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Optical and Mechanical Properties of Pure and Manganese Doped Strontium Tartrate Tetrahydrate Single Crystals

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ABSTRACT
In the present investigation, single crystals of strontium tartrate and manganese doped strontium tartrate tetrahydrate crystals were grown by the single diffusion gel growth technique. The growth conditions were optimized by varying the parameters such as pH, concentration of the gel, gel setting time and concentration of the reactants. Silica gel was used as the growth medium with test tubes as crystallization vessels. Crystals having different morphologies were obtained (transparent and few opaque). The lattice parameters of the grown crystals were determined by single crystal X-ray diffraction analysis. The UV-Vis spectrum was recorded to study the optical transparency of the grown crystals. The second harmonic generation measurements indicate that they are NLO active. Photoluminescence study was performed to know the luminescence property of the material. Atomic absorption spectroscopic measurements were also carried out to understand the presence of dopant in it. Mechanical strength of the grown crystals were analyzed by Vickers microhardness test. Details are presented.
Keywords: Gel technique, Strontium tartrate, SXRD, UV-Vis, PL, AAS, Microhardness.

I. Introduction

A systematic study of crystallization in gels begins with Liesegang's famous discovery of periodic crystallization in gels [1]. This technique is an alternative technique to solution growth with controlled diffusion and is free from convection. Tartaric acid may serve as a base for the development of new class of materials. Mainly tartrate crystals possess application as dielectric, ferroelectric and piezoelectric materials or show non-linear optical properties [2]. Because of these characteristics, the tartrate crystals are utilised in transducers, linear and non-linear mechanical devices, crystal oscillators and resonators and controlled laser emission [3,4]. Some tartrate compounds are used in military applications. Strontium tartrate crystal is an important ferro electric crystal [5,6]. The non-linear nature of ferro electric materials can be used to make capacitors with tunable capacitance. Nowadays great attention has been devoted to the growth and characterization of pure and doped tartrate crystals with the aim of identifying new materials for practical purposes [7]. Strontium tartrate is used in ammunition units. Strontium tartrate tetrahydrate crystal is reported to be orthorhombic. Strontium tartrate trihydrate is reported to be monoclinic. In the present study, we were interested in growing strontium tartrate tetrahydrate single crystals.

The effects of dopants on various properties of single crystals are of great interest for both solid state science as well as technological points of view [7]. Manganese tartrate crystals are useful in chemical temperature indicators [8]. In the present study, single crystals of pure and manganese doped strontium tartrate tetrahydrate crystals were grown by the gel technique. Optimum growth conditions were determined by varying gel concentration, pH, gel setting time and concentration of reactants. The grown crystals were characterized by carrying out PXRD, single crystal X-ray diffraction, UV-Vis absorption, photoluminescence and atomic absorption spectral, SHG and microhardness measurements. The results obtained are reported and discussed herein.

II. Growth of Sample Crystals

The test tube diffusion method was employed to grow pure and manganese doped strontium tartrate tetrahydrate crystals. The apparatus used for crystallization consists of borosilicate glass tubes placed in a stand. Silica gel was prepared by adding a solution of sodium meta silicate and tartaric acid by stirring slowly [9]. A fixed amount of gel solution with $1.03 g/cm^3$ specific gravity and pH was set at 4.0 by adding 0.5M tartaric acid and transferred to several test tubes. The test tubes were sealed. After gel setting, the supernatant solution, strontium chloride of 0.5M was poured over the gel slowly. The test tube was kept undisturbed at room temperature. The supernatant solution diffuses in to the gel column and reacts with the inner reactant, giving rise to the formation of strontium tartrate crystals [6]. We obtain pale yellowish crystals at the bottom of tubes along with transparent and faceted crystals near the gel surface [5]. The chemical reaction is [10]:

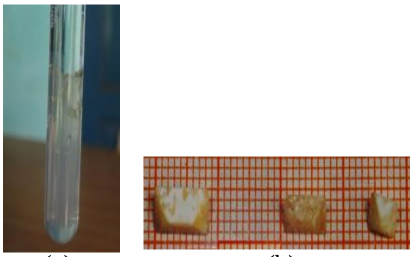
$$SrCl_2 + C_4H_6O_6 \longrightarrow SrC_4H_4O_6 + 2HCl$$

The yellowish crystals were strontium tartrate tetrahydrate and the transparent well faceted crystals were strontium tartrate trihydrate [5]. These two crystals differ and the study here is on the strontium tartrate tetrahydrate (SrT) which is orthorhombic. For the growth of manganese doped strontium tartrate crystals, the supernatant solution was a mixture of 0.5M strontium chloride and 0.0025/0.005M manganese chloride. Both the types of crystals were obtained and the study of manganese doped strontium tartrate tetrahydrate crystals (MS1/MS2) are discussed here.

These crystals are again orthorhombic. The optimum conditions obtained for the growth of pure and manganese doped strontium tartrate tetrahydrate crystals are given in Table 1. The crystallographic parameters obtained are provided in Table 2. Fig. 1-3 show the growing and grown crystals of pure and manganese doped strontium tartrate tetrahydrate (pure, MS1 and MS2).

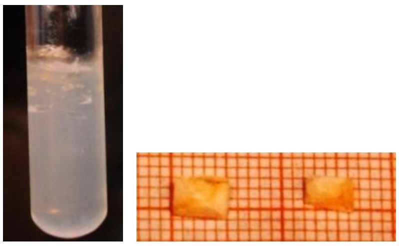
Table1: Optimum conditions obtained for the growth of pure and manganese doped strontium tartrate crystals

Parameters	Pure	MS1	MS2
Density of sodium meta silicate (g/cm^3)	1.03	1.03	1.03
Concentration of tartaric acid (M)	0.5	0.5	0.5
pH	4	4	4
Temperature (^0C)	30	30	30
Concentration of strontium chloride (M)	0.5	0.5	0.5
Concentration of manganese chloride (M)	---	0.0025	0.005
Gel setting time (week)	1	1	1
Crystal growth time (days)	25	25	25



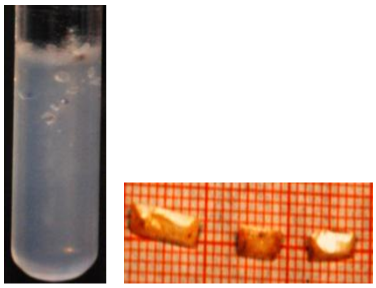
(a) (b)

Fig.1: Photographs showing the (a) growing pure crystals and (b) grown pure crystals



(a) (b)

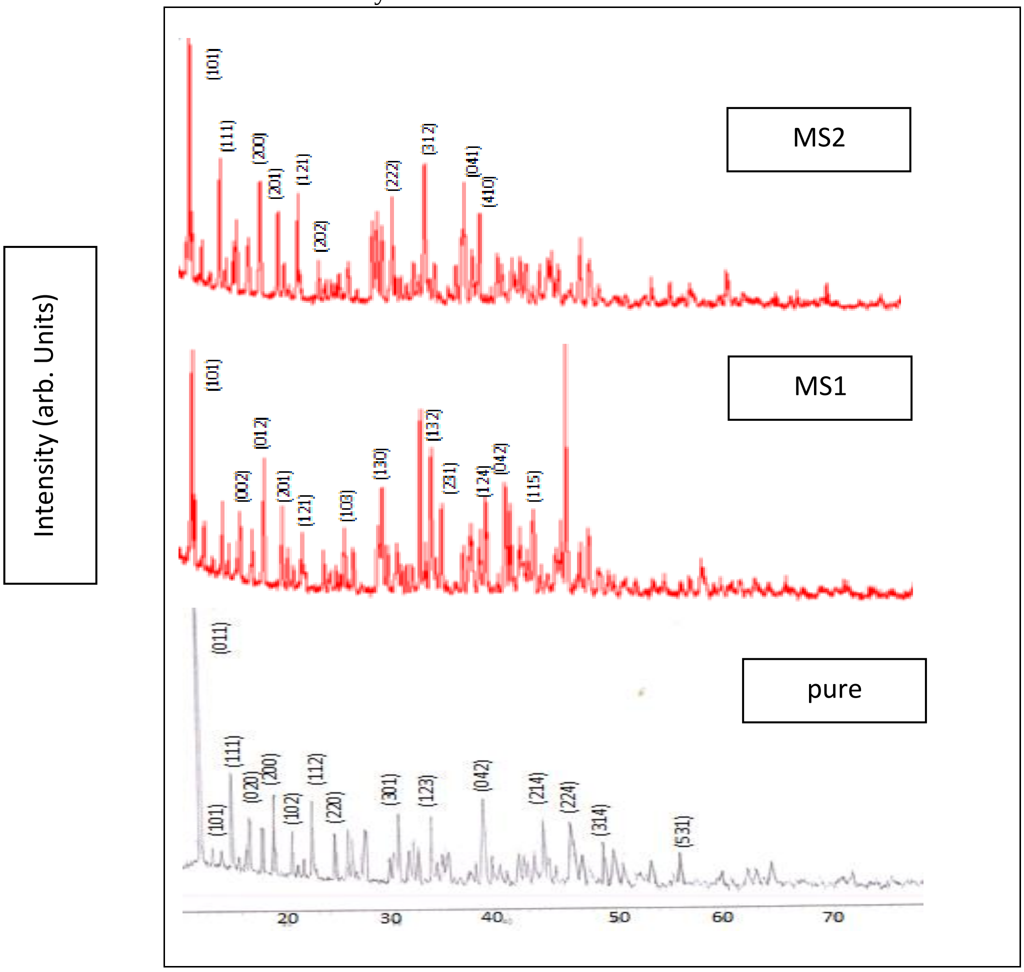
Fig.2: Photographs showing the (a) growing MS1 crystals and (b) grown MS1 crystals



(a) (b)

Fig.3: Photographs showing the (a) growing MS2 crystals and (b) grown MS2 crystals

The PXRD patterns were recorded using a diffractometer with Cu Kα (λ=1.54060Å) radiation. The powder X-ray diffraction patterns were indexed using a software (Fig.4). Sharp peaks confirm the crystalline nature of the sample crystals grown. Single crystal X-ray diffraction (SXRD) data were collected using a Enraf Nonius CAD4-F Diffractometer at room temperature. Lattice parameters were determined and crystal system was identified. The SXRD analysis indicates that the cell parameters obtained for the pure crystals are closely matching with the values already reported [11]. No significant variation of lattice parameters due to doping is observed which indicates that manganese doping does not lead to any lattice distortion. However, the small changes observed in the lattice volume indicates that the manganese atoms have entered into the strontium tartrate crystal matrix



2θ (degrees)

Fig.4: The PXRD patterns observed.

Table2: Crystallographic parameters for pure and manganese doped strontium tartrate tetrahydrate crystals

Parameters	Pure		MS1	MS2
	Reported [11]	Present work		
a(Å)	9.48	9.3854	*9.4354*	9.4335
b(Å)	10.96	10.9154	10.8954	10.9484
c(Å)	9.46	9.4722	9.48199	9.5355
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Volume($Å^3$)	982.9	970.4088	974.753	983.9466

Results of atomic absorption spectral (AAS) analysis carried out by using a Perkin Elmer spectrophotometer indicate the presence of manganese in the doped crystals. MS1 contains 5.32ppm and MS2 contains 8.33ppm. This is nearly proportional to the concentration considered in the solution used for the growth of single crystals.

III. Optical Properties

Single crystal is mainly used in opto-electronic applications. So, the optical transmission range and transparency cut-off wavelength are essential [12]. Transmittance spectra of pure and manganese doped strontium tartrate tetrahydrate crystals dissolved in water were recorded using a SHIMADZU UV-2450 UV-Visible Spectrophotometer over the wavelength range 200-700nm. From the spectra (see Figure 5), it can be seen that these crystals have sufficient transmission in the entire visible and most of the UV regions. There is a transparency around 250nm which shows that these crystals are suitable for second harmonic generations [13]. Efficient nonlinear optical crystals have an optical transparency lower cut off wavelengths between 200nm and 400nm. From this, it can be understood that these three crystals can be considered as promising nonlinear optical (NLO) crystals.

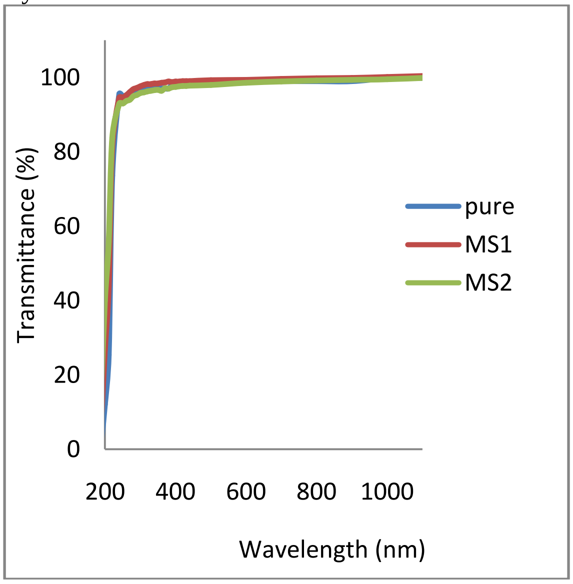


Fig.5: The observed UV – Vis spectra

The second harmonic generation property was tested for the grown crystals by passing the output of Nd-YAG Quanta ray laser through the crystalline powder sample. The second harmonic generation (SHG) efficiencies of the grown crystals are 0.545, 1.01 and 0.943 (in KDP unit) for pure, MS1 and MS2 respectively. The grown crystals are therefore observed to be NLO active.

Photoluminescence spectra (shown in Fig. 6) were recorded using a Perkin Elmer LS55 fluorescent spectrophotometer at room temperature. The spectra show three peaks at 390, 525 and 780nm. Most intense peak is at 390nm which is the violet emission. Peak at 525nm, the green emission is less intense and there is red emission at 780nm having sharp peak [2]. It can be seen that the grown crystals are having the fluorescent property.

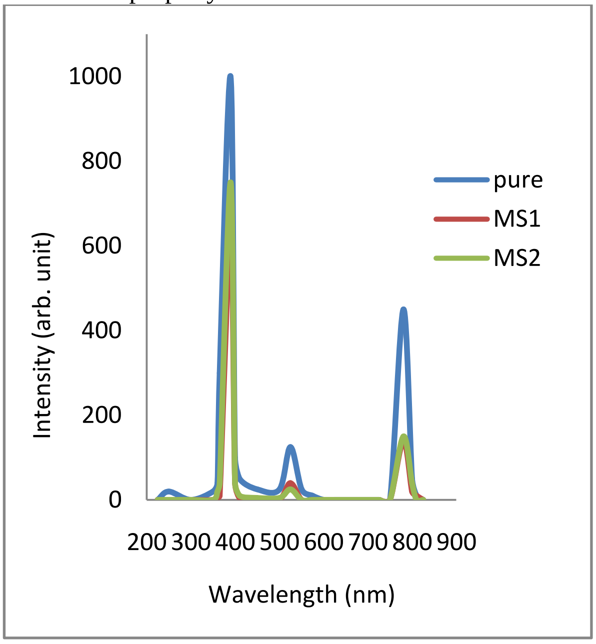


Fig.6: Emission spectra

IV. Mechanical Properties

The Vicker's hardness numbers (H_v) observed (by carrying out the microhardness measurements using a Shimadzu HMV-2 microhardness tester) for various loads(P) in the present study for all the 3 crystals grown are shown in Fig.7. It is found that the microhardness increases with the increasing load.

The work hardening coefficients (n), were determined from the slopes of log P vs log d Plots (not shown here). The values of n are found to be >2. Doping decreases the $H_v$value and the n values are found to be 3.18, 4.24 and 6.02 respectively for pure, MS1 and MS2. According to theory, if n<2 the materials are said to be hard ones and if n>2 the materials are said to be soft ones [14, 15]. The increase in H_v for increasing load (P) observed in the present study is in good agreement with the theoretical prediction and the grown crystals belong to soft materials.

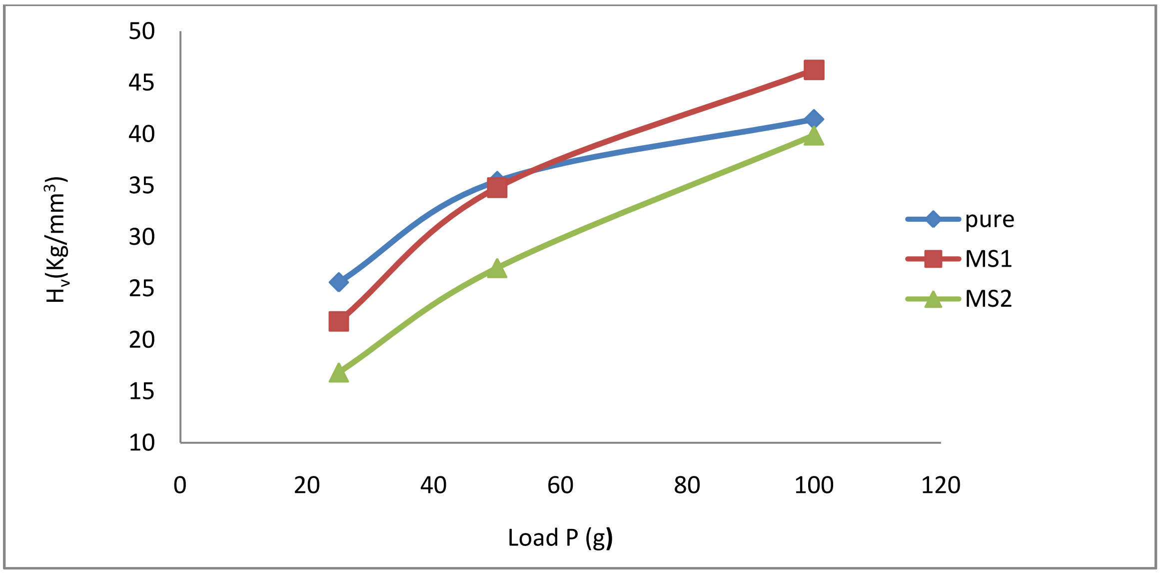


Fig.7: The hardness behaviour

V. Conclusions

Pure and manganese doped strontium tartrate tetrahydrate crystals have been grown successfully by the single diffusion gel growth technique. PXRD confirms the crystallinity of the grown samples. SXRD confirms the orthorhombic crystal system of the grown crystals. Unit cell parameters of the pure crystal match well with the reported SXRD standard values. AAS confirms the presence of manganese in the doped crystals. Also these crystals are found to be useful for the second harmonic generation. Photoluminescence spectra show that the grown crystals are having the luminescent nature. This property was found in the doped crystals also and it is clear that all the crystals are having the luminescent nature. Microhardness test reveals that the grown crystals belong to soft material category. It was found that due to the dopant, the number of grown crystals decreases. The pure and manganese doped strontium tartrate tetrahydrate crystals are found to be pale yellow and good quality crystals. Also the present study indicates that manganese doping leads to tuning the optical and mechanical properties of strontium tartrate tetrahydrate single crystals.

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