INTRODUCTION
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The study of optical properties of crystals has been found very useful in understanding the structural changes in terms of certain constants and low energy optical phonons. One of the popular ways employed to study optical properties of crystals is to measure their reflectivity in the far-infrared region. This technique is endowed with the uniqueness that it permits spectral measurements for thick single crystals and enables to get the frequency of longitudinal optical phonons whose excitation is not detected in the transmitted radiation. On the other hand the study of vibrational properties along with optical properties helps in understanding the dynamics of orientation of molecular groups and atoms in the crystals. Vibrational properties also provide information about their structure and the nature of forces that bind the various atomic and molecular units inside the crystal. The Raman scattering and infrared absorption spectroscopic measurements are being used to study the vibrational properties. These spectroscopic techniques provide the means of studying the effect of crystalline field on vibrations of the crystals through polarisation measurements. Distortions in molecular groups and ordering in crystals can best be estimated with the help of these techniques. The advantage of Raman scattering measurements over the absorption spectroscopy is that the entire vibrational spectrum (upto 4000 cm^{-1}) can be scanned in a single run of the spectrum whereas latter
requires separate measurements for far-infrared (FIR) and near-infrared (NIR) spectral regions.

The present work includes the study of optical and vibrational properties of three crystals, namely, \((\text{NH}_4)_3\text{H}(\text{SO}_4)_2\), \((\text{CH}_3\text{NH}_3)_2\text{ZnCl}_4\) and \((\text{NH}_4)_2\text{ZnBr}_4\) employing the above mentioned techniques. These compounds belong to three different classes of non-cubic crystals. \((\text{NH}_4)_3\text{H}(\text{SO}_4)_2\) is the crystal of the type \(A_3\text{HB}_2\), where \(A\) is an alkali atom or \(\text{NH}_4^+\) ion and \(B\) is \(\text{SO}_4^{2-}\) or \(\text{SeO}_4^{2-}\) ion. \((\text{CH}_3\text{NH}_3)_2\text{ZnCl}_4\) belongs to a family of crystals with general formula \((\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{MCl}_4\), where \(M = \text{Mn, Cd, Cu, Fe, Co or Zn}\) and \(X\) is a halide. \((\text{NH}_4)_2\text{ZnBr}_4\) belongs to the tetrahedrally coordinated crystals of the type \(A_2\text{BX}_4\) with \(A\) an alkali atom or \(\text{NH}_4^+\) ion; \(B = \text{Zn, Cd, Mn, Co or Cu}\) and \(X = \text{Cl, Br or I}\). Although \((\text{CH}_3\text{NH}_3)_2\text{ZnCl}_4\) belongs to a totally different class of metal-organic compounds, it is very much similar to crystals of the type \(A_2\text{BX}_4\) on account of its structure and symmetry. The dissimilarity, however, is due to the presence of organic ion. All the compounds have tetrahedrally coordinated molecular groups constituting their structure. The type of hydrogen bonding present in the crystals is different. The interesting property about the crystals is that they all exhibit structural phase transitions. Structural phase changes associated with phase transitions can be very well investigated by study of optical and vibrational properties of crystals. This makes their study further attractive.
The work presented concerns the measurement of FIR reflectivity and vibrational spectra of \((\text{NH}_4)^3\text{H}^{}(\text{SO}_4)^2\), \((\text{CH}_3\text{NH}_3)^2\text{ZnCl}_4\) and \((\text{NH}_4)^2\text{ZnBr}_4\) crystals. Details of the experimental techniques, the equipment used and theoretical concepts, on which interpretation of our results is based, are also discussed.

Chapter I describes the group theoretical methods for the classification of normal modes, classification of internal modes of vibration of molecular groups present in the crystals, theory of infrared reflection, absorption and Raman scattering and their selection rules. A brief review of various kinds of phase transitions occurring in solids is included in the chapter in view of the fact that crystals under study exhibit structural phase transitions.

Chapter II consists of details on crystal growing procedure, identification of crystal structure and a brief account of the equipment used for measurements.

Chapter III describes the results and analysis of reflection spectra in FIR region and vibrational spectra of \((\text{NH}_4)^3\text{H}^{}(\text{SO}_4)^2\) in the temperature range 10-300 K, covering its phases of structure below room temperature. Six phases of the crystal are denoted as I, II, III, IV, V and VI in order of decreasing temperature. Study of optical constants of the crystal in its phases (phase II to phase VI) suggests that LO modes play an important role in phase transition from phase III (220 K) to phase IV (135 K).
Variation of LO mode frequencies with temperature explains the abnormal behaviour of the dielectric constant of the crystal observed in phase IV. Vibrational spectra give the evidence of increase of local symmetry of molecular groups as the phase IV is approached both from lower and higher temperature sides. The role of hydrogen bonding is found to be crucial in the ferroelectric phase transition of the crystal resulting in an ordering of $\text{HSO}_4^-$ ions. The crystal shows most anharmonic behaviour in this phase due to the ordering of $\text{HSO}_4^-$ ion. The strength of hydrogen bonding increases with decreasing temperature.

Chapter IV deals with the measurements on $(\text{CH}_3\text{NH}_3)_2\text{ZnCl}_4$ crystal. FIR reflectivity data at room temperature and vibrational spectra for all of its phases have been analysed. Phase transitions in the crystal occur above room temperature. The FIR reflectivity spectra of the crystal for its phases other than the room temperature phase could not be recorded as the facility of measurement above room temperature was not available with the equipment used. The behaviour of damping constant evaluated from the classical oscillator fit of the reflectance data is found to form a basis for the identification of low-frequency optical phonon modes. Distortions in the molecular groups and correlation field effects are evident in the vibrational spectra. Phase transitions in the crystal seem to be characterized by the motion of methyl ammonium ion. A hindering of reorientational motion of the ion is suggested in the high
temperature phases. The effect of hydrogen bonding seems to be closely linked with the order of organic ions that leads to the phase transitions in the crystal.

Chapter V describes the results of \((\text{NH}_4)_2\text{ZnBr}_4\) crystals. Optical constants of the crystal are evaluated in FIR region at 300 and 105 K. The infrared absorption spectra at room temperatures have been recorded for the vibrational study. An extensive study of Raman scattering in the crystal has recently been made by others. The results of their measurements at room temperature are reproduced here for the completeness of the vibrational study. The analysis of optical constants suggests that hydrogen bonding is stronger in the low temperature phase which is further confirmed by the behaviour of vibrational modes of \(\text{NH}_4^+\) ion. Phase transitions in the crystal are characterized by the motion of \(\text{NH}_4^+\) ions. Vibrational analysis suggests a hindering of reorientational motion of \(\text{NH}_4^+\) ion in the crystal.