Investigations on Temperature Dependent Structural Evolution of Sodium Metaphosphate Glass

5.1. INTRODUCTION

Some family of phosphates both in glassy and crystalline state 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) [1]. Nasicon materials were studied widely due to their “net zero thermal expansion” behavior and these materials are useful for nuclear waste disposal. The procedure for the preparation of glassy Nasicon materials by conventional melt-quench method is tedious and requires at least 12 to 15 hours [2].

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 [3]. The unique microwave-absorbing ability of $\text{NaH}_2\text{PO}_4\cdot2\text{H}_2\text{O}$ was found to be useful for preparing crystal and glassy Nasicon as a component of batch mixtures. Although several crystalline and glassy Nasicon materials were prepared by
microwave heating method using NaH₂PO₄·2H₂O as a starting material [4]; the structure of sodium metaphosphate, NaPO₃ glass obtained by conventional melt quench and microwave heating from NaH₂PO₄·2H₂O as starting material and the structural evolution of sodium metaphosphate 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 transformations between phases and to probe the crystallization and glass transition phenomena [5-8]. The thermo Raman spectroscopic technique was utilized recently to monitor the dehydration, condensation and phase transformations involved upon heating the NaH₂PO₄·2H₂O [9]. However the capability of thermo Raman spectroscopy was not utilized earlier to probe the structural evolution during glass-crystalline transformation of sodium metaphosphate. Hence the thermo Raman spectroscopic technique was used in this work to probe the structural changes of NaPO₃ glass upon heating through glass transition.

The aim of this work is to prepare sodium metaphosphate glass both by conventional melt quench and microwave heating from NaH₂PO₄·2H₂O as a starting material, to probe their glassy nature and their structural evolution dynamically as a function of temperature by thermo Raman spectroscopic studies.
5.2. EXPERIMENTAL

5.2.1. Preparation of NaPO₃ glass

5.2.1.1. Conventional melt quench method

NaH₂PO₄·2H₂O (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 sodium metaphosphate glass was obtained and then it was ground into fine powder for further characterization.

5.2.1.2. Microwave heating process

NaH₂PO₄·2H₂O powder (5 g) taken in a silica crucible was exposed to microwaves inside a microwave oven (BPL) operating at 2.45 GHz. A "Step ladder" heating mechanism [4] has been proposed earlier to account for the high microwave absorbing ability of NaH₂PO₄·2H₂O. Dehydration of NaH₂PO₄·2H₂O 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 NaH₂PO₄ heats to high temperature. The second step of dehydration begins around 80 s and lasts up to 120 to 130 s. This second step of dehydration corresponds to the removal of
one more $\text{H}_2\text{O}$ 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 sodium metaphosphate glass obtained by this quenching process was ground into fine powder for further characterization.

5.2.2. Powder X-ray diffraction (PXRD) analysis

Powder X-ray diffraction (PXRD) (Rigaku-Mini Flex) patterns of the samples were taken with Cu-$\text{K}_\alpha$ radiation of wavelength 1.5418 Å with Ni filter. The PXRD pattern of the pre-melted $\text{NaH}_2\text{PO}_4\cdot2\text{H}_2\text{O}$, $\text{NaPO}_3$ glass prepared by microwave heating method and melt quench method are shown in Figs. 5.1a, b and c, respectively.

5.2.3. Thermal analysis

The differential scanning calorimeter (DSC) (Mettler DSC 821) thermogram of $\text{NaPO}_3$ glass prepared by melt quench and microwave heating method was measured under a flow of $\text{N}_2$ gas from 25 to 500°C at a heating rate of 5°C min$^{-1}$. The nature of the DSC thermogram of both $\text{NaPO}_3$ glass prepared by melt quench and microwave heating method were same. The DSC thermogram of $\text{NaPO}_3$ glass prepared by microwave heating method is shown in Fig. 5.2.
5.2.4. Impedance spectroscopic studies

The sodium metaphosphate glass was compacted as pellet of 10 mm diameter and 5mm thickness for impedance spectroscopic measurements. The temperature dependent impedance measurements were made dynamically in steps of 25°C in the temperature interval from 25 to 500°C in the frequency range 1-10⁶ Hz using impedance analyzer (HP4284A). The bulk conductivity of sodium metaphosphate glass calculated at various temperatures are presented in Fig.5.3.

5.2.5. Infrared spectroscopy

The Fourier transform infrared (FTIR) (Shimadzu FTIR-8700) spectrum of the NaH₂PO₄·2H₂O, NaPO₃ glass prepared by microwave heating and conventional melt quench and NaPO₃ glass sample (prepared by microwave heating method) heated to 400°C were recorded at room temperature and are depicted as Figs. 5.4a, b, c and d, respectively.

5.2.6. Thermo Raman spectroscopy

The powdered NaPO₃ 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. 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. 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. 5.5 - 5.7.

5.3. RESULTS AND DISCUSSION

The sharp peaks observed in the PXRD pattern presented in Fig. 5.1a clearly indicate the crystalline nature of pre-melted NaH₂PO₄·2H₂O.

Fig. 5.1. The powder X-ray diffraction patterns of the samples; a - pre-melted NaH₂PO₄·2H₂O; b - NaPO₃ glass prepared by microwave method; c - NaPO₃ glass prepared by melt quench method.
Non-observation of peaks and halos in the low angle region of the PXRD patterns in the Figs. 5.1b and 5.1c clearly indicate the glassy nature of the NaPO₃ sample prepared by microwave heating as well as melt quench method, respectively.

The DSC thermogram of NaPO₃ glass prepared by microwave heating shown in Fig. 5.2 indicated a broad peak at around 128°C corresponding to removal of water and deviation in the baseline of the thermogram in the temperature range at around 280°C corresponding to the onset of glass transition. As crystallization takes place the heat of crystallization is evolved, hence a sharp dip appears on the DSC thermogram at 330°C.

Fig. 5.2. The DSC thermogram of NaPO₃ glass prepared by microwave heating method.
The conductivity of sodium metaphosphate glass plotted against reciprocal temperature in Fig. 5.3 indicates steady increase in conductivity value from 25 to 275°C. An appreciable increase in conductivity was noticed in the temperature interval from 275 to 350°C and afterwards the conductivity drops. An appreciable increase in conductivity observed from glass transition temperature might be due to the nucleation of crystallites. The drop in conductivity observed after 350°C associated with the massive crystallization.

Fig. 5.3. The bulk conductivity of sodium metaphosphate calculated at various temperatures

The room temperature FTIR spectrum of NaH₂PO₄.2H₂O shown in Fig. 5.4a consist of a number of distinct and well separated groups of bands corresponding to vibrational modes of (PO₄H₂)⁻ ions. OH groups and water molecules. Infrared spectroscopy is very sensitive to the presence of water in
phosphate samples. A narrow band observed at 3530 cm\(^{-1}\) indicated the presence of loosely bounded crystal water in NaH\(_2\)PO\(_4\)·2H\(_2\)O.

Fig. 5.4. The Fourier transform infrared (FTIR) spectrum of: a - NaH\(_2\)PO\(_4\)·2H\(_2\)O; 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.
The FTIR spectrum of the NaPO₃ glass prepared by microwave heating and conventional melt quench shown in Figs. 5.4b and 5.4c, 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 NaPO₃ glass sample obtained by both the methods. The presence of broad and weak bands in P-O vibrational region in Figs. 5.4b and 5.4c reflects the glassy nature of the sample. The FTIR spectrum of NaPO₃ glass shown in Fig. 5.4b and 5.4c also clearly demonstrates the dramatic difference in the P-O vibrational region compared to the FTIR spectrum of NaH₂PO₄·2H₂O shown in Fig. 5.4a. For NaH₂PO₄·2H₂O, the ν₁, symmetric stretching vibrational mode of (PO₄)³⁻ was observed at 907 cm⁻¹ and ν₃, asymmetric stretching vibrational modes were observed at 962 and 1043 cm⁻¹. In contrast, the stretching modes of (PO₃)⁻ in NaPO₃ 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 NaPO₃ glass corresponding to the stretching modes of water indicated the presence of water when the NaPO₃ glasses were prepared in an open silica crucible with water producing raw material NaH₂PO₄·2H₂O. The FTIR spectrum of NaPO₃ glass heated to 400°C in Fig. 5.4d indicated considerable changes in the P-O vibrational region compared to the FTIR spectrum of as prepared NaPO₃ glass. The broad bands appeared in the glass phase split in to 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$_2$PO$_4$·2H$_2$O crystal belongs to space group P2$_1$2$_1$2$_1$ (D$_2^4$) with orthorhombic crystal structure [10]. In contrast to KH$_2$PO$_4$ (KDP) the four oxygen atoms of the PO$_4$ group in NaH$_2$PO$_4$·2H$_2$O are not equivalent. Two acidic hydrogens of (PO$_4$H$_2$)$_-$ form strong hydrogen bonds with the oxygen atoms of adjacent (PO$_4$H$_2$)$_-$ groups. The recent thermo Raman studies on NaH$_2$PO$_4$·2H$_2$O indicated two steps of dehydration, formation of Na$_2$H$_2$P$_2$O$_5$ at 220°C in the first condensation process, NaPO$_3$ formation in two steps at about 260°C and two phase transformation of NaPO$_3$ at the temperature of 345 and 515°C [9].

The thermo Raman spectra of NaPO$_3$ glass in the P-O vibrational region measured in two temperature interval from 25 to 145°C and 220 to 290°C are shown in Fig. 5.5. 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 NaPO₃ 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 NaPO₃ glass measured at 25°C shown in Fig. 5.5 indicated the non-bridging stretching modes at 1146 and 1260 cm⁻¹ and bridging stretching mode at 675 cm⁻¹.

Fig. 5.5. The thermo Raman spectra of NaPO₃ glass measured in the temperature interval from 25 to 145°C and 220 to 290°C.
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. 5.5 signalled 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. 5.5 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 onset of glass transition.

![Raman spectra](image)

**Fig. 5.6.** The thermo Raman spectra of NaPO\(_3\) glass measured in the temperature interval from 300 to 350°C.
The spectral variation observed in the temperature interval from 300 to 350°C shown in Fig. 5.6 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 NaPO₃ in glassy and crystalline phase in the 1100 cm⁻¹ region, which arises from the stretching modes of PO₃⁻ 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 ν₁ mode, the decrease in line width of this mode also observed during crystallization process. The ν₁ 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 shown in Fig. 5.7 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.
Fig. 5.7. The thermo Raman spectra of NaPO₃ glass measured in the temperature interval from 470 to 540°C.

The recent thermo Raman studies on NaH₂PO₄·2H₂O revealed that NaPO₃ formed after the condensation of Na₂H₂P₂O₇ was in phase III [9]. The transformation of NaPO₃ 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 [9]. The phase II of NaPO₃ 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 NaPO₃ was characterized by appearance of sharp band at 1161 cm⁻¹ instead of doublet observed in phase II of NaPO₃. The phase I of NaPO₃ 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. 5.8a, 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 NaPO₃ glass in a dynamical thermal process.

![Graph showing Raman spectra](image)

**Fig. 5.8.** The typical thermo Raman spectra observed at a. 25°C; b. 150°C; c. 300°C and d. 500°C during dynamical thermal process.

The thermo Raman spectrum measured at 500°C (Fig. 5.8d) correspond to crystalline NaPO₃ and is more similar to the Raman spectrum corresponding to phase I of NaPO₃ reported by Ghule et al [9] except a shift in the position of symmetric stretching mode. 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. 5.8d correspond to symmetric stretch of the O-P-O and P-O-P backbone species of sodium metaphosphate, respectively.

The bonding arrangement in phosphate glass structure was described earlier by Zachariasen [11] and Hagg [12]. According to Zachariasen's random work model the phosphate glass-forming tendency depend upon the development of random three dimensional networks. The Hagg's 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 [13]. The observation of absence of dramatic spectral variations in the thermo Raman spectra of NaPO\(_3\) glass as shown in Fig. 5.8 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.

5.4. 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 observation of
stretching modes of water in the FTIR spectrum of NaPO₃ glass prepared by both melt quench and microwave heating method strongly signals the presence of water in the NaPO₃ glass prepared in open silica crucible with water producing raw material NaH₂PO₄·2H₂O. 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 NaPO₃ 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. Impedance spectroscopic studies revealed the increase in conductivity from glass transition (Tₙ) to crystallization temperature (Tₓ) of sodium metaphosphate glass and latter on due to the massive crystallization the conductivity drops. The thermo Raman spectrum of crystalline NaPO₃ obtained after the glass transition indicated that this crystalline phase is more close to the phase I of NaPO₃. 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 NaPO₃ are based on the polymer like meta phosphate chains.
REFERENCES