CHAPTER 4

ANALYSIS OF FTIR SPECTRA OF NANOPARTICLES

4.1 Introduction

The vibrational spectrum of nanoparticles is generally different from the spectrum of the corresponding bulk materials.\(^1,2\) One reason for the change in vibrational spectrum is the size effect of small particles, which will cause the breakdown of vibrational selection rule k≠0 forbidden and as a result the vibrational lines may become broad and frequency shifted compared to those of the bulk crystals.\(^3\) Another reason is the surface effect of nanoparticles. The atomic arrangement on the surface of the particles will be quite different from the packing in the bulk of the crystal. Also the surface to volume ratio of atoms is large in nanoparticles. The vibrational spectra of small particles will be influenced by size effect\(^2\) and surface effect\(^4\) of nanoparticles.

The vibrational properties of small crystals can be studied with the help of infrared absorption spectroscopy.\(^3,5-8\) In the harmonic approximation method, an ionic crystal whose size is large compared to the wavelength of the light in the surrounding medium absorbs light only at a frequency \(\omega_T\). Here \(\omega_T\) is the frequency of long wavelength transverse optical mode. If the size of the crystal is small compared to the wavelength of light in the surrounding medium, the peak absorption frequency is changed to \(\omega_F\) by the polarisation charge at the crystal surface.\(^5\) It was shown that the mode of vibration with uniform polarisation in a small ionic sphere has the frequency given as

\[
\omega_F^2 = \omega_T^2 \left( \varepsilon_\infty + 2\varepsilon_m \right) / \left( \varepsilon_\infty + 2\varepsilon_m \right)
\]

where \(\omega_F\) is called the Frohlic mode, \(\varepsilon_\infty\) and \(\varepsilon_0\) are the high and low frequency dielectric constants of the sphere.\(^9\) \(\varepsilon_m\) is the dielectric constant of the surrounding medium. This mode is usually called a surface mode since its origin...
lies in the finite size of the particles.\textsuperscript{10} The scientists Fuchs and Kliewer\textsuperscript{11,12}, and Englman and Ruppin\textsuperscript{8} studied the scattering and absorption frequency modes on ionic spheres of arbitrary size. According to them there exists a series of surface modes with frequencies between \( \omega_s \) and \( \omega_T \), where \( \omega_s \) is defined as the frequency at which the real part of the dielectric constant equals minus \( \varepsilon_m \). The lowest frequency mode in the series is the Frohlich mode. Infrared measurements have been used by many scientists to study the surface modes in small crystals.\textsuperscript{13,14} IR transmission spectra of \( \text{ZnO}, \text{CdS} \) and \( \text{BeO} \) particles whose size is smaller than the wavelength of incident light has shown features specific to surface modes.\textsuperscript{14} Also in small crystals of \( \text{MgO, ZnO} \), etc. the experimental observation of surface phonon modes in the IR spectra has been made.

Infrared studies of small crystals have been conducted by many researchers.\textsuperscript{13-18} In the case of \( \text{NaCl} \) small crystals, the absorption band was found to be broad and the frequency of this band was different from the frequency of the bulk crystal.\textsuperscript{10} This change was attributed to the restoring force due to the polarisation of surface charge. In the case of nanoparticles, quantum confinement effect,\textsuperscript{19} size effect,\textsuperscript{19} dipolar interactions,\textsuperscript{10} interfacial effects,\textsuperscript{20} surface amorphousness,\textsuperscript{21} high internal stress,\textsuperscript{21} etc. are reported to be the reasons for the observed changes in vibrational frequencies. From all the above results, the conclusion obtained is that the optical absorption and scattering in the fundamental lattice absorption region are size dependent. In the present chapter, the mid-IR transmission spectra of \( \text{Ag}_3\text{PO}_4, \text{FePO}_4 \) and \( \text{ZnFe}_2\text{O}_4 \) nanoparticles are analysed compared to its bulk spectra. Far-IR transmission spectra of \( \text{ZnFe}_2\text{O}_4 \) are also analysed in detail for different particle sizes.

4.2 Experimental

Nanoparticles of \( \text{Ag}_3\text{PO}_4, \text{FePO}_4 \) and \( \text{ZnFe}_2\text{O}_4 \) were prepared by chemical method as described in section 3.2 of this thesis. XRD, TEM and SEM studies were carried out to estimate the particle size and structure of the crystallites. FTIR
spectra of the three samples, for three reactant concentrations each were recorded using a Bruker IFS 66V FTIR spectrometer. The mid-IR spectra were recorded for all the three samples and far-IR spectra were recorded for ZnFe₂O₄ particles.

4.3 Results of FTIR Spectra

4.3.1 Ag₃PO₄ Nanoparticles

Fig. 4.1a, b and c show the FTIR spectrum of 0.005M, 0.015M and bulk Ag₃PO₄ respectively. The band assignment corresponding to the stretching vibration of P-O (PO₄) in bulk Ag₃PO₄ is 975cm⁻¹ (fig 4.1c). For 0.005M and 0.015M, the stretching vibration frequency of P-O bond is 1017 and 1010cm⁻¹ observed from the figure. An increase in frequency of 42 and 35cm⁻¹ compared with bulk frequency 975cm⁻¹ is noted. Increase in frequency (blue shift) is a general phenomenon observed in nanophase materials due to its small size effect. Also the frequency shift is higher for low molarity sample, indicating smaller size for 0.005M Ag₃PO₄. It is reported that small changes in the environment of a chemical group will lead to small changes in the characteristic vibrational frequencies for this group.

Fig. 4.1a: FTIR spectrum of 0.005M Ag₃PO₄
Fig. 4.1b: FTIR spectrum of 0.015M $\text{Ag}_3\text{PO}_4$

Fig. 4.1c: FTIR spectrum of bulk $\text{Ag}_3\text{PO}_4$
4.3.2 FePO$_4$ Nanoparticles

Fig. 4.2 shows the FTIR spectrum of FePO$_4$ for three reactant concentrations (1M, 0.1M and 0.02M). The probable band assignments for bulk FePO$_4$ are stretching vibration of P-O (PO$_4$) around 1030 cm$^{-1}$, Fe-O vibrations around 630 cm$^{-1}$ and O-P-O bending around 420 cm$^{-1}$ excluding O-H (H$_2$O) vibrations.$^{16,17,23,24}$ Fig. 4.2 shows a broad band (1000-1200 cm$^{-1}$) indicating the coupling of basic structural units (PO$_4$) into a structural network and it is reported that the coupling is very strong for FePO$_4$ ($\alpha$-quartz like structure).$^{17}$ It can also be observed that the broadening is maximum for 0.02M sample having lowest molarity. It is noted that a change in frequency (blue shift) is observed for the basic (PO$_4$) structural vibration when the reactant concentration changes from 1M to 0.02M. For FePO$_4$ nanoparticles, small changes in the environment of the chemical group (PO$_4$) in addition to size effect may have led to small changes in the characteristic vibrational frequencies. Hence an increase in band frequency (blue shift) may have resulted in the case of nano FePO$_4$ particles indicating smallest particle size for 0.02M sample. In fig. 4.2, there are two nearby bands at 608 cm$^{-1}$ and 648 cm$^{-1}$ that are specific for FePO$_4$ structure and correspond to Fe-O vibrations$^{17}$ and these bands remain the same for all molarities. The bands below 500 cm$^{-1}$ are assigned to O-P-O bending vibrations. From FTIR study of nanoparticle FePO$_4$, it is observed that the P-O vibration band (PO$_4$ unit) is only affected by particle size variation, since other band frequencies remain the same.
4.3.3 ZnFe$_2$O$_4$ Nanoparticles

Fig 4.3 and 4.4 show the mid-IR and far-IR transmission spectra of 0.1M ZnFe$_2$O$_4$ nanoparticles annealed at different temperatures. From XRD studies it is found that particle size increases with annealing temperature and the size variation is given in table 3.3 of chapter 3. In normal zinc ferrite, there are four ($v_1$, $v_2$, $v_3$ and $v_4$) infrared lattice vibrations. The former two are high frequency bands ($v_1$ and $v_2$) and are very sensitive to changes in interaction between oxygen and cations in octahedral and tetrahedral positions. They appear in the ranges 600-540 and 450-400 cm$^{-1}$. The low frequency band $v_3$ normally appears close to 330 cm$^{-1}$ and $v_4$ near 200 cm$^{-1}$. The bands $v_3$ and $v_4$ correspond to divalent as well as oxygen and thermal vibrations respectively. From fig. 4.3 we can observe that as temperature increases the intensity of O-H vibration (1640 cm$^{-1}$, 3400 cm$^{-1}$) decreases attaining dehydrated state at 500°C. In our study $v_1$ band starts at 568 cm$^{-1}$ and decreases to 541 cm$^{-1}$ as the particle size increases. This is a consequence of size effect. In the present FTIR
spectrum as the particle size decreases the increase in frequency (blue shift) is beautifully observed. Similar behaviour is observed for frequencies $v_2$, $v_3$ and $v_4$.

**Fig. 4.3:** Mid-IR spectrum of ZnFe$_2$O$_4$ (0.1M) annealed at different temperatures

The frequency $v_2$ varies from 404 to 369 cm$^{-1}$, $v_3$ varies from 325 to 322 cm$^{-1}$ and $v_4$ varies from 168 to 164 cm$^{-1}$. In far-IR spectrum no vibration bands are observed for the sample annealed at 150$^\circ$C having particle size 4nm. From XRD pattern it was shown that this particle is having low crystallinity. This IR spectrum of sample at 150$^\circ$C shows minimum intensity (zero intensity) having smallest particle size and low crystallinity. Fig. 4.3 and 4.4 shows that as
annealing temperature increases (particle size increases) the intensity of the peak increases. It is noted that the change in value of \( v_3 \) is very small compared to other wave numbers. The same behavior was observed for \( \text{ZnFe}_2\text{O}_4 \) in the earlier report.\textsuperscript{25} The variation in the band position may be due to variation in the cation-oxygen bond length resulted from the change in particle size.\textsuperscript{18} It was reported that \( v_3 \) band is assigned to divalent \([\text{Zn}^{2+}]\) octahedral metal ion-oxygen group complexes.\textsuperscript{18} This is an indication that in nanophase \( \text{ZnFe}_2\text{O}_4 \), there is partial inversion of lattice sites and octahedral lattice sites are partly occupied by \( \text{Zn}^{2+} \) ions. Also the broadening of \( v_2 \) band with decrease in particle size may be due to the occupancy of cations of the different characters on the same site.\textsuperscript{18,28} From these observations it is assumed that as particle size decreases, the inversion nature of the spinel ferrite increases.

**Fig. 4.4:** Far-IR spectrum of \( \text{ZnFe}_2\text{O}_4 \) (0.1M) annealed at different temperatures
Fig. 4.5: Mid-IR spectrum of 0.002M, 0.01M and 0.1M ZnFe$_2$O$_4$ samples annealed each at 300°C

Fig. 4.5 shows the mid-IR spectrum of 0.002M, 0.01M and 0.1M ZnFe$_2$O$_4$ samples annealed each at 300°C. It is observed that the wavenumber increases from 549 to 559 cm$^{-1}$ as the reactant concentration decreases. This may be attributed to the decrease in particle size and hence the metal ion-oxygen bond distance.$^{18}$

Thus it is found that IR spectroscopic study is very effective in studying the size effect of nanoparticles and also an effective tool to study the inversion nature of ZnFe$_2$O$_4$ nanoparticles.

4.4 Conclusion

The FTIR spectra of nanoparticles of Ag$_3$PO$_4$, FePO$_4$ and ZnFe$_2$O$_4$ of three reactant concentrations each were analysed in comparison with the corresponding spectra of bulk material. Though the particle size variation with reactant concentration is small as evidenced from XRD analysis, a considerable
change in IR transmission spectroscopic wavenumber (blue shift) is observed with change in molarity (reactant concentration) and change in particle size. The changes in frequencies are attributed to size effect of nanoparticles.

4.5 References

3. Y. Bobovich, Appl. Spectrosc. 49 (1988) 869
15. J. T. Luxon, D. J. Mongomeri, R. Summit, Phys. Rev. 188 (1969) 1345