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Ionic conductivity and Raman investigations on the phase transformations of $Na_4P_2O_7$

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Abstract

The ionic conductivity and thermo-Raman spectra of anhydrous sodium pyrophosphate $Na_4P_2O_7$ were measured dynamically in the temperature range from 25 to 600 °C with a heating rate of 2 °C min^{-1} to understand the structural evolution and phase transformation involved. The DSC thermogram was also measured in the same thermal process for the phase transformation investigation. The spectral variations observed in the thermo-Raman investigation indicated the transformation of $Na_4P_2O_7$ from low temperature phase (ε) to high temperature phase (α) proceeded through pre-transitional region from 75 to 410 °C before the major orientational disorder at 420 °C and minor structural modifications at 511, 540 and 560 °C. The activation energies and enthalpies of the proposed phase transformations were determined. The possible mechanism for temperature dependent conductivity in $Na_4P_2O_7$ was discussed with the available data. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Inorganic materials; Optical properties; Ionic conduction; Optical spectroscopy

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1. Introduction

Phosphates are among the best glass formers. Their glass formation tendency can be associated with the ability of phosphates to form one or two-dimensional structures. To understand the ionic conductivity of mixed pyrophosphate systems, the detailed investigations on ionic conductivity and phase transformations of $Na_4P_2O_7$ are very much essential. Sodium pyrophosphate $Na_4P_2O_7$ exhibits rich variety of phase transformation from room temperature to 600 °C. Earlier investigations on the polymorphism of $Na_4P_2O_7$ indicated that there were at least 5–6 polymorphic structures. Farr [1] labeled the five phases of $Na_4P_2O_7$ as phase V, IV, III, II and I, reported the transformation temperatures were as:

$$Na_4P_2O_7(V) \xrightarrow{400\ ^\circ C} (IV) \xrightarrow{510\ ^\circ C} (III) \xrightarrow{520\ ^\circ C} (II) \xrightarrow{540\ ^\circ C} (I)$$

Recent thermal, X-ray and ionic conductivity studies indicated that before melting at 995 °C the $Na_4P_2O_7$ undergoes the following transformation [2,3].

$$Na_4P_2O_7(\varepsilon) \xrightarrow{390\ ^\circ C} (\delta) \xrightarrow{504\ ^\circ C} (\gamma) \xrightarrow{512\ ^\circ C} (\beta) \xrightarrow{550\ ^\circ C} (\alpha)$$

However, these two sets were the same.

Although the polymorphic structures and the phase transformation of $Na_4P_2O_7$ were studied by several techniques the nature and sequence of phase transformation are not known completely yet. Raman spectroscopy has the advantage in the identification of compositions and phases of a solid from vibrational bands. Raman spectra measured dynamically as a function of temperature is thermo-Raman spectroscopy (TRS) and has been applied successfully in the in-situ investigation of solid-state phase transformations and composition changes [4–9]. Hence in this work the thermo-Raman, ionic conductivity and thermal analysis DSC (differential scanning calorimetry) measurements were utilized extensively to derive a better microscopic understanding of the phase transformations and sequence of the phase transformations involved in $Na_4P_2O_7$.

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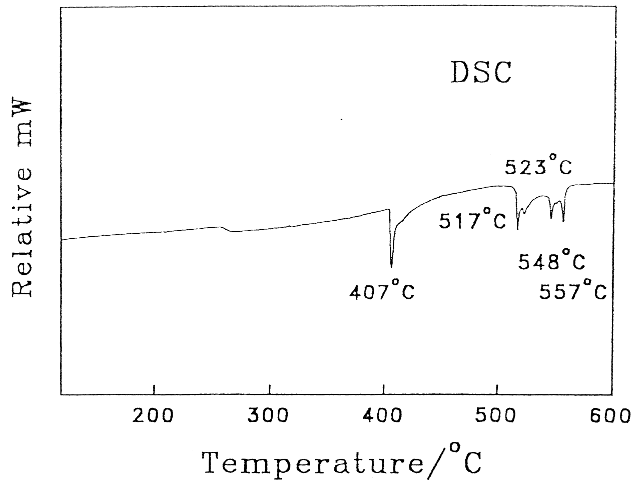

Fig. 1. DSC thermogram of $Na_4P_2O_7$.

2. Experimental

2.1. Sample preparation

Anhydrous $Na_4P_2O_7$ was prepared from analytical grade $Na_4P_2O_7 10H_2O$ (Showa Chemicals) by heating up to 150 °C with a heating rate of 1 °C min^{-1}. The sample was kept at 150 °C for 1 h for complete removal of hydrated water. Then this powder has been desiccated under vacuum. This anhydrous powder has been used for all the measurements.

2.2. Thermal analysis

The DSC (Seiko ISSC 5040) thermogram of anhydrous $Na_4P_2O_7$ measured from 25 to 600 °C with the heating rate of 2 °C min^{-1} in a flow of nitrogen with a flow rate of 100 ml min^{-1} is shown in Fig. 1. The DSC thermogram indicated five endothermic peaks at 407, 517, 523, 548 and 557 °C.

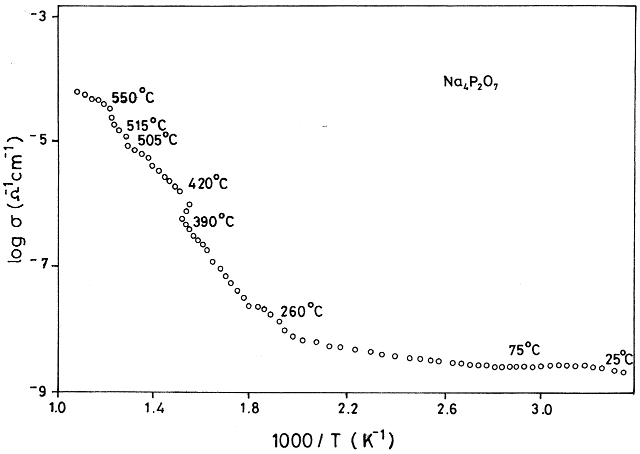

Fig. 2. Temperature dependence conductivity of $Na_4P_2O_7$.

2.3. Ionic conductivity measurements

The anhydrous sample from desiccator was compacted as pellets of 1 cm diameter and 0.6 mm thick; the applied pressure was 5.5 kbar. To ensure good homogeneity and to decrease the inner porosity of the pellets, a heat treatment at 250 °C for 48 h was applied. The pellet was introduced between silver electrodes of high purity. The contacts between pellet and electrode was improved by pressure applied through a steel compression spring arrangement. The bulk resistance of the sample from 25 to 600 °C was measured using Keithley meter. The bulk conductivity of $Na_4P_2O_7$ was calculated using the relation $\sigma = t/RA$, where t is the thickness of the sample, A is area of cross section of the electrode electrolyte contact. The temperature dependent conductivity plot of $Na_4P_2O_7$ in the form of log σ vs. 1000/T is shown in Fig. 2. The activation energy is calculated based on Arrhenius dependence of the conductivity from the slope of the log σ vs. 1000/T plot.

2.4. Thermo-Raman studies

Thermo-Raman spectra were measured by the excitation of the laser light (30 mW) at a wavelength of 514.5 nm from an argon ion laser (Coherent, Innova 100-15). The scattered light was collected at right angles, dispersed by a spectrometer (Spex, 0.5 m) and detected by a CCD camera (Princeton Instrument, 1024×1024 pixels). The sample from desiccator was packed in the sample holder and kept in a homemade oven. The thermo-Raman spectra were recorded under nitrogen atmosphere. For the phase transformation studies, the temperature range was set from 25 to 600 °C with a heating rate of 2 °C min^{-1}. The temperature was monitored by a thermocouple and controlled by a programmable controller. The positions of the spectral bands were calibrated using an argon spectral tube and the resolution was about 2 cm^{-1}. The typical thermo-Raman spectra of $Na_4P_2O_7$ observed in this investigation are presented in Fig. 3.

3. Results

3.1. Thermal analysis

The DSC thermogram of $Na_4P_2O_7$ shown in Fig. 1 indicates five endothermic peaks at 407, 517, 523, 548 and 557 °C. The enthalpy variation calculated for the endotherms in DSC at these temperatures were 9.4, 1.33, 0.54, 0.98 and 1.44 mJ mg^{-1}, respectively.

3.2. Ionic conductivity measurements

The temperature dependent conductivity plot of $Na_4P_2O_7$ shown in Fig. 2 indicates several temperature domains. Between room temperature and 75 °C the con-

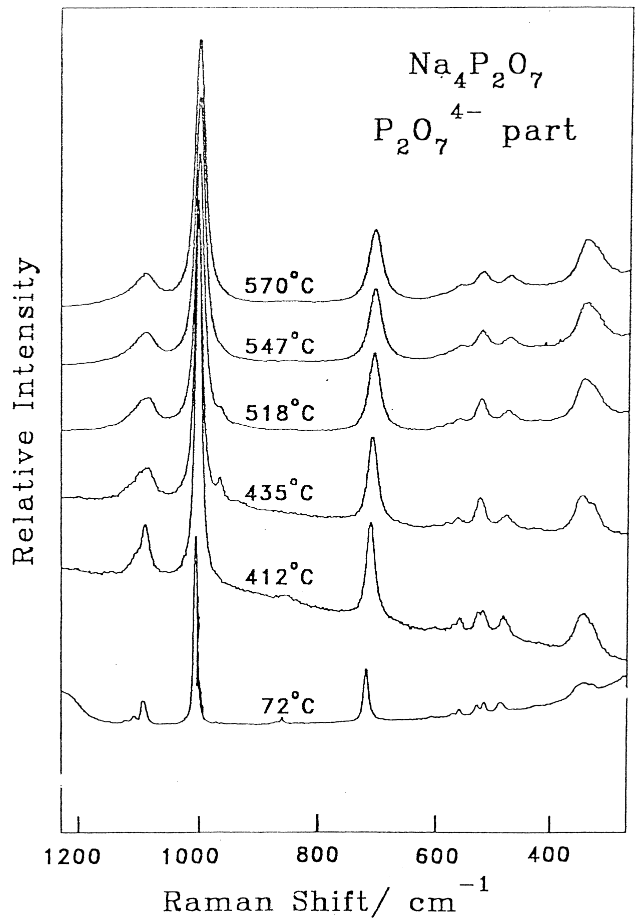

Fig. 3. Typical thermo-Raman spectra of $Na_4P_2O_7$.

ductivity of $Na_4P_2O_7$ does not vary much and the activation energy calculated in this range was 0.049 eV, which is very low, the characteristics of ε-phase of $Na_4P_2O_7$. With further increase in temperature it is clear that there is a gradual increase in the conductivity up to 260 °C and afterwards an appreciable increase in the conductivity was observed up to 390 °C and the activation energy in this temperature range was found to be 0.90 eV. After this, a jump in the conductivity curve was observed at around 420 °C with the drop of activation energy to 0.76 eV. Then a gradual increase in the conductivity was observed up to 545 °C except very slight jumps in the conductivity curve at around 505 and 515 °C. A change in the conductivity value was again observed at around 550 °C with the drop of activation energy to 0.92 eV. With further increase of temperature a slight deviation in the conductivity curve was observed in the range from 560 to 575 °C.

3.3. Thermo-Raman studies

The diphosphate ion $P_2O_7^{4-}$ consists of two PO_4 tetrahedra with a central P–O–P bridge bond [10]. The internal modes of $P_2O_7^{4-}$ are in the range from 300 to 1500 cm^{-1}. The stretching modes of PO_4 usually occur in the range from 1250 to 975 cm^{-1} and the bridge stretching modes of PO_4 are in the range from 975 to 675 cm^{-1}. Other bands can be grouped in to two regions from 450 to 620 cm^{-1} and around 340 cm^{-1} corresponding to the deformation modes of PO_4 and P–O–P, respectively. The symmetric stretching mode of PO_4 observed at around 1027 cm^{-1} is the most intense Raman band for the room temperature Raman spectrum of anhydrous $Na_4P_2O_7$. The band positions of Raman bands measured at various temperatures and their tentative vibrational assignments are given in Table 1.

Thermo-Raman spectra measured in the temperature interval from room temperature to 75 °C did not show any modification in the spectral profile. However, the spectral variation observed in the thermo-Raman spectra in the temperature interval from 75 to 415 °C as shown in Fig. 4 indicates the continuous but minute change in the spectral profile from 75 to 235 °C and appreciable modifications

Table 1
The band positions (in cm^{-1}) for different phases of $Na_4P_2O_7$

Phase ε[a] 25 °C	Phase ε_{PT} [a] 412 °C	Phase δ[a] 518 °C	Phase β[a] 535 °C	Phase α[a] 547 °C	Band assignment
1145					
1130	1128				
1116	1111	1110	1109	1108	PO_3 asym. str.
−1027	1023	1024	1022	1021	PO_3 sym. str.
		987	987		
881	875				
732	725	722	720	720	P–O–P sym. str.
616	614				
580	579	588	590		
567	566	571	568	567	
536	535	531	529	529	PO_3 sym. bend + P–O–P bend
523	524				
493	489	484	481	479	PO_3 asym. bend
338	342	347	343	342	PO_2 twist
327	327				

[a] Tentative assignment.

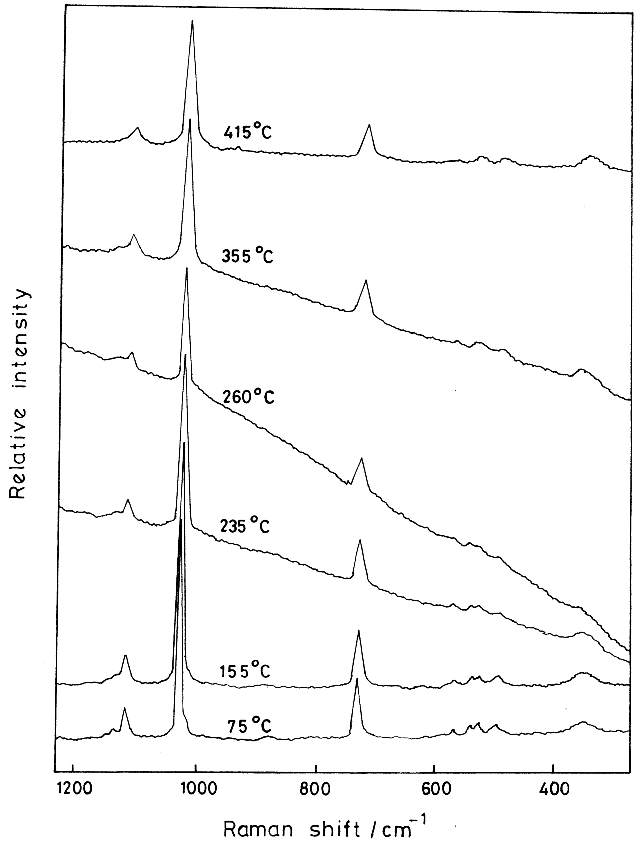

Fig. 4. Thermo-Raman spectra of $Na_4P_2O_7$ measured in the temperature interval from 75 to 415 °C corresponding to the transformation from ε-phase to ε-pretransitional phase.

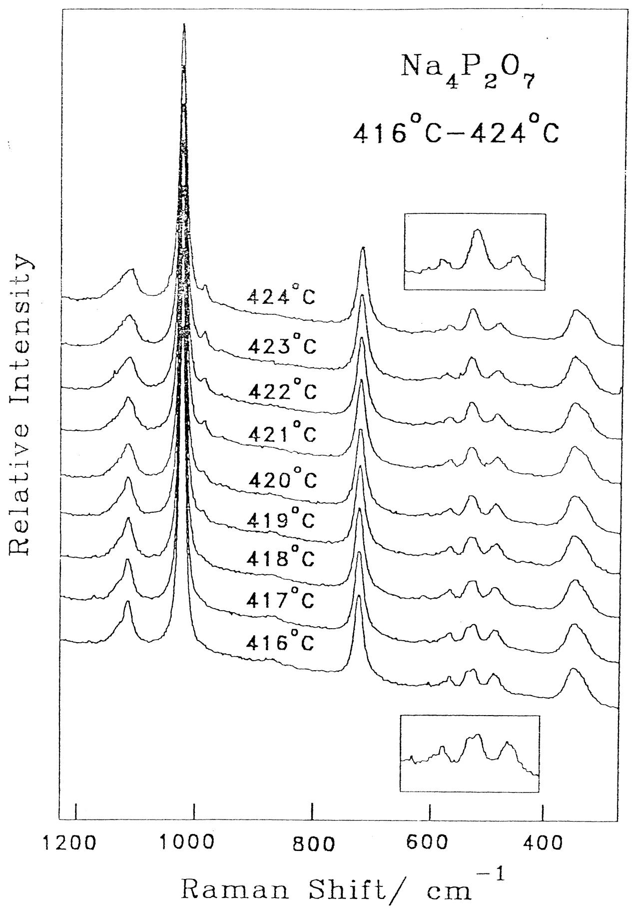

Fig. 5. Thermo-Raman spectra of $Na_4P_2O_7$ measured in the temperature interval from 416 to 424 °C corresponding to the transformation from ε-pretransitional phase to δ-phase.

afterwards up to 415 °C. The Raman spectrum measured at 415 °C clearly indicates the shift in the band positions of symmetric stretching mode of PO_4 from 1027 to 1023 cm^{-1}. During this course of change, three bands at 1145, 1130 and 1116 cm^{-1} became overlapped and appeared as a broad band centered at 1111 cm^{-1} with a shoulder at 1128 cm^{-1}. The band at 881 cm^{-1} shifted to 875 cm^{-1} and became broad and weak. The remaining weak bands were also broadened as shown in the Raman spectrum measured at 415 °C.

Thermo-Raman spectra observed in the temperature range from 416 to 424 °C as shown in Fig. 5 indicated a clear phase transformation. The most distinct variation in this temperature interval was the appearance of a small hump at 987 cm^{-1} close to the symmetric stretching band of PO_4 at 1024 cm^{-1} at around 420 °C. In addition to this major variation some more minor change also observed in the spectral profile. The bands observed at 579, 489 and 342 cm^{-1} shifted to 588, 484 and 347 cm^{-1}, respectively. The bands at 875 and 614 cm^{-1} had disappeared during this transformation. The temperature range covered for this transformation was from 418 to 423 °C.

The spectral variation in the temperature range from 509 to 515 °C indicated another phase transformation. The hump at 987 cm^{-1} became weak and observed as a shoulder to the symmetric stretching band of PO_4 at around 511 °C. In addition, the bands at 1110, 1024, 588, 484 and 347 cm^{-1} shifted to 1108, 1022, 590, 481 and 342 cm^{-1}, respectively. The temperature range covered for this transformation was from 509 to 513 °C.

As shown in Fig. 6 the thermo-Raman spectra measured in the temperature interval from 526 to 552 °C revealed the disappearance of the hump at 987 cm^{-1} and the band at 590 cm^{-1} and signaling another clear phase transformation. The temperature range covered by this transformation was from 532 to 548 °C and the transformation temperature was 540 °C. Thermo-Raman studies also indicate minor spectral variations, i.e. the broadening the bands at 720, 573, 533 and 480 cm^{-1} in the temperature interval from 550 to 570 °C. However, it was difficult to conclude these modifications were due to phase transformation, as there were only broadening of bands and no distinct variation in spectra.

4. Discussion and conclusion

According to Leung et al. [11] $Na_4P_2O_7$ crystallizes at ambient conditions in orthorhombic space group $P2_12_12_1$. Some studies also reported that it belongs to hexagonal

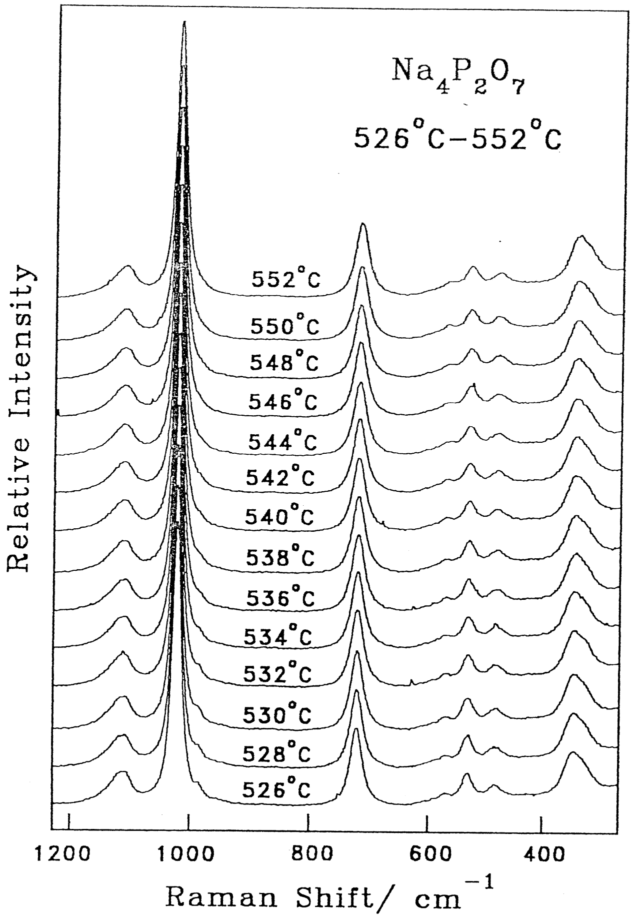

Fig. 6. Thermo-Raman spectra of $Na_4P_2O_7$ measured in the temperature interval from 526 to 552 °C corresponding to the transformation from β-phase to α-phase.

structure [12]. Although the exact crystal structures of other phases were not well known, the available crystallographic data signaled that they were more similar to each other and belong to the ordered version of hexagonal phase.

The DSC thermogram of $Na_4P_2O_7$ showed continuous deviation in the base line from 75 to 400 °C with a slight dip at around 260 °C. The ionic conductivity measurements carried out in this work also distinguish two temperature ranges in conductivity measurement below 260 °C with low activation energy (0.049 eV) and between 260 and 390 °C with high activation energy (0.90 eV). The thermo-Raman studies of $Na_4P_2O_7$ indicated the continuous but minute change in the spectral profile from 75 to 235 °C and appreciable modifications afterwards up to 415 °C. The observation of gradual modification in the vibrational bands in the P_2O_7 region in this temperature range before the first transformation was an indication of a pretransitional region in advance of the first structural transformation at around 420 °C. The pretransition is considered to be a preparatory stage caused by the structural changes not associated directly with the formation of the new phase. In the pretransitional region however there has been some rearrangements of atoms i.e. an onset rotation of P_2O_7, the skeleton structure was nearly the same as at room temperature.

The appearance of small but distinct hump at 987 cm^{-1} close to the strong symmetric stretching band of PO_4 at 1024 cm^{-1} in the thermo-Raman spectra in the temperature range from 416 to 424 °C signaled the clear disorder in the framework of P_2O_7. An appreciable jump in the conductivity value and an enthalpy variation of 9.4 mJ mg^{-1} for an endothermic peak in DSC in this temperature range also confirms the order disorder transformations. The observation of minor spectral variation in thermo-Raman, slight jump in conductivity value and weak endothermic peak with enthalpy variation of 1.33 mJ mg^{-1} in DSC implied moderate order disorder transformation in the temperature interval from 509 to 515 °C.

The major spectral variation of disappearance of the hump at 987 cm^{-1} and the band at 590 cm^{-1} in the thermo-Raman, an appreciable conductivity jump and an endothermic peak with enthalpy variation of 0.98 mJ mg^{-1} in the temperature at around 540 °C indicates an another possible order disorder transformation. The absence of distinct spectral variation except broadening of all the Raman active bands in the temperature interval from 550 to 570 °C indicated the modifications might be due to thermal effect.

The typical thermo-Raman spectra shown in Fig. 3 were probably from ε-phase (at 72 °C), ε-pretransitional phase (at 412 °C), δ-phase (at 435 °C), β-phase (at 518 °C) and α-phase (at 547 °C) of $Na_4P_2O_7$. The transformation observed in this work were for ε-phase to ε-pretransitional in the temperature intervals 75 to 410 °C, ε-pretransitional phase to δ-phase at around 420 °C, γ-phase to β-phase at 511 °C, β-phase to α-phase at 540 °C and α-phase to high temperature phase at 560 °C. Although the earlier studies predicted the phase δ to γ-transformation at around 505 °C, no distinct spectral variation was observed in the thermo-Raman for the phase transformation in this temperature range.

The ionic conductivity measurement in this work indicates the $Na_4P_2O_7$ materials behave as medium ionic conductors even at high temperature. The thermo-Raman spectra and activation energy measured in different temperature domains in this work may be useful to propose the mechanism of temperature dependent conductivity in this material. The temperature dependent conductivity of $Na_4P_2O_7$ depends on the number of mobile charge carriers available and possible sites for them. In $Na_4P_2O_7$ structure the P_2O_7 group consists of two PO_4 tetrahedra with a central P–O–P bridge bond constitute relatively rigid structure. Hence, for the diffusion of charge carriers, i.e. for the diffusion of sodium ions, the presence of defect is essential. The absence of dramatic spectral variation in the thermo-Raman during the transformation from ε-phase to ε-pretransition phase indicates the skeleton structure of $Na_4P_2O_7$ remains the same, except for the relative position and orientation of P_2O_7 group. During the ε-pretransition to δ-phase and β to α-phase transformations the thermo-Raman spectra indicated there is an appreciable disorder in the P_2O_7 group, hence, the sodium ions diffuse freely in the lattice and there is an increase in conductivity and drop in activation energy. However, with the available data it was difficult to probe the mechanism for the changes observed in the conductivity and activation energies in the remaining phases.

In all the spectral variations observed in thermo-Raman investigation, ionic conductivity measurement and thermal analysis indicate the transformation of $Na_4P_2O_7$ from low temperature (ε) to high temperature (α) phase proceeds through continuous modification in the crystal structure from 75 to 410 °C, major orientational disorder of P_2O_7 group at 420 °C and minor structural modification at 511, 540 and 560 °C. The spectral variations observed in the thermo-Raman studies signalled that except the major orientational disorder at 420 °C the other phase transformations involved very minor structural deviations. The thermo-Raman investigations carried out on $Na_4P_2O_7$ provided better microscopic understanding of the phase transformations compared to the earlier investigations.

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