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INFLUENCE OF ZINC DOPING ON THE STRUCTURAL AND THERMAL PROPERTIES OF STRONTIUM FORMATE DIHYDRATE CRYSTALS

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Abstract
Strontium formate dihydrate and zinc doped strontium formate dihydrate crystals were grown by slow evaporation method. The optimized growth parameters for growing these crystals were determined. The effect of zinc doping on the physic-chemical properties of strontium formate dihydrate crystals was studied by EDAX, PXRD, FTIR and TGA studies. EDAX studies confirmed the entry of the zinc into the crystal lattice. XRD studies showed that the lattice volume of strontium formate dihydrate crystals increase with doping concentration. Thermogravimetric analysis results obtained showed that the grown crystals were dihydrate.

Keywords: zinc doping, strontium formate crystals, physico-chemical properties, optical transmittance

Introduction

In recent years, the search for new non-linear optical (NLO) crystals has attracted the attention of many researchers due to their potential applications. Both organic and inorganic crystals were grown and characterized for NLO applications. Of the various varieties of crystals of studied so far, semi-organic crystals show high optical non-linearity with good thermal stability and excellent optical transmittance [1-3]. With an increasing demand of materials for NLO applications there is growing interest in investigations on crystallization and properties of new materials. Crystals of metal formates of I and II groups of the periodic systems exhibit marked nonlinear optical (NLO) properties comparable to that of the best nonlinear materials used for efficient frequency doubling of a YAG:Nd laser and for the phase matched SHG for ruby laser [4]. Deserno and Haussuh [5] have shown that orthorhombic $Sr(CHO_2)_2$ and $Sr(CHO_2)_2.2H_2O$ crystals allow phase-matched SHG and optical mixing in the near IR to UV region and low sensitivity with respect to aperture walkoff and beam divergence.

A thorough survey of the literature shows that very little work has been done on the effect of doping on the physico-chemical properties of strontium formate dihydrate crystals. Therefore in the present study we have attempted to study the effect of zinc doping on the structural, thermal and optical properties of strontium formate dihydrate crystals. The results obtained in the present study are reported herein.

Experimental

The synthesis of strontium formate dihydrate was reported by us elsewhere [6]. A saturated solution of strontium formate dihydrate mixed with zinc chloride ($ZnCl_2$) in the required concentration was kept in a

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magnetic stirrer at a temperature of 40°C for a period of 2 hours. The dopant concentrations were 0.005M ad 0.05M. The solution thus obtained was filtered and transferred to the growth vessel (100ml beaker) and kept in a constant temperature bath with an accuracy of ±0.1°C. The temperature of the bath was maintained at 40°C throughout the growth process.

Energy dispersive x-ray analysis (EDAX) was carried out at Central Electrochemical Research Institute, Karaikudi. Powder x-ray diffraction data of the grown crystals were obtained using JEOL-JDX X-ray diffractometer. FT-IR spectra were recorded using JASCO FT-IR spectrophotometer with ATR accessory in the range 400-4000cm^{-1}at a resolution of 4cm^{-1}. Thermal studies were carried out using TA Instruments thermal analyser in the temperature range ambient to 1000°C in nitrogen atmosphere at a heating rate of 10°C/min. UVVis spectrometer (JASCO, Japan) was used to record the optical transmittance spectra of the grown crystals.

Results and discussions

The optimum temperature for the growth of zinc doped strontium formate dihydrate crystals was found to be 40°C. Crystals of good quality and transparency appeared below the beaker in about 48 hours and grew in large crystals in about 7-8 days. The largest crystal was about 8 mm in length. It is observed that as the size of the crystal increases the transparency was reduced. The best crystal with good morphological perfection and transparency was about 6mm x 4mm x 3mm in size. The photograph of the grown crystals was displayed in fig.1.

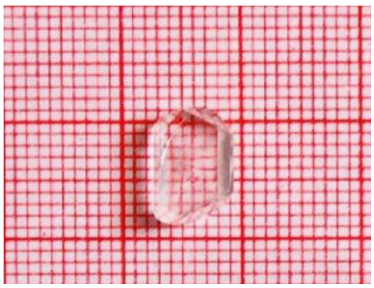

Figure 1: Photograph of zinc doped strontium formate dihydrate crystal

The results obtained from EDAX analysis are presented in fig. 2(a) to (c). The results confirm that the dopants have entered into the strontium formate dihydrate crystal lattice. The results show that there is reasonable agreement in the concentration of zinc ions in the grown crystals with that of actually taken for experiment. Introduction of Zn^{2+} ion into strontium formate crystal may lead to the formation of Zn^{2+} $HCOO^-$ dipoles (Zn^{2+} substitutes Sr^{2+}).

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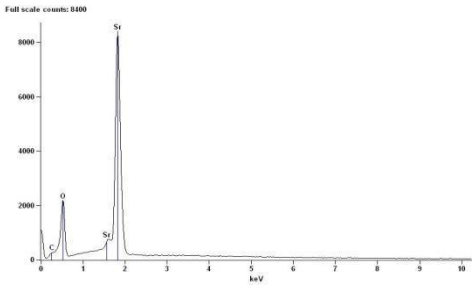
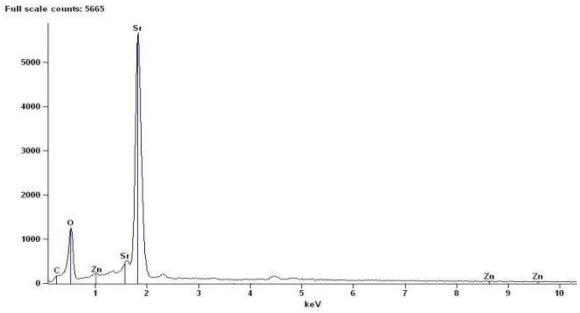


(a)



(b)

Figure 2: EDAX spectra of (a) strontium formate dihydrate crystals (b) zinc doped strontium formate
dihydrate crystals

EDX elemental maps of samples for Sr, O and Zn show homogeneous elemental distributions and no clustering of Zn was detected in the 0.05M doped crystal. The dopant concentration obtained from EDX analysis for the doped crystals are presented in Table 1. It is clear that the calculated dopant Zn concentration (from EDX) is significantly low when compared to experimental dopant concentration which indicates the amount of intake of Zn^{2+} ions or formation of dipole between Zn^{2+} and $HCOO^{-}$ is low in strontium formate crystal lattice. Similar results were obtained for magnesium doped strontium formate dihydrate crystals also [7].

Sample	Dopant concentration actually taken (in mole%)	Dopant concentration in the grown crystal (in mole%)
Zn-doped strontium formate dihydrate crystals	0.005	0.00069
	0.05	0.0146

Table 1: Dopant concentration in the grown crystals obtained from EDAX analysis

The material of the grown crystals was confirmed by x-ray diffraction studies. The grown crystals were confirmed to be strontium formate dihydrate crystals. The x-ray diffraction data compares very well with the JCPDS data of strontium formate dihydrate crystals (File No.14-0824). The lattice parameters of the grown crystals are given in Table 2. Lattice variation and increase in lattice volume further confirm the

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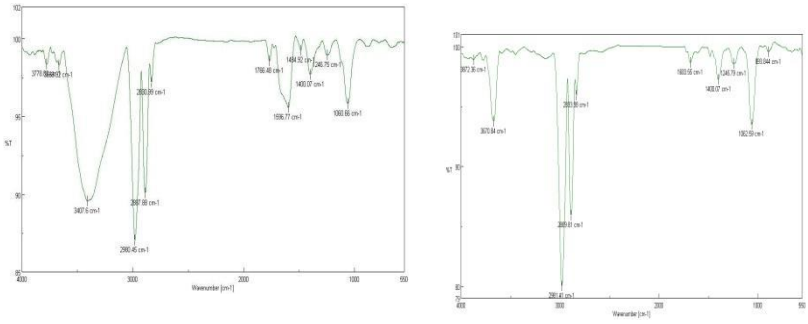
entry of the dopant into the crystal lattice. The lattice parameters for pure strontium formate dihydrate crystals obtained in the present study area = 7.351 (8) Å, b = 12.152(3) Å and c = 7.112(5) Å. The values reported in the literature [8] are a = 7.332 Å, b = 12.040 Å and c = 7.144 Å.

Sample	Dopant concentration (in M)	a (Å)	b (Å)	c (Å)	V (Å^3)
Pure	-	7.351(8)	12.152(3)	7.112(5)	635.31
Zn-doped	0.005	7.411 (32)	11.874(22)	7.298(12)	642.21
	0.05	7.412(52)	11.887(22)	7.294(41)	642.64

Table 2: Lattice parameters and lattice volume of zinc doped strontium formate dihydrate crystals

The FT-IR spectra of all the crystals grown in the present study are presented in Fig.3. In pure strontium formate dihydrate crystals, the absorption peaks at 3661 and 3416 cm^{-1} are due to water. The band at 2984 and 2885 cm^{-1} are attributed to the υ(C-H). The peak at 1591 cm^{-1} is due to υ(C-O). The peak at 1483 is due to υ(COO) and the peak at 1405 cm^{-1} are assigned to δ(C-H), C=O symmetric and δ (O-C=O) mode. The peaks at 1252, 1060 and 893 cm^{-1} are due to C-H bend, γ(C-H) and δ (COO). The absorption at 614 cm^{-1} is due to strontium-oxygen. The FT-IR spectrum obtained in the present study for pure crystal is similar to the IR spectrum of strontium formate dihydrate crystals reported earlier [9-10]. The FT-IR spectrum obtained for the doped crystals resemble that of the pure crystal. In addition to the peaks described above, few absorption peaks are observed between 500-660 cm^{-1} in the FT-IR spectra of the doped crystals. The spectra of doped crystals indicate an appreciable shift of peak positions to lower and higher values suggesting incorporation of dopants in the crystal lattice. These peaks are attributed to metal-oxygen bonds. It is noted from fig.3, the vibrational modes are unaffected in the doped crystals; indicating that there is no interaction between the formate ion and the dopant added.



(a) (b)

Figure 3: FTIR spectra of the grown crystals (a) strontium formate dihydrate (b) zinc doped strontium formate dihydrate

Thermo-gravimetric analysis (TGA) of pure and zinc doped strontium formate dihydrate crystals showed that the crystal was hydrated and the weight loss calculations clearly indicated that these crystals have two

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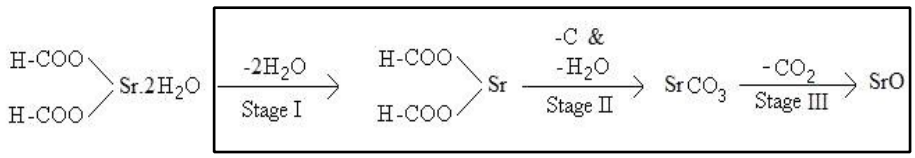
water molecules as water of hydration. This result is in accordance with our earlier work on copper and calcium and magnesium doped strontium formate dihydrate crystals [6]. As reported earlier by us, in the present study also we also we expect three stages of decomposition within the temperature range taken for study (ambient to 1200^{o}C). The decomposition stages may be as follows:



It was noticed that all the zinc doped strontium formate dihydrate crystal loses water of hydration and becomes anhydrous at 74^{o}C and thereafter it decomposes into strontium carbonate at 485^{o}C and finally turns into strontium oxide at 949^{o}C. The percentage of weight loss during the decomposition stages of zinc doped strontium formate dihydrate crystals is given in table 3. The incorporation of zinc into strontium formate dihydrate lattice did not make any significant change in the decomposition stages. However, some increase in the decomposition temperature is observed, though not much significant. It is expected that, increasing the doping concentration further more may lead to significant change in the decomposition temperature.

Stage	Temperature range (^{o}C)	Observed weight loss (%)	Calculated weight loss (%)	Loss of molecules in the stage
I	39-74	18.6	18.7	$2H_2O$
II	74-485	17.0	16.9	H_2O & C
III	485-949	29.2	29.9	CO_2

Table 3: Percentage of weight loss in the different stages of decomposition of zinc doped strontium formate dihydrate crystals

Conclusions

Zinc doped strontium formate dihydrate crystals were successfully grown by slow evaporation method. The grown crystals were characterized by EDAX, XRD, FTIR and thermal analysis. EDAX analysis confirmed the entry of the dopant into the crystal lattice. The results showed that there was reasonable agreement in the concentration of zinc ions in the grown crystals with that of actually taken for experiment. From FTIR spectra it was observed that the vibrational modes are unaffected in the doped crystals, indicating that there was no interaction between the formate ion and the dopant added. TGA studies showed that the grown crystals were dihydrate. Three stages of decomposition were observed for the grown crystals in the temperature range considered in the present study.

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