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RESEARCH ARTICLE

Effect of Magnesium Doping on the Physicochemical Properties of Strontium Formate Dihydrate Crystals

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Abstract: Magnesium doped strontium formate dihydrate crystals were grown by slow evaporation method. The optimized growth parameters for growing these crystals were determined. The grown crystals were characterized by EDAX, XRD, FTIR and TGA studies. EDAX studies confirmed the entry of the magnesium 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. We herein present the results obtained.

Keywords: Magnesium doping, Strontium formate crystals, Physicochemical properties

Introduction

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[1]. Deserno and Haussuh[2] 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. With an increasing demand of materials for NLO applications there is growing interest in investigations on crystallization and properties of new materials.

Strontium formate dihydrate is found to be orthorhombic[3] with space group $P2_12_12_1$. Strontium formate dihydrate crystals are of considerably interest, particularly for the basic studies of some of their interesting physical properties. A thorough survey of the literature shows that very little work has been done on the effect of doping on the physicochemical properties of strontium formate dihydrate crystals. Therefore in the present study we have attempted to study the effect of magnesium doping on the physicochemical 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 in our earlier work[4]. A saturated solution of strontium formate dihydrate mixed with magnesium chloride ($MgCl_2$) in the required concentration was kept in a magnetic stirrer at a temperature of 40 ^oC for a period of 2 hours. The dopant concentrations were 0.005 M ad 0.05 M. The solution thus obtained was filtered and transferred to the growth vessel (100 mL beaker) and kept in a constant temperature bath with an accuracy of ±0.1 ^oC. The temperature of the bath was maintained at 40 ^oC 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 400-4000 cm^{-1} at a resolution of 4 cm^{-1}. Thermal studies were carried out using TA Instruments thermal analyser in the temperature range ambient to 1000 ^oC in nitrogen atmosphere at a heating rate of 10 ^oC/min.

Results and Discussion

The optimum temperature for the growth of magnesium doped strontium formate dihydrate crystals was found to be 40 ^oC. Crystals of good quality and transparency appeared below the beaker in about 48 hours and grew in large crystals in about 8-10 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 8 mm x 4 mm x 3 mm in size. The photograph of the grown crystals was displayed in Figure 1.

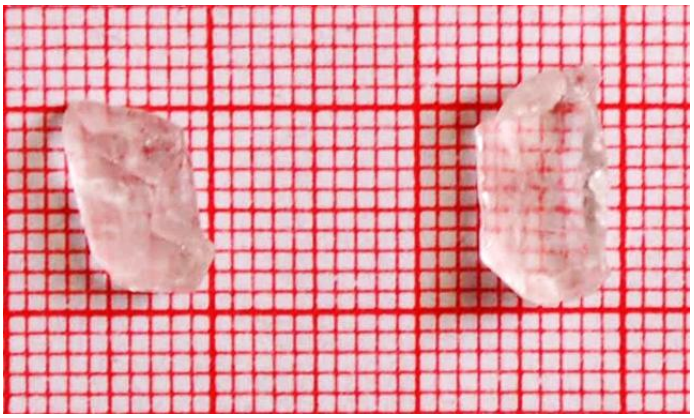
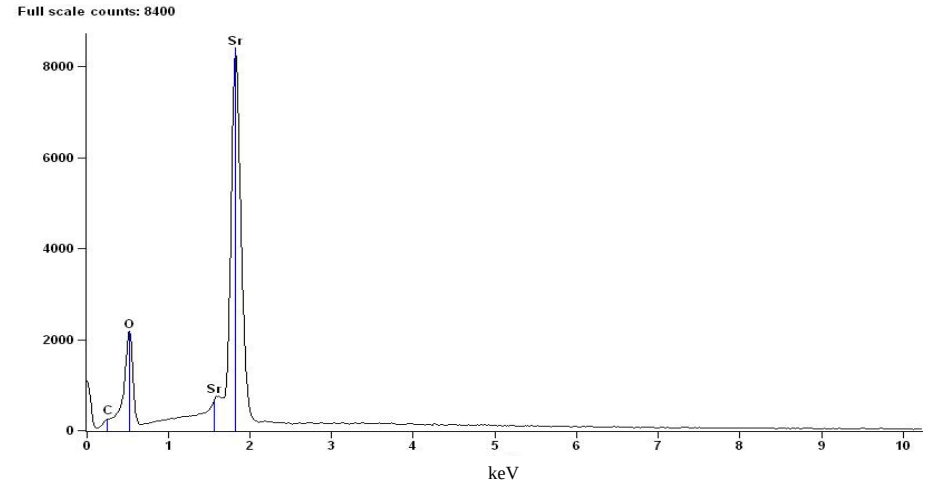


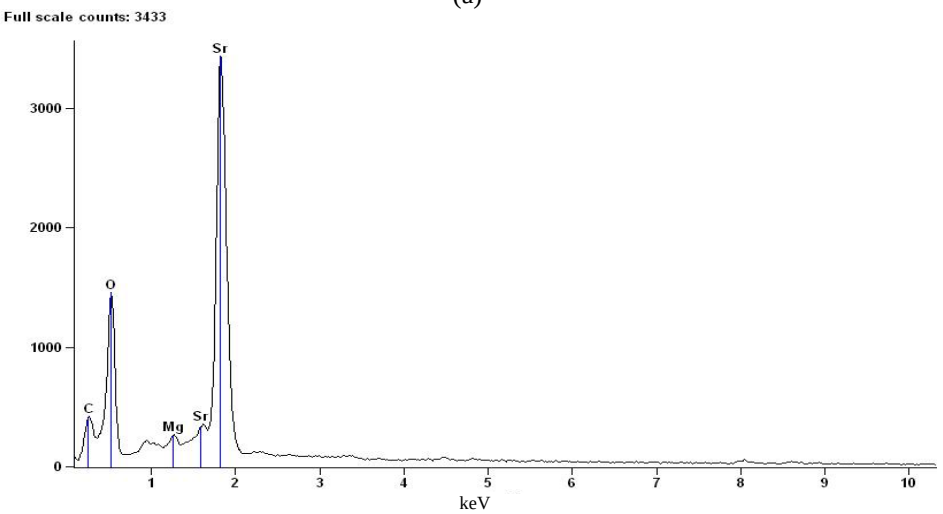
Figure 1. Photograph of the grown crystals

The results obtained from EDAX analysis are presented in Figures 2(a) to (c). The results confirm that the dopants have entered into the strontium formate dihydrate crystal lattice. From the results we infer that, the dopant taken in the form of $MgCl_2$ would dissociate into Mg^{2+} and Cl^- ions. Since the ionic radius of Mg^{2+} ion (ionic radius=0.72Å) is smaller than the ionic radius of Sr^{2+} ion (1.13 Å). Therefore, it is expected that Mg^{2+} ion can enter into the strontium formate dihydrate crystal lattice either by substituting Sr^{2+} ion or by occupying an interstitial position in the lattice, without affecting the overall charge neutrality. The results show that there is reasonable agreement in the concentration of magnesium ions in the grown crystals

with that of actually taken for experiment. Introduction of Mg^{2+} ion into strontium formate crystal may lead to the formation of Mg^{2+} $HCOO^-$ dipoles (Mg^{2+} substitutes Sr^{2+}). These results are in accordance with the results reported earlier for other Mg-doped metal formate crystals[5-6].



(a)



(b)

Figure 2. EDAX spectra of (a) strontium formate dihydrate crystals (b) magnesium doped strontium formate dihydrate crystals

EDX elemental maps of samples for Sr, O and Mg show homogeneous elemental distributions and no clustering of Mg was detected in the 0.05 M 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 Mg concentration (from EDX) is significantly low when compared to experimental dopant concentration which indicates the amount of intake of Mg^{2+} ions or formation of dipole between Mg^{2+} and $HCOO^-$ is low in strontium formate crystal lattice.

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

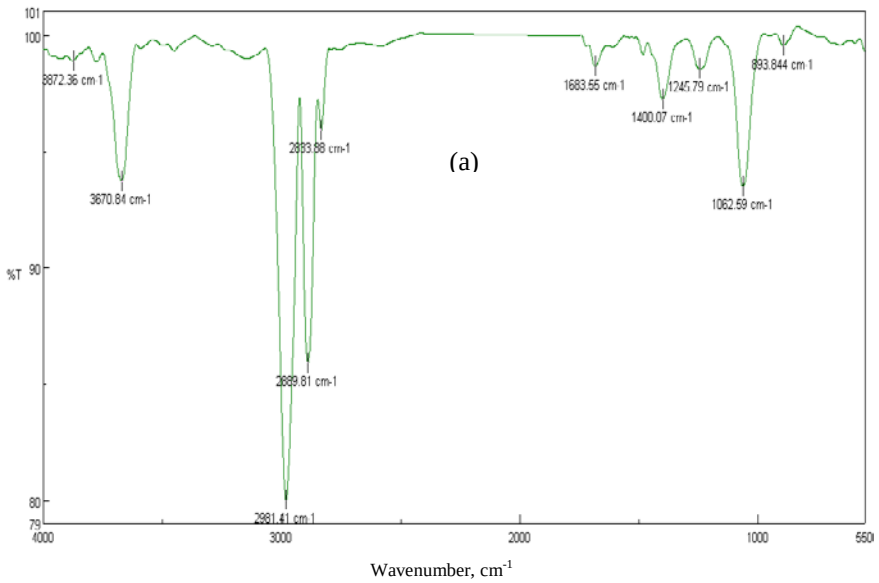
Sample	Dopant concentration actually Taken, mole%	Dopant concentration in the grown crystal, mole%
Mg-doped strontium formate dihydrate crystals	0.005	0.00066
	0.05	0.0099

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 entry of the dopant into the crystal lattice. The lattice parameters for pure strontium formate dihydrate crystals obtained in the present study are: a = 7.351(8) Å, b = 12.152(3) Å and c = 7.112(5) Å. The values reported in the literature were a = 7.332(1) Å, b = 12.040(1) Å, and c = 7.144(1).

Table 2. Lattice parameters and lattice volume of magnesium doped strontium formate dihydrate crystals

Sample	Dopant concentration, M	a (Å)	b (Å)	c (Å)	V (Å^3)
Pure	-	7.351	12.152	7.112	635.31
Mg-doped	0.005	7.412	12.098	7.218	647.24
	0.05	7.388	12.187	7.201	648.36

The FT-IR spectra of all the crystals grown in the present study are presented in Figure 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).



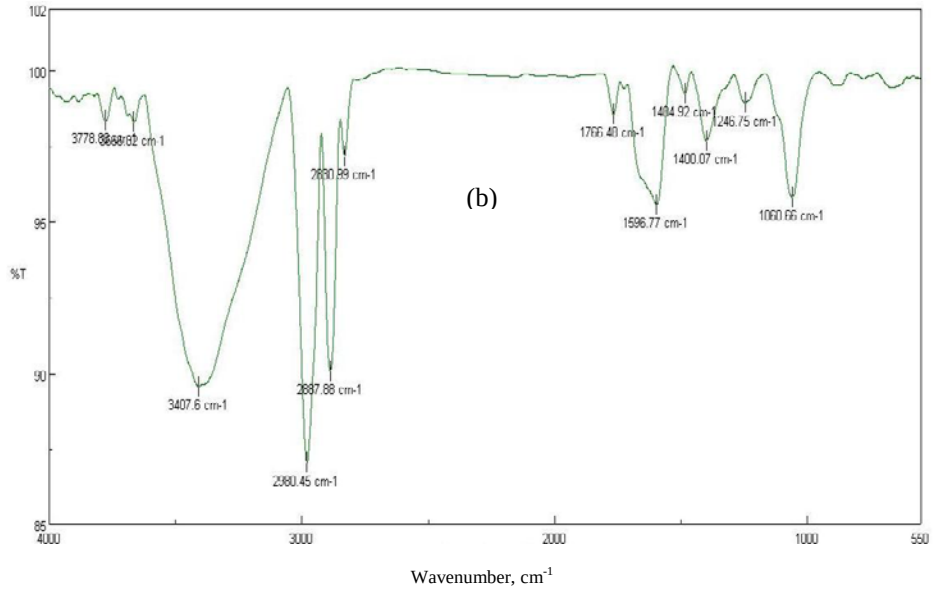
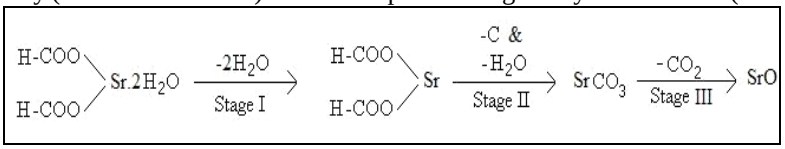


Figure 3. FTIR spectra of the grown crystals (a) strontium formate dihydrate (b) magnesium doped strontium formate dihydrate

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[7-8]. 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 Figure 3, the vibrational modes are unaffected in the doped crystals; indicating that there is no interaction between the formate ion and the dopant added.

Thermogravimetric analysis (TGA) of pure and magnesium doped strontium formate dihydrate crystals showed that the crystal was hydrated and the weight loss calculations clearly indicated that these crystals have two water molecules as water of hydration. This result is in accordance with our earlier work on copper and calcium doped strontium formate dihydrate crystals[4]. As reported earlier[4], we expect three stages of decomposition within the temperature range taken for study (ambient to 1200 ^oC). The decomposition stages may be as follows (Scheme 1):



Scheme 1

It was noticed that all the magnesium doped strontium formate dihydrate crystal loses water of hydration and becomes anhydrous at 74 ^oC 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 magnesium doped strontium formate dihydrate crystals is given in Table 3. The incorporation of magnesium 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.

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

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

Conclusion

Magnesium doped strontium formate dihydrate crystals were successfully grown by slow evaporation method. The grown crystals were characterized by EDAX, XRD and 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 magnesium 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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