SOLUTION GROWTH AND STUIDES OF STRONTIUM CHLORIDE DOPED AMMONIUM DIHYDROGEN PHOSPHATE CRYSTALS

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Abstract

Solution growth with slow evaporation technique was employed to grow the single crystals of strontium chloride doped ammonium dihydrogen phosphate (SCADP). Solubility of the sample was measured by gravimetric method at different temperatures. Single crystal X- ray diffraction technique was adopted to identify the crystal structure. Fourier Transform Infrared (FTIR) spectrum of SCADP crystal was recorded and analysed to find the functional groups present in the sample. Second harmonic generation (SHG) efficiency was measured by Kurtz-Perry technique. Hardness and work hardening coefficient of undoped and strontium chloride doped ADP crystals were evaluated by Vickers microhardness method.

Key words: ADP; doping; single crystal; solution growth; SHG; FTIR; Hardness; XRD; solubility

1. Introduction

Nonlinear optical, photonic and optoelectronic technologies need the suitable nonlinear optical materials with high Second Harmonic Generation (SHG) efficiency and high laser damage threshold. It is known that inorganic crystals like potassium dihydrogen phosphate (KDP), lithium triborate (LBO), β-barium borate (βBO), lithium niobate ($LiNbO_3$), potassium niobate ($KNbO_3$) etc have high SHG efficiency and laser damage threshold. Ammonium dihydrogen phosphate (ADP) is an inorganic NLO crystal which crystallizes in tetragonal crystal system like KDP and it is used as the second harmonic and third harmonic generating material. And this crystal is also used in electro-optic and acousto-optic applications [1-4]. Many researchers have done the research on the effect of many dopants on the various properties of ADP crystals [5-8]. Akhtar *et al*. have grown L-alanine doped ADP crystals and the properties like optical and electrical properties of the grown crystals have been studied [9]. Pattanaboonmee *et al.* have studied the effect of L-arginine on the properties of ADP crystals[10]. Hasmuddin *et al.* carried out structural, optical, electrical and hardness studies of L-proline doped ADP crystals [11]. Inorganic dopant like strontium chloride can enhance the NLO property, thermal stability and mechanical stability in the host organic and inorganic based crystals [12]. In this work, the effect of strontium chloride on the perfection, transmittance, electrical and NLO studies of ADP crystals is studied and reported.

2. Synthesis and growth of crystals

AR grade chemicals like ammonium dihydrogen phosphate (ADP), strontium chloride were purchased commercially from Merck chemical company, India. The salt of strontium chloride doped ADP was synthesized by aqueous solution method. 1 mole% of strontium chloride was added into the aqueous solution of pure ADP and solution was prepared and it was heated at 60 ^{o}C till the solvent evaporates to obtain the doped salt. Single crystals of the synthesized salt of strontium chloride doped ADP were grown from aqueous solution by slow evaporation technique. Saturated aqueous solution of the salt was prepared and the magnetic stirring for two hours was performed to obtain the homogenous solution. The solution was filtered using the Whatman filter papers and then the solution was taken in a growth vessel covered with a porous paper and kept in a dust free environment. Due to slow evaporation, the single crystals of SCADP were harvested after 30 days. The grown crystal of SCADP is shown in the figure 1.

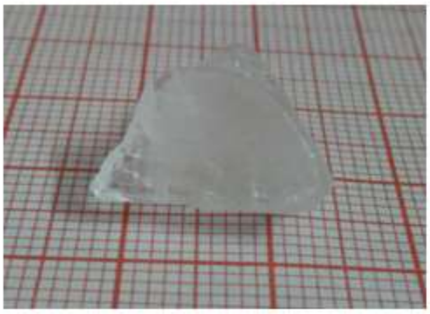

Fig.1. A single crystal of strontium chloride doped ADP

3. Results and discussions

3.1 Solubility studies

In the field of crystal growth, solubility measurement is essential because using the solubility data the saturated and supersaturated solutions can be prepared at a particular temperature and also these data can be used to carry out nucleation kinetic studies of the crystal. The solubility of undoped and strontium chloride added ADP crystals in double distilled water was measured by gravimetric method. The measured values of solubility at different temperatures are given in the figure 2. It is observed that the solubility increases with increase of temperature and hence these samples have positive temperature coefficient of solubility. The solubility is found to be decreasing when strontium chloride is added as the dopant into ADP crystal. It is reported that the solubility of crystalline samples is altered when organic and inorganic dopants have been added as the dopants [13-15]. The decrease nature of solubility of SCADP crystal indicates that the amount of solute required for saturation at a particular temperature decreases compared to that of undoped ADP crystal.

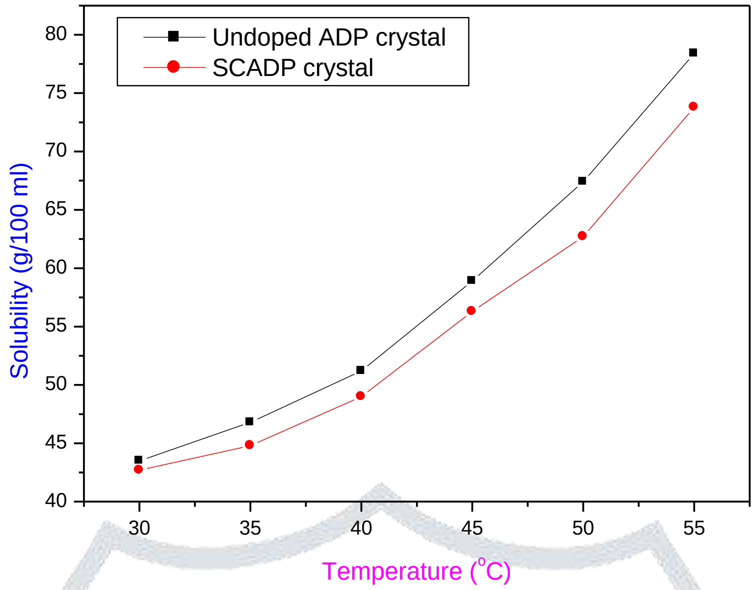

Fig.2. Solubility curves for undoped and strontium chloride doped ADP crystals

3.2Single crystal XRD studies

Finding the crystal structural analysis important after the growth of crystals and X-ray diffraction (XRD) method is the best method to find the crystal parameters and the crystal structure. There are two methods of XRD viz., powder XRD method and single crystal XRD method. Since the grown crystal of SCADP is a single crystal, single crystal XRD method was used here to carry out the structural analysis of the sample. Single crystal X-ray diffraction analysis was carried out using ENRAF NONIUS CAD-4 single crystal X-ray diffractometer. The data were collected at 293 K using MoK_{α} (λ = 0.71069 Å) radiation. The least square refinement of the reflections was done here. The crystallographic data for SCXRD crystal are given in the table 1 and for the comparison purpose, the lattice parameters of undoped ADP crystals are also given in the same table. From the data, it is found that SCADP crystal belongs to tetragonal crystal system with I-42d space group. It is seen that both undoped and strontium chloride doped ADP crystals crystallize in the same tetragonal system and the incorporation of dopant does not alter the crystal system. This is due the presence of dopant strontium chloride in the form of metal ions and halogen ions in the interstitial positions of the lattice of the host ADP crystal.

Table 1: Crystallographic data for undoped and strontium chloride doped ADP crystals

Crystal parameters	Undoped ADP crystal (JCPDS # 01-078-2414)	Strontium sulfate doped ADP crystal
a (Å)	7.485	7.479(4)
b (Å)	7.485	7.479(4)
c (Å)	7.538	7.584(5)

α	90°	90°
β	90°	90°
γ	90°	90°
Crystal system	Tetragonal	Tetragonal
Volume of unit cell	422.32 Å^3	424.22(2) Å^3
Bravais lattice	Body centered tetragonal	Body centered tetragonal

3.3 Microhardness studies

Measurement of hardness is an important characterization of crystalline samples and the hardness is the ratio of the applied load to the surface area generated due to indentation. Usually, it is observed that hardness of mixed and doped crystals always exceeds the that of the individual constituent materials. Hardness tests are commonly carried out to determine the mechanical strength of materials and it correlates with other mechanical properties like elastic constants and yield stress. Hardness measurements can also be defined as macro, micro and nano according to the forces applied and displacement obtained. Among the various methods of hardness measurements, static indentation test is the popular and simplest, in which a steady load is applied to an indenter. The indenter may be a ball or diamond cone or diamond pyramid. The hardness is calculated from the area or the depth of indentation produced. The indenter is made up of a very hard material to prevent its deformation by the test piece, so that it can cover materials over a wide range of hardness. For this reason either a hardened steel sphere or a cone diamond pyramid is employed. In the process of static indentation test, the indenter is pressed perpendicularly into the surface of a sample by means of an applied load. By measuring the correctional area or depth of indentation and knowing the applied load, the hardness number is evaluated. The undoped ADP and SCADP crystals were subjected to microhardness studies and for each load, several indentations were made and average value of indentation length was found. Vickers hardness test was used to find the microhardness number (H_v) and the relation employed is $H_v = (1.8544 * P) / d^2$ where P is the applied load and d is average indentation length and using the values of d, the microhardness number is evaluated. The variations of average indentation length (d) and the applied load for undoped and strontium chloride doped ammonium dihydrogen phosphate (SCADP) are presented in the figure 3. The results reveal that the average indentation length increases with increase of the applied load for both the samples and average indentation length is found to be less for SCADP crystal compared to that of undoped ADP crystal. The evaluated values of H_v for undoped and strontium chloride doped ADP crystals are presented in the figure 4. The results indicate that the hardness shows a nonlinear behaviour with the applied load for both the samples. The hardness is found to be increasing with increase of the applied load upto 50 g and it decreases upto 75 g and then again hardness increases until cracks are formed beyond 100 g. The increasing part is due to the tangled forest of dislocation lines and the work hardening mechanism. The subsequent decrease in hardness with increase in load was due to work softening mechanism which resulted from the activation of cross slip and the movement of piled-up dislocations. The movement of dislocations is responsible for the increase and decrease behaviour of the hardness in the samples [16].

The work hardening coefficient of the samples was determined using Meyer's law. This law connects the average diagonal indentation length (d), the applied load (P) and the work hardening coefficient (n) and it is given by $P = a\ d^n$. Taking log on both sides, equation obtained is $\log P = \log a + n \log d$ where a is a constant. Hence, if a plot of log P versus log d is drawn, the work hardening coefficient (n) could be found. Figs. 5 and 6 show the plots of log P versus log d for undoped and strontium chloride doped ADP crystals and the obtained values work hardening coefficient are 2.3992 and 2.2143 respectively. From careful observations on various materials, Onitsch and Hanneman pointed out that an ‘n’ lies between 1 and 1.6 for hard materials and it is more than 1.6 for soft materials. Hence, the grown crystals are the category of soft materials.

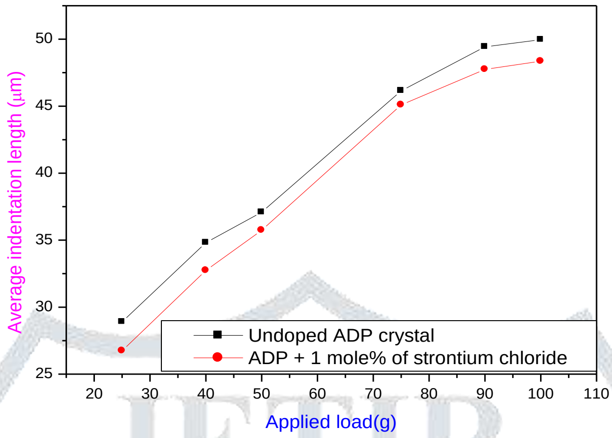

Fig.3. Variation of average diagonal indentation length with applied load for undoped and strontium chloride doped ADP crystals

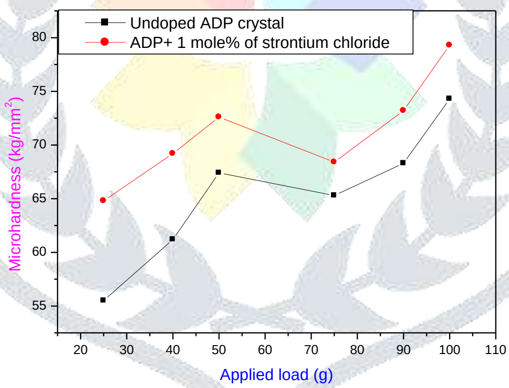

Fig.4. Variation of hardness with applied load for undoped and strontium chloride doped ADP crystals

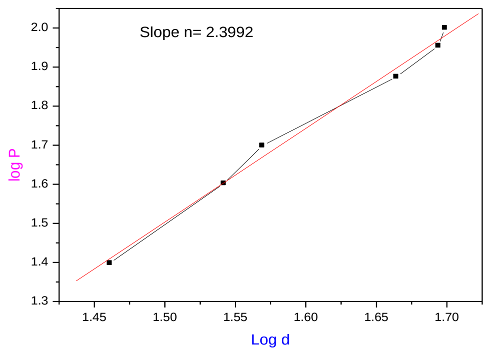

Fig.5. Plot of log(P) versus log(d) for undoped
ADP crystal

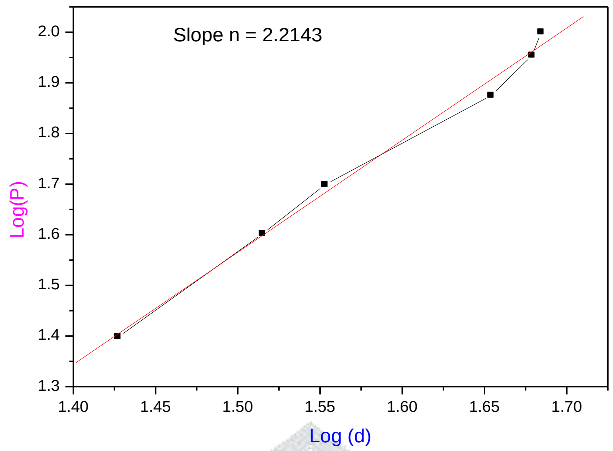

Fig.6. Plot of log(P) versus log(d) for strontium chloride
Doped ADP crystal

3.4. Second order NLO studies

Second order NLO studies were carried out by Kurtz and Perry powder technique. The level of SHG response of a given material is inherently dependent upon its structural attributes. A Q-switched Nd:YAG laser beam of wavelength 1064 nm was allowed to strike the samples normally. The second harmonic signal generated in the crystal was confirmed from the emission of green radiation by the crystal. The SHG radiation of 532 nm was collected by photomultiplier tube and converted into voltage output at the CRO. The input laser energy incident on the powdered samples was chosen to be 0.68 J/pulse and the output was found to be 16.8 mJ/pulse and 18.25 mJ/pulse for undoped and strontium chloride doped ADP crystals respectively and output of 8.8 mJ/pulse was observed from the KDP. Thus, the relative SHG efficiency of undoped ADP is found to be 1.9 and for SCADP is found to be 2.07 times that of KDP.

3.5 Dielectric constant and dielectric loss

A dielectric is an electrical insulator that is used to increase the capacitance of a capacitor. When a dielectric is placed in an electric field, electric charges do not flow through the material as they do in conductor, but only slightly shift from their average equilibrium positions causing dielectric polarization. Because of dielectric polarization, positive charges are displaced toward the field and negative charges shift in the opposite direction. This creates an internal electric field which reduces the overall field within the dielectric itself. If a dielectric is composed of weakly bonded molecules, those molecules not only become polarized, but also reorient so that their symmetry axis aligns to the field. The relative permittivity of a material under given conditions reflects the extent to which it concentrates electrostatic line of flux. It is the ratio of the capacitance of capacitor with dielectric to the capacitance of the capacitor without dielectric. The dielectric constant of any given material varies with temperature and also varies as a function of frequency. The amount of power losses in a dielectric material under the action of the voltage applied to it is commonly known as dielectric losses which usually mean the losses precisely under an alternating voltage. The dielectric loss angle is an important parameter both for the dielectric material and an insulated portion. The capacitance and dielectric loss factor (tan δ) measurements were carried out using the parallel plate capacitor at various frequencies in the range 10^2 – 10^6 Hz using an Agilent 4284A LCR meter. The dielectric constant of the crystal was calculated using the relation $\varepsilon_r = C/C_o$ where C is the capacitance of the crystal and C_o is the capacitance of the air medium of the same dimension as the crystal [17]. The variations of dielectric constant and dielectric loss of undoped and strontium chloride doped ADP crystals are shown in the figures 7 and 8. The dielectric constant of both the samples is observed to be decreasing with increase of frequency and also the same behaviour is noticed for dielectric loss. The low values of dielectric loss in the high frequency region indicates that both samples have high quality of insulating materials.When ADP crystals are doped with strontium chloride, it seems that dielectric properties are increasing and this is due to presence of dopants in the form of ions in host sample.

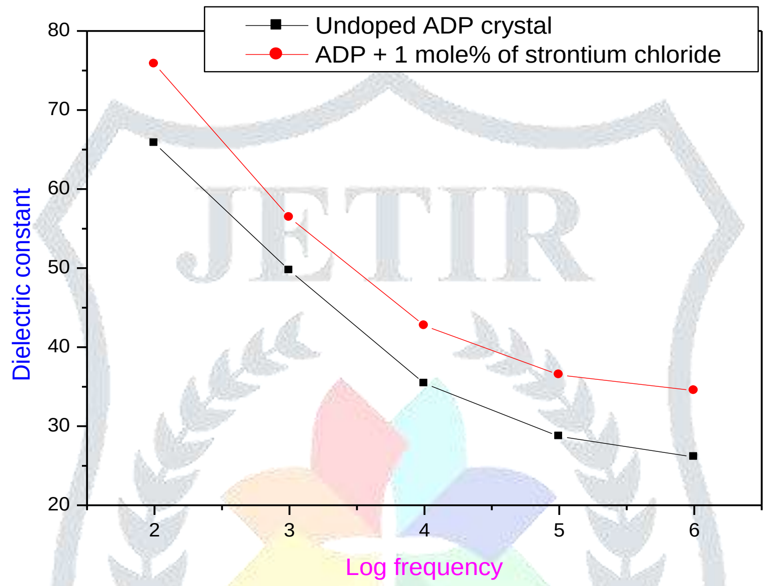

Fig.7. Frequency dependence of dielectric constant for undoped and strontium chloride doped ADP crystals

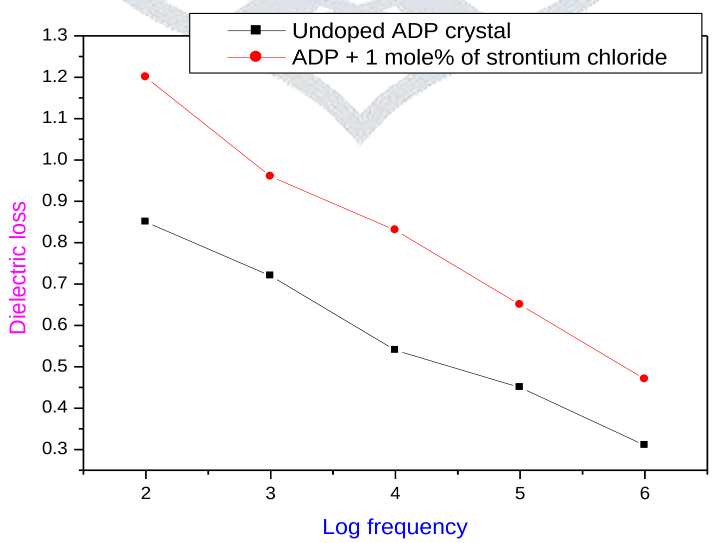

Fig.8. Frequency dependence of dielectric loss for undoped and strontium chloride doped ADP crystals

3.6 FTIR studies

Fourier Transform infrared (FTIR) studies were carried out for strontium chloride doped ADP crystal using a Bruker IR spectrometer in the wave number range 400-4000 cm^{-1}. This study helps to find the functional groups present in the sample. Here KBr pellet technique was adopted for the pelletized sample. The recorded FTIR spectrum SCADP crystal is shown in the figure 9. The broad absorption band in the wave number range 3400-3100 corresponds to OH stretching vibration of P-O-H group and N-H stretching of NH_4 group. The peak at 2369 cm^{-1} is due to P-H stretching. The peak at 1653 cm^{-1} is related to P=O stretching. The absorption peak at 1403 cm^{-1} is due to bending vibration of NH_4. The IR absorption peak at 1283 cm^{-1} corresponds to bending vibration of PO_4. The peak at 1106 cm^{-1} is related to bending vibration of P=O group. The peak observed at 903 cm^{-1} corresponds to bending vibration of P-O-H group. The peak at 539 cm^{-1} is due to bending vibration of PO_4 and the small peak at 461 cm^{-1} is also related to bending vibration of PO_4. Compared to FTIR spectrum of undoped ADP crystal as reported in the literature [18], the absorption peaks/bands in the FTIR spectrum of SCADP crystal are slightly broadened or narrowed and this is due to incorporation of strontium chloride in the host ADP crystal.

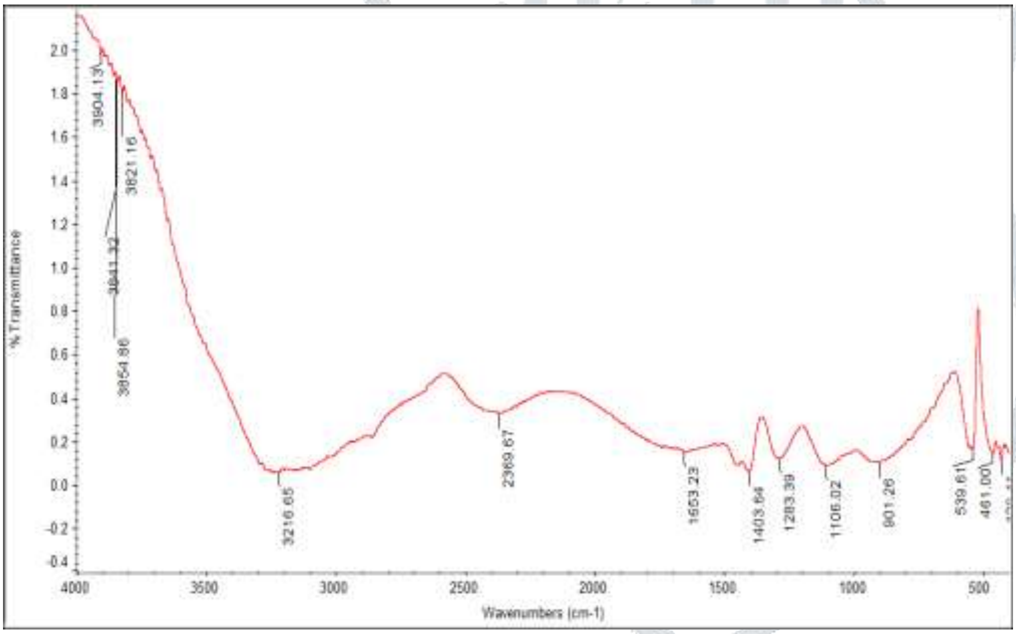

Fig.9. FTIR spectrum of SCADP crystal

4. Conclusions

Strontium chloride doped ADP crystals were grown by aqueous solution method. The XRD studies confirm that the crystal structure of SCADP is tetragonal and the crystal lattice parameters of the doped crystal are observed to be almost same as those of the undoped ADP crystal. The slightly different values obtained for the unit cell parameters reveals that the dopant does not distort the basic crystal structure of ADP crystal. Doping of strontium chloride into ADP crystal has effect of increasing the hardness and SHG efficiency. The relative SHG efficiency of SCADP crystal is found to be 2.07 times that of KDP. Solubility of SCADP crystal is found to be more than that of unodped ADP crystal. The functional groups of SCADP crystal were identified by FTIR spectral analysis. Dielectric parameters such as dielectric constant and dielectric loss factor are observed to increasing when ADP crystals are doped with strontium chloride.

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