GROWTH AND PHYSICAL PROPERTIES OF PURE AND MANGANESE DOPED STRONTIUM TARTRATE TRIHYDRATE SINGLE CRYSTALS

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Abstract

Pure and manganese doped strontium tartrate trihydrate single crystals (a total of 3) were grown by the single diffusion gel growth technique. The growth conditions were optimized by varying the parameters such as pH, concentration of gel, gel setting time and concentration of reactants. Crystals having different morphologies were obtained with a maximum size of 10x5x 3 mm^3. The grown crystals were characterized by carrying out PXRD, SXRD, FTIR spectral, UV- Vis-NIR spectral, SHG, PL spectral, AAS, micro hardness and thermo gravimetric measurements. The crystals belong to the monoclinic crystal system and are optically transparent, NLO active, mechanically soft and thermally stable at least up to 100 ^oC. AAS measurement revealed the presence of Mn atoms in the doped crystals. Results indicate that Mn doping significantly increases the PL yield and SHG efficiency. Details are presented.

Keywords: *Single crystals, Doped crystals, Gel technique, Strontium tartrate, X-ray diffraction, Optical properties, Mechanical properties.*

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1. INTRODUCTION

Single crystals are the backbone of the modern technological revolution. Tartaric acid may serve as a base for the development of new class of materials. The presence of two hydroxyl as well as two carbonyl groups in tartaric acid permits the ready incorporation of monovalent, divalent or trivalent metal ions [1]. Mainly tartrate crystals possess application as dielectric, ferroelectric and piezoelectric materials [1-14]. They are used in the fabrication of nonlinear optical (NLO) devices such as crystal oscillators and resonators based on their optical second harmonic generation (SHG), optical transmission characteristics, and controlled laser emission[2]. Some tartrate compounds are used in military applications. Manganese tartrate crystals are used in chemical temperature indicators[3]. Among the several tartrate compounds, strontium tartrate has received greater attention on account of its ferroelectric, nonlinear optical and spectral characteristics[1,2,7-11,13,14].

Currently, great attention has been devoted to the growth and characterization of pure and doped metal tartrate crystals with the aim of identifying new materials for device applications. Investigating the effect of dopants on various properties of single crystals is of great interest in the technological point of view[1]. In the present study single crystals of pure and manganese doped strontium tartrate trihydrate crystals were grown by the gel technique and the grown crystals were characterized by carrying out powder X-ray diffraction (PXRD), single crystal X-ray diffraction (SXRD), Fourier transform infrared (FTIR) spectral, UV-Vis-NIR spectral, photoluminescence (PL) spectral, atomic absorption spectroscopic (AAS), thermo gravimetric (TG/DTA), SHG and micro hardness measurements. The results obtained are reported herein and discussed.

2. EXPERIMENTAL DETAILS

2.1 Growth of Single Crystals

A systematic study of crystallization in gels begins with Lissegang's famous discovery of periodic crystallization in gels [15]. This technique is an alternative technique to solution growth with controlled diffusion. The test tube diffusion method was employed to grow strontium tartrate single crystals in a gel medium. The growth of pure and doped strontium tartrate crystals was achieved by controlled diffusion of strontium ions through silica gel impregnated with tartaric acid [2,8,14]. 0.5M sodium meta silicate having specific gravity 1.03g/cm^3 was titrated with 0.5 M tartaric acid till the mixture attained the pH of 4. This was allowed to set in glass tubes placed vertically on wooden stands undisturbed at room temperature. The solution was found to strongly depend on pH. Within a week the gel was set. The supernatant solution used was 0.5 M strontium chloride. It diffused into the gel column and reacted with the inner reactant, giving rise to the formation of single crystals. The expected chemical reaction was [7]

$SrCl_2+C_4H_6O_6 \rightarrow SrC_4H_4O_6 + 2HCl$

Tiny crystals were visible within a day and the size and number of crystals increased in about a week. It is known that different parameters such as concentration of reactants, pH of gel solution, gel concentration and gel setting time have considerable effects on the growth rate[15]. On increasing the pH value large number of tetrahydrate crystals were obtained and on decreasing the pH value below 4, trihydrate crystals were obtained in large number. But when the pH was set as 4, both types of crystals were obtained, those crystals near the gel surface were transparent (trihydrate) and near the bottom were pale yellow (tetrahydrate) [14]. After 25 days the crystals were harvested. We consider here only the strontium tartrate trihydrate which belongs to the monoclinic crystal system [7,11]. For the growth of manganese doped strontium tartrate crystals, the supernatant solution used was a mixture of 0.5M strontium chloride and 0.0025/0.005M (as required) manganese chloride (i.e. in 1:0.005 and 1:0.010 molar ratios). We represent here the three grown strontium tartrate trihydrate crystals as Pure for the pure strontium tartrate trihydrate, M31 for the 0.005 Mn doped and M32 for the 0.010 Mn doped.

2.2. Characterizations

PXRD data were collected using an automated X-ray powder diffractometer with Cu Kα (λ=1.54056 Å) radiation. The PXRD patterns were indexed using a software. SXRD data were collected using an EnrafNonius CAD4 F diffractometer at room temperature. FTIR spectra were recorded by employing a SHIMADZU spectrometer in the wave number range 400-4000 cm^{-1}. The UV-Vis-NIR transmittance spectra were recorded for all the three crystals dissolved in water in the wavelength range 200-1100 nm by using a SHIMADZU UV-250 UV-Vis-NIR spectrophotometer. PL spectra were recorded using a Perkin Elmer LS55 fluorescence spectrophotometer at room temperature. The SHG property was tested (using the Kurtz and Perry technique) for the grown crystals by passing the output of Nd-YAG Quanta ray laser through the crystalline powder sample. AAS analysis was carried out by using a Perkin Elmer spectrophotometer. Vicker's hardness measurements were carried out on all the three grown crystals using a SHIMADZU HMV-2 microhardness tester. TGA/DTA analysis was carried out from room temperature to 800 °C in an atmosphere of air by using a thermal analyser (model SDT-Q600) for the Pure and M32 crystals.

3. RESULTS AND DISCUSSION

3.1. Crystals Grown

Highly transparent crystals with good morphological perfection appeared near the gel-solution interface within 25 days. Best quality Pure, M31 and M32 crystals were obtained with pH 4.0 - 4.5, gel density 1.03 g/cc, growth temperature 30 °C and concentration 0.5 M. A change in pH of the gel solution other than this range resulted in poor quality crystals. Crystals up to a size of about 10x5x3 mm^3 could be harvested. Figure 1 shows the photographs of sample crystals grown in the present study.

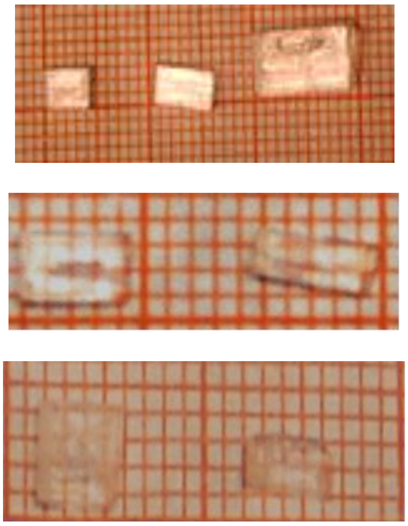

Fig.1 : Photographs of the sample crystals grown (From top - Pure, M31 and M32)

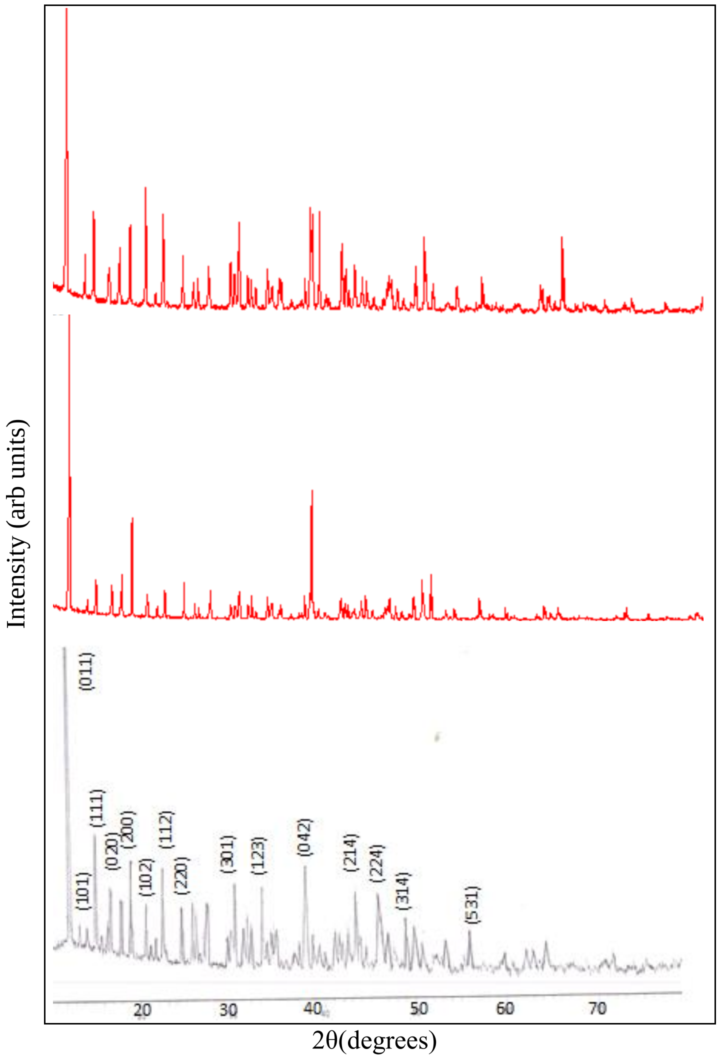

Fig 2: The observed PXRD patterns

3.2. Lattice Parameters

The indexed PXRD patterns observed in the present study are shown in Figure 2. Sharp peaks observed confirm the crystalline nature of the crystals grown. The crystallographic parameters obtained through SXRD measurements are provided in Table 1 along with that reported for the Pure in the literature [11]. The lattice parameters observed in the present study for the Pure crystal agree well with the literature values. Change in volume due to doping indicates that the impurity (Mn) atoms have entered into the host crystal matrix [14]. The dopant atoms are expected to replace the Sr atoms mainly and, to some extent, to occupy the interstitials. The Mn atom contents (see Table 2) observed through AAS analysis confirm this.

Table 1: Crystallographic parameters for pure and manganese doped strontium tartrate trihydrate crystals

Parameters	Pure		M31	M32
	Reported [11]	Present work		
a(Å)	7.55	7.47	7.49	7.56
b(Å)	10.06	10.03	10.03	10.14
c(Å)	6.47	6.44	6.44	6.47
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$	$P2_1$	$P2_1$
Volume($Å^3$)	491.42	482.51	484.17	495.97

3.3. FTIR Spectra

The FTIR spectra recorded for the grown crystals are shown in Figure 3. Due to the small dopant concentration, there is no significant difference observed for the doped crystals. The functional groups identified from the FTIR spectra confirm the material of the grown crystals as strontium tartrate. The OH stretching frequency due to free water symmetry appears at around 3400 cm^{-1} indicating the presence of water in all the three crystals considered. The strong C-O stretch is found at around 1399cm^{-1}. The bending mode of water has been observed at around 476cm^{-1} [14]. C-O-C asymmetric strong stretching has been observed in the range 1300-1270cm^{-1}[14]. The asymmetric stretch of water has been observed at around 1591cm^{-1}[14]. The spectra observed in the present study for the strontium tartrate trihydrate are in good agreement with that reported for barium tartrate [4].

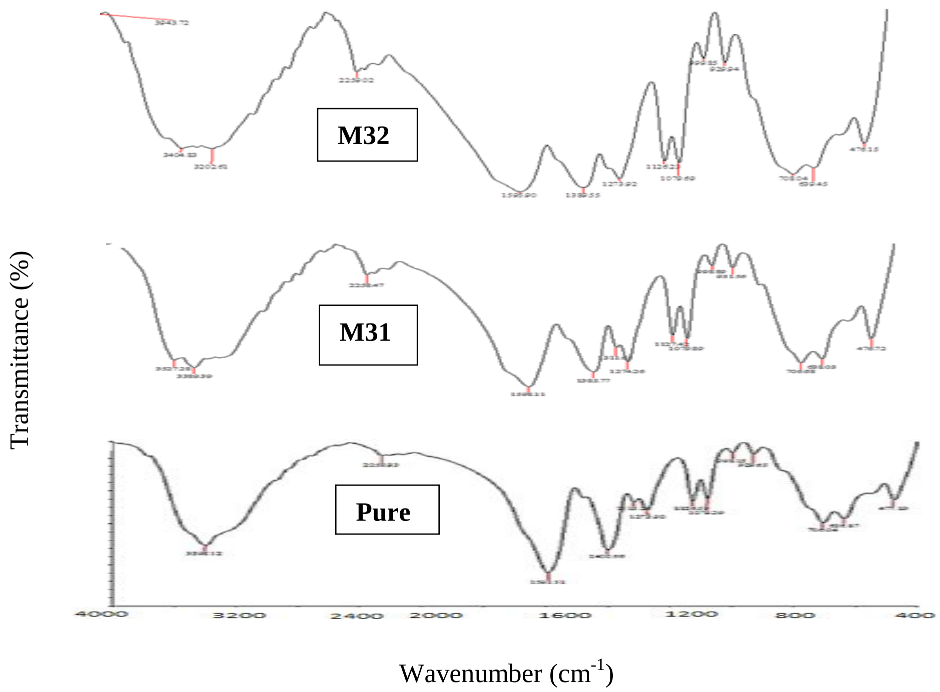

Fig 3 : The observed FTIR spectra

3.4. Optical and Mechanical Properties

Dielectric crystals are mainly used in opto-electronic and photonic applications. So, the optical transmission (wavelength) range and transparency cut-off wavelength are essential. Figure 4 shows the UV-Vis-NIR spectra observed in the present study. It can be seen that these crystals have sufficient transmission in the entire visible, near infrared and most of the UV regions. Even though the optical measurement was carried out on aqueous solutions of the crystals, the observed transparent wavelength range starting from around 250 nm shows that these crystals are suitable for second harmonic generation. Efficient nonlinear optical crystals are expected to have optical transparency lower cut-off wavelengths between 200 and 400 nm [16]. So, all the three crystals grown in the present study can be considered as promising NLO materials.

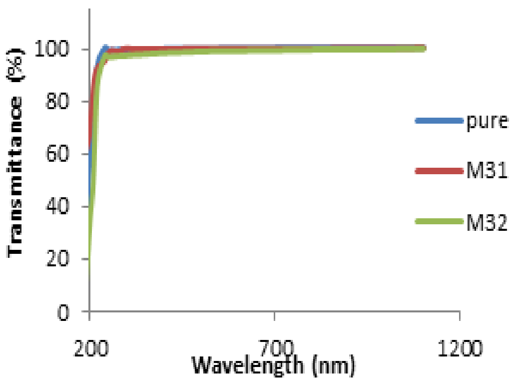

Fig.4: The observed UV-Vis-NIR spectra

SHG efficiencies of the grown crystals (in KDP unit) observed in the present study are provided in Table 2. Results obtained indicate that the crystals grown are NLO active. Moreover, it is found that Mn doping increases the SHG efficiency significantly.

The observed PL spectra are shown in Figure 5. The spectra shows three peaks at 385, 520, 780 nm. The most intense peak is at 385 nm which is the violet emission. Peak at 520 nm indicates green emission. Peak at 780 nm is the least intense red emission [12]. It is found that Mn doping increases the PL yield significantly. The SHG and PL spectral measurements indicate that Mn doping leads to significant improvement in the NLO and PL properties of strontium tartrate trihydrate.

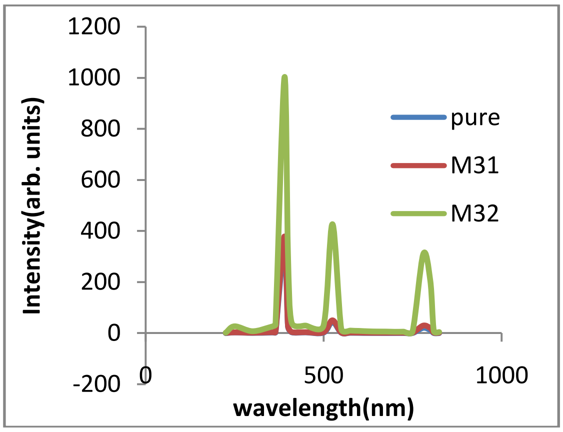

Fig.5: The observed PL spectra

The Vicker's hardness number (H_v) is defined as [16] $H_v = 1.8544(P/d^2)$ kg/mm^2 where P is the load applied and d is the diagonal length of the indentation made on the crystal surface. Results obtained in the micro hardness measurement are shown in Figure 6. It is found that the hardness number increases with the increasing load for all the three crystals considered. The Meyer's law is expressed as [16] $P = k_1 d^n$ where k_1 is the material constant and n is the Meyer index or work hardening co-efficient.

The work hardening coefficients (n) were determined from the slopes of log P vs log d plots [not shown here]. The values obtained are given in Table 2. They are found to be >2. According to Onitsch and Hanneman 'n' should lie between 1.0 and 1.6 for hard materials and above 1.6 for soft ones [16]. The increase in Hv for increasing P observed in the present study is in good agreement with the theoretical prediction exhibiting the normal size indentation effect. Also, the grown crystals belong to soft materials category

Moreover it is found that Mn doping increases the hardness number significantly.

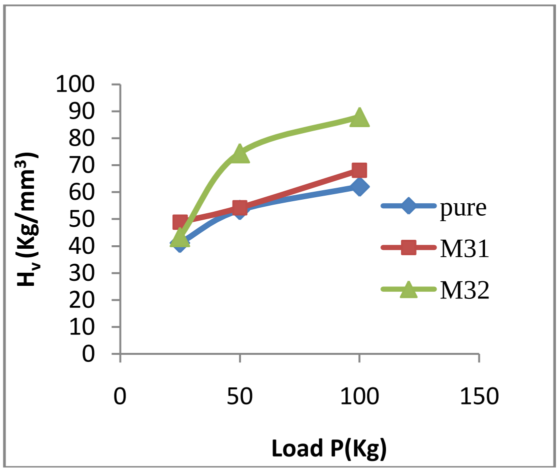

Fig. 6: The observed hardness behaviour

The present study, in effect, indicates that the optical and mechanical properties of strontium tartrate trihydrate single crystals can be tuned significantly by doping with Mn atoms.

Table 2: The observed SHG efficiencies, work hardening coefficients (n) and Mn atom contents (from AAS analysis)

Name of the crystal	SHG efficiency (KDP unit)	n	Mn atom content (ppm)
Pure	0.579	2.7	-----
M31	0.852	2.6	6.34
M32	0.840	3.8	11.44

3.5. Thermo Gravimetric Analysis

The TGA and DTA patterns recorded for the Pure and M32 crystals in the temperature range 50 to 800 °C are shown in Figure 7. It can be seen that the crystals are thermally stable at least up to 100 °C. The three different stages identified along with the corresponding temperature ranges and mass losses are provided in Table 3. The first stage corresponds to the removal of water molecules (dehydration process) [13]. The second stage corresponds to the formation of strontium oxalate (SrC_2O_4) (decomposition process). The third stage corresponds to the formation of strontium carbonate ($SrCO_3$) (decomposition process) [9]. The energy required to dislodge water molecules depends upon how strongly they are locked up in the lattice. The water molecules ejected during the first stage indicates the presence of three water molecules which is in agreement with the results obtained through the FTIR spectral analysis. The DTA patterns also indicate the above dehydration and decomposition processes clearly.

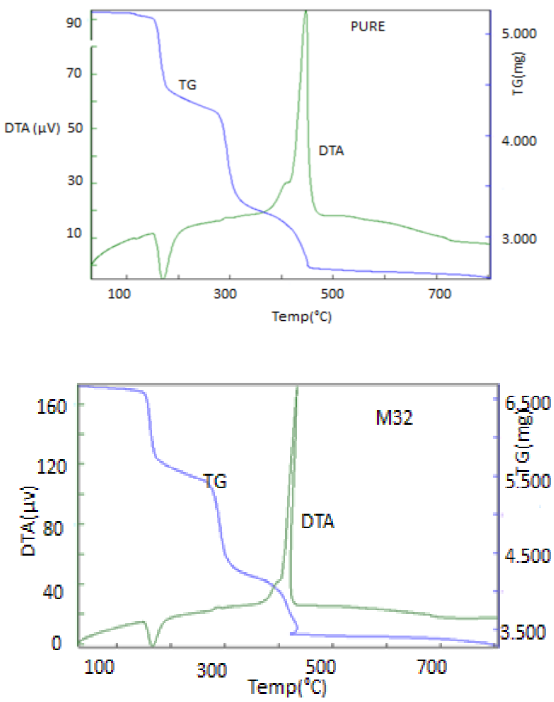

Fig.7: The observed TG/DTA patterns

Table 3: The results of thermo gravimetric analysis made on pure and M32 crystals

Stage	Sample	Temperature (° C)	Mass loss (%)
I	Pure	100-220	17.14
	M32	120-210	16.12
II	Pure	270-350	20.95
	M32	270-350	20.16
III	Pure	390-470	10.47
	M32	380-440	9.67

4. CONCLUSIONS

Single crystals of pure and manganese doped strontium tartrate trihydrate have been grown successfully by the gel technique. Results obtained through PXRD, SXRD, FTIR spectral, AAS and thermo gravimetric measurements indicate that the material of all the 3 crystals (pure and 2 Mn doped) grown in the present study are basically strontium tartrate trihydrate and the Mn atoms have entered into the crystal matrix of the doped crystals. All the 3 crystals exhibit wide optical transparency, NLO activity, PL and normal size indentation effect and are thermally stable at least up to 100 °C. Results of SHG and PL spectral measurements indicate that Mn doping increases significantly the SHG efficiency and PL yield of the strontium tartrate trihydrate crystal. The present study, in effect, indicates that Mn doping makes strontium tartrate trihydrate crystals more useful in photonics device applications.

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