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Ion charge transfer in $\text{Na}_2\text{Ca}_{0.5}\text{PO}_4$

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Abstract. The Vogel–Fulcher–Tammann (VFT) ($\sigma \propto \exp[-E_a/k(T - T_0)]$) temperature dependence of ionic conductivity has been found for the $\text{Na}_{3-2x}\text{Ca}_x\text{PO}_4$ orientational glass at $x = 0.5$. The VFT behaviour of σ is accounted for within a two-level phenomenological model including attractive interactions between the mobile ions. In this case, an increase in the E_a -value for the phase transition of $\text{Na}_2\text{Ca}_{0.5}\text{PO}_4$ to a modulated state ($q_{1,2} = 0.167a^*$ and $q_3 = 0.263a^*$, where a^* is the reciprocal-lattice cell constant of the cubic modification of the crystal) at about 518 K is due to a deepening of the low-energy level.

1. Introduction

$\text{Na}_{3-2x}\text{Ca}_x\text{PO}_4$ solid solutions belong to materials derived from sodium orthophosphate (Na_3PO_4) with substitution of sodium by calcium [1]. The distinguishing feature of the crystal structure of sodium orthophosphate is the orientational disorder of the PO_4 tetrahedra, at least in the high-temperature cubic modification of the compound [2]. This means that Na_3PO_4 belongs to orientationally disordered crystals [3]. The relatively high value of ionic conductivity of the compound ($\sigma_{600\text{K}} \simeq 10^{-3} \text{ S cm}^{-1}$ [4]) also suggests disorder of its sodium sublattice. As was shown earlier, the disordered state of the sodium orthophosphate can be preserved down to room temperature either by quenching the crystals [2] or by heterovalent substitution of either Na^+ or P^{5+} ions by other cations [4, 5].

It would be of interest to study the processes of ion charge transfer in the statically disordered state (i.e. in the substituted phases at relatively low temperatures) taking into account the significant ionic conductivity of Na_3PO_4 in the dynamically disordered state.

The electrophysical properties of $\text{Na}_{3-2x}\text{Ca}_x\text{PO}_4$ solid solutions have never been studied before. So they were chosen for these investigations. This paper presents data on the ionic conductivity of the $\text{Na}_2\text{Ca}_{0.5}\text{PO}_4$ (i.e. $x = 0.5$).

2. Experimental details

All the samples under investigation were obtained by the conventional solid state synthesis technique. Na_2CO_3 , CaCO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$ were used as the initial reagents. A mixture of the reagents in the appropriate amounts was fired at 1500 K for 24 h with subsequent milling and refring. X-ray powder diffraction analysis (Rigaku Geigerflex D3; $\lambda = 1.5405 \text{ \AA}$) was used for phase control of the products of the chemical reaction.

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Ionic conductivity measurements were carried out with pellet-like ceramic samples $\text{Na}_2\text{Ca}_{0.5}\text{PO}_4$ (10–12 mm thick and 2–4 mm diameter) coated with graphite electrodes. The measurements were performed in the frequency range $5\text{--}5 \times 10^5$ Hz (Tesla BM-507) and temperature interval 290–700 K. The thermal capacitance of the samples has been studied using the DSC technique (Perkin–Elmer DSC-7 unit).

3. Results and discussion

Figure 1 shows the temperature dependence of the ionic conductivity of a $\text{Na}_2\text{Ca}_{0.5}\text{PO}_4$ ceramic. As can be seen from figure 1, the $\sigma(T)$ curve deviates from the Arrhenius law in the entire temperature range. The behaviour of the ionic conductivity of the solid solution can be described using the Vogel–Fulcher–Tammann (VFT) law [6–8] (figure 2). VFT-type behaviour is usually observed in supercooled liquids and glasses above the glass transition point [9]. This means that the origin of the VFT law has a connection to dynamical processes which become ‘frozen in’ above 0 K (see for example [10] and references therein).

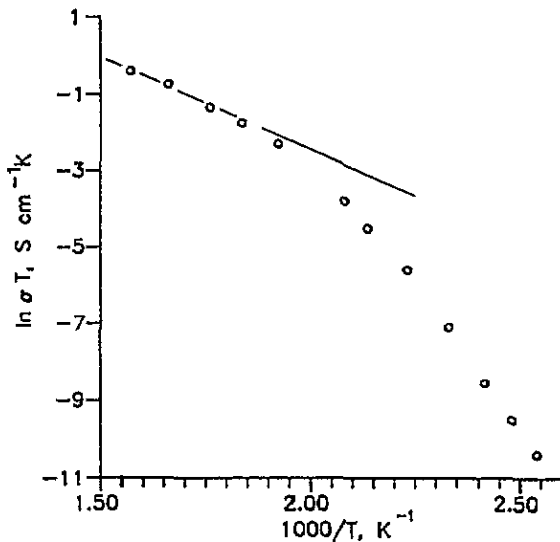


Figure 1. Temperature dependence of ionic conductivity of $\text{Na}_{2.5}\text{Ca}_{0.5}\text{PO}_4$ on an Arrhenius plot.

Below 520 K the experimental data can be fitted with

$$\sigma = 1.29 \times 10^3 \exp[-0.22/k(T - T_0)] \quad (1)$$

where T_0 is the characteristic VFT temperature (250 K for $\text{Na}_2\text{Ca}_{0.5}\text{PO}_4$). Above 520 K the pre-exponent and activation energy values in (1) are changed. Thus, the following equation is satisfied in the high-temperature range:

$$\sigma = 62 \exp[-0.15/k(T - T_0)]. \quad (2)$$

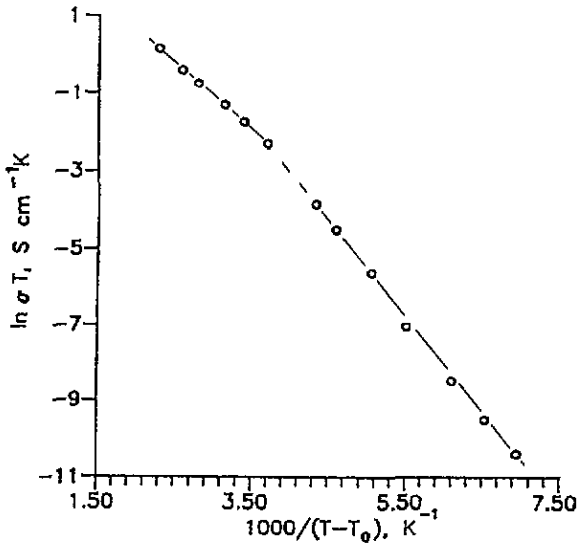


Figure 2. Temperature dependence of ionic conductivity of $\text{Na}_{2.5}\text{Ca}_{0.5}\text{PO}_4$ on a $\ln \sigma T$ versus $T - T_0$ plot.

It is noteworthy that data obtained earlier on the ionic conductivity of the phases related to sodium orthophosphate [4, 5, 11] indicate that a VFT-type behaviour can be observed for almost all these materials. However, in the original papers the analysis of these data has been carried out within the Arrhenius approach which was believed to be universal for a description of the ion charge transfer in solids (see, for example, [12] and references therein).

This 'universality' does not seem to extend to superionic solids. Thorough analysis of the experimental data on the ionic conductivity of the solid electrolytes shows that deviations from the Arrhenius law are observed approximately as frequently as the Arrhenius law itself [13].

The VFT approach is one of these deviations. In principle, the VFT law corresponds to the Arrhenius model in the case of the temperature-dependent value of the activation energy for ion transport:

$$E_a = E_a^0(1 - T_0/T)^{-1}. \quad (3)$$

A simple analysis of equation (3) shows that in the high-temperature range the activation energy tends to its smallest value E_a^0 and becomes weakly dependent on T . On the other hand, the activation energy increases with decreasing temperature and tends to infinity at $T \rightarrow T_0$. However, it is hardly possible to accept the idea of an infinite increase in E_a in the vicinity of T_0 . Indeed, the magnitude of E_a within the Arrhenius approach is defined by the height of the potential barrier between the adjacent positions of mobile ions. So, (3) means an infinite increase in the height at $T = T_0$.

From the general point of view the σ -value is defined by the number n of charge carriers, their mobility μ and their charge q ($\sigma = n\mu q$). The value of n is usually suggested to be temperature independent in superionics (changes in the number of mobile ions occur only under the structural phase transitions). However, from the general point of view the observed dramatic decrease in σ in the vicinity of T_0 could be due to a significant decrease in n instead of the usually suggested decrease in μ .

In this case, the well known [14–16] two-level model for superionics can be used to describe the situation. Figure 3 represents this model schematically. E_{gs} corresponds to the ground state of the mobile ions and E_{es} corresponds to the excited state of the ions; so the difference $E = E_b - E_{es}$ is the activation energy for translational motion of the charge carriers (the probability of the ground-to-ground hops is assumed to be insignificant for simplicity). In the absence of interactions between the mobile ions the population of the excited level increases with increasing temperature in accordance with the Arrhenius law

$$n_{es} = n_{gs} \exp(-\delta/kT) \quad (4)$$

where n_{gs} is the number of ions in the ground state, δ is equal to $E_{es} - E_{gs}$, k is the Boltzmann constant and T is the temperature.

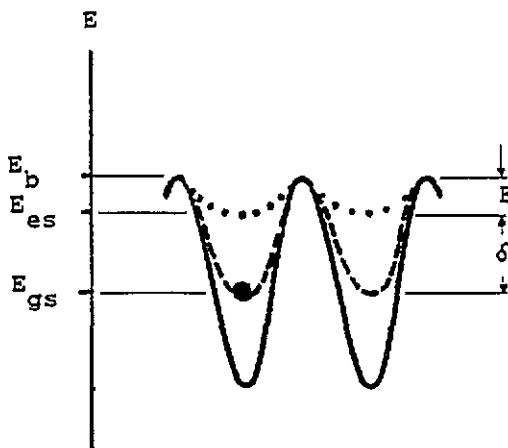


Figure 3. A schematic representation of a two-level model of a superionic material. The notation is explained in the text.

Taking into account that the interactions between the mobile ions take place in both the ground and excited states one has to add a term λn to the exponent of (4):

$$n_{es} = n_{gs} \exp\{-[\delta - \lambda(n_{es} - n_{gs})]/kT\} \quad (5)$$

where λ is a constant of energy dimension characterizing the strength of the interactions [14–16]. The case $\lambda > 0$ corresponds to an attraction between ions, and $\lambda < 0$ corresponds to ion–ion repulsion. As was mentioned elsewhere [16], the situation after introduction of the interactions is similar to the case of ferromagnetism in solids (the Weiss model [17]).

An expression of type (5) has no precise analytical solution. Thus one will obtain an approximate solution assuming that the exponent is not large. Then, expanding (5) in a series, i.e.

$$n_{es} = n_{gs} \{1 - [\delta - \lambda(n_{es} - n_{gs})]/kT + \dots\} \quad (6)$$

one obtains

$$n_{es} \simeq n_{gs} [1 - \delta/k(T + T_0)] \quad (\lambda < 0) \quad (7)$$

$$n_{es} \simeq n_{gs} [1 - \delta/k(T - T_0)] \quad (\lambda > 0) \quad (8)$$

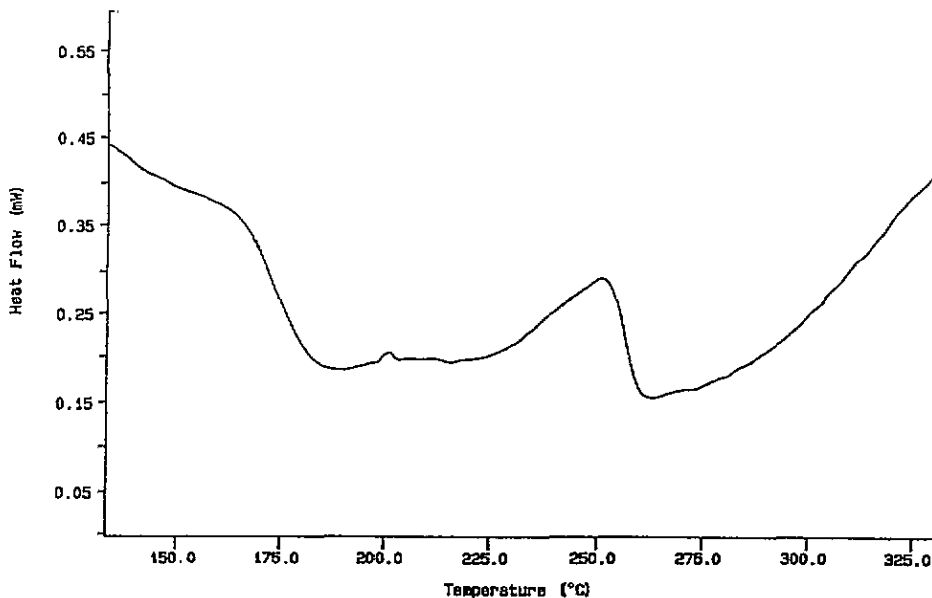


Figure 4. Temperature dependence of the heat capacity of $\text{Na}_{2.5}\text{Ca}_{0.5}\text{PO}_4$.

where $T_0 = \lambda n_{\text{gs}}/k$ (n_{gs} is the total concentration of the potentially mobile ions; i.e. this is either the population of the ground state at $T \rightarrow 0$ K ($\lambda > 0$) or excited state at $T \rightarrow \infty$ ($\lambda < 0$)).

Within the approach the interactions between mobile ions will inevitably cause the E_a -value to vary because of a shift in the E_{es} level with respect to E_b . Thus

$$\sigma = \sigma_0 \exp[-(E_a - \lambda n_{\text{es}})/kT]. \quad (9)$$

Substituting (7) or (8) into (9), one obtains

$$\sigma = \sigma_0 \exp[-E^*/k(T \mp T_0)] \quad (10)$$

where $E^* = [(T \mp T_0)(E_a \mp kT_0) + \delta T_0]T^{-1}$. It can be easily seen that the VFT law is a special case of (10) for attractive interactions between the mobile ions.

As was mentioned above, the VFT-type behaviour of σ means that below T_0 the ionic conductivity of $\text{Na}_2\text{Ca}_{0.5}\text{PO}_4$ disappears because the population of the excited level equals zero. However, one should keep in mind the possibility of ground-to-ground hops which for simplicity was neglected in the model considered. So, a situation when σ exists below T_0 (but its value is much lower than above T_0) seems to be more realistic.

It should be stressed that the aim of the above analysis was to show in principle that interaction between the mobile ions has to result in deviations from the Arrhenius law. To use the obtained expressions in as wide a range of the corresponding parameters (T , T_0 , n_i and so on) as possible, one should either find a more precise solution of (5) (e.g. through differential equations) or use the numerical calculations in each individual case.

As can be seen from figure 2, the value of E^* changes in the vicinity of 518 K. This temperature is close to the temperature of the order-disorder phase transformation in the $\text{Na}_{3-2x}\text{Ca}_x\text{PO}_4$ solid solutions (529 K) found elsewhere [1]. So, it can be suggested that $\text{Na}_2\text{Ca}_{0.5}\text{PO}_4$ undergoes a phase transition at 518 K. This is confirmed by the DSC data (figure 4), revealing an anomaly in C_p with a maximum at about 525 K.

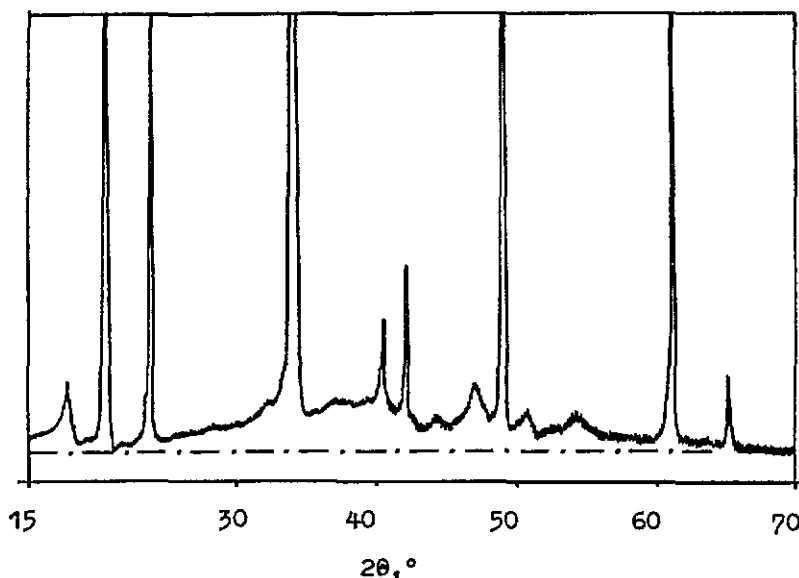


Figure 5. Powder diffraction pattern of $\text{Na}_{2.5}\text{Ca}_{0.5}\text{PO}_4$ at 293 K. The contribution from diffuse scattering is separated from the background by the chain line.

Figure 5 shows the typical x-ray diffraction pattern of $\text{Na}_2\text{Ca}_{0.5}\text{PO}_4$ at 293 K. As can be seen from figure 5, there are two points of interest in the data obtained.

First of all, there is a significant contribution of the diffuse x-ray scattering to the total intensity of the diffracted beam. This indicates that a significant structural disorder exists in $\text{Na}_2\text{Ca}_{0.5}\text{PO}_4$ even at a relatively low temperature. When the very low value of σ at 293 K (see figure 1) is taken into account it seems that orientational disorder of the PO_4 tetrahedra causes diffuse scattering of x-rays.

The second point is the marked separation of the Bragg peaks into two groups which differ in both FWHM and intensity. Analysis of the Bragg peaks show that all high-intensity peaks are narrow and can be described within cubic symmetry (spacegroup, $Fm\bar{3}m$; $a \simeq 7.4$ Å). This symmetry and the value of the lattice cell parameter correspond well to the crystal structure of the high-temperature modification of Na_3PO_4 [2].

However, the Bragg peaks belonging to the second group (which are less intensive and more 'diffuse' than the peaks of the first group) do not correspond to cubic symmetry. The whole diffraction pattern can be described within tetragonal symmetry ($a = 44.381(5)$ Å; $c = 28.154(3)$ Å).

Taking into account the above-mentioned character of the peaks belonging to the second group, we suggest a three-dimensional commensurate modulation of the crystal structure of the solid solution. The corresponding modulation vectors are $q_{1,2} = 0.167a^*$ and $q_3 = 0.263a^*$, where a^* is the reciprocal-lattice vector of the cubic lattice of $\text{Na}_2\text{Ca}_{0.5}\text{PO}_4$. It should be mentioned that all the $q_{1,2,3}$ -vectors or any couple(s) of them can be projections of the more complicate modulation vector in the corresponding planes. However, the powder diffraction data are insufficient to analyse precisely the character of the modulation. It should be mentioned that the modulations along the a and b axes seem to have a commensurate character, while the modulation along the c axis has an incommensurate character.

From the general point of view, ordering of a crystal structure will result in deepening of the potential wells (due to a contribution of the entropy term in the expression for the

Helmholtz free energy). Within the approach under consideration it should result in a shift in the ground state to lower values of energy and a corresponding increase in δ . In this case, the value of E^* should increase in accordance with (9) in the ordered phase of the material. As was mentioned above, the increase in E^* indeed takes place below the phase transition point. So, the suggested two-level model describes the behaviour of the ionic conductivity of $\text{Na}_2\text{Ca}_{0.5}\text{PO}_4$ well in the entire temperature range.

It is interesting to note that the nominally undoped sodium orthophosphate exhibits an Arrhenius [18] or a non-Arrhenius [19] temperature behaviour of σ . The non-Arrhenius behaviour of σ found in [19] was attributed in [18] to the presence of NaOH, H_2O and/or Na_2CO_3 in the sample. However, our analysis indicates that the experimental data in [19] obey the VFT law with $T_0 = 330$ K and $E_a^{\text{VFT}} = 0.18$ eV.

The nature of this behaviour can be caused, from our point of view, by ordering processes. Indeed, in the case of almost perfect order, the value of δ will be high. This will result in a decrease in the occupation of the excited state in accordance with (7). Thus the main contribution to the ionic flow will be due to ground-to-ground hops of the sodium ions. In this case the temperature dependence of σ will obey the Arrhenius law.

Under annealing at relatively low temperatures the phases related to Na_3PO_4 are ordered [20]. So, when the values of the synthesis temperatures for the Na_3PO_4 samples studied in [19] (about 1620 K) and [18] (about 1100 K) are taken into account the suggestion made above can be considered to be plausible.

4. Conclusions

Therefore the VFT behaviour of the temperature dependence of ionic conductivity of the $\text{Na}_2\text{Ca}_{0.5}\text{PO}_4$ solid solution is due to the existence of attractive interactions between the sodium ions. Ordering of the crystal structure of the solid solution results in a decrease in the entropy and consequent deepening of the ground-state energy level for the sodium ions.

Acknowledgment

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