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Dielectric and thermal characteristics of gel grown single crystals of ytterbium tartrate trihydrate

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Abstract Dielectric and thermal characteristics of gel grown single crystals of ytterbium tartrate trihydrate have been carried out. The dielectric constant has been measured as a function of frequency in the range 2 kHz–1 MHz and temperature range 30–300 °C. The dielectric constant increases with temperature, attains a peak near 215 °C, and then decreases as the temperature exceeds 215 °C. The dielectric anomaly at 215 °C is suggested to be due to phase transition brought about in the material. The dielectric behaviour of the material is correlated with the results on thermal analysis. Thermogravimetric and differential thermal analysis have been used to study the thermal characteristics of the material. The experimental results show that the material is thermally stable up to 200 °C. The decomposition process occurs in two stages until ytterbium oxide is formed at 700 °C. The non-isothermal kinetic parameters e.g., activation energy and the frequency factor have been evaluated for each stage of thermal decomposition by using the integral method, applying the Coats–Redfern approximation.

Introduction

The salts of tartaric acid belong to an important class of materials because of their interesting physical properties such as Ferroelectricity, Piezoelectricity and non-linear optical properties (Second Harmonic Generation) [1–7]. The Ferroelectricity was first discovered in 1921 in the double salt of tartaric acid i.e., $NaKC_4H_4O_6 \cdot 4H_2O$ [8]. Subsequently, other types of double salts of tartaric acid were investigated for their dielectric behaviour [9, 10]. Dielectric and thermal properties of many tartrate salts with monovalent cations; such as rubidium hydrogen tartrate [11], sodium tartrate [12] and ammonium tartrate [13] and divalent cations; such as calcium tartrate [14], cadmium tartrate [1] manganese tartrate [15], zinc tartrate [16] and strontium tartrate [17, 18] have been investigated. Some of these materials have shown to be ferroelectric [1, 8–10, 14] while others are non-ferroelectric [12, 13]. The spherulitic polycrystals of rare earth tartrates bearing the formula $R_2\,(C_4H_4O_6)_3 \cdot H_2O$ (where R = Y, Sm) were shown to be thermally unstable and start decomposing at a temperature of about 50 °C [19]. Studies on thermal decomposition of lanthanum tartrate decahydrate have been reported, which shows the material to be unstable even at room temperature [20]. In this paper we describe the dielectric and thermal behaviour of single crystals of ytterbium tartrate trihydrate: $Yb\,(C_4H_4O_6)(C_4H_5O_6) \cdot 3H_2O$, which is a trivalent tartrate salt. The single crystals of ytterbium tartrate trihydrate are thermally stable up to a temperature of about 200 °C as compared to most divalent tartrate salts that decompose at much lower temperatures [14–17]. The results obtained on dielectric studies are correlated with the thermal studies viz., thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the crystals. The material under study is proposed to show the ferroelectric behaviour. Thermal characteristics of the material have been studied using thermogravimetry and differential thermal analytic techniques.

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Experimental

Single crystals of ytterbium tartrate trihydrate (YbTT) were grown by single gel diffusion method [21, 22] using two types of gels: an inorganic (silica) gel and an organic (agar–agar) gel. The details of various experiments on the growth of these crystals have been published elsewhere [23]. The crystals obtained from all experiments were of small size and thus it was not possible to carry out direct measurement of dielectric properties on a single crystal. Therefore, the dielectric measurements were carried out on powdered samples in the form of pellets. To obtain the pellet samples, the single crystals were finely ground and the resulting powder was compressed into a die 13 mm in diameter and 1–1.3 mm in thickness under a pressure of 5 tons/cm^2 using a hand operated hydraulic press. The samples were silver electroded by using a fine paintbrush to coat both faces of the pellets with a thin layer of silver paint. The dielectric measurements were carried out in the frequency range 2 kHz–1 MHz and over the temperature range 30–300 °C using a Hewlett–Packard impedance analyzer LF 4192A and further automated by using a computer for data recording, storage and analysis. A microprocessor-based furnace fitted with a temperature controller and a specially designed two-terminal sample holder was used to heat the sample. The impedance analyzer directly provides the values of capacitance (C) and, so the dielectric constant (ε') is computed using the relation;

$$\varepsilon' = C\, t/\varepsilon_o A$$

where C is the capacitance (in farad), t is the thickness (in m), A the area (in m^2), $\varepsilon_o = 8.854 \times 10^{-12}$ F m^{-1} and f is the frequency (in Hz) of the applied electric field.

X-ray powder diffraction analysis of ytterbium tartrate trihydrate was carried out using Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å). The FT-IR spectra of the material in the wave number range of 400–4,000 cm^{-1} were recorded on a Bruker Vector 22 spectrometer using KBr pellet technique. Thermal behaviour (thermogravimetric analysis and differential thermal analysis) of the material was investigated using a Perkin–Elmer thermal analyser in N_2 atmosphere at a heating rate of 10 °C/min.

Results and discussion

Powder X-ray diffraction results

The powder X-ray diffractogram of YbTT crystals is shown in Fig. 1. The occurrence of intense peaks at specific Bragg angles 2θ indicates the crystallinity of the grown material. The powder diffraction pattern of YbTT was indexed with the TREOR program [24], using the 20 most intense peaks. A tetragonal unit cell was found with cell parameters a = 5.885(4) Å, c = 35.801(1) Å, $\alpha = \beta = \gamma = 90°$, V = 1239.9(5) Å^3, where the numbers in the parentheses are standard deviations in the last significant digits. The calculated cell parameters are consistent with those of reported isomorphous materials [25–27].

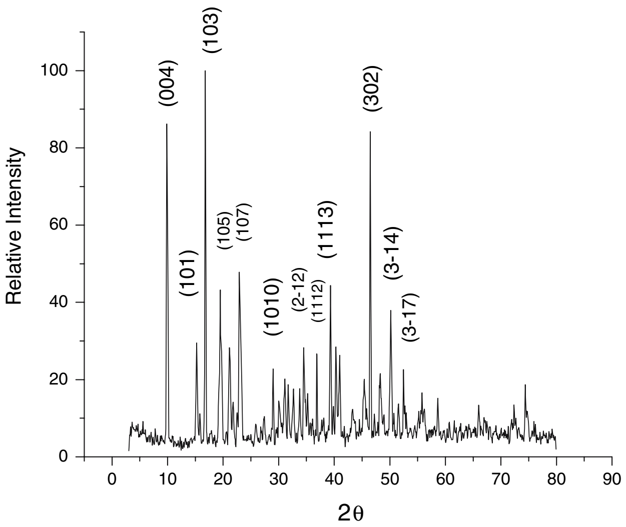


Fig. 1 Powder X-ray diffractogram of ytterbium tartrate trihydrate crystals

Dielectric characteristics

The dependence of real dielectric constant (ε') on temperature at various frequencies of the applied a.c. field is studied in the temperature range of 30–300 °C and frequency range of 2 kHz–1 MHz. The results are described as follows.

Figure 2 shows the variation of real dielectric constant (ε') with temperature at four frequencies (2, 10, 100 and 1,000 kHz) of the applied a.c. field. It is clear from Fig. 2 that in the temperature range $30 < T < 180$ °C, the dielectric constant of ytterbium tartrate trihydrate is practically temperature independent in the higher frequency range 100–1,000 kHz whereas it shows slight dependence at the lower frequencies of 2 and 10 kHz. Other tartrate salts also have been reported to show this type of behaviour [1, 14]. Beyond 180 °C, the dielectric constant increases almost suddenly with temperature, attains a peak around 215 °C, and then decreases as the temperature exceeds 215 °C. The occurrence of this peak may suggest a phase transition in the material near 215 °C. To account for this behaviour, we have two possibilities. The first possibility is that on heating the sample up to 225 °C, there is loss of some water molecules and because of this dehydration a

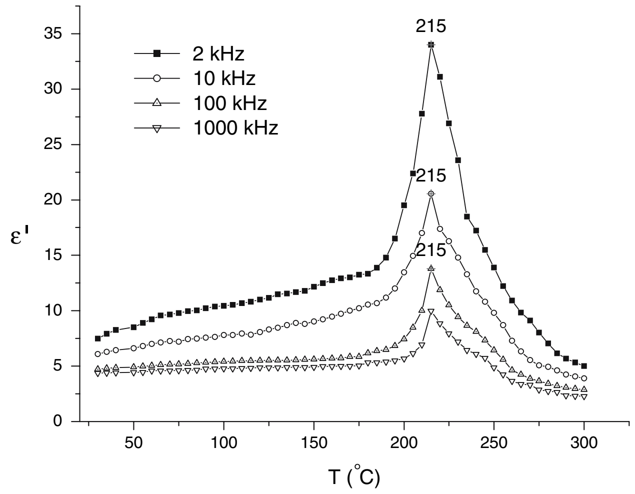


Fig. 2 Variation of dielectric constant with temperature at frequencies 2, 10, 100 and 1,000 kHz

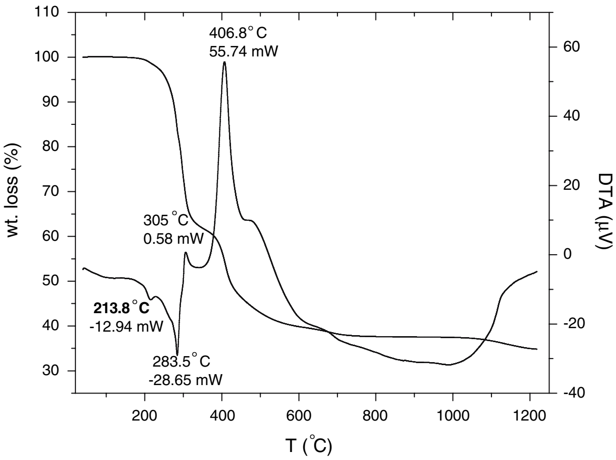


Fig. 4 TG and DTA curves of ytterbium tartrate trihydrate

transition appears to have occurred at about 215 °C. The phase transition due to loss of water molecules as well as due to structural changes has been reported by Torres et al. [1] in the case of cadmium tartrate crystals. However, the possibility of phase transition exclusively due to loss of water molecules is ruled out in the light of the results of thermal behaviour of the material under consideration. Figure 3 shows thermogravimetric (TG) and DTG curves of ytterbium tartrate trihydrate. The material loses about five water molecules (three from coordinated water and two from intramolecular; observed weight loss: 17.4%, calculated weight loss: 17.15%) in the temperature range of 200–285 °C. Up to a temperature of about 225 °C, there occurs a loss of about 0.5 H_2O (observed loss: 1.8%; calculated loss: 1.72%). Corresponding to this loss there is an endothermic peak at about 213.8 °C as shown by the DTA curve of Fig. 4. A further loss of 4.5 water molecules occurs in the temperature range of 225–285 °C (observed loss: 15.6%; calculated loss: 15.43%). Therefore, it may appear that there should be at least two transitions; first in the temperature range 200–225 °C (corresponding to DTA peak: 213.8 °C) and second in the temperature range 225–285 °C (corresponding to DTA peak: 283.5 °C). However, in the present case the only transition that has been observed in the dielectric constant versus temperature curve (Fig. 2) is around 215 °C. Therefore, the possibility of the material showing the phase transition near 215 °C exclusively due to loss of water molecules may be ruled out. The second possibility is that dielectric anomaly near 215 °C is due to a crystallographic change/polymorphic phase transition brought about in the material (including due to loss of 0.5 H_2O molecules). The DTA curve of Fig. 4 shows an endothermic peak near 213.8 °C, thereby, suggesting a phase transition in the material. This temperature is close to the transition temperature (215 °C) observed in the dielectric constant versus temperature curve (Fig. 2). Therefore, it may be suggested that the material shows a ferroelectric behaviour up to the temperature of 215 °C. The characteristic feature of rare earth tartrate salts is that in all these crystal structures, rare earth cations and hydrogen bonds of O–H···O type involving water ligands, hydroxyl O and the carboxylate O atoms, link the tartrate anions into layers parallel to (001); these layers are linked together by hydrogen bonding between adjacent tartrate molecule [25–27]. It is believed that the hydroxyl groups in the tartrate ions make the major contribution to the spontaneous polarization in salts of tartaric acid .The spontaneous polarization results from the two possible positions for hydrogen atoms, which are believed to lie in intrinsically asymmetric double minimum potential well [28].

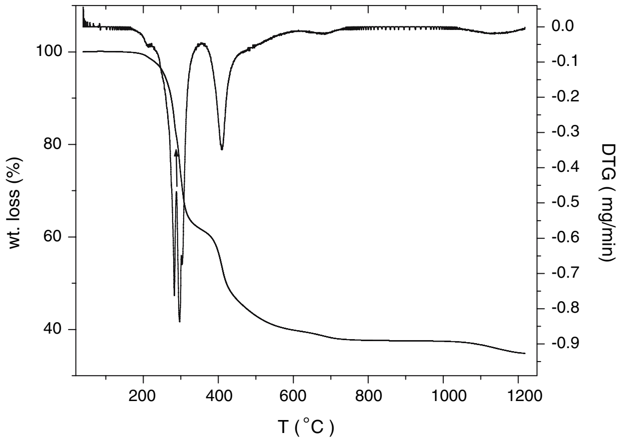
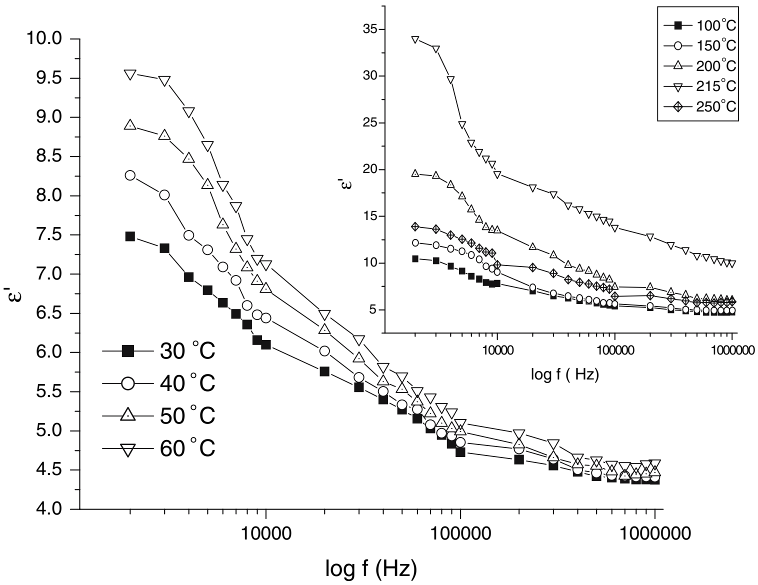


Fig. 3 TG and DTG curves of ytterbium tartrate trihydrate

The variation of dielectric constant as a function of frequency is shown in Fig. 5. The inset of Fig. 5 shows the variation of dielectric constant with frequency at high temperatures. It is clear from Fig. 5 that dielectric constant

Fig. 5 Variation of dielectric constant with frequency. The inset of the figure shows variation of dielectric constant with frequency at temperatures of 100, 150, 200, 215 and 250 °C



of ytterbium tartrate trihydrate decreases gradually with increasing frequency. The decrease of dielectric constant with increase of frequency is a normal dielectric behaviour and can be explained on the basis of various polarization mechanisms. There are four primary mechanisms of polarization in materials i.e., electronic, ionic or atomic, dipolar or orientational and space charge or interfacial polarization. At low frequencies, all the mechanisms of polarization contribute to the dielectric constant and with the increase in frequency, the contributions from different polarizations start decreasing. For example, at very high frequencies (10^{15} Hz), only electronic polarization contributes to the dielectric constant, while ionic polarization takes place at IR frequencies (~10^{13} Hz). In the material under present investigation the high rise of dielectric constant at lower frequencies may be attributed to space charge polarization due to crystal lattice defects. The gradual decrease in dielectric constant with frequency suggests that ytterbium tartrate trihydrate has domains of different sizes and hence varying relaxation times.

Thermal characteristics

Simultaneous recording of TG and DTA was made in the temperature range 40–1,200 °C .The results thus obtained are shown in Figs. 3 and 4. Figure 3 shows the TGA/DTG curves of ytterbium tartrate trihydrate crystals. From the TG curve, it is observed that the material remains stable up to a temperature of about 200 °C. In the temperature range 200–354 °C, the material loses five water molecules and two CO_2 molecules, leading to the formation of ytterbium acrylate [29] (calculated weight loss: 34%, observed weight loss: 35.4%). A close look at the DTG curve reveals that the first stage of decomposition (200–354 °C) actually consists of two sub stages (225–285 °C and 285–354 °C). The first sub stage (200–285 °C) is due to dehydration resulting in the elimination of five water molecules from the material. This includes three coordinated and two intramolecular water molecules. The dehydration temperature range (200–285 °C), which seems to be high, suggests the presence of coordinated water in the compound [30]. The measured weight loss in the first sub-stage is about 17.4% (calculated loss, 17.15%). Corresponding to this dehydration step there are two endothermic peaks in the DTA curve at about 213.8 and 283 °C, respectively (see Fig. 4). The loss of two intramolecular water molecules results into the dehydration of the tartrate, thus leading to the formation of ytterbium-fumarate complex. In the second sub-stage (285–354 °C), there occurs a loss of two CO_2 molecules and the ytterbium-fumarate complex decomposes to ytterbium acrylate. Corresponding to this sub-stage (285–354 °C), there is an exothermic peak in DTA, at about 305 °C. The formation of acrylate complex was confirmed by carrying out CHN analysis of the intermediate obtained at 360 °C (Calculated; C = 20.82%, H = 1.45%, Observed; C = 19.96%, H = 1.5%). The FT-IR spectrum of ytterbium tartrate trihydrate (curve 1) and the intermediate product (curve 2) obtained at 360 °C is shown in Fig. 6. The strong peak at 1,718 cm^{-1}, as shown in curve 1, is due to free carbonyl stretch v (C=O), which shows that besides ionized COO^- group there is also presence of unionized carboxyl groups (COOH) in the compound [31]. A band centred at approximately 1,587 cm^{-1} is due to C=O asymmetric stretch of carbonyl group. The absorption at 1,410 cm^{-1} is attributed to C=O symmetric vibration. In the FT-IR spectrum of intermediate (ytterbium acrylate, curve 2) an absorption peaks at 1595.20 cm^{-1} and 1,418 cm^{-1} corresponds to symmetric and anti symmetric stretch of C=O and the absorption peak at

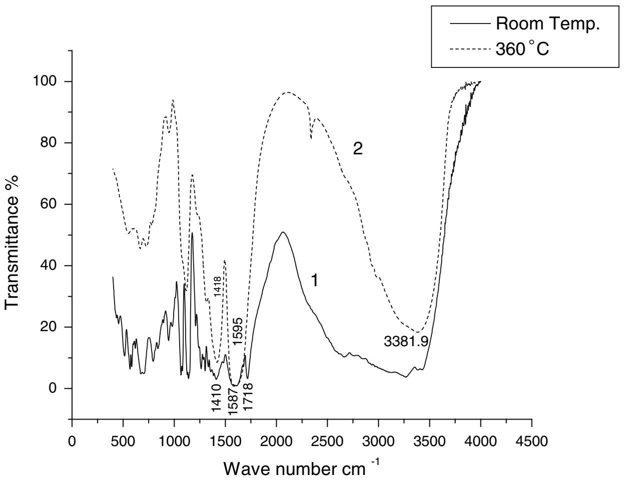


Fig. 6 FT-IR spectrum of ytterbium tartrate trihydrate crystals obtained at room temperature (curve 1) and at 360 °C (curve 2)

3381.9 cm^{-1} is attributed to the stretching vibration of hydroxyl group. Thus the FT-IR spectrum obtained at 360 °C is in conformity with the proposed product i.e. ytterbium acrylate. In the second stage between temperature 385 and 700 °C, the acrylate of ytterbium decomposes and gets reduced to ytterbium oxide, which is clear from the saturation of TG curve from 700 °C onwards. The second stage of decomposition corresponds to the elimination of two CO_2 and two $CH_2{=}CH_2$ molecules from the material. The observed weight loss in this stage is about 26.86% (calculated weight loss: 28.29%). Corresponding to this stage there is an exothermic peak at about 406.8 °C. The thermal decomposition of ytterbium tartrate trihydrate that occurs through the reactions I, II, and III are given below. Based on the reported isomorphous materials [25–27], we suggest the molecular structure of the compound under investigation to be the one shown on the L.H.S of reaction (I).

The temperature written above the arrow corresponds to the maximum decomposition rate as shown by DTG curve. It may be emphasized here that the proposed molecular structure agrees well with the decomposition steps of ytterbium tartrate trihydrate as shown above.

The non-isothermal kinetic parameters have been worked out for the complete stage 1 (200–354 °C) and stage 2 (385–700) using the integral method by applying the Coats–Redfern approximation [32]:

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left(\frac{AR}{E\beta}\left(1-\frac{2RT}{E}\right)\right) - \frac{E}{RT} \qquad (1)$$

where α is the fraction of reactant used, $g(\alpha)$ is the conversion function dependent on the mechanism of the reaction, R is the gas constant (=8.314 J K^{-1} mol^{-1}), E is the activation energy (kJ mol^{-1}), T the absolute temperature (K), β the linear heating rate (K s^{-1}) and A is the frequency factor (s^{-1}).This equation is most often used to describe the kinetics of thermal decomposition of solids in general. A plot of $\ln\left[\frac{g(\alpha)}{T^2}\right]$ versus 1/T gives a straight line for the correct model.

The statistical parameter; correlation coefficient r and Snedecor's variable F were calculated to aid the selection of the g (α) function best describing the experimental results [33]. The values of the kinetic and statistical parameters for all analysed models are listed in Table 1. The Arrhenius plot for the best-fitting curve for the stage 1 and stage 2 is shown in Fig. 7 and 8, respectively. It is clear from the Table 1 that the best fitting expression for the stage 1 is that of random nucleation model F1 with activation energy of 103.6 kJ/mol whereas for stage 2 the second order reaction model F2 fits best to the experimental results with activation energy 136.33 kJ/mol.

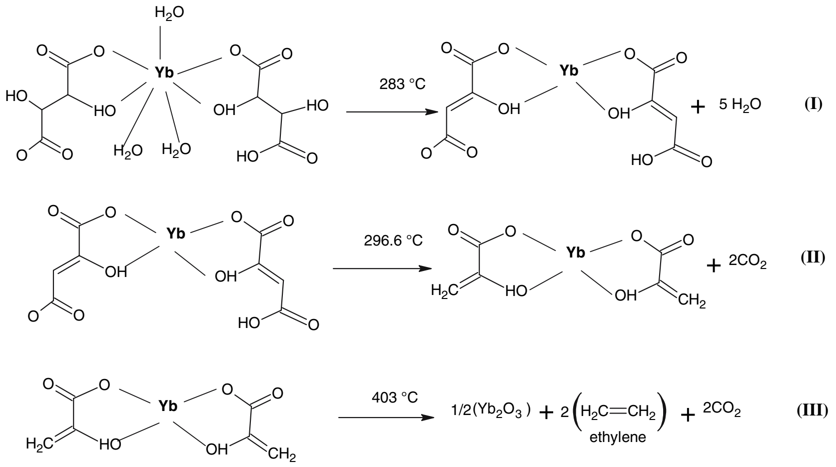


Table 1 Kinetic and statistical parameter values for stages 1 and 2

Stage	Model	E (kJ/mol)	A (s^{-1})	|r|	F
1	D1	159.58	$7.27E \times 10^{11}$	0.97435	15,917
	D2	172.75	9.07×10^{12}	0.98192	22,838
	D3	41.325	9.53×10^{4}	0.98702	32,067
	D4	179.06	9.27×10^{12}	0.98529	28,225
	F1	103.6	1.73×10^{7}	0.9954	91,735
	F2	155.23	4.82×10^{12}	0.97629	17,272
	A2	47.26	1.55×10^{4}	0.99439	75,049
	A3	44.42	7.50×10^{5}	0.99302	60,161
	R2	86.825	1.38×10^{5}	0.98555	28,744
	R3	91.745	3.11×10^{5}	0.98977	40,847
2	D1	69.30	$4.4E \times 10^{7}$	0.8378	2,532
	D2	72.52	2.0×10^{7}	0.84078	2,592
	D3	15.43	2.4×10^{7}	0.80161	1,933
	D4	80.85	2.3×10^{4}	0.86763	3,273
	F1	59.90	3.1×10^{4}	0.93897	8,010
	F2	136.33	7.5×10^{7}	0.95082	10,131
	A2	23.76	4.9×10^{6}	0.90604	4,928
	A3	11.66	1.8×10^{7}	0.8424	2,627
	R2	11.77	7.6×10^{5}	0.84645	27,167
	R3	43.32	1.3×10^{6}	0.88542	3,901

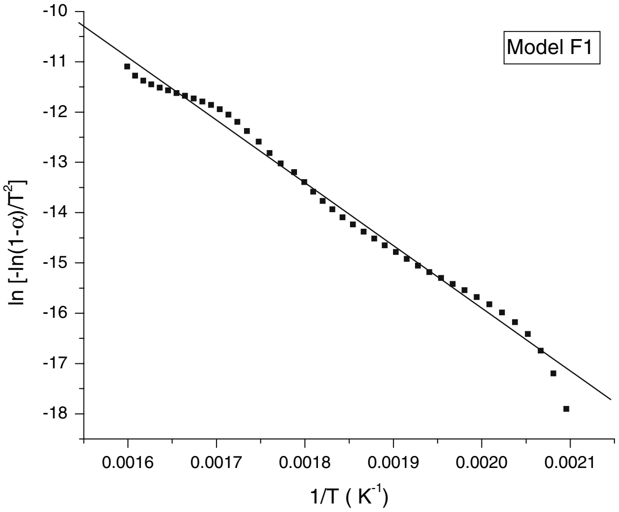


Fig. 7 Arrhenius plot of the best fitting function g (α) for stage 1 (200–354 °C)

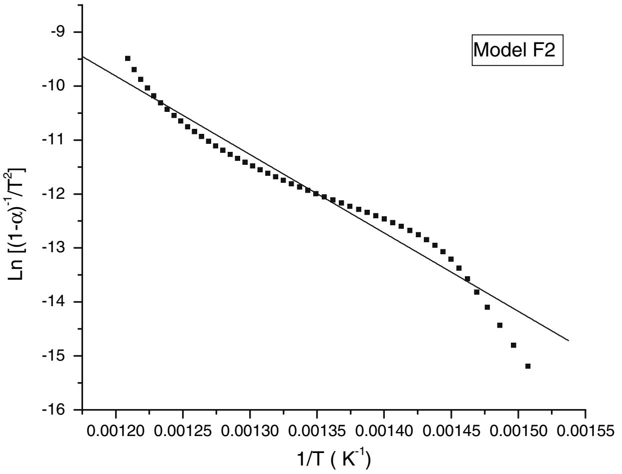


Fig. 8 Arrhenius plot of the best fitting function g (α) for stage 2 (385–700 °C)

Conclusions

The study of the dielectric behaviour of ytterbium tartrate trihydrate crystals shows the strong dependence of dielectric constant on temperature. The dielectric constant (ε') varies with the temperature and attains a peak value around 215 °C after which it decreases, thus establishing this temperature as the transition temperature of the material. X-ray diffraction results suggest that the crystals belong to tetragonal system with cell parameters: a = 5.885 Å, c = 35.80 Å, $\alpha = \beta = \gamma = 90°$, V = 1239.86 Å^3. Thermogravimetric analysis shows that the material is thermally stable up to a temperature of about 200 °C. Decomposition of ytterbium tartrate trihydarte occurs in two complete stages ultimately leading to the formation of ytterbium oxide. The reaction corresponding to stage 1 is governed by random nucleation model F1 with activation energy

103.6 kJ/mol and frequency factor 1.73×10^{7} s^{-1} whereas that of stage 2 by second order reaction model F2 with activation energy 136.33 kJ/mol and frequency factor 7.5×10^{7} s^{-1}.

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