The concentration dependences of the specific electroconductivity at a constant temperature and the activation energy for conduction in the \((\text{Na}_1-\text{xK}_x)_3\text{s}\text{Ca}_0.1\text{P}_2\text{O}_7\) system are presented in Figs. 4a and 5, respectively. The \(\text{Na}_3\text{P}_2\text{O}_7\) samples \((x = 0.6)\) have the structure of \(\gamma\)-\(\text{K}_4\text{P}_2\text{O}_7\) at temperatures exceeding 485, 540, and 470°C for \(M = \text{Ca}, \text{Sr, and Cd}\), respectively, [2]. Therefore, the electroconductivity values given in Fig. 4 at lower temperatures are obtained by an extrapolation of the high-temperature linear parts of the \(\log \sigma\) vs. \(1/T\) dependences. The dependences in Figs. 4a and 5 have a clear-cut extremum character: one has a minimum, and the other has a maximum near \(x = 0.6\). Positions of the extremums coincide with those in the \((\text{K}_1-\text{Rb})_3\text{sP}_2\text{O}_7\) system [4]. In the other systems studied here, we failed to determine the position of extremums, due to relatively narrow single-phase ranges of solid solutions. However, even in

Fig. 2. Diffractograms for (1) \((\text{Na}_{0.8}\text{K}_{0.2})_3\text{s}\text{Ca}_0.1\text{P}_2\text{O}_7\) at \(548°C\) and (2) \((\text{Na}_{0.3}\text{K}_{0.7})_4\text{P}_2\text{O}_7\) at room temperature.