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THE ENERGETICS OF PHASE TRANSITIONS IN THE SYSTEM $Na_{1+X}Zr_2Si_XP_{3-X}O_{12}$, $1.9 \leq X \leq 2.5$

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ABSTRACT

The temperatures and enthalpies of phase transitions in the system $Na_{1+X}Zr_2Si_XP_{3-X}O_{12}$ with $1.9 \leq X \leq 2.5$, have been determined by differential scanning calorimetry. Second-order phase transitions were observed in all samples except for $X = 2.5$. The transition temperatures decreased systematically with X, varying from approximately 423 K for $X = 1.9$ to 375 K for $X = 2.3$. The enthalpies of transition followed a similar trend, 2.11 kJ mol^{-1} for $X = 1.9$ and 0.52 kJ mol^{-1} for $X = 2.3$.

INTRODUCTION

In recent years many studies have been made on the solid solution system $NaZr(PO_4)_3$–$Na_4Zr_2(SiO_4)_3$. The interest in this system was motivated by the discovery of fast alkali-ion transport in certain compositions, with the highest conductivity occurring for $Na_3Zr_2PSi_2O_{12}$ [1]. This material is more commonly known as NASICON (Na super-ionic-conductor). The ionic conductivity of NASICON is comparable to that of sodium β-alumina and this ceramic has potential for use as a solid electrolyte in sodium–sulfur batteries.

The two end-members of the $Na_{1+X}Zr_2Si_XP_{3-X}O_{12}$ system, i.e. $X = 0$ and $X = 3$, are rhombohedral ($R\bar{3}c$); fast ionic conductivity is observed in the range $1.8 \leq X \leq 2.4$ with the maximum occurring at approximately $X = 2$ [2]. All the compositions showing fast ionic Na transport are characterized by a structural phase transition at low temperatures, typically close to 400 K. The low temperature structure of these compositions is monoclinic ($C2/c$) transforming to the higher temperature rhombohedral structure via a second-order transition [3,4]. Because single crystals of the solid solutions

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have proven difficult to prepare, details of the Na positions in these phases have provided a source of much investigation and controversy [5]. There has also been a considerable degree of discussion in the literature as to the optimum synthetic route for preparing homogeneous samples with the correct stoichiometry.

Arrhenius plots of the conductivity of NASICON materials show characteristic breaks in slope at temperatures corresponding to the monoclinic–rhombohedral transition. The activation energy below the transition is significantly lower than that after the transition [3]. It is presumed that this results from a significant disordering of the Na ions during the phase transition. Most work has concentrated upon the $X = 2$ compound. The energetics and character of the phase transition in $Na_3Zr_2PSi_2O_{12}$ have been studied by Von Alpen et al. [4]. In their work they found the phase transition was second order and characteristically broad, occurring over a range of approximately 80°C. In this paper we report the results of a study of the transition temperatures and enthalpies of a series of compositions with $1.9 \leq X \leq 2.5$, using differential scanning calorimetry.

EXPERIMENTAL

NASICON samples were prepared by milling $Na_3PO_4 \cdot 12H_2O$, SiO_2 and ZrO_2 under acetone. Appropriate amounts of $Na_2CO_3 \cdot H_2O$ or $Na_4P_2O_7 \cdot H_2O$ were added for values of $X > 2$ or $X < 2$, respectively. After milling, the mixture was dried in air to remove the acetone and then under vacuum to dehydrate the hydrated phosphates without forming a liquid phase. The dried materials were calcined in fused-silica containers at 1140°C for about 2 h. The calcined material was milled under acetone for 30 h. The milled powder was then granulated for fabrication. Powders were iso-statically pressed into pellets and sintered by heating to 400°C at 80°C h^{-1} then to 1230°C at 400°C h^{-1} and finally held at 1230°C for 16 h. In this system it is difficult to eliminate traces of a free ZrO_2 phase, weak peaks were observed in X-ray diffraction. However, in all samples it was estimated that the volume fraction of ZrO_2 was less than 3%.

The energetics of the phase transitions for compositions with $1.9 \leq X \leq 2.5$ were measured on 200–350 mg samples using a Setaram DSC 111. Measurements of the heat flow were made from 220 to 520 K at a scanning rate of 5°C min^{-1}. Starting the scans well below the transitions using a sub-ambient nitrogen-cooled system, and stopping more than 50°C past their completion allowed accurate baseline determination for each run. Multiple scans were made for each composition to check the reversibility of the transitions and also to check the consistency of the transition temperatures and enthalpies.

RESULTS AND DISCUSSION

Our results for $Na_3Zr_2PSi_2O_{12}$ ($X = 2$) were in general agreement with those previously reported [4]. Thus, as shown in Fig. 1, the transition in this ceramic is broad, being spread over a range of approximately 100 K, and has all the characteristics of a second-order phase transition. The transition showed no apparent hysteresis. The transition temperature was calculated by extrapolation of the steepest slope of the thermal anomaly to the pre-transition baseline. The enthalpy accompanying the transition was calculated by digitizing the area under the peak. The peak area was obtained by extrapolation of both the pre- and post-transition baselines. Our value for the enthalpy was in agreement with that of Von Alpen [4], and the calculated transition temperature, 424.6 K, was also close to the value, 420 K, previously reported, though see ref. 5 for a discussion of heat treatment effects upon the nature of the transition in this material. Because in this study we were primarily interested in the trends in the variation of T_{trans} and ΔH_{trans} with X, we used the transition enthalpy of 2.07 kJ mol^{-1} previously reported as a standard and calculated all other enthalpies with respect to that value.

Broad thermal effects were observed for samples with $X = 1.9$, 2.1, 2.2, 2.3 and 2.4. All were characteristic of second-order behavior. Although the transition in the sample with $X = 2.4$ was detectable, it was too small to accurately determine a transition temperature or enthalpy. No transition was detected in the $X = 2.5$ sample. A summary of the transition temperatures and their associated enthalpies is given in Table 1.

The variation of T_{trans} with X is shown in Fig. 2. The transition temperature varies systematically with composition, with the highest temperature occurring for $X = 1.9$ and 2.0, and the lowest for $X = 2.3$. Although the transition temperature could not be reliably determined for $X = 2.4$, due to the inherent weakness of the thermal anomaly, it appeared to follow this general trend.

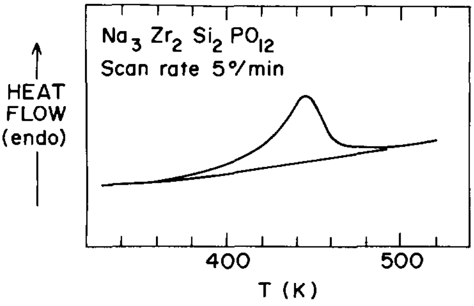

Fig. 1. Thermal characteristics of the phase transition in $Na_3Zr_2Si_2PO_{12}$.

TABLE 1

Transition temperatures and enthalpies in the system $Na_{1+X}Zr_2Si_XP_{3-X}O_{12}$

X	1.9	2.0	2.1	2.2	2.3
T_{trans} (K)	422.9	424.6	415.5	388.0	374.6
ΔH (kJ mol^{-1})	2.11	2.07	1.61	1.25	0.52

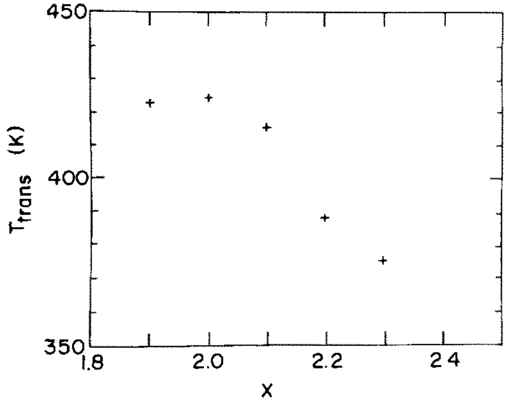

Fig. 2. Plot of the variation of the transition temperatures in $Na_{1+X}Zr_2Si_XP_{3-X}O_{12}$ as a function of X.

The corresponding enthalpies of transition are plotted in Fig. 3. A similar trend is observed. The largest enthalpies occur for $X = 1.9$ and $X = 2.0$ and then decrease systematically to $X = 2.4$ where the transition is barely detectable.

The variations in the transition temperatures and enthalpies seem to follow previously reported observations of a monoclinic–rhombohedral

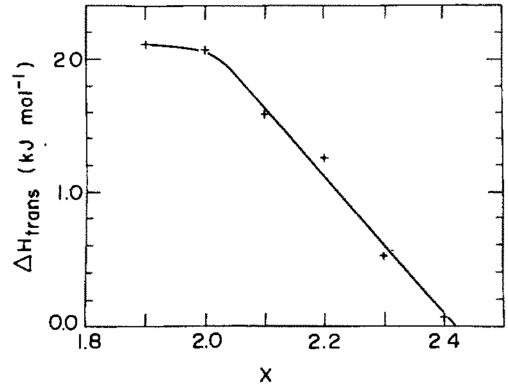

Fig. 3. Variation of the enthalpy of the phase transition, ΔH_{trans} (kJ mol^{-1}), in $Na_{1+X}Zr_2Si_XP_{3-X}O_{12}$ as a function of X.

transition within the range $X = 1.9–2.4$ [6]. All samples outside this range remain rhombohedral at all temperatures. The absence of a thermal anomaly at $X = 2.5$ is in agreement with those results. We also find a direct correlation between the magnitude of the conductivity and the anomalies in the Arrhenius plots, and the energetics of the transitions. If the phase transition results in part from the disordering of the sodium ions then its enthalpy should be directly related to the magnitude of the conductivity of the system. Thus from our calorimetric results we would predict, in agreement with the previous conductivity work [3], that the compositions $X = 1.9$ and 2.0 should show higher conductivities than samples with larger values of X.

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