

Structure, surface morphology and thermal study of strontium tartrate crystals grown in silica gel by single diffusion method

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ABSTRACT

In this analysis, crystals were grown by adopting simple gel technique by single diffusion method. Effect of various parameters like gel pH, gel aging, gel density and concentration of reactants on the growth of these crystals was studied. Crystals having different morphologies and habits were obtained. Whitish, pale yellow semi-transparent crystals of strontium tartrate were obtained. Maximum size of grown crystals is 6mm x 6mm x 3mm. The grown crystals were characterized by XRD, SEM, EDAX, thermogravimetry and UV Visible spectroscopy. The crystal structure is monoclinic and crystalline perfection of the crystals is extremely good. SEM image showed plate like morphology and EDAX study revealed that grown crystals are of strontium tartrate, indeed. UV-Visible spectrum indicates that strontium tartrate crystals have non linear optical property as it has sufficient transmission in the entire UV region. The absorption coefficient is high at lower wavelength and the wide transparency from 270 nm suggested their suitability for second and third harmonic generations.

Keywords: Crystal growth; X-ray diffraction; Scanning electron microscopy, SEM; Energy dispersive X- ray spectroscopy, EDAX; Thermo gravimetric analysis/Differential thermal analysis, TGA/DTA; UV-Visible spectroscopy.

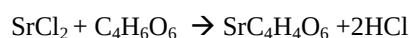
INTRODUCTION

Crystals are the pillars of modern technology. Crystals of different materials have several applications. Hence industry has taken interest in the field of crystal growth. In early days, mineral crystals were available to meet requirements, but now the natural source is found to be quite inadequate. To solve this acute problem, the synthesis of the material in the form of crystal is necessary. Hence production of artificial crystal is now considered as a “new agriculture”. The increase in crystal growth activity throughout the world is reflected in the national and international conferences on crystal growth and establishment of national and international organizations of crystal growth [1-2]. Single crystals and polycrystalline form of materials of great interest, from both solid state sciences as well as technological point of view have grown by several researchers by gel technique [3]. For growing single crystals of substances which are sparingly soluble in water and decompose before their melting point, gel method is a promising technique [4]. In the recent years, the technology and science of crystal growth has advanced rapidly for the development of new nonlinear optical materials. The desire to utilize the properties of these materials in applications such as telecommunications, optical data storage and optical information processing has created need for new materials with very large second order susceptibilities [5-7]. Tartrate materials are used mostly, for their dielectric, ferroelectric, piezoelectric or nonlinear optical properties [8-9]. Hence they are used in transducers, linear and nonlinear mechanical devices [10-11]. Nonlinear optics is expected to play a major role in the technology of photonics. Reflection, refraction, diffraction and absorption are commonly observed interactions of light with matter. During these processes the optical properties of the material such as refractive index and absorption coefficient remain unaffected by electromagnetic radiation. When the light used is in the form of powerful laser

beams, some materials manifest marked changes in their optical properties as a result of interaction with the strong electromagnetic field of the radiation. This interaction effects a modification of the frequency phase or amplitude of the light transmitted through the material. Such interactions arising out of multiphoton effects are known as nonlinear optical (NLO) processes and the materials in which such processes can be carried out efficiently are called NLO materials [12-14].

MATERIALS AND METHODS

Good quality crystal can be grown in gels in a variety of ways; the single diffusion method was employed in the present work for the growth of strontium tartrate crystals. The growth process involves the diffusion of strontium chloride solution into a gel in which tartaric acid is impregnated beforehand. The silica gel is used as a growth medium. The chemicals used for growth of tartrate crystal were tartaric acid, strontium chloride, and sodium meta silicate. All chemicals were of AR grade. The crystallization apparatus consist of borosilicate glass test tubes of length 25 cm and diameter 2.5cm placed vertically on wooden stand. The tartaric acid and strontium chloride solution is prepared by dissolving these compounds in an appropriate amount of distilled water to give the required molarities. Gels of required specific gravity were prepared by adding a calculated amount of redistilled water to the solution of sodium meta silicate. A stock solution was kept ready for doing further experiments. Tartaric acid solution of particular strength was taken in a 100 ml beaker and sodium meta silicate solution of suitable gravity was added drop wise using a tephlon cock burette, constantly stirring the solution in a beaker by magnetic stirrer. Stirring is done to avoid the excessive local ion concentration which may otherwise cause premature local gelling and make the final medium inhomogeneous and turbid. Here tartaric acid acted as a lower reactant. The solution after noting pH values, being allowed to fall along the side of a test tube without giving chance for the formation of the bubbles. Test tubes were then closed with rubber corks or cotton to prevent evaporation and contamination of the exposed surface of the gel by dust particles of the atmosphere. The solution was found to be strongly dependent on pH and room temperature. After confirming the gel setting, an aqueous solution of strontium chloride (0.2 to 1.2M) 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. The strontium ions diffuse through the narrow pores of the gel to react with tartrate ions, which are present in the gel as lower reactant giving rise to the formation of strontium tartrate crystals [15-21]. The following reaction takes place in the gel medium.



RESULTS AND DISCUSSION

Different parameters such as concentration of reactants, pH of gel, gel setting time, gel aging time, concentration programming etc. have considerable effect on growth rate. The size of these crystals varied from 6 – 7 mm. Few diamond shaped crystals were obtained. Some crystals were whitish and few were pale yellow. Most crystals were semi-transparent. Higher concentration of supernatant increased the nucleation density. Perfect crystals were obtained for pH values, between 4 and 5. It was found that strontium tartrate does not nucleate at pH values less than 3. Most of the crystals were larger in size and few crystals close to the gel solution interface were smaller in size. The crystals growing deep into the gel were larger in size Density of nucleation was reduced and size of the crystals growing deep into the gel was increased by concentration programming. Aging period reduced the nucleation density and improved the quality of the grown crystals. The various optimum conditions for the growth of crystals were obtained and are reported in table 1. Figure1 shows strontium tartrate crystals inside test tube under varied concentration o f reactants. Figure 2 shows few pyramidal shaped and few diamond shaped crystals. Figure 3 shows single crystal of strontium tartrate in magnified form.

Table 1: Optimum growth conditions

Various process parameters	Optimum conditions
Density of sodium meta silicate	1.04 gm/cm ³
Concentration of Tartaric acid	1.2 M
Volume of Tartaric acid	5 ml
Volume of sodium meta silicate	17 ml
pH of gel	4.4
Concentration of Strontium chloride	1.2 M
Temperature	Room temperature
Gel setting time	48 hrs
Gel aging time	36 hrs
Period of crystal growth	1week



Figure 1. Optical photograph showing strontium tartrate crystals in test tube



Figure 2. Optical photographs illustrating varied morphologies of Strontium tartrate crystals grown under different growth conditions

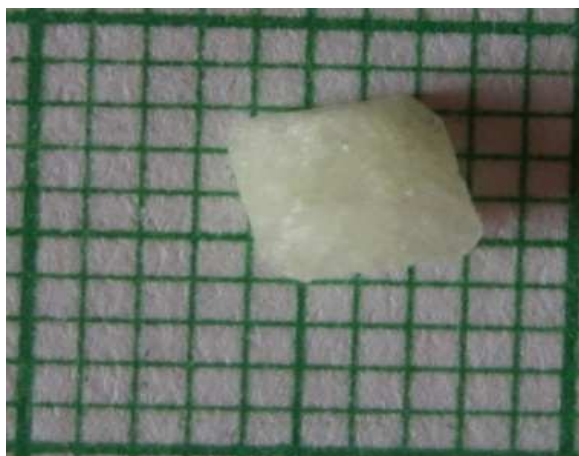


Figure 3. Strontium tartrate crystal in magnified form

Characterization

Strontium tartrate crystals were characterized by XRD, SEM, EDAX, TGA/DTA, UV.

3.1 X-ray powder diffractogram

The crystals of strontium tartrate were carefully removed, dried and powdered. X-ray powder diffractogram (XRD) recorded with $\text{CuK}\alpha$ radiation ($1.5418\text{\AA}$) is shown in figure 4. The observed d-values and hkl were computed. The computer program POWD (an interactive powder diffraction data interpretation and indexing program version 23.0550), was used to calculate 'd' values. The 'd' values of grown material obtained from the XRD matched well with the values obtained by POWD Program. The observed peaks in diffractogram show that the strontium tartrate

crystal has monoclinic structure, $a \neq b \neq c$, $\alpha = \gamma = 90^\circ \neq \beta$. The data observed from powder diffraction is well correlated with data available in the literature [22-23]. Table 2 shows the unit cell parameters.

Table 2: Unit cell parameters

System	Monoclinic
a	7.55Å
b	10.06Å
c	6.47Å
β	102°

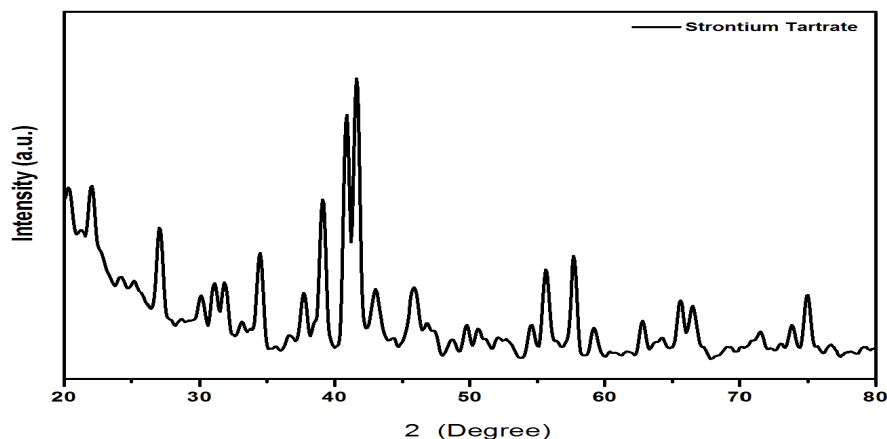


Figure 4. XRD of Strontium Tartrate crystals

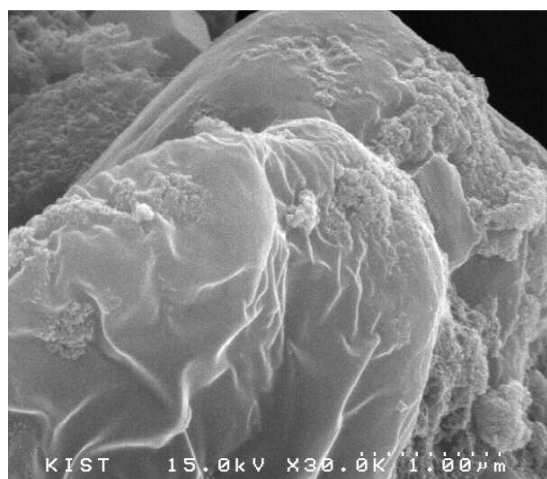


Figure 5. (a) SEM image of Strontium tartrate crystal

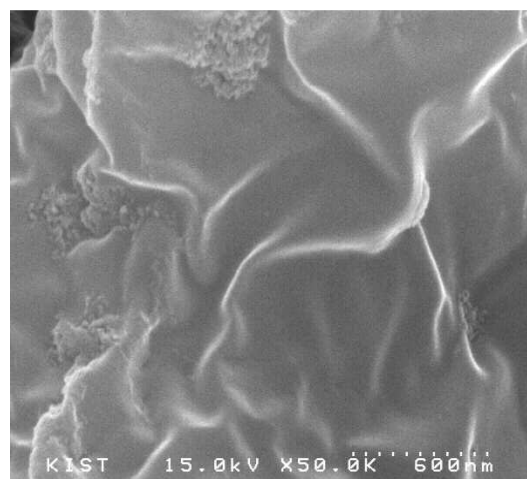


Figure 5. (b) Magnified SEM image of Strontium tartrate crystal

3.2. Scanning Electron Microscope (SEM)

In the present work powdered sample of strontium tartrate crystals was examined by using SEM technique. The study of the surface of the crystal gives valuable information about its internal structure. Figure 5(a) illustrates SEM photographs of crystals of strontium tartrate crystal. An enlarged SEM image is shown in figure 5 (b). This technique combines the resolution and analytical power with ease of operation. Images can be formed from a very wide range of materials, from metals to ceramics, semiconductors to polymers. These materials can be examined with low energy secondary electrons, with high energy back scattered electrons or with other emission such as light, heat and sound. The high depth of field of the SEM images makes it especially suitable for the study of the fracture and complex microstructure such as those found in composite materials [24-30]. Figure 5(a, b) shows plate like crystal morphology. Boundaries of the plate like structure are not very sharp. These crystals are grown by layer deposition. Thick and thin layers are seen in figure. The individual plates of samples are flat and the some plates with the sharp edges were observed. On some plates further plate like growth was observed. The presence of small grain structures, along with the plate like microstructures; interlocked with each other is observed. On higher magnification plate like structure is clearly seen. The average particle size measured is to be 1.0 µm to 600nm as shown in figure 5 (a), (b).

3.3. Energy dispersive X- ray spectroscopy (EDAX)

Figure 6 shows EDAX spectrum of strontium tartrate crystals. The peaks show the presence of oxygen, hydrogen, carbon and strontium in the crystals. This clearly indicates that the crystals are of the strontium tartrate indeed. Table 3 shows the elemental and atomic percentage of the elements O, H, C and Sr. It was observed that the atomic % of Sr, O, H and C are in good agreement with stoichiometrically expected atomic % 10.69, 30.88, 35.65 and 22.65 respectively [31].

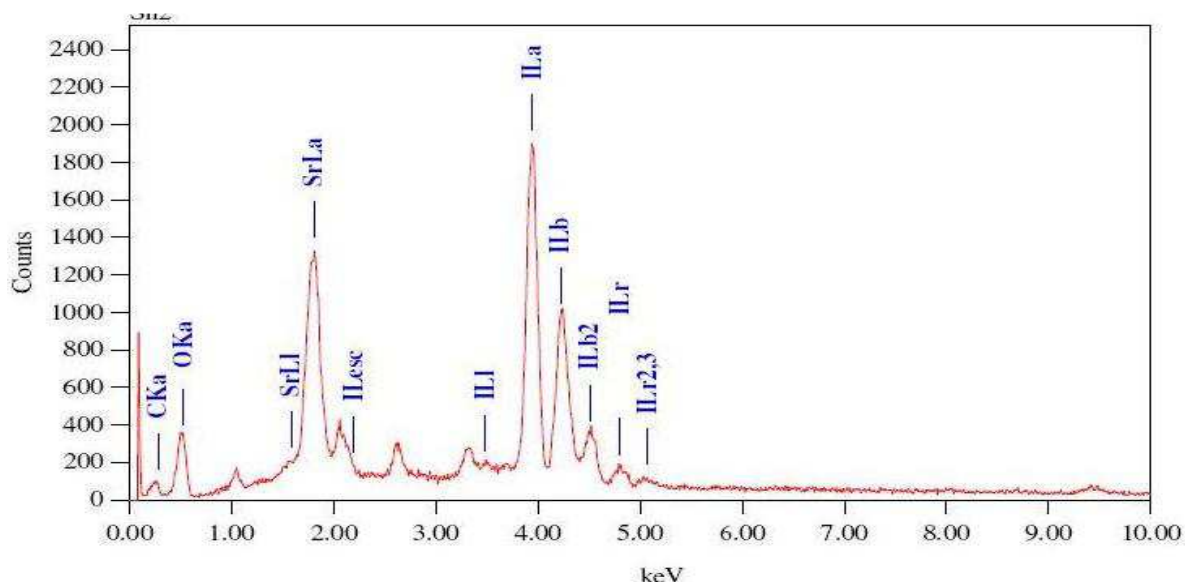


Figure 6. Energy dispersive spectrum of Strontium tartrate crystal

Table 3: ZAF Method Standard less Quantitative Analysis

Sr. No	Element	Mass %	At. %
1	Sr	15.04	10.69
2	O	7.93	30.88
3	H	72.69	35.65
4	C	4.39	22.65

3.3. Thermal analysis

Strontium tartrate crystals were characterized by TGA and DTA analysis to determine thermal stability.

3.3.1 Thermogravimetry Analysis (TGA)

The TGA curve for strontium tartrate crystal is shown in figure 7. The percentages of the weight loss in the different stages of decomposition of strontium tartrate are presented in table 4. There is a good agreement between the observed and calculated weight losses [32-33]. Strontium tartrate is water coordinated compound. Therefore, there is a possibility that this crystal may loose some of its water molecules while heating. TGA of strontium tartrate showed clearly four stages of decomposition as expected, 1) Dehydration. 2) Decomposition of strontium tartrate to strontium oxalate. 3) Decomposition of strontium oxalate to strontium carbonate. 4) Decomposition of strontium carbonate to oxides of strontium. Observations are known from the literature on Rochelle salt and rare earth tartrates [34].

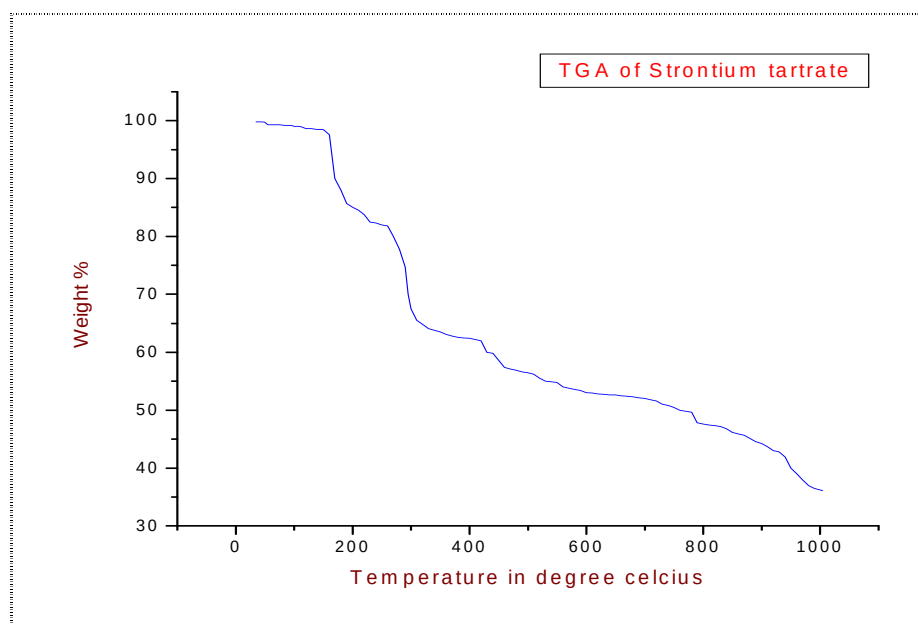


Figure 7. TGA curve for strontium tartrate

The first stage of decomposition (45°C to 150°C) results in the elimination of water molecules. The second stage is between 150°C and 200°C , corresponds to the loss of water molecules and results in the formation of anhydrous strontium tartrate. In the third stage of decomposition is between 200°C and 285°C , the anhydrous strontium tartrate reduces to strontium oxalate. In fourth stage of decomposition in the temperature range from 285°C to 310°C , the material loses CO molecules. In the fifth step, between 310°C and 890°C , decomposition further gives a stable intermediate compound as strontium carbonate. The last step is between 890°C and 1004°C , results in further decomposition into oxide of strontium. Table 4 indicates the results of decomposition process of strontium tartrate crystals.

Table 4: TGA data of strontium tartrate

Stage	Temperature range $^{\circ}\text{C}$	Observed % weight loss	Calculated % weight loss
I	45 – 150	2.1	1.9
II	150-200	14.9	14.1
III	200-285	3.2	3.0
IV	285-310	17.9	18.0
V	310-890	19.1	19.0
VI	890 -1004	9.1	9.0

3.3.2 Differential Thermal Analysis (DTA)

The DTA curve for strontium tartrate gel grown crystals is shown in the figure 8. In DTA curve, we observed three endothermic peaks at 185°C , 590°C , and 920°C , and exothermic peaks at 280°C and 430°C . The endothermic peaks are due to the decomposition of hydrated strontium tartrate into anhydrous strontium tartrate. In the first stage of decomposition, peak at 185°C is attributed to the loss of first water molecules followed by another endothermic peak at 590°C which corresponds to loss of more water molecules. The first exothermic peak at 280°C is attributed to the loss of carbon molecule and is attributed to the decomposition of anhydrous strontium tartrate into strontium oxalate. The exothermic peak at 430°C is due to the reduction of strontium oxalate into strontium carbonate. This is attributed to the loss of 2CO_2 . The endothermic peak at 920°C is due to further decomposition into oxide of strontium. These endothermic peaks observed in the DTA curve correspond to the total weight loss of water molecule in the TG curve.

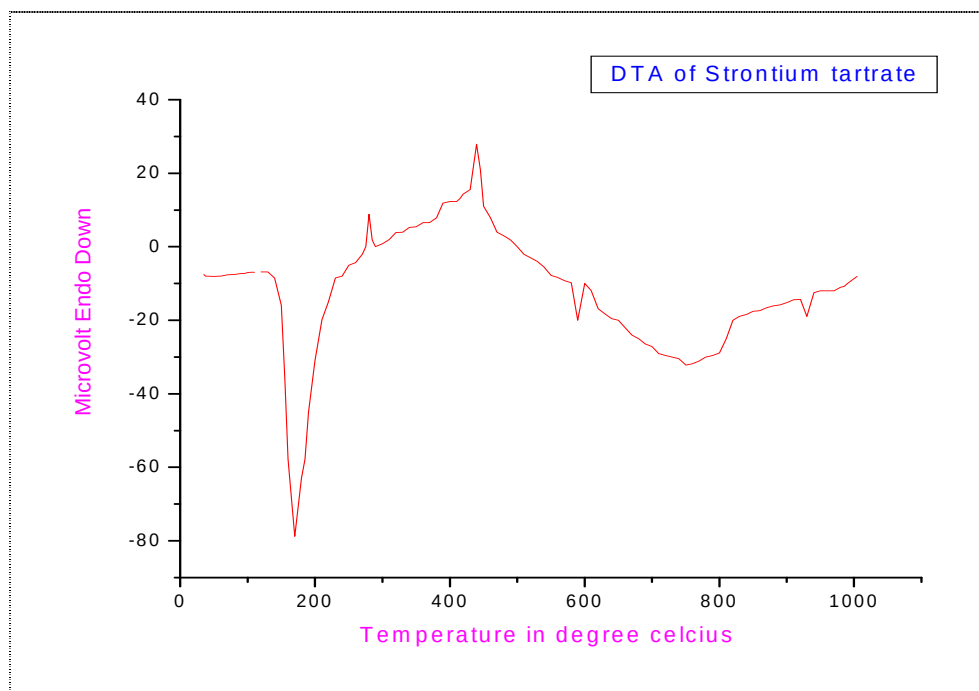


Figure 8. DTA curve for strontium tartrate

3.4 UV-VIS Spectrophotometer

Absorption spectra of strontium tartrate crystals were recorded over the wavelength range 200nm – 450nm. Figure 9 shows UV absorption spectrum of strontium tartrate crystals. From the spectrum, it has been inferred that strontium tartrate crystals have sufficient transmission in the entire UV-visible region. The absorption coefficient is high at lower wavelength and the wide transparency from 275 nm suggests their suitability for second and third harmonic generations and their non linear optical nature [35-41]. The band gap energy of the strontium tartrate crystals with the obtained wavelength is calculated using the following simple conversion equation;

Band gap energy (eV) = $1240/\text{wavelength (nm)}$.

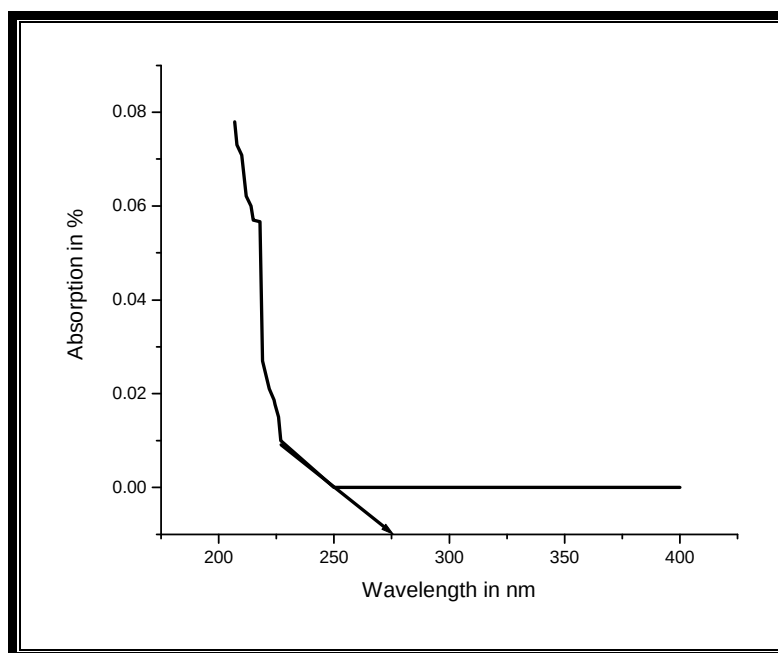


Figure 9. Optical absorption spectrum of strontium tartrate

Band gap energy is presented in the table 5. From table 5 it is observed that gel grown strontium tartrate crystals, have wide band gap energy.

Table 5: Band gap energy of strontium tartrate

Crystal	λ (nm)	Band gap energy (eV)
Strontium tartrate	275	4.50

CONCLUSION

Crystals of strontium tartrate can be grown by single diffusion method using silica gel as growth medium. Transparent, semitransparent, well isolated crystals of strontium tartrate were grown at 1.04 gm/cm^3 density and pH of 4.4. The average length of the grown crystals was found to be 6-7 mm. X-ray diffractogram reveals that strontium tartrate crystal has monoclinic structure, $a \neq b \neq c$, $\alpha = \gamma = 90^\circ \neq \beta$. The SEM studies suggested 2-dimensional, layer deposition growth. EDAX studies reveals that grown crystals are strontium tartrate indeed. Water of crystallization present in grown crystals is confirmed by TGA and DTA. UV-Visible absorption spectrum clearly indicates that strontium tartrate crystals have sufficient transmission in the entire UV- visible region. High absorption coefficient at lower wavelength and the wide transparency from 275 nm suggested their suitability for second and third harmonic generations and confirmed non linear optical nature of the substance.

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