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Comparative Study of Manganese doped Sulphamic acid, Tristhioureazinc(II)sulphate, Ammonium dihydrogen phosphate Crystals

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Abstract

Ammonium dihydrogen phosphate, ZTS and Sulphamic acid being a potential semi organic nonlinear optical material is doped with Manganese sulphate (1:1). Good quality crystals in the presence of Manganese sulphateare grown by slow evaporation solution technique (SEST). FTIR spectral analysisconfirm that there is slight distortion in crystal structure due to doping. The surface morphology of the as-grown specimen which is changed with the nature and concentration of dopant is studied by scanning electron microscopy (SEM). Single crystal XRD indicates that the inclusion of Manganesesulphate isnot to an appreciable extent, there is only a slight changes in the cell parametervalues of the doped specimen. TGDTA confirms the stability and temperature resistance of the formed crystal.

Keywords: Single Crystal XRD, Manganese, NLO material, SEM-EDS, SEST.

Introduction

Latest studies report that Ammoniumdihydrognphosphate (ADP) is one of the available nonlinear optical crystals needed for laser radiation conversion in laser fusion system[1]. The lattice studies on the ADP crystals still attract interest because of their unique nonlinear optical, dielectric and anti-ferroelectric properties and their varied uses as electro-optic modulator, harmonic generators and paramagnetic generator[2-13]. ADP, being an inorganic nonlinear optical materials has made the researchers to study about its optical transparency, good susceptibility and low thermal and mechanical stability[14]. The enhancement of optical transmission[15], effect of complexing agent[16], dopant effect of KCl andOxalic acid[17]. Studies have also been made about the effect of mixing of divalent and trivalent impurities on the growth, habit modification and structure of ADP[18-21]. Manganese is one of the metallic elements which appear in biologicial apatite like bone and teeth. Its important effect on the growth and development of bone has been well known[22]. The Mn d-electron states act as an efficient luminescent centres. Mn emission was red shifted from 584-600 nm[23]. Further because of its transparency, it may be of use in laser production in the green region based on $3d^{5}\,{}^{4}T_1 \rightarrow {}^{6}A_1$ transition of Mn (II)[24]. A good number of investigations are reported on manganese as dopants. The unusual ferromagnetic properties of manganeseorthovanadate is studied[25]. The magnetic properties of nano crystals of Mn doped ZnO is recently reported[26].Recent fact reveals that doping influences the electrical, mechanical, electroopticalproperties, also the nature of host material and the dopant is influenced by their surface morphology27-39. A promising senmiorganic NLO material is suitable for Nd:YAG laser with high SHG efficiency laser damage threshold. Its SHG and laser damage threshold values are 1.2[40] times that of KDP [41]. Being a good engineering materials for SHG device application and laser fusion experiments, with a novel metal organic crystal with potential application in electro-optic modulation, ZTS belongs to orthorhombic system with the space group Pca2, (point group mm2) though the crystal growth, kinetics and characterization of ZTS are reported[42-46] . All though many reports are there showing the effect of many metals doped

onSulphamicacid,Tristhioureazinc(II)sulphate,Ammoniumdihydrogenphosphate,Manganese sulphate crystals, there is no study on the Manganese as impurity which couldinfluence the physical properties ,particularly on thiourea crystals has been reported. Sulphamic acid belongs to orthorhombic structure and the relevant lattice parameters are a = 8.078 (Å), b = 8.116 (Å) and c = 9.268 (Å)[47]. Among all amino acids, sulphamic acid and derivatives exhibited large industrial applications[48-50]. Dopant play vital role to enhance the physical properties of single crystals. Few authors reported the effect of dopants on the growth and physical properties of inorganic SA single crystal[51-55]. From the literature survey it was observed that addition of metal enhances the optical, ferroelectric and dielectric properties of the crystals. Incorporation of small amount of impurities in the form of cationic dopant K^+ and Na^+ increases the growth rate, physical and chemical properties of the crystals

Our present investigation mainly focus on the study of equimolar concentration effect of doping manganese sulphate on sulphamic acid, ADP and ZTS and the grown crystals are subjected to various experimental techniques like SEM-EDS, Single crystal XRD, FTIR.

Results and discussion

Synthesis and crystal growth

The Complex crystal is synthesized by mixing the commercially available materials sulphamicacid, AmmoniumdihydrogenPhosphate, Tristhioureazinc(II)sulphate and manganese sulphate at an equimolar concentration and stirred using magnetic stirrer in theconical flask 250ml for about 3 to 5 hours using triply distilled water as solvent. After 5hours stirring, the contents in the conical flask are filtered using funnel and whattmannfilterpaper.Thefiltrateisthencollectedinthe450mlbeakerandcoveredwith a transparent colourless polyethene sheet and tiny holes are made over the polyethene sheet.This is kept under the shadow of the sunlight for slow evaporation and the techniquefollowed here in this synthesis is slow evaporation solution growth technique (SEST). The seed crystals are formed at the bottom of the beaker around 7-14 days and its slowly grows

to a complex single crystal making the process of crystal growth complete. This is thenseparated by filtration technique without any scratch on it and collected and packed in a ziplock cover after drying. The 20th day bulk crystal which was clear in growth medium are images of asgrown doped crystals is shown in the fig.1(a)

Fig.1Imagesof (a) Mn doped ADP/ZTS/Sulphamic acid crystal

SCANNING ELECTRON MICROSCOPE WITH ENERGY DISPERSIVE SPECTROSCOPY (SEM-EDS):-

Surface Morpholoy of the sample is observed using JEOL JSM 5610LV scanningelectron microscope (SEM), EDS, a chemical microanalysis technique with cobalt as astandard, is performed in conjuction with resolution 3.0nm, accelerating voltage 20KV and maximum magnification 3,00,000 times. The investigation of influence of sulphamicacid and manganese sulphate doping on the surface morphology of Ammonium dihydrogenphosphate, Tristhioureazin(II)sulphate reveals the formation of structure defect centres. The incorporation of (Mn) Manganese in the crystalline matrix results in more scatter centres as shown in the figure-2.

EDS analysis is an analytical tool used to screen the chemical compositions of different elements in a solid sample and to determine the relative abundance of such chemical elements. The existence of manganese (Mn) may be noted from EDS graph which is shown in the figure-2. This presence of manganese confirms doping of manganese sulphate to ADP/ZTS/Sulphamic acid.

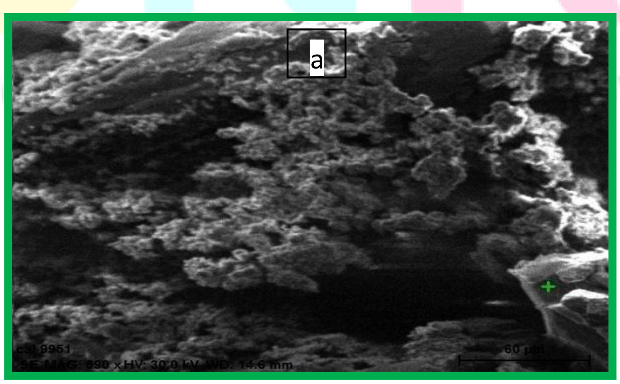

Fig.2SEM incorporation of Mn doped ADP/ZTS/Sulphamic acid

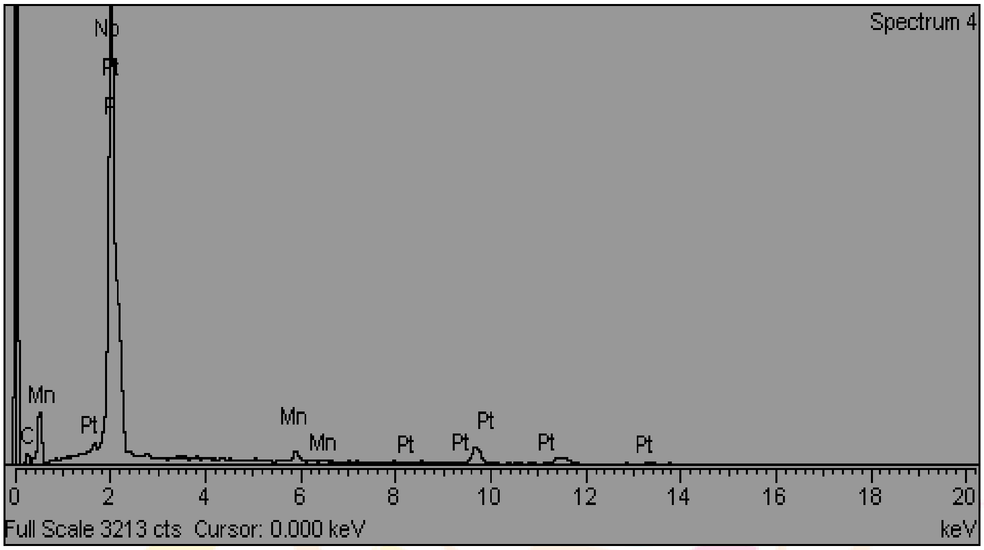

Fig.2 EDS incorporation of Mn doped ADP/ZTS/Sulphamic acid

SINGLE CRYSTAL XRD ANALYSIS:

The Single crystal X-ray diffraction analysis is done by Bruker AXS (Kappa ApexII) X-ray diffractometer. Here the unit cell values are determined along with structuralalignmentifnecessary.The cellparameter valuesof a mixture of sulphamic acid, Ammoniumdihydrogenphosphate, Tristhioureazinc(II)sulphate and Manganesesulphate crystals are tabulated as follows in Table-1. From the table we can conclude that the angles for both pure and doped mixed crystal of sulphamicacid+ADP+ZTS+MnSO4 are same as α=β=γ=90˚. The cell parameter values of pure ADP is a=7.502A˚, b=7.480A˚, c=7.554A˚ and v=421A˚^{3} crystallizing with orthorhombic system. For pure ZTS the cell parameter values differs from a=7.794A˚, b=11.152A˚,c=15.494A˚ and v=1348A˚ crystallizing with orthorhombic system. For the mixed crystalsof sulphamic acid with Ammonium dihydrogen phosphate, ZTS and Sulphamic acid are a=7.810A˚, b=11.19A˚,c=15.59A˚, v=1362A˚^{3} possessing orthorhombic system with angle α=β=γ=90˚. Thus wecan conclude that there is no vast difference in their crystal lattice structure and there is only slight modificationin the alignment of the mixed crystals structure.

Table-1- cell parameters values of Sulphamic acid, Ammoniumdihydrogenphosphate, Tristhioureazinc(II)sulphate, Manganesesulphate crystals,

Lattice ParameterValue	**a0A**	**bA0**	**c0A**	**V A03**	**System**
ADP	7.502	7.480	7.554	421	Orthorhombic
ZTS	7.794	11.152	15.494	1348	Orthorhombic
Mixed Crystal(Sulphamicacid+ADP+ZTS+$MnSo_4$)	7.810	11.19	15.59	1362	Orthorhombic

FOURIER TRANSFORM INFRARED SPECTROSCOPY:-

The broad peak around 3200-2500cm^{-1} is responsible for the presence of water and also it belongs to free water symmetric stretching. The asymmetric stretch of sulphate appears between 1292-31cm^{-1} and 947.05cm^{-1}. Usually four normal modes are present in the infrared region for the sulphate anion (SO42-): a non degenerate symmetric bending(947.05cm^{-1}),a doubly degenerate symmetric bending (605.65cm-1), triplydegenerate symmetric stretching (1028.06cm-1) and triply degenerate symmetric bending(1141.86cm-1) changes in protonation, metal complexation and solvation of $SO4^{2-}$can modify S-O bond length and it changes the symmetry of the anion as a result. This leads to a shift in the vibrational band to different wave numbers and causes the degenerate vibrations into non degenerate. In addition the IR spectrum contain the peaks corresponding to the functional groups of Sulphamicacid, Ammoniumdihydrogenphosphate and tristhioureazinc(II)sulphate. A sharp intense band at 1641.42cm^{-1}, 1625.99cm^{-1} and 1622.13cm^{-1} may be due to presence of acid group. A short peak at 1481 and 1516.05cm^{-1} is due to c-c stretching vibration and symmetric. The peak at 2349.30 and 2713.84cm^{-1} arises due to NH3 symmetric stretching vibration. The intense and sharp band at 3180.62cm^{-1}is assigned to the NH3^{+} asymmetric stretching vibration. A minute peak at

3481.51cm-1 indicates the presence of NH3 asymmetric stretching vibration. A broad peak at 3373.50cm^{-1}and 3313.71cm^{-1} shows the presence of OH stretching.

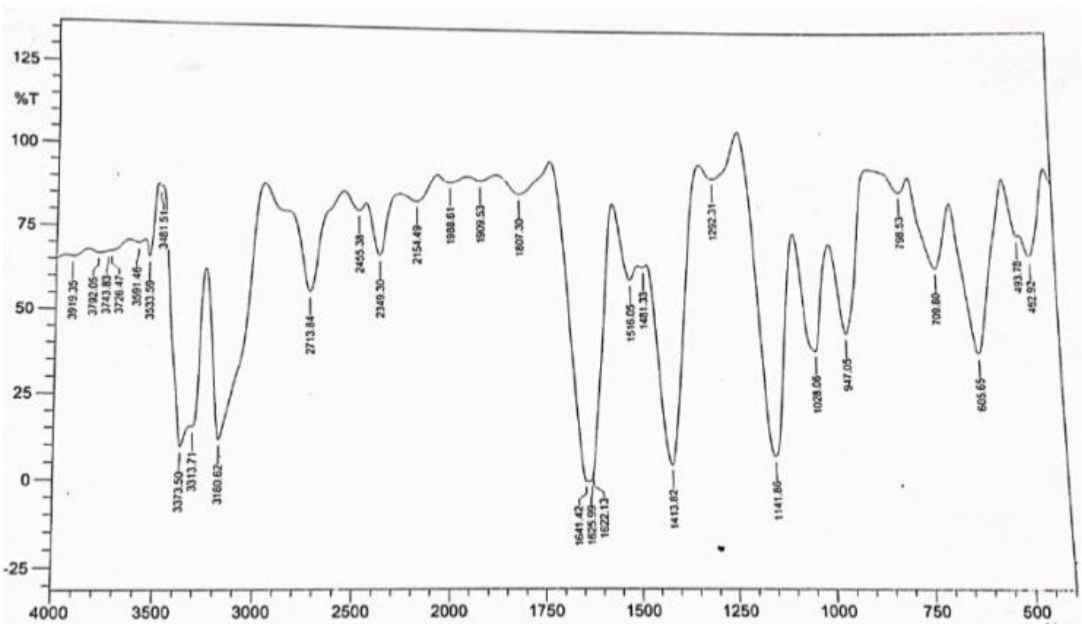

Fig.3.5 FTIR Spectra of SA, ADP, ZTS & $MnSO_4$

CONCLUSION:

Sulphamic acid is mixed with Ammoniumdihydrogenphosphate, Trithioureazinc(II)sulphate, Manganese sulphate to form crystal by the process of slowevaporation solution growth technique (SEST). Thus formed crystal is characterized byvarious techniques like Single crystal X-ray diffraction analysis, Fourier Transform infrared spectroscopy (FTIR) and ScanningElectronMicroscopy-Energydispersivespectroscopy(SEM-EDS). The single crystal XRD shows that mixed crystals of sulphamic acid with Ammonium dihydrogen phosphate, ZTS and

Sulphamic acid are a=7.810A˚, b=11.19A˚,c=15.59A˚, v=1362A˚[3] possessing orthorhombic system with angle α=β=γ=90˚. Thus wecan conclude that there is no vast difference in their crystal lattice structure and there isonlyslight modificationin thealignment ofthemixed crystalsstructure. FTIR shows that due to heavy doping, the peaks are shifted to higher frequency range. The incorporation of (Mn) Manganese in the crystallinematrixresultsinmorescatteredcentre, SEM shows a slight disturbance in the surface. The existence of manganese (Mn) may be noted from EDS graph confirming the presence of manganese doping of manganese sulphate to ADP/ZTS/Sulphamicacid.

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