Structural, thermal, optical & dielectric characterization of solution grown pure and doped semi organic sodium phthalate single crystals

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ABSTRACT

Nonlinear optics (NLO) has been recognized for several decades as promising fields with important applications in the area of opto-electronics, photonics, memory devices, etc. High performance electro-optical switching elements for telecommunications and optical information processing are based on the material properties. Hence, there is always a continuous search for new and better materials. Second order nonlinear optical (SONLO) materials have recently attracted much attention because of their potential applications in emerging optoelectronic technologies. Materials found in non-centrosymmetric, or acentric crystal classes, i.e. crystal classes lacking a center of inversion, can exhibit a variety of technologically important physical properties. Semi-organic crystals have attracted considerable interest due to their large non linear optical coefficients, high resistance to laser induced damage, low angular sensitivity and excellent mechanical hardness.

Semi organic hydrogen phthalate crystals are one of the best NLO crystals which are well known for their common use as analyzer for x-ray spectrometers and electro optic processes. These crystals are also used as substrate for deposition of thin film of polymers and conjugated molecules. A large number of phthalate crystals like potassium hydrogen phthalate (KHP), Rubidium hydrogen phthalate (RHP), Cesium hydrogen phthalate (CHP), Ammonium hydrogen phthalate (AHP) etc. have been investigated in pure and doped form. Sodium hydrogen phthalate (SP) is also a promising NLO candidate of the phthalate family. However, limited information on doped form of SP crystals is available; therefore this material can be investigated in detail in pure and doped form. It has been observed that the second harmonic generation (SHG) efficiency of sodium hydrogen phthalate is double that of potassium hydrogen phthalate crystals.

In this thesis, the growth, structural, optical, thermal and dielectric properties of pure and transition metal doped sodium hydrogen phthalate single crystals have been investigated to study the influence of transition metals on the physical properties and crystalline perfection of pure sodium phthalate crystals. This thesis consists of eight chapters as follows:
The first chapter gives a brief description of the importance and growth mechanism of crystals and their use in the modern technology. Various phenomena like nucleation, metastable zone width, thermodynamics in crystal growth etc. are also discussed which play a vital role during crystal growth. Different crystal growth techniques like melt growth, solution growth and vapor growth are discussed in detail. Slow evaporation solution growth technique used for growth of crystals of thesis work is discussed in detail.

The second chapter gives the literature survey on organic, inorganic and semi organic nonlinear optical (NLO) crystals. A major portion of this chapter consists of gist of the earlier work carried out on organic, inorganic and semi organic compounds. In addition; aim and basic outline of the whole thesis is also discussed in this chapter.

The third chapter describes the experimental techniques needed to grow as well as to characterize these crystals. A complete experimental procedure used to grow crystals of thesis work by slow evaporation solution growth technique is discussed. In the present work, solution growth method was used to grow pure and transition metal (Fe, Zn, Ni, Mn) doped sodium phthalate crystals. Preliminary characterization techniques like powder X-ray diffraction, optical transmission, photoluminescence, dielectric spectroscopy, atomic absorption spectroscopy, second harmonic generation, thermo gravimetric studies, laser induced damage etc. used for characterizing the grown crystals are described briefly.

The fourth chapter contains details of single crystal growth and characterization of pure and iron (Fe) doped sodium hydrogen phthalate. The morphology of the crystals found to change from bi-pyramidal to rectangular shape as a result of the entrance of Fe ion impurities in the host structure. The actual amount of Fe-impurity entered in the Fe-doped SP crystals was found to be 6.5 ppm which was ascertained by AAS. Vibrational bands present in the crystals were assigned in FTIR and Raman spectra on the basis of the vibrational bands present in phenyl ring and carboxylate ion of phthalic acid. All the bands assignment confirmed the formation of required compound. It was found that Fe inclusion did not have any effect on the vibrational band position. Fe inclusion in SP crystals resulted in an absorption band at 370 nm in UV region which make it a potential candidate for holographic data storage applications. There is an increase in transmittance in entire visible region of doped crystals making them suitable for second
harmonic generation. Fe-doping did not have any adverse effect on the cut-off wavelength (~325 nm) and optical band gap of pure SP crystals. Intensity of photoluminiscence peaks at 412 nm and 522 nm was enhanced due to Fe-doping with inhomogeneous broadening in both peaks. SHG efficiency of doped SP crystal was found to be twice of pure SP crystals and comparable to that of KDP. LDT values were found to be 0.32 GW cm$^{-2}$ and 0.28 GW cm$^{-2}$, for pure and iron doped crystals respectively. Dielectric studies showed lower dielectric tensor component ($\varepsilon_{33}$) and higher dielectric loss in Fe-doped crystals compared to pure SP crystals. This may be due to smaller size of Fe-ion as compared to Na-ion. For both crystals, dielectric tensor and dielectric loss increases with temperature. From thermal analysis it was observed that Melting point (286 °C) and thermal stability (129 °C ) of FSP crystal is higher than that of pure SP crystals (211 & 117 °C).

**Fifth chapter** describes the growth and characterization of pure and Zn-doped sodium phthalate crystals. Zn-doped crystals were found to exhibit prominent morphological changes (bi-pyramidal to pentagon) in different crystallographic planes due to anisotropic distribution of dopant. XRD analysis revealed that presence of metallic dopant (Zn) in sodium phthalate lattice did not have any effect on the basic structure (orthorhombic) of the parent crystal. The presence of various functional groups and chemical bonding present in the crystals was identified and assigned qualitatively by FTIR and Raman analysis. Incorporation of dopant into the crystalline matrix was confirmed quantitatively (2.72 ppm) by AAS. UV-Vis studies indicate the low percentage of absorption in doped crystals in the visible region, thereby confirming the enhancement of non-linear optical (NLO) property. From PL spectra, it was found that due to Zn-dopant intensity of peak 412 nm remain unchanged whereas intensity of peak at 522 nm increases with inhomogeneous broadening. Second harmonic generation efficiency also gets enhanced as a result of metal ion zinc doping. From laser damage threshold studies, LDT values were found to be 0.32 and 0.25 GW/cm$^2$ for pure and Zn-doped sodium phthalate crystals, respectively. Dielectric analysis revealed that on zinc doping dielectric tensor ($\varepsilon_{33}$) and loss decreases significantly. Thermal analysis indicates that the melting point (295 °C) and thermal stability (124 °C) of Zn-doped sodium phthalate crystals is higher as compared to pure sodium phthalate crystals.

**Sixth chapter** deals with the growth and characterization of Ni-doped sodium phthalate single crystals. Ni-doped sodium phthalate crystal exhibits the same
orthorhombic structure with change in morphology (rhombic bipyramidal to hexagonal). Powder XRD revealed very slight changes in peak intensities and lattice parameters due to Ni-dopant in SP lattice. All vibrational bands present in doped crystals were assigned and confirmed by using FTIR and Raman analysis. From AAS studies, amount of Ni in the doped SP crystals was found to be 3.5 ppm. From UV-Vis studies, it was found that there is no appreciable change in the cut-off wavelength and optical band gap. However, transmittance increases appreciably in the visible region due to inclusion of nickel in SP crystalline matrix implying chances of higher SHG efficiency in doped crystals. PL studies showed that Ni dopant in SP matrix did not have much effect on photoluminescent properties of crystals. SHG efficiency increased to almost double that of pure SP crystals. LDT value was found to be 0.32 GW/cm² which is similar to that of pure sodium phthalate crystals. Dielectric constant and dielectric loss decreases appreciably due to Ni-doping in SP crystals. Melting point (301 °C) and thermal stability (122 °C) are enhanced significantly in NSP crystals as compared to pure SP crystals.

**Seventh chapter** explains the effect of manganese doping on the crystalline perfection and physical properties of pure sodium phthalate crystals. Doped crystals exhibit prominent morphological changes (rhombic bipyramidal to hexagonal) in different crystallographic planes. Incorporation of Mn in SP crystals has been estimated qualitatively and quantitatively by FTIR, Raman and AAS analysis, respectively. Lattice parameters were determined by powder X-ray diffraction analysis and slight change in lattice parameters of doped crystals was observed. UV-Vis studies revealed appreciable increase in transmittance in entire visible region in MSP crystals as compared to pure SP crystals. From photoluminescence studies, it was observed that PL intensity of both peaks at 412 and 522 quenched as a result of Mn-doping in SP crystals. SHG efficiency increased due to inclusion of Mn ions in SP crystalline matrix. From laser damage threshold studies, LDT value calculated to be 0.27 GW/cm² for MSP crystals. Dielectric constant and dielectric loss decreased by Mn-doping in sodium phthalate crystals. Thermal stability and melting point of MSP crystals (120 & 303 °C) are higher than that of pure SP crystals.

The general conclusion and comparative discussion on pure and doped crystals are given in **chapter 8** along with possible future work that could be performed on these crystals.