STRUCTURAL STUDIES OF PURE AND MAGNESIUM MIXED STRONTIUM TARTRATE CRYSTALS GROWN BY GEL TECHNIQUE

N. H. Tandel[1], Dr. I. B.Patel[2]

[1,2]*Department of Physics, Veer Narmad South Gujarat University, Surat, Gujarat, India*

ABSTRACT

Single crystals of pure and magnesium mixed strontium tartrate crystals were grown by single diffusion technique at room temperature. The obtained micro crystals were transparent. The powder XRD analysis showed these crystals to have orthorhombic crystal system. From FTIR spectral analysis the presence of water of crystallization and related groups and bonds were confirmed. The presence of expected elements in relative crystals was confirmed by carrying out EDAX spectrum analysis. UV-Vis-NIR spectral study reveals these crystals to be transparent and suitable for second harmonic generations. The scanned images show these crystals to be grown by layer deposition.

Keywords: *Gel growth, PXRD, EDAX, UV-Vis-NIR, FTIR, SEM.*

1. INTRODUCTION

Tartrate single crystals have many interesting and useful properties such as ferroelectric, piezoelectric, dielectric, optical and other technological characteristics [1-8]. Among various tartrate compounds strontium tartrate crystals have received great attention due to their useful properties such as ferroelectric, non-linear optical and spectral characteristics [9]. Growth and characterization of pure and mixed strontium tartrate crystals have been reported by various researchers [10-13]. Because of its wide applications several types of mixed crystals of strontium tartrate were grown and studied. But in literature survey, to the best of our knowledge, no report has been made on the growth and characterization of magnesium mixed strontium tartrate crystal. In present work, single crystals of pure and magnesium mixed strontium tartrate crystals were grown by gel technique and the grown crystals were characterized by carrying out various structural and spectroscopic analysis such as powder XRD, EDAX spectral, UV-Vis-NIR spectral, FTIR spectral and SEM.

2. EXPERIMENTAL DETAILS

2.1 Crystal growth

Single crystals of pure and magnesium mixed strontium tartrate crystals were grown by gel technique. The silica gel was used as a growth medium. The chemical used for the growth were tartaric acid, strontium chloride, magnesium chloride and sodium metasilicate. All chemicals were AR grade. The crystallization apparatus consists of borosilicate glass test tubes having dimensions of 20 cm x 1.5 cm were placed vertically on a wooden stand. The solutions of tartaric acid, strontium chloride and magnesium chloride were prepared by dissolving these compounds in an appropriate amount of distilled water to get the required molarities. The solutions were stirred and filtered using filter paper. The solution of sodium metasilicate was prepared by adding its compound in to distilled water in appropriate amount. It was stirred and kept for a day so that all the impurities settle down. Then the solution is filtered and kept aside. To get the required specific gravity of gel, the calculated amount of distilled water is added into sodium metasilicate solution. Silica gel is prepared by acidifying sodium metasilicate solution with tartaric acid drop by drop with continuous stirring to avoid excessive local ion concentration which may cause premature local gelling and make the final solution inhomogeneous and turbid. The pH of the gel was adjusted to attain the value of 4.5. The gelling mixture was transferred in to test tubes and allowed to set by keeping undisturbed. The open end of the test tubes was closed using cotton plug to prevent excess evaporation and contamination from the exposed

surface of the gel. Here the tartaric acid acted as lower reactant. After confirming the gel setting, an aqueous solution of strontium tartrate was carefully poured along the walls of the test tube with the help of pipette over the set gel in order to avoid any gel breakage.

To grow magnesium mixed strontium tartrate crystals, the aqueous solution of magnesium chloride was mixed with the solution of strontium chloride in certain proportion. The solution was centrifuged up to 1500 rpm for 90 minutes. Then this solution was poured over the set gel carefully using pipette and kept undisturbed. The following reactions are expected to take place in gel medium.

$$SrCl_2 + C_4H_6O_6 \rightarrow SrC_4H_4O_6 + 2HCl \quad \text{……...….(1)}$$

$$_{(1-x)}SrCl_2 + _{(x)}\ MgCl_2 + C_4H_6O_6 \rightarrow Mg_{(x)}Sr_{(1-x)}C_4H_4O_6 + 2HCl \quad \text{…….……...…...(2)}$$

(Where, x= 5% of total volume)

2.2 Characterization techniques

The grown strontium tartrate (ST) and magnesium mixed strontium tartrate (MST) crystals were subjected to the powder crystal XRD studies using Rigaku Miniflex X-ray Diffractometer with CuKα radiation (λ=1.54 Å). The sample was scanned over a required range for 2Θ values (0-80̊). The elemental analysis was carried out by using EDAX spectral analysis. The FTIR spectra were recorded for the powdered sample in the range 400-4000cm^{-1} using Perkin Elmer (Model: Spectrum BXw) spectrophotometer by using KBr pallet technique. The UV-Vis-NIR absorption spectra were recorded for all the three grown crystals using Shimadzu UV-1700 spectrophotometer in the wavelength range of 200-1100 nm. Surface morphology of grown crystals was studied by using Hitachi S-3400N scanning electron microscope.

3. RESULT AND DISCUSSION

3.1 Crystal growth

Both the crystals were harvested after 42 days. They were washed and cleaned by using distilled water. The crystals were different in size. The pure crystals of ST were transparent having maximum size of 1.5x0.5x0.5 mm^3 and grown mixed MST crystals were having maximum size of 1x1x0.5 mm^3. Growth condition is shown in table 1. Figures 1, 2 and 3 show the images of the grown ST crystals, while figures 4, 5 and 6 show the images of the grown MST crystals.

The sizes of mixed crystals were comparatively smaller than the pure crystals. Thus, it was found from experiment that addition of dopant increased the nucleation time with reduction in crystal size.

Table-1: Growth conditions

Sp. density of Sodium meta silicate	1.048 gm/cc
Concentration of Tartaric acid	0.5 M
pH of the silica gel	4.5
Concentration of Strontium Chloride	0.5 M
Concentration of Magnesium Chloride	0.5 M
Gel setting period	5 days
Gel aging period	2 days
Period of crystal growth	42 days
Temperature	Ambient Temperature

Fig-1: Growing ST crystal

Fig-2: Grown ST crystals

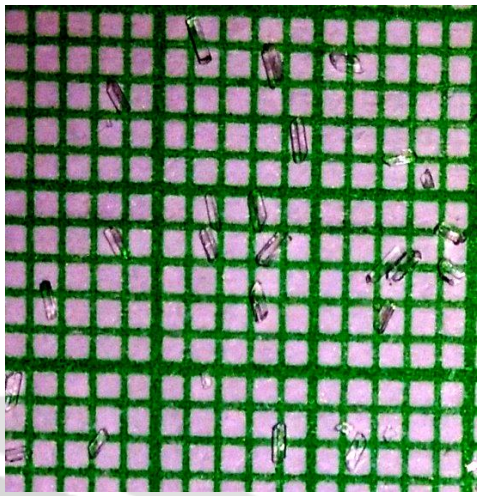

Fig-3: Size of ST crystals

Fig-4: Growing MST crystals

Fig-5: Grown MST crystals

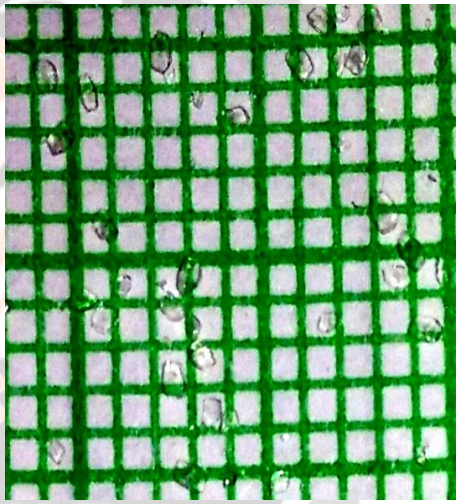

Fig-6: Size of MST crystals

3.2 Powder XRD analysis

From the obtained XRD data, the observed prominent peaks confirm the crystalline nature of the grown ST and MST crystals. The d values of Pure ST crystals matched well with those of reported data of strontium tartrate tetrahydrate crystals [14]. The d values correspond to the orthorhombic crystal system for pure ST crystals. From the reported data [14] the lattice parameters are, a = 9.48 Å, b= 10.96 Å and c = 9.46 Å. The hkl values for ST crystals were obtained using lattice parameters by using the formula;

$$1/d^2 = (h^2/a^2) + (k^2/b^2) + (l^2/c^2) \quad \text{.....(3)}$$

The d values of mixed MST crystals were quite similar with those of pure ST crystal. Few new peaks were also found in XRD spectra of MST crystals. The XRD spectra for both the crystals are shown in figure 7. The relative intensities and (hkl) of ST and MST crystals are tabulated in table 2. From this data we can see the relative intensities are different for same hkl plane.

Table-2: Relative intensities, d values and hkl planes of pure ST and MST crystals

Relative intensity I/I_0 [ST]	Relative intensity I/I_0 [MST]	d (Å) [ST]	d (Å) [MST]	(hkl)
100	100	7.88	7.85	110
12	36	4.94	4.89	120
35	18	3.95	3.92	112
11	16	3.80	3.77	030
22	9	2.64	2.63	140
6	31	2.23	2.23	303
7	17	2.08	2.08	151

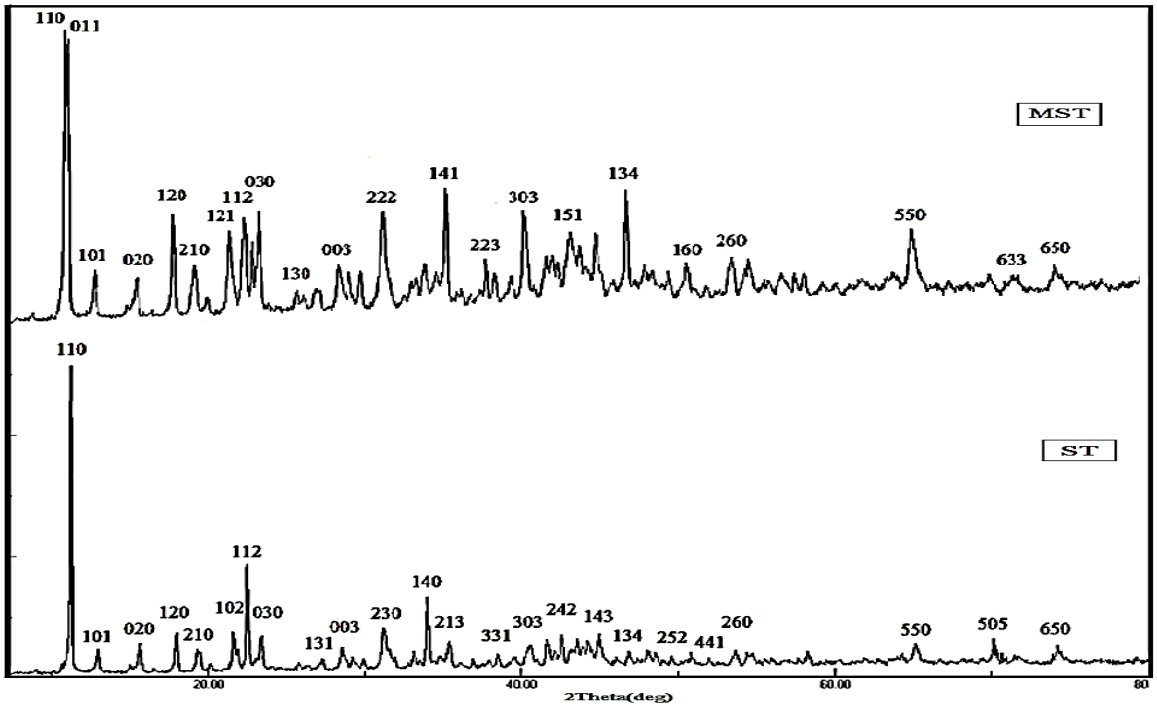

Fig-7: XRD Spectra of ST and MST crystal

3.3 Elemental analysis

The spectra obtained from Energy Dispersive X-ray analysis confirm the presence of various elements in the grown crystals as shown in figure 8 and 9. The presence of strontium in pure ST crystal is confirmed. Also, the presence of both magnesium and strontium elements are confirmed in mixed MST crystal. In the strontium tartrate crystal sample, the peak ranging from 1.8 KeV to 2.0 KeV clearly indicates the presence of strontium. The relative weight is 39.35%. In magnesium mixed strontium tartrate crystal, the peak ranging from 1.1 KeV to 1.3 KeV indicates the presence of magnesium and peak ranging from 1.8 KeV to 2.0 KeV indicates presence of strontium. The relative weight of magnesium is 0.13% and that of strontium is 29.80%.

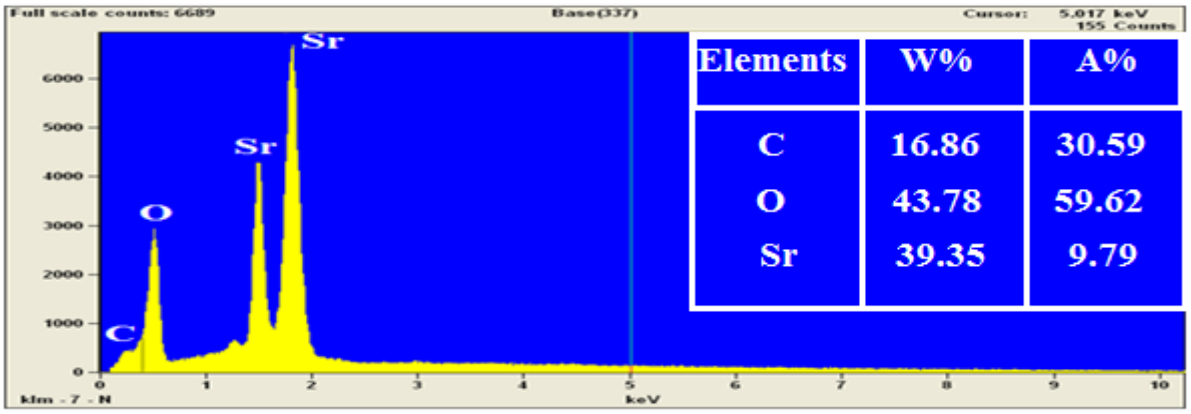

Fig-8: EDAX graph of ST

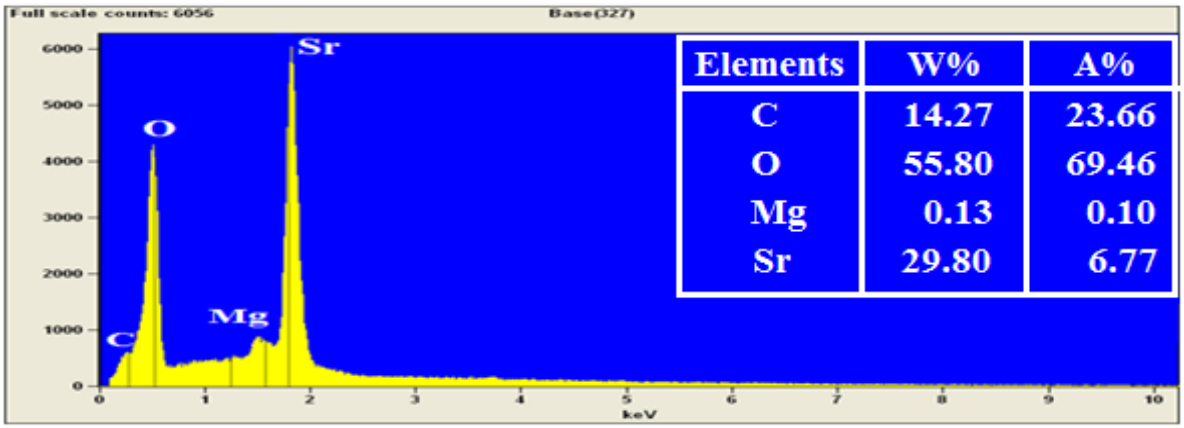

Fig-9: EDAX graph of MST

3.4 FTIR spectral analysis

For both crystals, the observed absorption bands/peaks and their respective assignments are reported in table 3. The assignments for the absorption bands/peaks of FTIR spectra of the grown pure ST crystals in the present study are in good match with the previously reported data [15]. Comparative FTIR spectra of ST and MST can be seen in figure 10.

Table-3: IR assignments for ST and MST crystals

Wave numbers in cm^{-1}		Peak assignments
ST	**MST**	
3449, 2896	3448, 2896	Water, OH stretch & C-H stretch
-	2362, 2344	Combination and overtone bands
1579	1578	C=O stretch
1443	1443	C-O stretch
1383	1382	C-OH in-plane bend
1309	1309	In-plane and out of C-H bend
1125	1125	O-H deformation out of plane
1085	1085	C-O(H) stretch
933	-	C-C stretch
630, 533, 482	630, 532, 483	Metal-Oxygen bonding

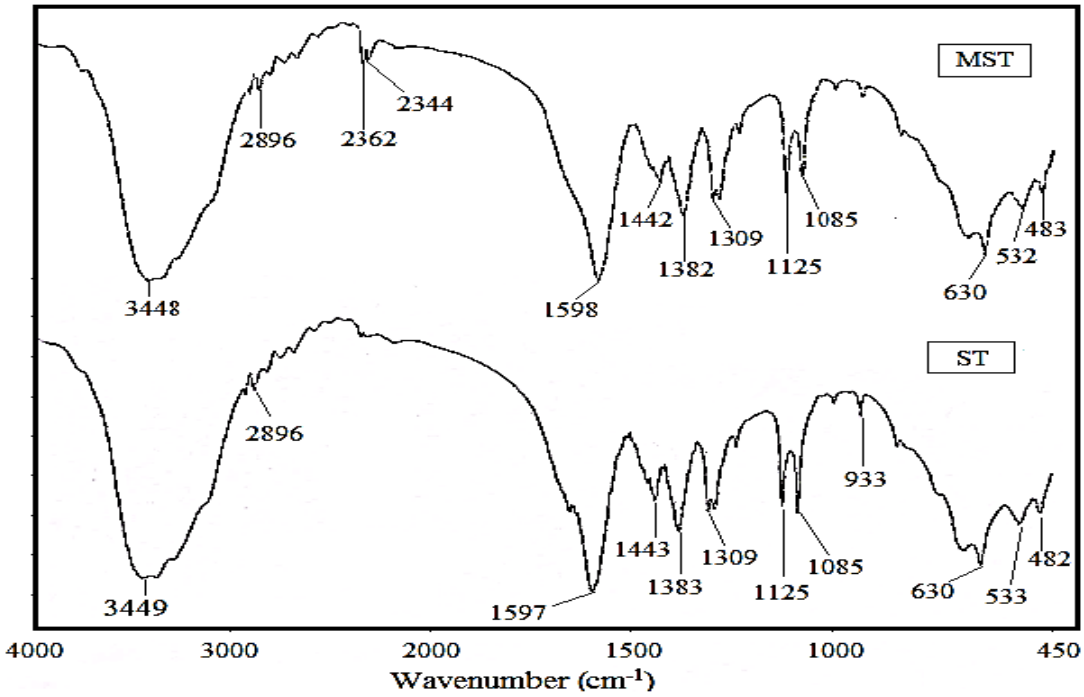

Fig-10: FTIR spectra of ST and MST

3.5 UV-Vis-NIR spectral analysis

The UV-Vis absorption patterns obtained are shown in figure 11 & 12. Both the spectra show wide transmission window in the visible region which enables them to be potential candidates for opto-electronic application. The presence of low cut off wavelength and the wide optical transmission window range are the most desirous properties of materials possessing NLO activity. The low absorption in the visible region confirms the suitability of the grown crystals for NLO applications.

From the lower cut off wavelength, band gap energies were calculated using the formula:

$$\mathbf{E = hv = hc/\lambda} \quad \text{..... (4)}$$

Where, $h = 6.623 \times 10^{-23}$ Js, $c = 3 \times 10^{8}$ ms^{-1}.

The observed cut off wavelengths and the obtained band gap energy values in the present study are provided in table 4.

Table-4: Band-gap energies of ST and MST crystals

Sample	Cut-off wavelength λ (nm)	Band-gap Energy E (eV)
ST	248	5.007
MST	240	5.174

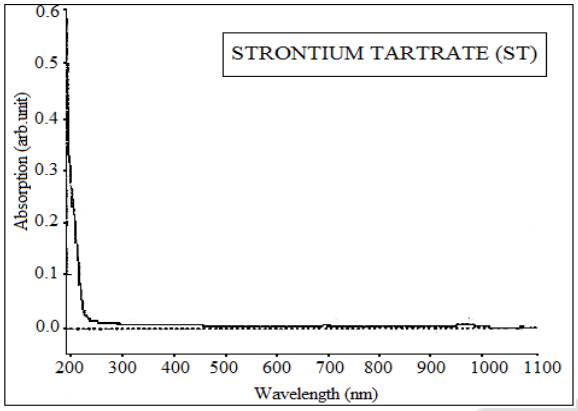

Fig-11: UV-Vis spectrum for ST

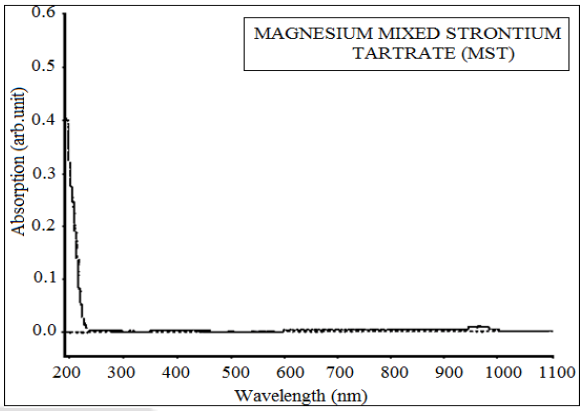

Fig-12: UV-Vis spectrum for MST

3.6 Structural analysis

From the obtained scanned images, thick and thin growth layers on the crystal surfaces were observed in both crystals as shown in figures 13 & 14, which indicate that both crystals were grown by layer deposition technique. On higher magnification, some plate like microstructures attached on the crystal surface was observed in the scanned images of powdered samples of both crystals as shown in figures 15 & 16. Here, for pure ST and mixed MST crystals, the secondary crystal growth on the (100) face of primary crystal were observed, which indicates that the surface of a crystal sometimes work as elegant centers for initiation of growth layers. Also, gel particles attached with crystal particle were seen in some crystal images as shown in figures 17 & 18, which indicate that the crystals were not properly cleaned while removing from the crystallization system.

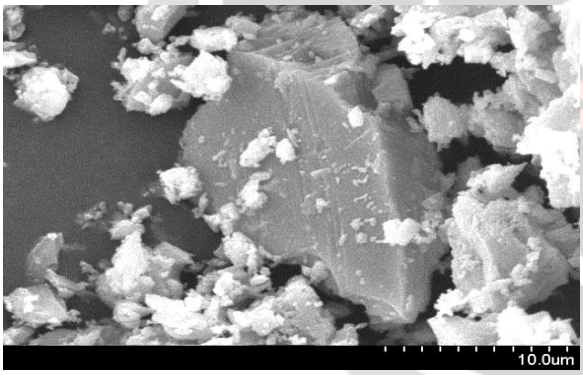

Fig-13: Growth layers on ST

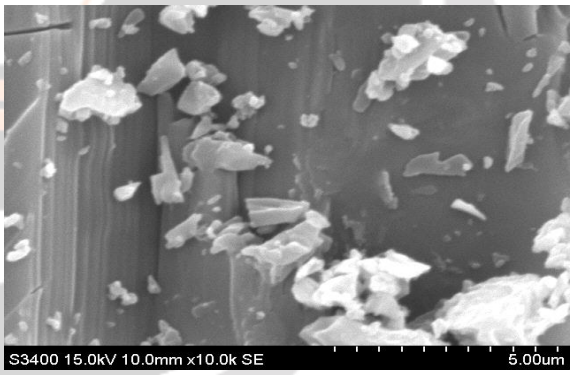

Fig-14: Growth layers on MST

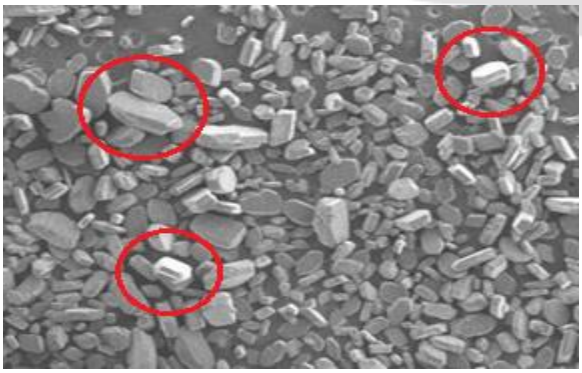

Fig. 15: Secondary crystal growth on ST crystal

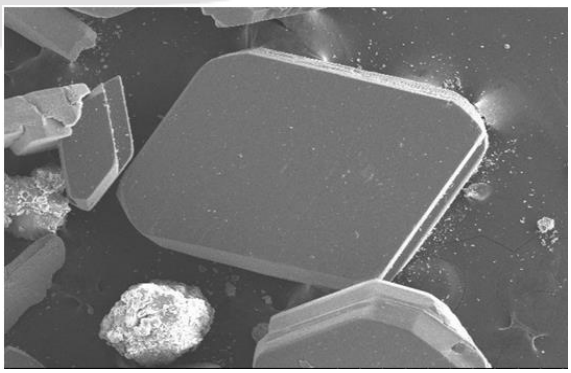

Fig. 16: Secondary crystal growth on MST crystal

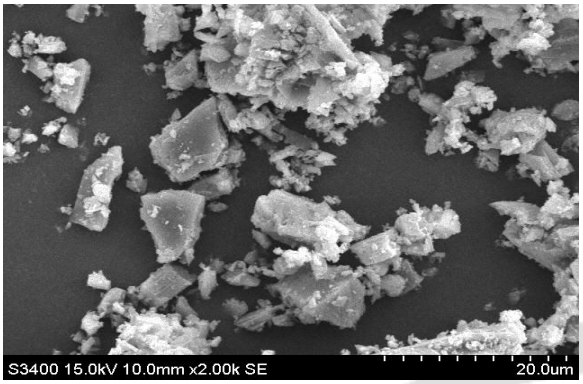

Fig-17: Presence of gel particles in ST

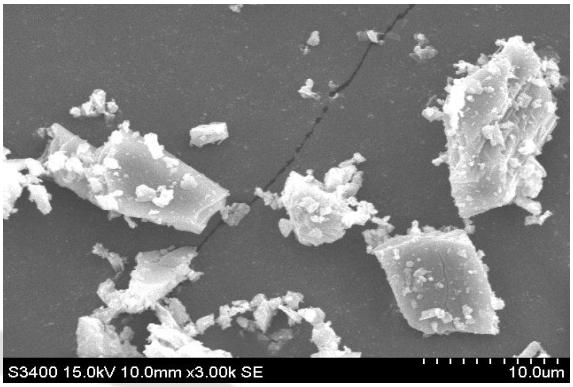

Fig-18: Presence of gel particles in MST

4. CONCLUSION

Pure strontium tartrate and magnesium mixed strontium tartrate crystals have been grown in silica gel at ambient temperature. It was found from experiment that the addition of dopant increased the nucleation time with reduction in crystal size. From PXRD spectra, the sharp peaks declare the perfect crystalline nature of crystals. All crystals were found to have orthorhombic crystal system. From EDAX spectra, the presence of all the expected elements was confirmed. From FTIR spectral analysis, the presence of water of crystallization and related groups and bonds were confirmed. It is inferred from the UV-Vis-NIR spectrum that both crystals have low absorbance in the entire visible & NIR regions and show maximum absorption at UV region. From these it can be considered as promising nonlinear optical (NLO) crystals. The scanned images show these crystals to be grown by layer deposition.

5. ACKNOWLEDGEMENTS

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