PREFACE

Raman and IR spectroscopic techniques have attained considerable attention in the field of molecular spectroscopy. These techniques are also used as a powerful tool for many applications in the field of biology, medicine, forensic science, industry etc. In crystals Raman spectral studies provide valuable information regarding structure, hydrogen bonding, molecular symmetry, order-disorder phenomenon and phase transition. Raman spectra recorded in \textit{in situ} electric field provide information on the ionic and proton conductivities of crystals and their changes in polarizability. In this thesis Raman and IR spectra of a few phosphates including both doped and undoped KTP crystals and a few bromates are presented. The effect of electric field on the Raman spectra of KTP crystals is also investigated.

This thesis contains nine chapters. The first chapter gives the basic principles of Raman and IR spectroscopy and the instrumentation. A brief review of the earlier studies in phosphates with particular emphasis to those in potassium titanyl phosphate (KTP) and bromates are also presented.

The second chapter deals with the vibrational spectra of undoped and La and Pr doped KTP crystals. The internal modes of TiO$_6$ octahedra and PO$_4$ tetrahedra are assigned. An attempt is made to remove certain ambiguities related to the assignments of some of the bands in the KTP crystal. The dopants La and Pr do not affect significantly the wavenumber values of the TiO$_6$ and PO$_4$ vibrations. But Raman bands of KTP, LKTP and PKTP in the same polarization geometries show
intensity variations. The presence of La and Pr atoms affect the polarizability leading to changes in intensities. The TiO$_6$ octahedra and PO$_4$ tetrahedra in these crystals are considerably distorted.

The IR and Raman spectra of Eu and Nd doped KTP crystals are described in the third chapter. The optical second harmonic generating properties of undoped and Eu and Nd doped KTP crystals are also investigated. Intensity changes in Raman spectra in different scattering geometries of the doped crystals, as compared to those of KTP indicate the changes in polarizability of the doped crystals. Raman spectra of the doped crystals ruled out major structural changes due to doping. The dopants (Eu and Nd), with $d^0$ cations can be used as suitable dopants for modifying SHG property of the KTP crystal.

Raman spectra of the KTP single crystal in in situ ac and dc electric fields are recorded and analysed in the fourth chapter. Spectra with laser beam focused near the cathode end, anode end and the centre of the crystal are recorded. Cathode end of the crystal develops a small spot known as 'grey track' where the laser beam is focused after a lapse of 5 hours from the application of a dc electric field of 38 V/cm. Spectra recorded at the cathode end after the application of field shows variations in intensity of bands. Changes in band intensities are explained on the basis of changes in polarizability of the crystal due to the movement of K$^+$ ions along the polar axis. K$^+$ ions accumulate at the cathode end. 'Grey track' formation occurs there. The intensity enhancement observed for almost all bands in ac field is attributed to the improvement of crystalline quality.
The \( \text{KMg}_{13}\text{Nb}_{23}\text{PO}_5(\text{KMNP}) \) is a KTP analogue without NLO properties. The detailed vibrational analysis of this crystal is presented in Chapter 5. The observed bands are assigned in terms of vibrations of \( \text{PO}_4 \) tetrahedra and \( \text{NbO}_6 \) octahedra. The bands of \( \text{NbO}_6 \) octahedra are compared to those of \( \text{TiO}_6 \) octahedra in KTP to explain why nonlinear optical properties are absent in KMNP.

The sixth chapter deals with the vibrational spectra of three thallium niobyl phosphates. For \( \text{Tl}_3\text{NaNb}_4\text{O}_9(\text{PO}_4)_2 \) and \( \text{Tl}_2\text{NbO}_2\text{PO}_4 \), the bands are assigned in terms of vibrations of \( \text{NbO}_6 \) octahedra and \( \text{PO}_4 \) tetrahedra while those in \( \text{TINbOP}_2\text{O}_7 \) are assigned in terms of vibrations of \( \text{NbO}_6 \) octahedra and \( \text{P}_2\text{O}_7^{4-} \) anion. The \( \text{NbO}_6 \) octahedra in the all title compounds are found to be corner-shared and distorted. Larger distortion of the \( \text{NbO}_6 \) octahedra is observed in \( \text{Tl}_2\text{NbO}_2\text{PO}_4 \) and \( \text{TINbOP}_2\text{O}_7 \) as compared to those in \( \text{Tl}_3\text{NaNb}_4\text{O}_9(\text{PO}_4)_2 \), from the appearance of stretching modes in the higher wavenumber side. The distortion of \( \text{PO}_4 \) tetrahedra in the \( \text{Tl}_2\text{NbO}_2\text{PO}_4 \) is slightly higher than in \( \text{Tl}_3\text{NaNb}_4\text{O}_9(\text{PO}_4)_2 \). The symmetry of \( \text{P}_2\text{O}_7^{4-} \) anion in \( \text{TINbOP}_2\text{O}_7 \) is lowered. Bands indicate that the P-O-P bridge in the above compound has a bent P-O-P bridge configuration.

The superionic phosphates with general formula \( \text{HNaM}_2\text{PO}_7(M=\text{Co},\text{Zn},\text{Pb}) \) are investigated in chapter 7. The non-coincidence of the majority of the IR and Raman bands agree with the centrosymmetric space group \( \text{P}\overline{1} \). The \( \text{P}_2\text{O}_7^{4-} \) anions
in all the compounds have a non-linear P-O-P bridge. Bands indicate a staggered configuration in CoP and an eclipsed configuration in PbP for the \( \text{P}_2\text{O}_7^{4-} \) anions. The presence of protons attached to an oxygen atom of \( \text{P}_2\text{O}_7^{4-} \) ion is confirmed by the appearance of OH vibrations in all the crystals.

The IR and Raman spectra of copper and aluminium hexa-aqua complex with bromate ions are recorded and analysed to get information on the nature of hydrogen bonding in them (Chapter 8). Temperature dependent Raman spectra of the single crystals of \([\text{Cu}(\text{H}_2\text{O})_6](\text{BrO}_3)_2\) show that hydrogen bonds in the crystal are rearranging themselves leading to a reorientation of the \( \text{BrO}_3^- \) ions and a consequent phase transition at about 447 K in the crystal.

Chapter 9 gives the Raman and IR spectra of two rare-earth bromates, \( \text{Tb}(\text{BrO}_3)_3.9\text{H}_2\text{O} \) and \( \text{Eu}(\text{BrO}_3)_3.9\text{H}_2\text{O} \). The \( \text{BrO}_3^- \) anion in the first compound is distorted and the symmetry is lowered due to the activation of \( \text{BrO}_3^- \) modes in symmetry forbidden orientations. \( \text{Eu}(\text{BrO}_3)_3.9\text{H}_2\text{O} \) bands contain electronic transitions in \( \text{Eu}^{3+} \). An attempt is made to assign these transitions.