CHAPTER - VI
SUMMARY, CONCLUSIONS AND FUTURE SCOPE

6.1 Summary and Conclusions

Nonlinear optical (NLO) materials are used in fields of fiber optic communication, laser technology, optical signal processing, opto-electronics, optical computing and optical storage devices. Among NLO materials, the second harmonic generating (SHG) crystals play an important role in the domain of opto-electronics and photonics. In this modern era there is a great demand to grow new NLO materials with large nonlinear optical coefficients.

Sodium chlorate, sodium bromate and mixed sodium chlorate and sodium bromate crystals are NLO materials and they can be used as second harmonic generators of laser light. These materials have commercial applications in frequency conversion, electro-optics and so on. The physical properties of crystals can be modified for tailor made applications by adding suitable impurity.

In the present investigation, the isomorphous crystals such as pure sodium chlorate, sodium bromate and mixed crystals of sodium chlorate and sodium bromate were grown. The effect of dopants such as sodium chloride, ammonium chloride, lithium nitrate and nickel sulphate has been studied in the crystallization of sodium chlorate and sodium bromate single crystals. Also, the effect of the dopants such as nickel sulphate and lithium nitrate has been studied in the crystallization of the mixed crystals of sodium chlorate and sodium bromate.

Commercially purchased sodium chlorate and sodium bromate salts were re-crystallized in double distilled water to improve the purity. The dopants were added separately to the re-crystallized salts in three different concentrations of 0.5, 1 and 1.5 mol %. The solubility of pure and doped salts in double distilled water was determined. It is found that the solubility of all the samples of this work in water increases with increase of temperature. In accordance with the solubility data, the saturated solutions of pure, doped and mixed salts were prepared and single crystals were grown by slow evaporation technique. The chemical composition of the the grown pure, doped and mixed crystals was checked by using energy dispersive analysis by X-rays (EDAX) which confirms the presence and replacement of additives in the crystal matrix.

The powder X-ray diffraction studies were performed on the pure and sodium chloride, ammonium chloride, lithium nitrate and nickel sulphate doped sodium chlorate single crystals. The powder X-ray diffraction data collection from powdered samples of pure and sodium chloride, ammonium chloride, lithium nitrate and nickel sulphate separately doped sodium bromate crystals were analyzed. Also, powder study for mixed and doped crystals of sodium chlorate and sodium bromate was carried out. The reflection peaks of the XRD patterns were indexed using JCPDS data and unit cell software package. The unit cell parameters were calculated. The diffracted peaks are observed to be similar for the doped crystals when compared to that of pure sodium chlorate and sodium bromate crystals. But the intensities of the diffracted peaks vary and the slight shifts in the '2θ' values in the XRD patterns of the doped crystals show slight disturbance in crystal lattice comparing with pure sodium chlorate crystal structure.

The mechanical strength of the grown crystals of this work was studied by subjecting the crystals to microhardness measurements. It is observed that the hardness values are found to increase while increasing the loads for all the samples. The hardness values of the crystals are varied with the dopants used. The work hardening coefficient values for samples of the work were calculated and found to be altered when the sodium chlorate and sodium bromate crystals are doped with sodium chloride, ammonium chloride, lithium nitrate and nickel sulphate separately and it is found that the work hardening coefficient is greater than 1.6 for all the samples. The yield stress and stiffness constant values were also determined for the pure and doped crystals.

The FTIR transmission spectra have been recorded in the range of 400-4000 cm^{-1} for all the grown crystals. The functional groups associated with pure sodium chlorate and sodium chloride, ammonium chloride, lithium nitrate and nickel sulphate separately doped sodium chlorate along with their respective absorption bands and peaks have been identified and assigned. Also, the functional groups associated with pure sodium bromate and sodium chloride, ammonium chloride, lithium nitrate and nickel sulphate doped sodium bromate crystals and the mixed crystals were identified by FTIR studies. The broadening, narrowing, shift of absorption peaks and the appearance of new peaks in the spectra of doped sodium chlorate and sodium bromate crystals may be due to the incorporation of the dopants into crystal matrix.

The UV-Vis-NIR transmission spectra were recorded in the range 190–1100 nm for pure, mixed and doped crystals and from the results it is observed that the crystals were found to be transparent in the entire visible and near IR region. Pure sodium chlorate crystal has a wide transmission with a transparency of 85%. The transparency was increased for sodium chloride and nickel sulphate doped sodium chlorate crystal with transparency 90% and 86% respectively. The transparency was decreased for ammonium chloride and lithium nitrate having transparency 75% and 70%. Tauc's plots were drawn for the samples and the optical energy band gap is found to be altered when sodium chlorate and sodium bromate crystals are doped with dopants like sodium chloride, ammonium chloride, lithium nitrate and nickel sulphate.

The mixed and lithium nitrate, nickel sulphate doped mixed crystals have good transparency and it was studied by UV-Vis-NIR transmission spectrum. The optical band gap and transmittance values are found to be increased for the doped mixed crystals with respect to the component crystals.

The SHG measurements on the grown crystals reveal that the SHG efficiency is increased for sodium chloride and nickel sulphate doped sodium chlorate single crystals. The efficiency was decreased for ammonium chloride and lithium nitrate doped sodium chlorate crystals. The SHG efficiency of lithium nitrate and nickel sulphate doped sodium bromate crystals was found to be increased and ammonium chloride and sodium chloride doped sodium bromate crystals was decreased when compared to the pure crystals. The SHG efficiency is varied with respect to the selected dopant materials for mixed crystals.

The surface morphology of the grown crystals was studied by scanning electron microscope (SEM). The micrographs of pure and 0.5 mol% of sodium chloride, ammonium chloride, lithium nitrate and nickel sulphate separately doped sodium chlorate and sodium bromate single crystals were presented and it is observed that surface of the crystals is smooth and clear with or without crystallites. It is noticed that the mixed and lithium nitrate doped crystals have cloudy growth on the surfaces.

Electrical properties were studied by dielectric measurements. The capacitance and dielectric loss tangent (tanδ) measurements were carried out for all the samples of this work using a precision LCR meter at various temperatures and at frequencies. The dielectric loss and the calculated values of the dielectric constant and AC electrical conductivity for the pure and the doped crystals in the present study were found to increase with increase in temperature and decrease with addition of dopants. Low values of dielectric loss represents that the grown crystals are of good quality and can be used in the microelectronics industry. The dielectric loss and dielectric constant decreases with increase of frequency and this is due to space charge polarization and other polarization effects. The AC conductivity of the crystals increases smoothly with increase of temperature and the activation energy was calculated and it is found to be decreased for doped crystals of this work on comparing with the undoped crystals.

Thermogravimetric (TG) and differential thermal analysis (DTA) have been carried out to study the thermal behaviour of pure, mixed and doped sodium chlorate and sodium bromate crystals. The thermal studies reveal that the values of decomposition temperature decreases while adding dopants to pure crystals. Slight changes were observed in the melting point while adding dopants to the component crystals. The stability was increased while doping with pure sodium bromate. Slight changes were observed in the melting point and decomposition temperature and this indicates that the dopants have entered into the doped samples.

In conclusion, the experimental results of the present investigation reveal that the pure, mixed and doped crystals could be successfully grown. All the grown doped crystals have enhanced the properties such as optical transparency, mechanical strength, nonlinear optical property, thermal stability and good surface features. The values of dielectric constant (ε_r) have been decreased so that the doped crystals can be categorized under low 'ε_r' materials.

6.2 Suggestions for future work

The present research has only been focused on the studies related to the influence of inorganic dopants on growth and properties of sodium chlorate, sodium bromate and mixed sodium chlorate, sodium bromate crystals grown by slow evaporation solution growth method. The influence of organic dopants may be studied for the growth of sodium chlorate and sodium bromate crystals. In the future, these crystals can be grown by other methods like slow cooling and melt growth methods. Efforts can also be made to grow the crystals of this work by gel technique. Third harmonic generation studies for all the samples of this work can be carried out in the future and this kind of research will lead the crystals into more technological applications. The DC conductivity measurements can be made along the a, b and c axes. The etching studies can be carried out using different solvents to understand dislocation density and growth mechanism of the crystals of this work in the future.