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# Thermal conductivity and diffusivity of sodium orthophosphate

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## Abstract

The transient hot-disc method is used to measure the thermal conductivity and thermal diffusivity simultaneously for polycrystalline sodium orthophosphate ( $\text{Na}_3\text{PO}_4$ ) in the temperature range 300–800 K. The thermal conductivity and diffusivity showed a gradual decrease up to the transition temperature  $T_c = 598$  K and then rose rapidly, reaching a peak at 617 K, followed by a decreasing tendency identified with lower peaks up to 800 K. These data were compared with previous thermal conductivity and diffusivity measurements of pure  $\text{Li}_2\text{SO}_4$ . In the pure  $\text{Li}_2\text{SO}_4$  case, the possibility of linking the heat conduction to the paddle-wheel mechanism has been reported. However, in the present case, the link was not so obvious, in spite of the fact that, in other non-thermal studies, it has been well justified. Possible reasons are given to explain the lack of sensitivity in the thermal behaviour of  $\text{Na}_3\text{PO}_4$  for it to be linked to this mechanism. These reasons were attributed to the detailed microstructure and to the effect of replacing the anions  $(\text{PO}_4)^{3-}$  by  $(\text{SO}_4)^{2-}$  and/or replacing the cations  $\text{Na}^+$  by  $\text{Li}^+$  in the two cases.

## 1. Introduction

Solid phosphates range from being highly crystalline to being glassy. They are generally durable and non-toxic, and they have a wide range of actual and potential materials applications such as catalysis, non-linear optical materials or bio-materials [1]. A variety of crystalline phosphates are good ionic conductors. Notably, NASICON (NA super ionic conductor) solid solutions of  $\text{Na}$ ,  $\text{Na}_{1+x}\text{Zr}_2(\text{PO}_4)_{3-x}(\text{SiO}_4)_x$ , could have very high sodium ion conductivity in the range  $1.8 < x < 2.2$  (a maximum conductivity of  $0.2 \text{ S cm}^{-1}$  at  $300^\circ\text{C}$  for  $x = 2$ ). The orthophosphate group  $(\text{PO}_4)^{3-}$  is the most common phosphorus oxoanion. All four oxygen atoms are usually co-ordinated to cations in solid orthophosphate, leading to strongly bonded extended structures. An example of this group is the sodium orthophosphate  $\text{Na}_3\text{PO}_4$ , which

has a first-order transition at 598 K [2]. The high-temperature form of  $\alpha$ - $\text{Na}_3\text{PO}_4$  is both plastic and a good sodium ion conductor [2]. The orientationally disordered anions form a face-centred cubic (fcc) lattice in which the Na cations occupy all the tetrahedral and octahedral interstices [3]. Due to the observed high cationic mobility and anionic rotational disorder above the phase transition, the material belongs to the ionically conductive rotor solids.

In general, characterization of phosphates can be performed using several techniques [1]. The usual structural techniques of x-ray or neutron diffraction and electron microscopy can be used to reveal the structure of these solids. Vibrational and NMR spectroscopies are both very useful for studying solid phosphates, especially poorly crystalline materials. For example, the features in the P–O stretching region ( $700\text{--}1400\text{ cm}^{-1}$ ) are of greatest diagnostic use. Di- and polyphosphates are distinguished from orthophosphates by the vibrations of the P–O–P bridge. The choice of the sodium orthophosphate  $\alpha$ - $\text{Na}_3\text{PO}_4$  as a candidate for our study is due to the relatively low transition temperature and the rather good relative air stability for anhydrous  $\text{Na}_3\text{PO}_4$ . This is characterized by the dynamic rotational disorder of its polyatomic anions and by the translation mobility of its cations (see the discussion section). To our knowledge, there is a lack of thermal conduction studies on ionic rotor solids. We are interested in studying the effect of the rotational and translational dynamics due to phase transition in such solids. In other words, we will investigate the structural transition anomalies that are connected with the absorption or release of energy and the properties of the phases between the corresponding structural transitions. In this work, we have used the transient hot-disc method [4] to measure the thermal conductivity and thermal diffusivity simultaneously and to investigate the thermal conduction processes that might take place during the phase transition of the sodium orthophosphate.

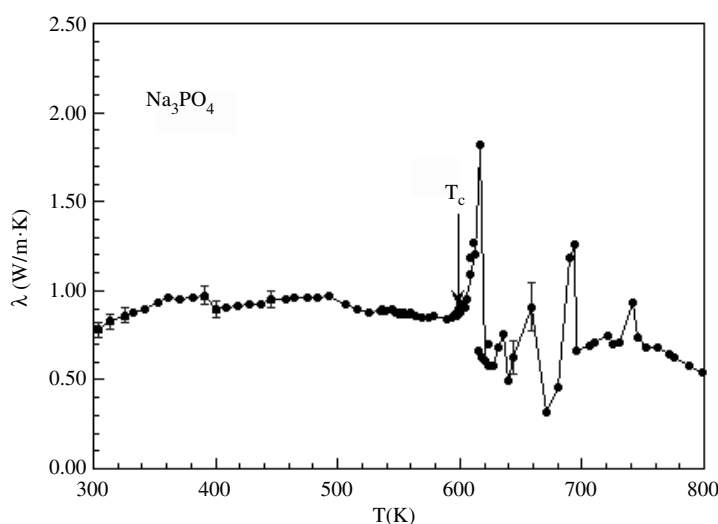
## 2. Experiment

### 2.1. Sample preparation

A powder sample of pure  $\text{Na}_3\text{PO}_4$  was obtained by solid-state reaction of  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_4\text{P}_2\text{O}_7$  at  $800\text{ }^\circ\text{C}$  for 48 h [5]. Since  $\text{Na}_3\text{PO}_4$  is hygroscopic, careful handling of the powder is necessary in a dry environment so that water will not be built into the crystal structure. The powder is used at room temperature (in a dry environment) to make two pellets of 28 mm diameter by applying a uniaxial load ranging between 8 and 12 kN. The sample consisted of two identical disc-shaped pellets with a diameter of 28 mm and a thickness of 5 mm. An average value of the apparent density was calculated by using the accurate dimensions and weights of the pellets.

## 3. Measurements

The transient hot-disc method [4] was used to perform simultaneous measurements of the thermal conductivity ( $\lambda$ ) and thermal diffusivity ( $\kappa$ ) over the temperature range from 300 to 800 K. In this method, a resistive heater pattern, cut from a thin sheet of Ni covered on both sides with a thin layer of insulating mica, is used both as a heat source and temperature sensor. The thickness of the sheet and the mica layer are 10 and  $100\text{ }\mu\text{m}$ , respectively. The method is based on three-dimensional heat flow inside the sample, which can be regarded as an infinite medium by limiting the total time of the transient recording. With this basis, the method eliminates the photon component (heat lost by radiation) of the thermal conductivity, which is a feature of utmost importance for high-temperature measurements. The experimental arrangement is set up by sandwiching the hot disc between the pellets. The experiment was performed by



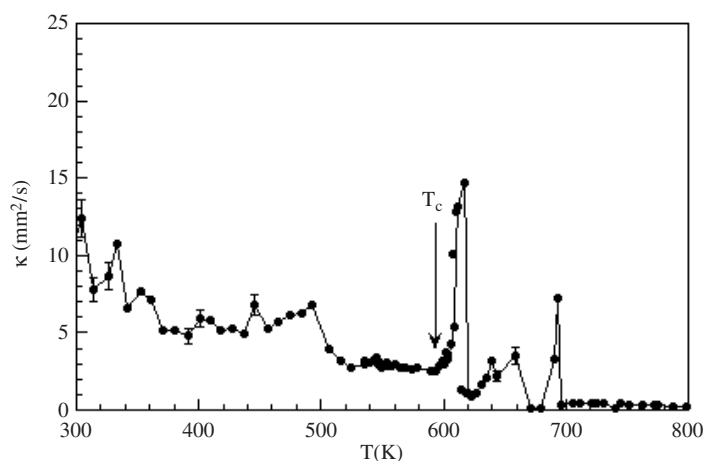
**Figure 1.** The temperature dependence of the thermal conductivity of sodium orthophosphate. The arrow indicates the transition temperature  $T_c$ .

recording the voltage (resistance) variation over the hot disc while its temperature is raised slightly by a pulsed electrical current. The time-dependent resistance data of the hot disc are then used to evaluate the thermal conductivity and diffusivity of the sample. The temperature coefficient of the hot disc's resistance was determined from separate calibration measurements of the disc. The measurement error did not exceed 10% for  $\lambda$  and 12% in  $\kappa$ , except for some of the data points assigned by the error bars. More details on the experimental procedures are given elsewhere [6].

#### 4. Results

Figures 1 and 2 show the measured data of the thermal conductivity  $\lambda(T)$  and thermal diffusivity  $\kappa(T)$ , respectively. A trend of decreasing  $\lambda(T)$  was observed as the temperature increased to about 598 K, at which point there was a drastic change in the slope. This is in agreement with the behaviour of other similar materials that undergo structural phase transition [7, 8]. As stated above, the present material should have a first-order phase transition at 598 K [2]. It is worth mentioning that there might be a slight shift in our data due to some microstructure defects. Our sample was made of polycrystalline powder. The type and number of non-equilibrium defects, mosaic structure and the morphology of the internal boundary surfaces determine the microstructure of such samples. Therefore, solids of the same chemical composition may exhibit a broad variation with regard to their reactivity and most of their physical properties, including a possible shift in the phase transition temperature.

The thermal conductivity values started to increase at the transition temperature  $T_c$  (indicated by the arrow in figure 1) and then first rose rapidly, reaching a peak at 617 K, followed by a rapid decrease, characterized by a gradual decline with two smaller peaks at 694 and 741 K, respectively. The diffusivity  $\kappa(T)$  shows a faster decrease, characterized by peaks similar to those observed in the conductivity data. The clear tendency of a general decrease in heat conduction is characteristic behaviour for non-metallic crystals in this temperature range. Their values were thus lowered due to phonon–phonon scattering, since  $\lambda(T)$  can be



**Figure 2.** The temperature dependence of the thermal diffusivity of sodium orthophosphate. The arrow indicates the transition temperature  $T_c$ .

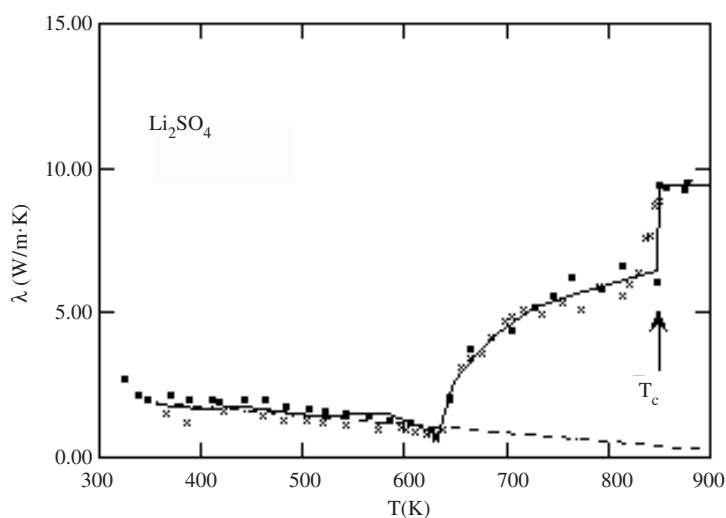
approximated as being inversely proportional to the temperature. The reduction of the thermal conductivity after the peaks might be due to the formation of local elastic inhomogeneities during the phase transformation. These local elastic inhomogeneities may act as additional scattering centres to the phonons, and they take up a fraction of the heat conduction volume affecting the thermal conduction processes (see discussion).

The range of  $\lambda(T)$  values of these data coincides with other measurements [9] and with previous measurements made by us to elucidate the effect of increasing  $\text{Na}^+$  by increasing the  $\text{Na}_2\text{SO}_4$  contents in the  $\text{Li}_2\text{SO}_4$ – $\text{Na}_2\text{SO}_4$  system [10, 11]. In our previous measurements of the thermal properties of pure lithium sulfate [6], belonging to the same class of ionic rotor solids, we obtained much higher  $\lambda(T)$  values, while pre-transition behaviour had been seen in this properties (see figure 3). We will compare the observed changes in the behaviour of the thermal properties, both in the low-temperature and high-temperature phases, for  $\text{Li}_2\text{SO}_4$  and  $\text{Na}_3\text{PO}_4$ .

## 5. Discussion

As general background, an ionic conductor is characterized by the ability to conduct electricity via the migration of ions through its structure. The requirements for ionic conduction in solids are low ionic migration activation energies and/or access to vacant sites for the ions to move into. Solids that conduct ions well are referred to as fast ion conductors (see below). The conductivities of such solids are typically in the range  $10^{-3}$ – $10^1$   $\text{S cm}^{-1}$  at the temperature in question and their structures have special features that enable the relatively facile motion of one set of ions between sites [12].

According to Wilmer *et al* [2], the high-temperature  $\alpha$ -phase of  $\text{Na}_3\text{PO}_4$  is characterized by dynamic rotational disorder of its polyatomic anions and by the translational mobility of its cations. It has a lack of vacancies and free space for the sodium ion hopping. In other words, in its structure all of the interstices are filled with cations and percolation-type mechanisms are hard to visualize, creating a favourable situation for detecting correlated anion/cation dynamics. Therefore,  $\text{Na}_3\text{PO}_4$  makes a very good candidate for the study of the interplay of anion rotation and cation hopping which can be linked to the paddle-wheel



**Figure 3.** The temperature dependence of the thermal conductivity of lithium sulfate. The arrow indicates the transition temperature  $T_c$ . The dashed line is an extrapolation of the phonon-scattering effect on the thermal conductivity—for more details, see [6].

mechanism [13]. In a recent study by Witschas *et al* [14], the anionic and cationic motion was probed individually over a wide range of experimental time-scales. They used five different techniques to probe the dynamics: three to characterize the rotational motion of the anions—namely, coherent quasi-elastic neutron scattering, temperature-dependent  $^{17}\text{O}$  NMR line-shape and relaxation spectroscopy—and the other two to characterize the cation motion—namely, high-frequency conductivity and  $^{23}\text{Na}$  NMR relaxation measurements. They concluded that the dynamic measurements provided clear evidence for strong dynamic interplay between anions and mobile cations in  $\alpha\text{-Na}_3\text{PO}_4$ . Furthermore, the interplay is not only operative in the non-translational high-amplitude movements of neighbouring ions, but is certainly also essential when sodium ions are moving on from one neighbourhood to another in a translational chain mechanism. Their observation of constant conductivity up to microwave frequencies rules out the possibility of a simple transport mechanism, with individual cations performing independent hops. In other words, it appears that the paddle-wheel mechanism has been well justified by their findings. It should be mentioned that there have also been some studies of cation transport in solid phases with other types of polyatomic anions [15, 16]. We are, at present, not making any comparisons with salts with polyatomic anions, but mechanisms of ion conduction in such systems have been discussed thoroughly by Funke [17].

Regarding heat conduction in the  $\alpha$ -phase of  $\text{Na}_3\text{PO}_4$ , we are interested in the extent to which heat transport is influenced by the cations and the polyatomic anions. This is the first study of heat transport in a fast-ion-conducting plastic phase of the polyatomic (phosphate) anions. It is evident from figures 1 and 2 that, for both the conductivity and the diffusivity, there are peaks at 617 K as well as at 694 K. Furthermore, it is also evident that, for  $T < T_c$ , in the low-temperature range both parameters decreased slightly when the temperature was increased, which is an indication that a simple phonon-transport theory can be applied to the ‘low-temperature’ part before the phase transition.

At this stage, it might be reasonable to start to compare this data with other materials that have ionic bonds and for which measurements have been made on both sides of a phase transition. The peak in thermal conductivity due to a phase transition is in agreement with other

similar investigations of ionic conductive samples [18, 19]. However, if we try to compare this data to our previous measurements of a pure  $\text{Li}_2\text{SO}_4$  sample [6], where the thermal transport was linked to the paddle-wheel mechanism, then this link is not clear in the  $\text{Na}_3\text{PO}_4$  case in spite of the fact that other non-thermal studies [2, 13] have justified the link. There are several reasons that might make the link to the paddle-wheel mechanism through the thermal behaviour of this sample not quite obvious. Before we make any comparison between the measurements for the two compounds—namely,  $\text{Li}_2\text{SO}_4$  and  $\text{Na}_3\text{PO}_4$ —we must look at two major differences in the chemical compositions of these compounds. Although they both belong to the ionically conductive rotor solids, the cations are  $\text{Li}^+$  in the former and  $\text{Na}^+$  in the latter, while the anions groups are  $(\text{SO}_4)^{2-}$  and  $(\text{PO}_4)^{3-}$ , respectively. We will try to elucidate the effect of these two major differences and their combination on the electrical conduction and activation energies of the conducting ions with the possible relation to thermal conduction processes.

According to Jansen [20],  $\text{Na}_3\text{PO}_4$  already has an overcharged cation substructure, leading to changes in the potential of the corresponding lattice site and thus effects, inter alia, a more or less strong deformation of its surroundings and lowers the mobility of the charge carrier.

Moreover, the replacement of the phosphate anion by the sulfate anion, while retaining the structure, has essentially the following effects with regard to the cation conductivity:

- (i) increasing the concentration defects in the cation substructure;
- (ii) changing the so-called free transport volume for the cations;
- (iii) increasing the rotational motion of the complex anion.

In addition, we may also consider the possible different trapping of the cations in the proximity of different anions.

All of the above-mentioned reasons are justified by the temperature dependence of the sodium ion conductivity in the  $\text{Na}_3\text{PO}_4/\text{Na}_2\text{SO}_4$  mixed-crystal system [20]. The abrupt change in the conductivity at the transition point was smeared out as the mole fraction of  $\text{Na}_2\text{SO}_4$  is increased (see figure 9 in [20]). The activation energy of the sodium conductivity is also decreased as the mole fraction of  $\text{Na}_2\text{SO}_4$  is increased in this mixed-crystal system (see figure 15 in [20]). Both figures in [20] may indicate that the major effect on the electrical conduction is due to replacing the phosphate anion by the sulfate anion. This is in direct correspondence to our comparison between the thermal conduction of  $\text{Li}_2\text{SO}_4$  and  $\text{Na}_3\text{PO}_4$ .

Furthermore, from the theoretical point of view there are two reports. One concerns a study of two-component systems of non-equilibrium dynamic simulation [21]. This study revealed that the major contributions to the heat flux are from the fluxes of the kinetic and collisional energies and that the main mechanism of heat transport is collision between particles (the motion of the cations). This process may be directly related to anharmonicity of the lattice and disordered motion in ionic systems, depending on the type of cations in the system. The other report concerns a study of the thermal conductivity in superionic conductors [22] based on the lattice gas model with a hopping term. It has been shown that the contribution of mobile ions to the thermal conductivity is of Arrhenius type and is of the same order as that of lattice conduction. This is in agreement with our studies on the thermal properties of a mixed system of  $\text{Li}_2\text{SO}_4/\text{Na}_2\text{SO}_4$  [10, 11, 23], which indicate the smearing of the pre-transition behaviour in the thermal conduction data as the mole fraction of  $\text{Na}_2\text{SO}_4$  is increased. In these studies, the onset temperature is independent of the crystal structure as well as of the cation concentrations. However, both the conductivity and diffusivity are larger for lithium sulfate than for sodium sulfate, while the mixtures fall in between. This might be due to the fact that the hexagonal pure  $\text{Na}_2\text{SO}_4$  has lower conductivity than the cubic pure  $\text{Li}_2\text{SO}_4$ . However, the conductivity of pure  $\text{Na}_2\text{SO}_4$  can be enhanced by doping with lithium ions, because there are cation sites that are too small for the sodium ions but can host lithium ions [24].

It should be noted that the  $\alpha$ -phase of  $\text{Na}_3\text{PO}_4$  is isostructural with fcc  $\text{Li}_2\text{SO}_4$ . The difference is that all cation sites are occupied in the phosphate while one third are vacant in the sulfate. This may also affect the contribution of Na in the thermal processes of heat conduction in this material. In addition, according to a recent paper by Wilmer *et al* [25], increasing the sulfate content in  $x\text{Na}_2\text{SO}_4(1-x)\text{Na}_3\text{PO}_4$  not only enhances the cation transport in the ionic conductivity but also speeds up the anion reorientational motion.

Other lithium-containing analogues, such as  $\text{LiM}_2(\text{PO}_4)_3$  with  $\text{M}^{4+} = \text{Zr}, \text{Ti}, \text{Ge}$  and  $\text{Hf}$ , also have NASICON-type structures. According to Robertson *et al* [26] and references therein, these structures consist of corner-sharing  $\text{MO}_6$  and  $\text{PO}_4$  polyhedra which form a rigid  $[\text{M}_2(\text{PO}_4)_3]$  framework and the lithium ions move through tunnels in a three-dimensional pathway. There are two different lithium ion sites in the structure, labelled I and II. In stoichiometric  $\text{LiM}_2(\text{PO}_4)_3$ , the type I sites are full and the type II sites are empty. It has been postulated that lithium loss during sintering at high temperatures causes a significant reduction in the conductivity of undoped  $\text{LiTi}_2(\text{PO}_4)_3$  [27]. A study of the thermal properties of such a compound may reveal the direct relation between the Li ions and the phosphate group and their effect on the thermal conduction processes.

Finally, it is assumed that the heat carriers in such materials are mainly phonons, which are greatly affected by the heat scattering centres within the crystal lattice such as point defects, dislocations, isotropic inhomogeneities, admixtures, grain boundaries etc. In general, the mean free path of phonons is determined by these scattering centres and by the mean length of elastic waves excited at a given temperature inside the crystal. A detailed discussion of the phonon-dispersion relation (acoustic and optical modes) in ionic crystals is given in [6]. Under these circumstances, the thermal behaviour of what appears to be similar samples can lead to different results that might as well depend on the preparation procedures. Thus, the technology of making the pellets might influence lattice conduction in both pure- or mixed-crystal systems.

## 6. Conclusions

Using the transient hot-disc method, we have measured the temperature dependence of the thermal conductivity and diffusivity of a polycrystalline sample of sodium orthophosphate. We tried to associate our measurements in this case with the previously measured case for pure  $\text{Li}_2\text{SO}_4$ . For the pure  $\text{Li}_2\text{SO}_4$ , we have observed a pre-transition behaviour that leads to the enhancement of thermal conduction, which was linked to the paddle-wheel mechanism. Other measurements, rather than thermal measurements, have shown that, for both cases, this mechanism may play a dominant role in the electrical conduction processes. However, regarding thermal conduction, we could not see similar behaviour in  $\text{Na}_3\text{PO}_4$  and the link was not obvious. It seems that the reason is due to the microstructure differences, and the role of the anions and cations, in these two ionic rotor solids. The heat carriers in such materials are mainly phonons, which are more sensitive to these differences and are greatly affected by the heat scattering centres (defects) within the crystal lattice. It appears that the concentration of defects and the ionic mobility are both key parameters related to the ionic transport in ionic systems such as  $\text{Na}_3\text{PO}_4/\text{Na}_2\text{SO}_4$  mixed crystal. These parameters are directly related to the correlated anion/cation dynamics and thus to the anharmonicity (distortion) of the lattice. Furthermore, it is not obvious which is the governing (dominant) parameter, even in pure substances such as the  $\alpha$ -phase of  $\text{Na}_3\text{PO}_4$ , which has a strong dynamic interplay between anions and mobile cations. A study of heat conduction for  $\text{LiTi}_2(\text{PO}_4)_3$  may reveal a direct association with the dynamic interplay between the Li ions and the phosphate group and their effect on the thermal conduction processes.



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