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INVESTIGATIONS ON TEMPERATURE DEPENDENT STRUCTURAL EVOLUTION OF $NaPO_3$ GLASS

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Abstract

The understanding of molecular level structural information of phosphate glasses is very much essential. The unique microwave-absorbing ability of $NaH_2PO_4{\cdot}2H_2O$ was found to be very useful for preparing crystal and glassy sodium super ionic conductors (Nasicon's) as a component of batch mixtures. In this work $NaPO_3$ glass was prepared by both conventional melt quench and microwave heating from $NaH_2PO_4{\cdot}2H_2O$ as a starting material. The structure of $NaPO_3$ glass and their structural evolution upon heating through glass transition were probed by combination of complementary techniques like differential scanning calorimetry (DSC), powder X-ray diffraction (PXRD), Fourier transform infrared (FT-IR) and thermo-Raman spectroscopy.

Keywords: $NaPO_3$ glass, structural evolution, thermo-Raman spectroscopy

Introduction

Phosphates are among the best glass formers and have been widely investigated in recent times [1]. Their glass formation tendency can be associated with the ability of phosphates to form one or two dimensional polymeric structures in the form of meta and ultra phosphate units. Some of the crystalline phosphates of the general formula $A_1B_2(PO_4)_3$, where A is Na ion and B is generally a metal with valency of four or more are called as sodium super ionic conductor (Nasicon).

The single-short microwave assisted approach to the preparation of a number of important crystalline and glassy materials with Nasicon structure is attracted in terms of its simplicity, rapidity and general applicability. The unique microwave-absorbing ability of $NaH_2PO_4{\cdot}2H_2O$ was found to be useful for preparing crystal and glassy

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Nasicon as a component of batch mixtures. Although several crystalline and glassy Nasicon materials were prepared by microwave heating method using $NaH_2PO_4{\cdot}2H_2O$ as a starting material; the structure of $NaPO_3$ glass obtained by conventional melt quench and microwave heating from $NaH_2PO_4{\cdot}2H_2O$ as starting material and the structural evolution of $NaPO_3$ glass upon heating through glass transition are not investigated earlier in detail.

Raman spectroscopy is one of the most convenient and powerful tools to unravel details about local and cooperative changes during transitions between phases and to probe the crystallization and glass transition phenomena [2, 3]. Thermo-Raman spectroscopy (TRS) in which Raman spectra are measured dynamically as a function of temperature has been applied successfully in the in situ investigation of solid state phase transitions and composition changes [4–15]. The thermo-Raman spectroscopic technique was utilized recently to monitor the dehydration, condensation and phase transitions involved upon heating the $NaH_2PO_4{\cdot}2H_2O$ [16]. However the capability of Raman spectroscopy was not utilized earlier to probe the structural evolution during glass-crystalline transition of $NaPO_3$. Hence the thermo-Raman spectroscopic technique was used in this work to probe the structural changes of $NaPO_3$ glass upon heating through glass transition.

The aim of this work is to prepare $NaPO_3$ glass both by conventional melt quench and microwave heating from $NaH_2PO_4{\cdot}2H_2O$ as a starting material, to probe their glassy nature and their structural evolution dynamically as a function of temperature by thermo-Raman spectroscopic studies.

Experimental

Preparation of $NaPO_3$ glass

Conventional melt quench method

$NaH_2PO_4{\cdot}2H_2O$ (5 g) sample taken in open silica crucible was heated up to 70°C in a furnace. The remaining sample in the silica crucible was taken out and it was ground. The grounded powder in open silica crucible was kept inside the furnace and heating process was continued till melting. Constant stirring was adopted to have homogenous melt. The resulting melt was allowed to cool rapidly at room temperature. The transparent hygroscopic nature $NaPO_3$ glass was obtained and then it was ground into fine powder for further characterization.

Microwave heating process

$NaH_2PO_4{\cdot}2H_2O$ powder (5 g) taken in a silica crucible was exposed to microwaves inside a BPL microwave oven operating at 2.45 GHz. A ‘Step ladder’ heating mechanism [17] has been proposed earlier to account for the high microwave absorbing ability of $NaH_2PO_4{\cdot}2H_2O$. Dehydration of $NaH_2PO_4{\cdot}2H_2O$ appears to take place in two steps; the first step which apparently starts within 30 s of exposure and is completed within 50 to 60 s for the loss of two water molecules. The microwave absorption continues to occur even after dehydration and anhydrous NaH_2PO_4 heats to high temperature. The second step of dehydration begins around 80 s and lasts upto 120 to 130 s. This second step of dehydration corresponds to the removal of one more H_2O molecule from the structure by condensation reaction. The entire material was melted within 150 s and turns red hot. The melt was allowed to cool rapidly at room temperature. A transparent and hygroscopic nature $NaPO_3$ glass obtained by this quenching process was ground into fine powder for further characterization.

Powder X-ray diffraction (PXRD) analysis

PXRD patterns of the samples were taken using Rigaku-Mini Flex system with CuK_α radiation of wavelength 1.5418 Å with Ni filter. The PXRD pattern of the pre-melted $NaH_2PO_4 \cdot 2H_2O$, $NaPO_3$ glass prepared by microwave heating method and melt quench method are shown in Figs 1a, b and c, respectively.

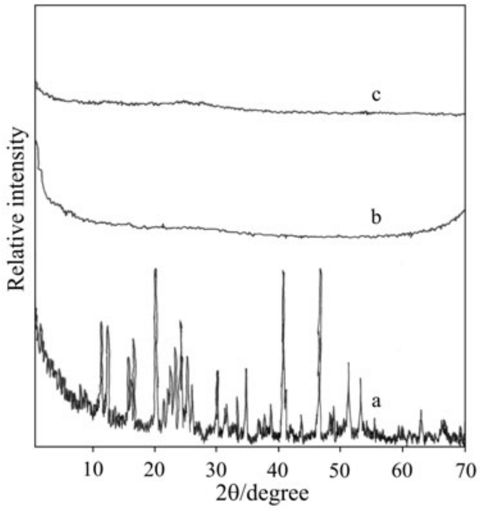

Fig. 1 The powder X-ray diffraction patterns of the samples; a – pre-melted $NaH_2PO_4 \cdot 2H_2O$; b – $NaPO_3$ glass prepared by microwave method; c – $NaPO_3$ glass prepared by melt quench method

Thermal analysis

The differential scanning calorimeter (DSC) curve of $NaPO_3$ glass prepared by melt quench and microwave heating method was measured using Mettler DSC 821 under a flow of N_2 gas from 25 to 500°C at a heating rate of $5°C\ min^{-1}$. The nature of the DSC curve of both $NaPO_3$ glass prepared by melt quench and microwave heating method were same. The DSC curve of $NaPO_3$ glass prepared by microwave heating method is shown in Fig. 2.

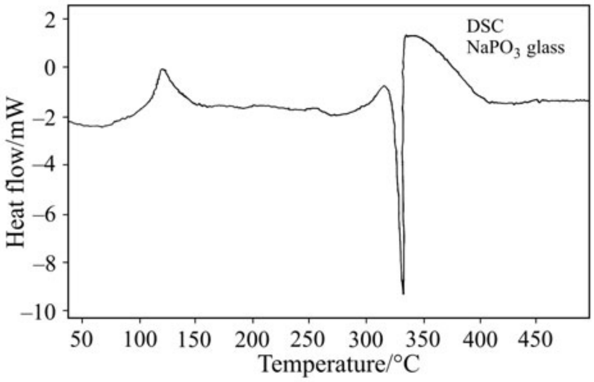

Fig. 2 The DSC curve of $NaPO_3$ glass prepared by microwave heating method

Infrared spectroscopy

The Fourier transform infrared (FTIR) spectrum of the $NaH_2PO_4 \cdot 2H_2O$, $NaPO_3$ glass prepared by conventional melt quench and microwave heating and $NaPO_3$ glass sample (prepared by microwave heating method) heated to 400°C were recorded by Shimadzu FTIR-8700 spectrometer at room temperature and are depicted as Figs 3a, b, c and d, respectively.

Thermo-Raman spectroscopy

The experimental set-ups utilized for the thermo-Raman studies were described in detailed earlier [2, 11]. The powdered $NaPO_3$ glass sample was pressed into a shallow pit on a sample holder attached to a thermocouple in a homemade oven covered with glass. A programmable controller was used to control the temperature. The uncertainty in measuring the temperature was about 1°C. Thermo-Raman spectra were measured using excitation by laser light of 50 mW power operating at a wavelength of 514.5 nm, from an argon ion laser (Coherent, Innova 100–15). The scattered radiation was collected, analyzed by a 0.5 m spectrophotometer (Spex) and detected by a CCD camera (Princeton Instruments, 1024×1024 pixels). Thermo-Raman spectra were taken continuously with suitable exposure times, such that each spectrum covered 1°C in a dynamical thermal process, heating from 25 to 600°C at the rate of 5°C min^{-1}. A low laser power of 10 mW was employed for thermo-Raman studies to avoid any heating effects due to laser irradiation. The spectral resolution was about 2 cm^{-1}. The thermo-Raman spectra measured in different temperature intervals are presented in Figs 4–6.

Results and discussion

The sharp peaks observed in the PXRD pattern presented in Fig. 1a clearly indicate the crystalline nature of pre-melted $NaH_2PO_4 \cdot 2H_2O$. Non-observation of peaks and

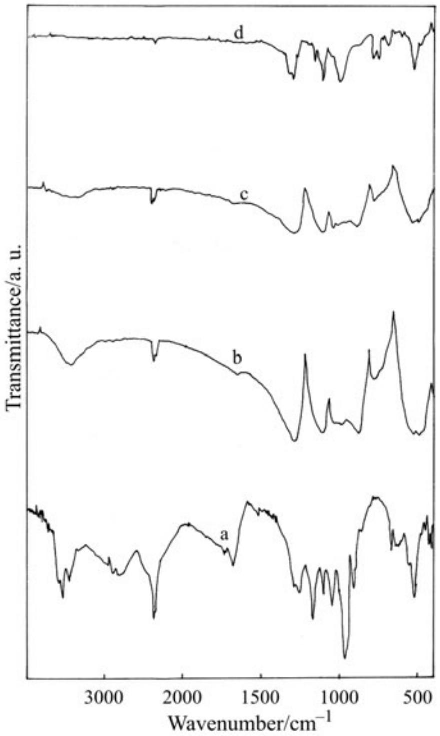

Fig. 3 The Fourier transform infrared (FTIR) spectrum of; a – $NaH_2PO_4{\cdot}2H_2O$; b – $NaPO_3$ glass prepared by microwave heating; c – $NaPO_3$ glass sample prepared by conventional melt quench and d – $NaPO_3$ glass sample (prepared by microwave heating method) heated to 400°C

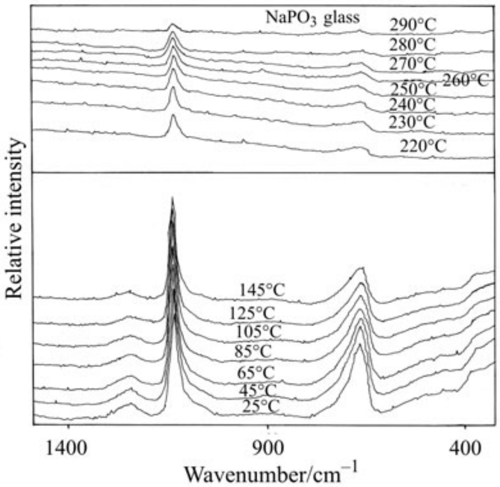

Fig. 4 The thermo-Raman spectra of $NaPO_3$ glass measured in the temperature interval from 25 to 145°C and 220 to 290°C

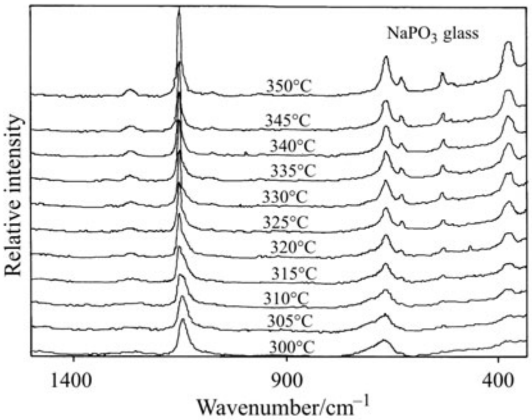

Fig. 5 The thermo-Raman spectra of $NaPO_3$ glass measured in the temperature interval from 300 to 350°C

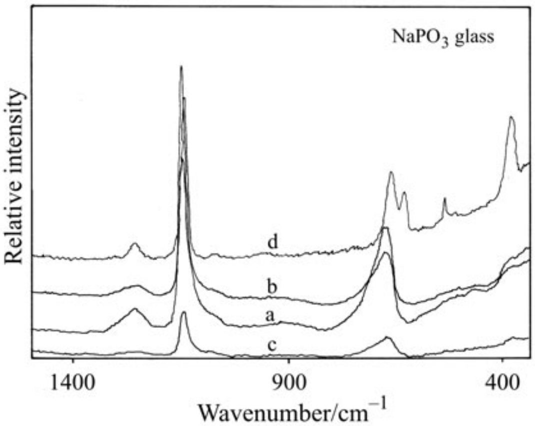

Fig. 6 The typical thermo-Raman spectra observed at a – 25°C; b – 150°C; c – 300°C and d – 500°C during dynamical thermal process

halos in the low angle region of the PXRD patterns in the Figs 1b and c clearly indicate the glassy nature of the $NaPO_3$ sample prepared by microwave heating as well as melt quench method, respectively.

The DSC curve of $NaPO_3$ glass prepared by microwave heating shown in Fig. 2 indicated a broad peak at around 128°C corresponding to removal of water and deviation in the baseline of the curve in the temperature range at around 280°C corresponding to the outset of glass transition. As crystallization takes place the heat of crystallization is evolved, hence a sharp dip appears on the DSC curve at 330°C.

The room temperature FTIR spectrum of $NaH_2PO_4{\cdot}2H_2O$ shown in Fig. 3a consist of a number of distinct and well separated groups of bands corresponding to vibrational modes of $(PO_4H_2)^-$ ions, OH groups and water molecules. Infrared spectroscopy is very sensitive to the presence of water in phosphate samples. An asymmetric band observed at 1672 cm^{-1} corresponds to bending vibrations and a broad band at 3450 cm^{-1} corresponds to stretching vibrations of crystal water in $NaH_2PO_4{\cdot}2H_2O$. A narrow band observed at 3530 cm^{-1} indicated the presence of loosely bounded crystal water in $NaH_2PO_4{\cdot}2H_2O$. The FTIR spectrum of the $NaPO_3$ glass prepared by microwave heating and conventional melt quench shown in Figs 3b and c, respectively, indicate both the spectra are very similar except slight change in their band positions at lower wave number side and hence reveals the close similarity of the $NaPO_3$ glass sample obtained by both the methods. The presence of broad and weak bands in P–O vibrational region in Figs 3b and c reflects the glassy nature of the sample. The FTIR spectrum of $NaPO_3$ glass shown in Figs 3b and c also clearly demonstrates the dramatic difference in the P–O vibrational region compared to the FTIR spectrum of $NaH_2PO_4{\cdot}2H_2O$ shown in Fig. 3a. For $NaH_2PO_4{\cdot}2H_2O$, the ν_1, symmetric stretching vibrational mode of $(PO_4)^{3-}$ was observed at 907 cm^{-1} and ν_3, asymmetric stretching vibrational modes were observed at 962 and 1043 cm^{-1}. In contrast, the stretching modes of $(PO_3)^{-}$ in $NaPO_3$ glass were observed at 1095 and 1274 cm^{-1}, respectively. The observation of weak broad band at 3425 cm^{-1} in the FTIR spectrum of $NaPO_3$ glass corresponding to the stretching modes of water indicated the presence of water when the $NaPO_3$ glasses were prepared in an open silica crucible with water producing raw material $NaH_2PO_4{\cdot}2H_2O$. The FTIR spectrum of $NaPO_3$ glass heated to 400°C in Fig. 3d indicated considerable changes in the P–O vibrational region compared to the FTIR spectrum of as prepared $NaPO_3$ glass. The broad bands appeared in the glass phase split into many sharp bands in the crystalline phase. The prominent and broad band observed at 472 cm^{-1} corresponding to the bending modes of PO_3^- in the glass phase appeared just as a weak band at 482 cm^{-1} in the crystalline phase. The presence of this prominent band in the glass phase strongly signaled the network features of phosphate species present in the glass phase.

The Raman spectra measured as a function of temperature, during the dynamical thermal process can provide valuable information for the in situ investigation of PO_3 environment in the samples because of the availability of spectra in the time scale of seconds and temperature scale of 1°C. $NaH_2PO_4{\cdot}2H_2O$ crystal belongs to space group $P2_12_12_1$ (D_2^4) with orthorhombic crystal structure [18]. In contrast to KH_2PO_4 (KDP) the four oxygen atoms of the PO_4 group in $NaH_2PO_4{\cdot}2H_2O$ are not equivalent. Two acidic hydrogens of a $(PO_4H_2)^{-}$ form strong hydrogen bonds with the oxygen atoms of adjacent $(PO_4H_2)^{-}$ groups. The recent thermo-Raman studies on $NaH_2PO_4{\cdot}2H_2O$ indicated two steps of dehydration, formation of $Na_2H_2P_2O_7$ at 220°C in the first condensation process, $NaPO_3$ formation in two steps at about 260°C and two-phase transition of $NaPO_3$ at the temperature of 345 and 515°C [16].

The thermo-Raman spectra of $NaPO_3$ glass in the P–O vibrational region measured in the temperature interval from 25 to 145°C are shown in Fig. 4. Bands in the 1000–1400 cm^{-1} range are due to the symmetric and asymmetric stretching modes of P–O non-bridging bonds, whereas the bands observed in 620–820 cm^{-1} are due to the symmetric and asymmetric stretching modes of bridging oxygens. There are several bands common to both Raman and FTIR spectrum of the $NaPO_3$ glass measured at room temperature. But it is difficult to identify and compare quantitatively the various bands due to their large bandwidths. In phosphate glasses the number of tetrahedral linkages in the network of glass is based on the ratio of oxygen to phosphorus. The Raman spectrum of $NaPO_3$ glass measured at 25°C shown in Fig. 4 indicated the non-bridging stretching modes at 1146 and 1260 cm^{-1} and bridging stretching mode at 675 cm^{-1}.

The spectral variation of slight shift and appreciable broadening of the bands at 675 and 1146 cm^{-1} observed in the temperature interval from 85 to 145°C as shown in Fig. 4 signaled the removal of water in this temperature interval. The absence of any appreciable change in spectral profile of $NaPO_3$ glass after the removal of water indicated that this hygroscopic water is not strongly bonded to the phosphate species. Although this hygroscopic water is not strongly bonded to the phosphate species it has some influence on the $NaPO_3$ glass network.

The presence of broad and weak Raman bands for the spectrum measured at 220°C in Fig. 4 signals the glassy nature of the sample even after the removal of adsorbed water. With further increase of temperature at around 280°C all the dominant glassy Raman bands exhibit further broadening with reduction in their intensity which signals the on set of glass transition.

The spectral variation observed in the temperature interval from 300 to 350°C shown in Fig. 5 clearly reveals the crystallization growth process in the temperature interval from 305 to 335°C. Some major differences can be seen between the Raman spectra of the $NaPO_3$ in glassy and crystalline phase in the 1100 cm^{-1} region, which arises from the stretching modes of PO_3^- units. The increase in intensity of all the Raman bands due to an increase in concentration of crystalline phase and decrease in line width of the dominant modes, due to increase in the correlation length of the vibration are consistent with the crystallization process. In addition to the increase in intensity of ν_1 mode, the decrease in line width of this mode also observed during crystallization process. The ν_1 mode also shifted from 1146 to 1152 cm^{-1} during this temperature interval. The weak broad band observed at 668 cm^{-1} in the glassy phase became medium intense band along with a shoulder band at 628 cm^{-1} after the crystallization. The observation of medium strong band at 369 and weak band at 529 cm^{-1} for the spectrum measured at 350°C also confirms the formation of crystalline phase. However, the spectral variation observed in the temperature interval from 470 to 540°C (not shown) reveals no major change in spectral profile but an appreciable increase in intensity of the bands due to an increase in concentration of crystalline phase.

The recent thermo-Raman studies on $NaH_2PO_4{\cdot}2H_2O$ revealed that $NaPO_3$ formed after the condensation of $Na_2H_2P_2O_7$ was in phase III [16]. The transition of $NaPO_3$ from phase III to phase II and then from phase II to phase I was observed in the temperature interval from 325 to 360°C and from 490 to 520°C, respectively [16]. The phase II of $NaPO_3$ was characterized by sharp band at 1165 cm^{-1} with a medium shoulder around 1152 cm^{-1} and another doublet at 694 and 676 cm^{-1}. The phase I of $NaPO_3$ was characterized by appearance of sharp band at 1161 cm^{-1} instead of doublet observed in phase II of $NaPO_3$. The phase I of $NaPO_3$ also consists medium strong band at 672 cm^{-1} with shoulder at 638 cm^{-1}, medium strong band at 374 cm^{-1} and weak band at 537 cm^{-1}.

The typical thermo-Raman spectra observed in the present study at 25, 150, 300 and 500°C are depicted in Figs 6a, b, c and d, respectively. The spectrum measured at 25, 150, 300°C correspond to the as synthesized, after the removal of water and during the glass transition of $NaPO_3$ glass in a dynamical thermal process. The thermo-Raman spectrum measured at 500°C (Fig. 6d) correspond to crystalline $NaPO_3$ is more similar to the Raman spectrum corresponding to phase I of $NaPO_3$ reported by Ghule *et al*. [16] except a shift in the position of symmetric stretching mode of PO_2. The basic units in crystalline phosphates are the P-tetrahedra that link through covalent bridging oxygens to form various phosphate anions. The bands at 1152 and 668 cm^{-1} in Fig. 6d correspond to symmetric stretch of the PO_2 and O–P–O–P–O backbone species of cyclic metatriphosphate.

The bonding arrangement in phosphate glass structure was described earlier by Zachariasen [19] and Hagg [20]. According to Zachariasen's random work model the phosphate glass-forming tendency depend upon the development of random three dimensional networks. The Hagg model for the description of phosphate glass is based on the distribution of molecular species. Anyhow these two models predict the structure of both glasses and crystal of identical compositions should have similar local bonding arrangements [21]. The observation of absence of dramatic spectral variations in the thermo-Raman spectra of $NaPO_3$ glass as shown in Fig. 6 clearly signals the close similarity in the local bonding arrangement of glassy and crystalline $NaPO_3$. The observation of dominant non-bridging stretching mode only in the region from 1146 to 1152 cm^{-1} in the entire temperature range i.e. from 25 to 600°C also clearly signals both the glassy and crystalline $NaPO_3$ have similar local bonding arrangement based on polymer like metaphosphate chains of Q^2 tetrahedra linkages.

Conclusions

The PXRD pattern, FT-IR spectra and Raman spectra of $NaPO_3$ glass sample obtained by both the microwave heating and melt quench method revealed the close similarity of both the samples. The presence of the prominent bending mode of PO_3^- in the FT-IR spectrum of $NaPO_3$ glass phase strongly signaled the network features of phosphate species in the glass phase. The observation of stretching modes of water in the FTIR spectrum of $NaPO_3$ glass prepared by both melt quench and microwave heating method strongly signals the presence of water in the $NaPO_3$ glass prepared in open silica crucible with water producing raw material $NaH_2PO_4\cdot 2H_2O$. The minor spectral variations observed in the thermo-Raman spectra during the dehydration process also indicated that this hygroscopic water is not strongly bounded to the phosphate species. Thermo-Raman studies on $NaPO_3$ glass clearly indicate the removal of water in the temperature interval from 85 to 145°C, glass transition at around 280°C and the crystallization process at around 330°C. The thermo-Raman spectrum of crystalline $NaPO_3$ obtained after the glass transition indicated that this crystalline phase is more close to the phase I of $NaPO_3$. The observation of dominant non-bridging stretching modes only in the region from 1146 to 1153 cm^{-1} in the glass phase during glass transition and after crystallization indicated that the local bonding arrangement in the glassy and crystalline $NaPO_3$ are based on the polymer like meta phosphate chains of Q^2 tetrahedra linkages.

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