

Synthesis and characterization of gel-grown cobalt tartrate crystals

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Abstract. Crystals of cobalt tartrate are grown from the gel using chemical reaction method. The functional groups are found from Fourier transform infrared spectroscopy (FTIR). The OH stretching mode owing to water, carbonyl group, CH stretching modes and metal–oxygen stretching are identified. The unit cell dimensions, interaxial angles and unit cell volume are found from powder X-ray diffraction studies (XRD) which show the orthorhombic nature of the crystal. The magnetic study is used to find the magnetic susceptibility and magnetic moment of the grown crystal. It reveals the magnetic nature of the crystal. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are done to find the thermal properties of the crystal which manifest the water of hydration in the crystal. The variation of dielectric constant with respect to the applied frequency shows the polarization property of the crystal. The AC conductivity is increased proportionally with increase in frequency. The reverse nature is found for the AC resistivity. The nature of the composition of the crystals affects the dielectric properties.

Keywords. Gel growth; cobalt tartrate; Fourier transform infrared spectroscopy; powder X-ray diffraction studies; magnetic studies; thermal analysis; dielectric properties.

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1. Introduction

Crystals are the unknown pillars of modern technology. The present technological developments depend greatly on the availability of suitable single crystals, whether it is for semiconductors, optical devices, or for telecommunications, etc. In spite of great technological advancements in modern days, we are still nowhere with respect to the growth of several important crystals such as diamond, silicon carbide, gallium nitride and so on. Unless the science of growing these crystals is understood precisely, it is impossible to grow them as large single crystals that can be used in modern industry. There is great

demand to grow large single crystals with high purity and symmetry. These crystals find applications in electronics, optics and industries. A series of pure and mixed crystals have been grown by several researchers with the aim of identifying new materials for practical and industrial purposes [1–5]. Compounds of tartaric acid find several practical applications in science and technology because of their interesting dielectric, ferroelectric, piezoelectric and non-linear optical properties [6–8]. The art of growing crystals in gel is simple, cheap and crystals can be grown at ambient temperature. But the challenges and opportunities in understanding the growth features and morphology of grown crystal remain there. Crystals of great interest from solid-state science as well as technological point of view have been reported by many investigators using the gel method [9–11]. The chemical reaction, chemical reduction, reduction of solubility and complex dilution are the popular methods for growing crystal in gel. Gel media prevent turbulence and help in the formation of crystals by providing a framework of nucleation sites. These media are unique due to their characteristics of suppression of nucleation centre. The convection is absent in the gel media and it is an alternative method for those substances which are sparingly soluble in water. The crystals grown by this technique have high degree of perfection. The method is extremely simple and inexpensive. Potassium dihydrogen phosphate and ammonium dihydrogen phosphate were grown by the reduction of solubility method. A few researchers reported the growth of crystals of strontium tartrate tetrahydrates and trihydrates based on their second harmonic generation characteristics [12–15], crystals of lithium-doped strontium tartrate on the surface of the gel [16], crystals of pure and nickel-doped strontium tartrate tetrahydrates in silica [17] and crystals of cadmium tartrate in silica hydrogel [18].

Cobalt tartrate crystals have been grown by gel technique using sodium metasilicate as the medium with the aim of identifying new materials for practical and industrial purposes. Cobalt tartrate crystals have several applications in semiconductors, medicine, optics, gold industries, veterinary drugs, etc. Hence, it was thought worthwhile to undertake investigations on the growth of cobalt tartrate crystals and their characterization by different methods. Spherulitic crystals with dimensions of several mm can be grown in a period of 3 to 4 weeks. It is pertinent to point out here that, so far, no work has been reported on the growth of cobalt tartrate in the gel medium. We report here the growth of cobalt tartrate in gel medium for the first time. The growth procedure and its various characterizations are discussed in detail here. Fourier transform infrared spectroscopy (FTIR) was used to find the functional groups, the unit cell dimensions, interaxial angles and unit cell volume were found from powder X-ray diffraction studies (XRD), magnetic study was used to find magnetic nature of the crystal, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were done to find the thermal properties of the crystal and dielectric studies were done to find dielectric properties.

2. Experimental method

Cobalt tartrate shows poor solubility in water and hence it was thought worthwhile to grow it by chemical reaction method using the gel technique. The crystallization apparatus for the growth of cobalt tartrate consists of borosilicate glass tube of 20 cm length and 2.5 cm diameter cm placed vertically on a plastic stand. Silica gel was prepared by

acidifying pure sodium metal silicate (Na_2SiO_3) of specific gravity 1.04 g/cm^3 , with tartaric acid of a concentration in accordance with the requirement of a particular pH value. The tartaric acid solution was added slowly to sodium metasilicate solution with continuous stirring to avoid any local ion concentration which would otherwise cause premature local gelling making the final solution inhomogeneous. Here, tartaric acid acts as a lower reactant. Fixed quantities of gel solution with desired value of pH were then transferred to several test tubes. The test tubes were sealed with cotton to prevent fast evaporation and contamination of the exposed surface of the gel. The solution was then allowed to set. The time taken by the gel to set was found to be strongly dependent on the pH. Gel with high pH value takes lesser time to set than gel with low pH value. After confirming the gel setting, an aqueous solution of cobalt nitrate of a particular molarity was poured along the sides of the test tube, to avoid breaking the gel surface. Here, cobalt nitrate acts as the upper reactant. Slow diffusion of the upper reactant ions through the narrow pores of the silica gel leads to reaction between these ions and the ions present in the gel as lower reactant.

The following reaction was expected in the gel:



The grown cobalt tartrate crystals are dark brownish with spherical shape. The grown crystals are shown in figure 1.

3. Results and discussion

3.1 FTIR spectroscopy

In this investigation, KBr pellet method was used. The instrument used was Thermo Nicolet Avatar 370. The spectrum was recorded in the region $4000\text{--}400 \text{ cm}^{-1}$ at room temperature. The infrared radiations promote transitions in a molecule between rotational and vibrational energy levels of the ground electronic energy state [19].

The FTIR spectra of cobalt tartrate crystals are shown in figure 2. The observed bands with intensity and their vibrational assignments are given in table 1. The peak observed at 3320.7 cm^{-1} is due to OH stretching mode. The bands at 2649.9 cm^{-1} and 2578.5 cm^{-1} are attributed to the CH stretching mode of tartaric acid. The strong peak at 1627.9 cm^{-1} is due to C=O stretching mode of vibration. The band at 1349.9 cm^{-1} is attributed to $\lambda(\text{C}=\text{O}) + \delta(\text{O}-\text{C}=\text{O})$. The absorption peak at 1314.2 cm^{-1} is assigned to OH plane bending. The strong peak at 1114.1 cm^{-1} is attributed to $\delta(\text{C}-\text{H}) + \pi(\text{C}-\text{H})$ modes of vibration [20, 21]. The band observed at 607.8 cm^{-1} is attributed to CO_2 deformation. Absorption wave numbers below 500 cm^{-1} are assigned for Co–O mode or metal–oxygen stretching.

3.2 Powder XRD

The grown crystals were characterized by powder X-ray diffraction using a Bruker D8 Advance, Germany instrument with $\text{CuK}\alpha$ radiation (1.5406 \AA). The sample was scanned in the range of 15° to 90° at the scan rate of 1° min^{-1} . The powder X-ray diffractogram

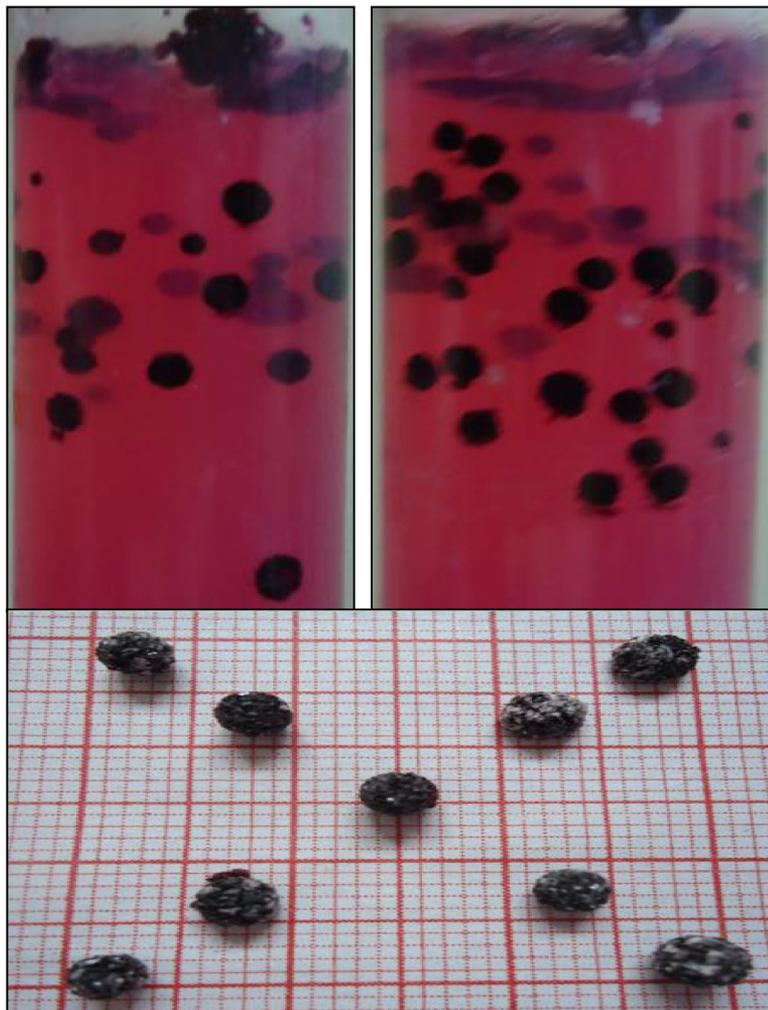


Figure 1. Crystals of cobalt tartrate grown in gel at room temperature.

of cobalt tartrate crystals is shown in figure 3. The crystallinity of the crystal is quite clear from the diffractogram because of the occurrence of sharp peaks at specific Bragg's angles [22]. The indexed XRD data for cobalt tartrate crystals are shown in table 2. The indexing was done and confirmed using the JCPDS file (CAS:66904-98-1). The unit cell dimensions and interaxial angles were found out from the crysfire software. Calculation of cell parameters reveals that the crystal belongs to orthorhombic crystal system having space group $P2_12_12_1$. The unit cell dimensions of the cobalt tartrate crystals are found to be $a = 9.9873 \text{ \AA}$; $b = 7.8973 \text{ \AA}$; $c = 10.9832 \text{ \AA}$ and the interaxial angles are $\alpha = \beta = \gamma = 90^\circ$.

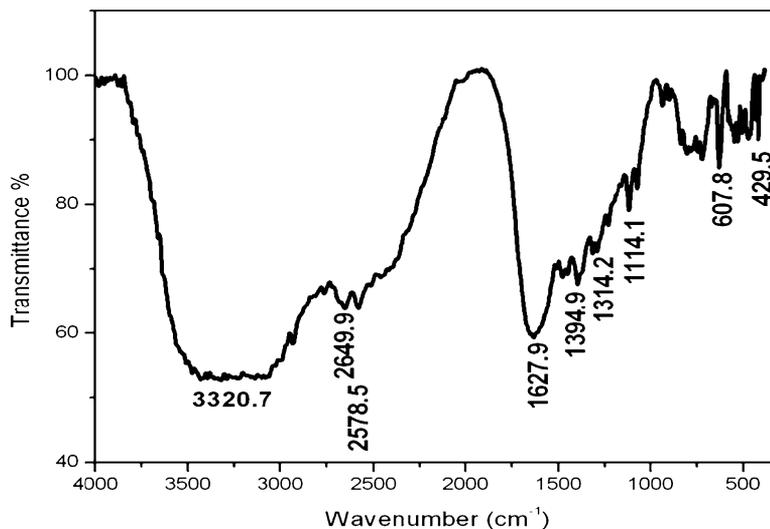


Figure 2. FTIR spectrum of cobalt tartrate crystal.

3.3 Magnetic properties

The cobalt tartrate crystals were finely ground, crushed and the resulting powders were packed in a Gouy tube of known magnetic susceptibility. These experiments were repeated five times and the change in weight was calculated for the given magnetic field. The readings of Gouy balance was recorded when the values became steady. These values are given in table 3. The magnetic susceptibility of the sample was calculated using the equation $mg = (A/2)\chi H^2$, where m is the mass of the substance, A is the area of cross-section of the glass tube, H is the magnetic field between the pole pieces and χ is the magnetic susceptibility of the substance. A graph is drawn between m and H^2 and

Table 1. FTIR assignments for cobalt tartrate crystals.

Absorption in wave number (cm^{-1})	Assignment
3320.7	OH stretching
2649.9	CH stretch
2578.5	CH stretch
1627.9	C=O stretch
1349.9	$\lambda(\text{C}=\text{O}) + \delta(\text{O}-\text{C}=\text{O})$
1314.2	OH plane bending
1114.1	$\delta(\text{C}-\text{H}) + \pi(\text{C}-\text{H})$
607.8	CO_2 deformation
429.5	Metal-oxygen stretching

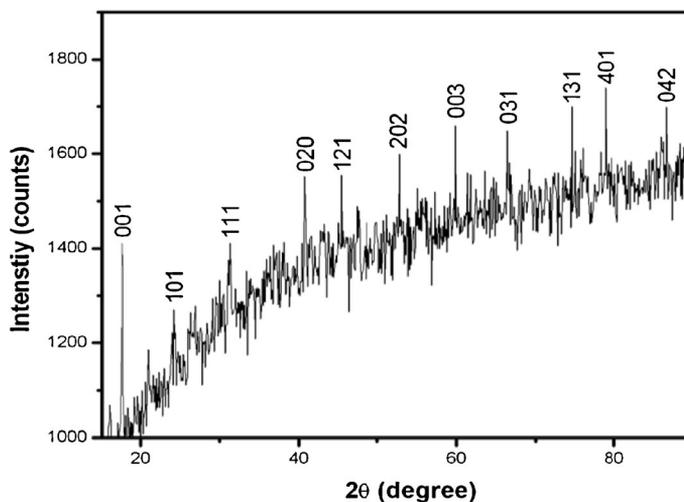


Figure 3. Powder XRD spectrum of cobalt tartrate crystal.

the slope gives $A\chi/2g$. Hence the susceptibility χ is calculated [23]. This is shown in figure 4. The slope is found out at the linear region of the graph. The magnetic moment μ of cobalt tartrate crystal was calculated using the formula $\mu = 2.828(x \times T)^{1/2}\text{BM}$, where T is the room temperature in Kelvin. The susceptibility and magnetic moment of the cobalt tartrate crystal were calculated to be 33.966×10^{-6} e.m.u. and 2.854 BM respectively.

3.4 Thermal analysis

Thermogravimetric analysis relies on a high degree of precision in three measurements: change in mass, temperature, and change in temperature. Therefore, the basic instrumental requirements for TGA are a precision balance with a pan loaded with the sample and

Table 2. Indexed XRD data for cobalt tartrate crystals.

<i>hkl</i>	2θ
001	17.0234
101	25.1238
111	32.0495
020	40.1108
121	45.9210
202	51.9818
003	60.0101
031	69.5212
131	73.0812
401	78.9023
042	86.9821

Table 3. Change in mass with respect to the applied magnetic field for cobalt tartrate crystals.

Name of the crystal	Magnetic field (kG)	Mass (kg)
CoC ₄ H ₄ O ₆	1	0.0523
	2	0.0519
	3	0.0515
	4	0.0511
	5	0.0507

a programmable furnace. The furnace can be programmed either for a constant heating rate, or for heating to acquire a constant mass loss with time.

The TGA curve for cobalt tartrate crystals is shown in figure 5. There are four stages of decomposition starting from room temperature of 40°C. The first stage of decomposition starts from 40°C and continues up to 200°C where the weight loss is about 25%. The second stage of decomposition starts from 200°C and continues up to 270°C where the weight loss is about 20%. The third stage of decomposition starts from 270°C and continues up to 700°C where the weight loss is about 12%. The fourth and the final stage of decomposition starts from 700°C and continues up to 1000°C where the weight loss is about 24%. Comparing the observed and calculated percentage weight losses suggests chemical formula for the given crystal to be CoC₄H₄O₆5H₂O and there is enough evidence for five water molecules in the crystal [24]. The TGA result for cobalt tartrate is shown table 4.

The DSC can be used to obtain the thermal critical points like melting point, enthalpy, specific heat or glass transition temperature of substances. The DSC analysis was done

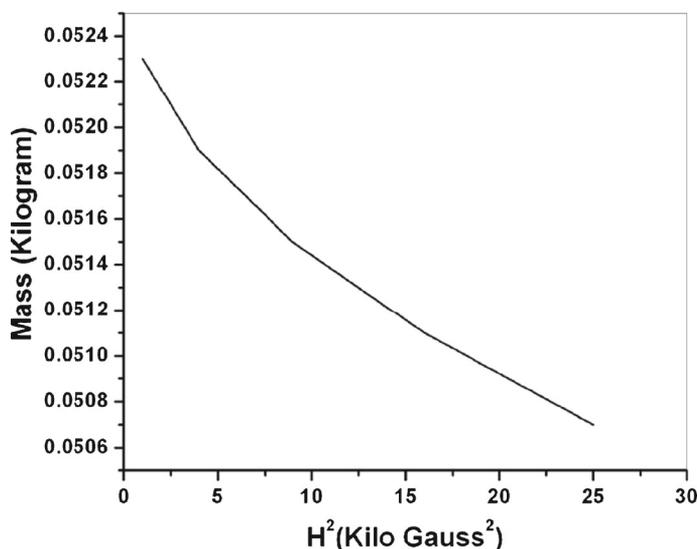


Figure 4. Graph between m and H^2 for cobalt tartrate crystal.

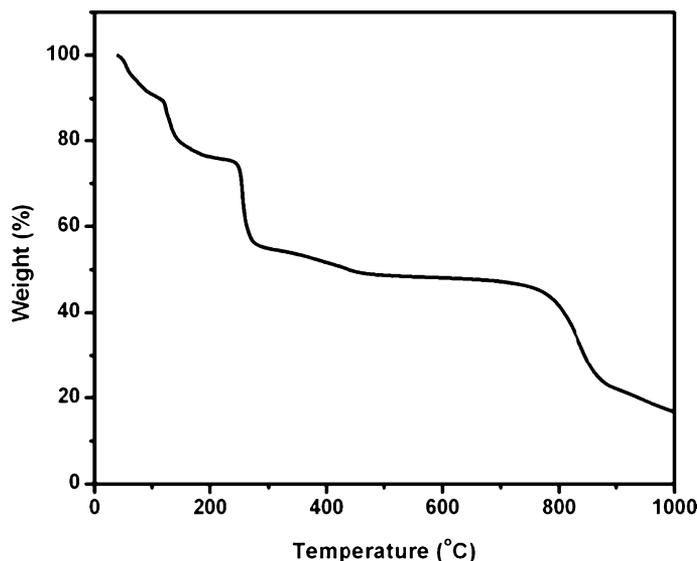


Figure 5. TGA curve for cobalt tartrate crystal.

between 40°C and 1000°C at a heating rate of 20°C min⁻¹ in nitrogen atmosphere. The DSC trace for cobalt tartrate crystal is shown in figure 6. The endothermic peaks at 120°C, 269°C, 384°C, and 825°C confirm various decomposition stages of the crystal under investigation.

3.5 Dielectric properties

The dielectric study of pure, Cu²⁺, Fe²⁺, and Mg²⁺-doped cadmium tartrate crystals were taken using HIOKI 3532-50 Icr histesteter instrument and a conventional sample holder (westphal). Silver paint was applied to the surfaces of the samples to ensure good electrical contact between the sample and the electrodes. Dielectric measurements were done in the frequency range 50 Hz–5 MHz at room temperature (305 K).

Figure 7a gives the plots of dielectric constant vs. frequency for cobalt tartrate crystals. From the plots it can be seen that the dielectric constant increases in the beginning but for most part of the graph it decreases as the frequency of the applied field increases. The electronic exchange of the number of ions in the crystals gives local displacement

Table 4. TGA result for cobalt tartrate crystals.

Name of the crystal	Stage	Temperature range (°C)	Weight loss(%)		Reaction
			Observed	Calculated	
Cobalt tartrate	I	40–200	25.1	24.7	CoC ₄ H ₄ O ₆ 5H ₂ O → CoC ₄ H ₄ O ₆
	II	200–290	20.1	19.87	CoC ₄ H ₄ O ₆ → CoC ₂ H ₄ O ₂
	III	290–700	12.0	12.13	CoC ₂ H ₄ O ₂ → CoCH ₃ O
	IV	700–1000	24.12	25.14	CoCH ₃ O → CoO

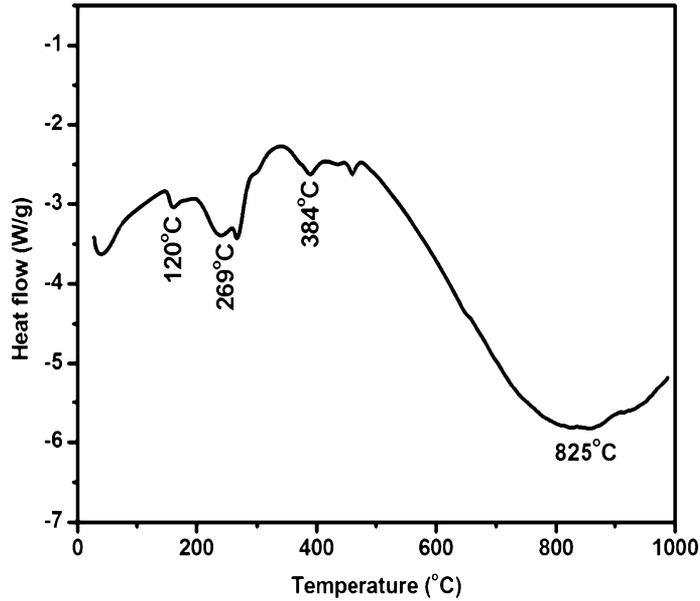


Figure 6. DSC trace for cobalt tartrate crystal.

of electrons in the direction of the applied field, which in turn gives rise to polarization. As the frequency increases, a point will be reached where the space charge cannot sustain and comply with the variation of external field. Hence, polarization decreases, which gives rise to diminishing values of dielectric constant. Thus, the crystal exhibits a smooth

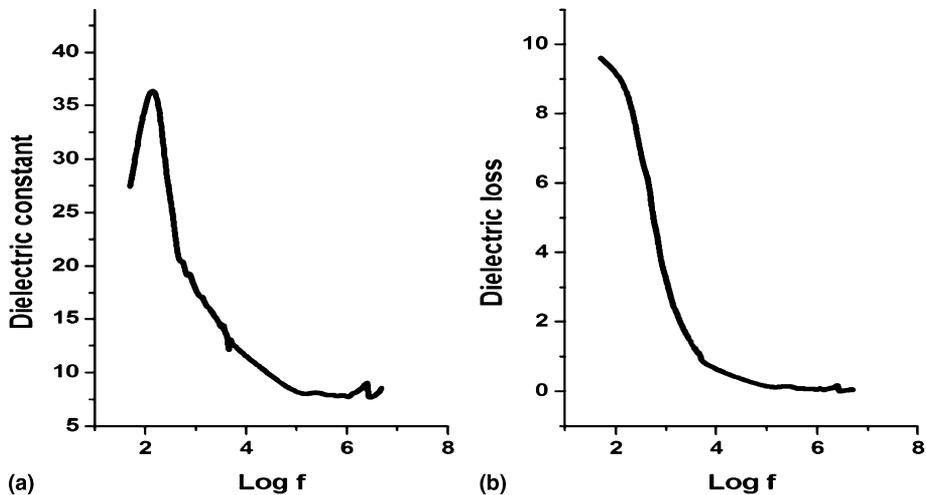


Figure 7. Plots of (a) dielectric constant vs. frequency and (b) dielectric loss vs. frequency.

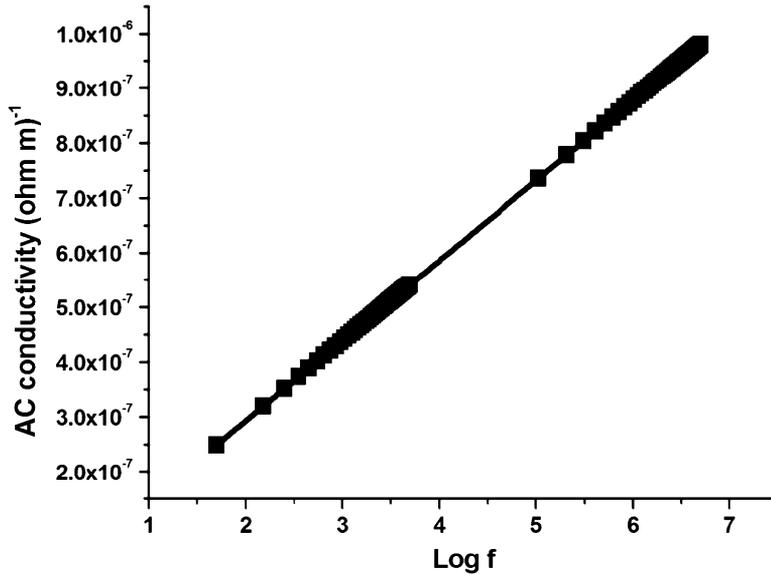


Figure 8. The plots of AC conductivity vs. frequency for cobalt tartrate crystals.

decrease in the value of dielectric constant with increase in frequency. This is in confirmation with the dielectric study of zinc tartrate crystals [25] and strontium tartrate crystals [26]. Similarly, figure 7b gives the variation of dielectric loss vs. applied frequency for

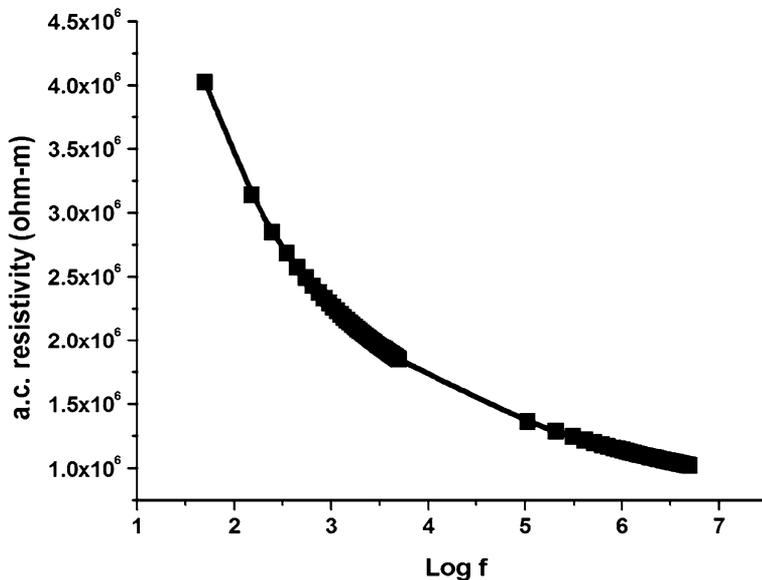


Figure 9. The plots of AC resistivity vs. frequency for cobalt tartrate crystals.

cobalt tartrate crystals. It is observed that in the beginning the dielectric loss decreases with increase in frequency and then it almost remains constant.

The variation of AC conductivity (σ_{AC}) and AC resistivity (ρ_{AC}) with frequency of the applied field is shown in figures 8 and 9, respectively. The AC conductivity is increased proportionally with increase in frequency. It is the reverse for the AC resistivity. The nature of the composition of the crystals affects the dielectric properties.

4. Conclusions

Crystals of cobalt tartrate were grown using sodium metasilicate gel by chemical reaction method for the first time. The functional groups such as OH stretching mode owing to water, carbonyl group, CH stretching modes and metal–oxygen stretching were identified using the FTIR spectroscopy. The unit cell dimensions, interaxial angles and unit cell volume were found out from powder XRD which revealed the orthorhombic nature of the crystal. The unit cell volume of the grown crystal was found to be 866.27 \AA^3 . The magnetic study was used to find the magnetic susceptibility and magnetic moment of the grown crystal. It revealed the magnetic nature of the crystal. TGA and DSC were taken to find the thermal properties of the crystal which showed the water of hydration in the crystal. The variation of dielectric constant with respect to the applied frequency showed the polarization property of the crystal. The AC conductivity was increased proportionally with increase in frequency. The reverse nature was found for the AC resistivity. The nature of the composition of the crystals affects the dielectric properties.

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References

- [1] S K Arora and B Chudasama, *Cryst. Res. Technol.* **41**, 1089 (2006)
- [2] L A Patil and P A Wani, *Cryst. Res. Technol.* **36**, 371 (2001)
- [3] B B Parekh, M J Joshi and A D B Vaidya, *Curr. Sci.* **93(3)**, 373 (2007)
- [4] D P Dobson and Jacobsen, *The American Mineralogist* **89**, 807 (2004)
- [5] X Jiayue, S Minli, L Baoliang, L Xinhua and W Anhua, *J. Crystal Growth* **292**, 391 (2006)
- [6] P Shenoy, K V Bangerla and G K Shivakumar, *Cryst. Res. Technol.* **45(8)**, 825 (2010)
- [7] M V John and M A Ittayachen, *Cryst. Res. Technol.* **36(2)**, 141 (2001)
- [8] B B Parekh, R M Vyas, S R Vasant and M Joshi, *Bull. Mater. Sci.* **31(2)**, 143 (2008)
- [9] P Gao, M Gu and X Lin-Liu, *Cryst. Res. Technol.* **43(5)**, 496 (2008)

- [10] A Firdous, I Quasim, M M Ahman and P N Kotru, *J. Crystal Growth* **311**, 3855 (2009)
- [11] B B Parekh, V S Joshi, V Pawar, V S Thaker and M J Joshi, *Cryst. Res. Technol.* **44**(1), 31 (2009)
- [12] V Siva Shankar, R Siddheswaran, R Sankar, R Jayavel and P Murugakoothan, *Curr. Appl. Phys.* **9**, 1125 (2009)
- [13] D K Sawant, H M Patil, D S Bhavsar, J H Patil, K D Girase, *Arch. Appl. Sci. Res.* **3**, 404 (2011)
- [14] S K Arora, A J Kothari, R G Patel, K M Chauhan and B M Chudasama, *J. Phys.: Conf. Ser.* **28**, 48 (2006)
- [15] S K Arora, V Patel, A Kothari and B Amin, *Cryst. Growth Des.* **4**, 343 (2004)
- [16] S K Arora, V Patel and A Kothari, *Mater. Chem. Phys.* **84**, 323 (2004)
- [17] S K Arora, V Patel, B M Chudasama and B Amin, *J. Crystal Growth* **275**, 657 (2005)
- [18] A R Patel and S K Arora, *J. Mater. Sci.* **12**, 2124 (1977)
- [19] B Suresh Kumar, M H Rahim Kutty, M R Sudarshana Kumar and K R Balu, *Bull. Mater. Sci.* **30**, 349 (2007)
- [20] I Quasim, A Firdous, N Sahni, S K Khosa and P N Kotru, *Cryst. Res. Technol.* **44**, 539 (2009)
- [21] P P Pradyumnan and C Shini, *Indian J. Pure Appl. Phys.* **47**, 199 (2009)
- [22] F Jesu Rethianam, D Arivu Oli, S Ramasamy and P Ramasamy, *Cryst. Res. Technol.* **28**, 861 (2006)
- [23] V Mathivanan and M Haris, *Optik - Int. J. Light Electron Opt.* **124**(20), 4614 (2013), DOI: [10.1016/j.ijleo.2013.01.101](https://doi.org/10.1016/j.ijleo.2013.01.101)
- [24] S J Joshi, B B Parekh, K D Vohra and M J Joshi, *Bull. Mater. Sci.* **29**(3), 307 (2006)
- [25] R M Dahbi, B B Parekh and M J Joshi, *Indian J. Phys.* **79**, 503 (2005)
- [26] S K Arora, V Patel, B Amin and A Kothari, *Bull. Mater. Sci.* **27**, 141 (2004)