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Growth and Thermal, Electrical, Structural Characterization of Mixed Hydrated Single Crystal

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Summary: Mixed single crystal was made by mixing saturated aqueous solutions of $NiSO_4 \cdot 6H_2O$ and $CuSO_4 \cdot 5H_2O$ by volume (80:20) and the mixture was kept to form the crystals at room temperature by slow evaporation process. After some days, big pieces of greenish blue, dark colored crystals were grown. To determine the weight of $NiSO_4 \cdot 6H_2O$ and $CuSO_4 \cdot 5H_2O$ in the crystal, Ni-DMG complexiometrical and EDTA gravimetrical analysis was done respectively. From this analysis it was concluded that 5.8 molecules of water of crystallization is present in the mixed single crystal. The crystals were characterized by UV-Visible, FTIR and single crystal X-ray diffraction studies. From single crystal XRD lattice parameters have been calculated. All these structural analysis confirms formation of new single crystal. Further, DTA-TGA, dc electrical conductivity and dielectric constant studies were done from the room temperature to 400 °C.From DTA studies it was observed that 5.8 molecules of water of crystallization get dehydrated in four major steps at temperature 115 °C, 150 °C, 240 °C and 325 °C respectively corresponding to the detachment of 1 mole, 3 moles, 1 mole and 0.8 mole of water of crystallization. DC electrical conductivity and dielectric constant studies also show close agreement to the dehydration steps. The observed peaks in the conductivity verses temperature graph have been explained on the basis of release of water molecules and subsequent dissociation of these released water molecules into H^+ and OH^- ions.

Keywords: dc electrical conductivity; dielectric property; DTA-TGA; FTIR; mixed single crystals; Single crystal XRD; UV-Visible

Introduction

A variety of compounds results from combination of materials with water. Metal hydrated salts have wide applications in the biomedical fertilizers. The thermal and electrical measurements have proven to be convenient methods for studying deaquation steps in many metal salt hydrated systems. The dynamic thermogravimetry (TG) is one of the best methods for studying the dehydration in hydrated salts. The sequence of deaquation steps in many polyhydrated metal sulphates has been reported by Ben-dot and Margalith[1] consist of two definite steps: first all but one water molecule are evolved at relatively low temperature (beginning at 60 °C) then after significant rise in temperature the last molecule is evolved.

K.R. Ghormare and et al. have reported that $K_2CO_3.1.5H_2O$ crystal dehydrates in steps of 0.5 moles and 1 mole at 235 °C and 273 °C respectively.[2] BaC_2O_4. 0.5 H_2O gets dehydrated completely in the temperature range of 142 °C to 217 °C.[3] Dehydration steps of Potassium magnesium sulfate hexahydrate was reported.[4] Phenomenon of dehydration of crystals of Iron-manganese laevo-tartrate mixed in different proportions was discussed by Joshi and Parekh.[5] It is noted that in the electrical

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conductivity and the height of the conductivity peak is dependant on both the heating rate and rate of diffusion of water molecules. The trapped H^+ and OH^- ions get detached at the deaquation temperature and move towards the respective electrodes and giving rise to changes in electrical conductivity.

The peaks in the dielectric constant at the transition temperature arise due to space charge polarization by trapped charges. Availability of charged particles increases the conductivity whereas the formation of space charge increases the dielectric constant.[6] P. N. Nandi and V. G. Kher have reported that crystal of $NiSO_4.6H_2O$ get dehydrates after heating in 4 steps.[7] Crystals of $NiSO_4.6H_2O$ grown at room temperature get dehydrated as 1 mole, 2 mole, 2 mole, 1 mole at 129 °C, 187 °C, 214 °C and 390 °C respectively. P. N. Nandi and et.al have reported that the crystals of $CuSO_4.5H_2O$ get dehydrate during heating in 4 distinct steps.[8] Crystals of $CuSO_4.5H_2O$, grown at room temperature gives deaquation steps as 1 mole, 1 mole, 2 moles and 1 mole at 111 °C, 124 °C, 190 °C and 275 °C temperatures respectively. In both the cases, the rate of heating was maintained at 5 °C rise per minute.

$NiSO_4.6H_2O$ crystallizes in the monoclinic form whereas $CuSO_4.5H_2O$ crystallizes in triclinic form.[7] The deaquation steps depend on the type of bonding, bond length and temperature at which they grow.

In this paper, we are reporting mixed single crystal analysis. Saturated solutions of $NiSO_4.6H_2O$ and $CuSO_4.5H_2O$ were mixed by 80:20 proportions by volume. The grown crystals were characterized by single crystal XRD, FTIR, UV-visible, TG, DTG analysis. Dielectric constant and dc electrical conductivity measurements have been carried out.

Experimental Part

Sample Preparation

Powdered form of $NiSO_4 \cdot 6H_2O$ was taken from BARGOYNE chemicals of 99% purity and $CuSO_4 \cdot 5H_2O$ was taken AREN chemicals of 99.1% purity. Saturated solutions were made separately and allowed them undisturbed to settle down for one day. Next day both the solutions were decanted. Then both the solutions were mixed by 80:20 and stirred. The mixed solution was allowed to crystallize the solutions at room temperature by slow evaporation process.

After some days bluish green colored crystals were grown.

Analysis of Weight

As the crystals were made by mixing the two solutions by volume, weight of $NiSO_4.6H_2O$ and $CuSO_4.5H_2O$ was estimated. To determine the weight of $NiSO_4.6H_2O$ and $CuSO_4.5H_2O$ in the crystal, Ni-DMG complexiometrical analysis was done. From this analysis weight of Ni was calculated. Copper was estimated by using EDTA gravimetrical analysis was done.

Thermo Gravimetric Studies

The thermo gravimetric measurements of the mixed single crystal were carried out from 30 °C to 400 °C. For this purpose locally fabricated furnace was used whose temperature can be varied up to 500 °C with accuracy of 1 °C. Monopan balance (sensitivity 0.1 mg) was also used for thermo gravimetric study. The crystal was freely suspended from the monopan balance such that it occupies the central position of the furnace. The furnace was heated at constant rate of heating of 5 °C/min in static air. The rate of heating was maintained constant throughout the experiment. The mass of the crystal with temperature and also the time for each 5° rise in temperature was recorded. The change in mass Δm [g] as well as the rate of change in mass $\Delta m/\Delta t$ [g/min] for entire temperature range was calculated.

FTIR

Fourier Transform Infrared spectroscopic studies were carried out on the grown mixed single crystal in order to understand the structure and bonding in them. The spectrum of mixed single crystal was recorded on a Shimadzu spectrometer using KBr pellet technique in the wave number range 400–4000 cm^{-1}.

XRD

Single crystal XRD was carried out using Enraf Nonius MACH (Bose Institute, Kolkata) 3 Cu (Kα) Mo (Kα) sources. The lattice parameters are determined *i.e.* values of d spacing, a, b, c, and the angles α, β, γ.

UV- VIS Spectroscopy

The UV-VISIBLE spectrum was recorded from 250–1000 nm using Shimadzu UV-1700 series spectrophotometer in which transmission and absorbance spectrum was recorded.

DC Electrical Conductivity Measurements

The dc electrical conductivity was measured using nanoammeter. The crystal was kept in a metallic sample holder. This sample holder was connected to the digital nanoammeter and constant power supply. Again the sample was heated from 30 °C to 350 °C with constant rate of heating of 5 °C per minute. The current and time for each 5 °C rise temperature with time have also been recorded.

Dielectric Constant Measurements

The dielectric constant ε was measured by using digital LCR meter [PACIFIC company] at fixed frequency. The crystal was held in a metallic sample holder and introduced in a furnace which was heated from 30 °C to 350 °C at constant rate of heating of 5 °C per minute. The capacitances were measured using LCR meter for every 5 ° rise in temperature.

Result and Discussion

EDTA

From above standard method it was found that, each crystal contain weight of $NiSO_4 \cdot 6H_2O$ is 82% and weight of $CuSO_4 \cdot 5H_2O$ is 18%. That means 4.9 water molecules from $NiSO_4 \cdot 6H_2O$ and 0.9 water molecules from $CuSO_4 \cdot 5H_2O$ were simultaneously involve in single crystal. It was concluded that 5.8 molecules of water of crystallization are tightly bonded in each crystal.

Thermo Gravimetric Analysis

In the thermo gravimetric study two graphs were plotted 1) temperature T (°C) verses change in mass Δm [g] called as TG shown in Figure (1) (2) temperature T (°C) verses rate of change in mass $\Delta m/\Delta t$ [g/min] called as DTG as shown in Figure 2. From TG curve of crystal of mixed single crystal (shown in Figure 1) it was observed that weight of the 5.8 water molecules are lost in different steps.

Figure 2 indicates that differential thermo gravimetry shows five major peaks. The 5.8 water molecules detached at temperatures 115 °C, 150 °C, 240 °C and 325 °C respectively corresponding to the detachment of 1 mol, 3 mol, 1mol and 0.8 mol of water of crystallization. These peaks are fitted, as explained below, first of all the loss in mass after complete dehydration is calculated and is compared with the actual loss in mass corresponding to loss of 5.8 water molecules as from theoretical calculations. The second peak consists of three very small peaks involving release of one water molecule in each. However, because these peaks occur in a very small temperature range and they are very close to each other, they can broadly overlap into one peak. The occurrence of DTG peak is because of the release of water molecules due to the thermal energy received by the crystal.

P. N. Nandi and V. G. Kher have reported that crystal of $NiSO_4 \cdot 6H_2O$ get dehydrates after heating in 4 steps.[7] Crystals of $NiSO_4.6H_2O$ grown at room temperature get dehydrated as 1 mole, 2 mole, 2 mole, 1 mole at 129 °C, 187 °C, 214 °C and 390 °C respectively. P. N. Nandi and et.al have reported that the crystals of $CuSO_4 \cdot 5H_2O$ get dehydrate during heating in 4 distinct steps.[8] Crystals of

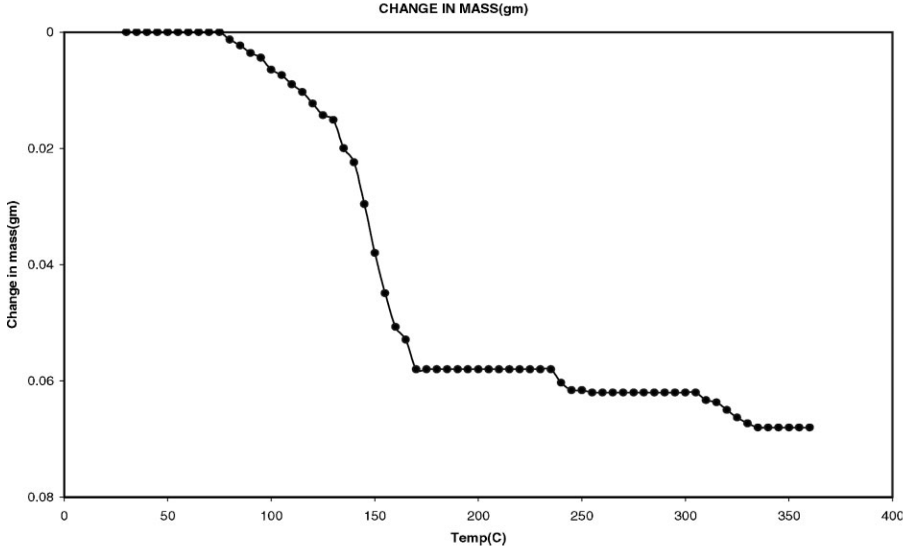

Figure 1.
Graph of TG of mixed single crystal form.

$CuSO_4.5H_2O$, grown at room temperature gives deaquation steps as 1 mole, 1 mole, 2 moles and 1 mole at 111 °C, 124 °C, 190 °C and 275 °C temperatures respectively. In both the cases, the rate of heating was maintained at 5 °C rise per minute. Mixed single crystal gets dehydrated relatively at low temperature than the consecutive crystals.

The moisture absorbed on the surface of the crystal is getting removed before 80 °C that is why the peaks occurring below 80 °C are not due to the dehydration but could be due to removal of initial moisture of the crystal.

FTIR

Figure 3 shows FTIR spectra of pure and grown mixed crystal. Mixed single crystal shows some new bands and some shifts. Mixed single crystal is showing some such peaks which are shown by pure crystals but

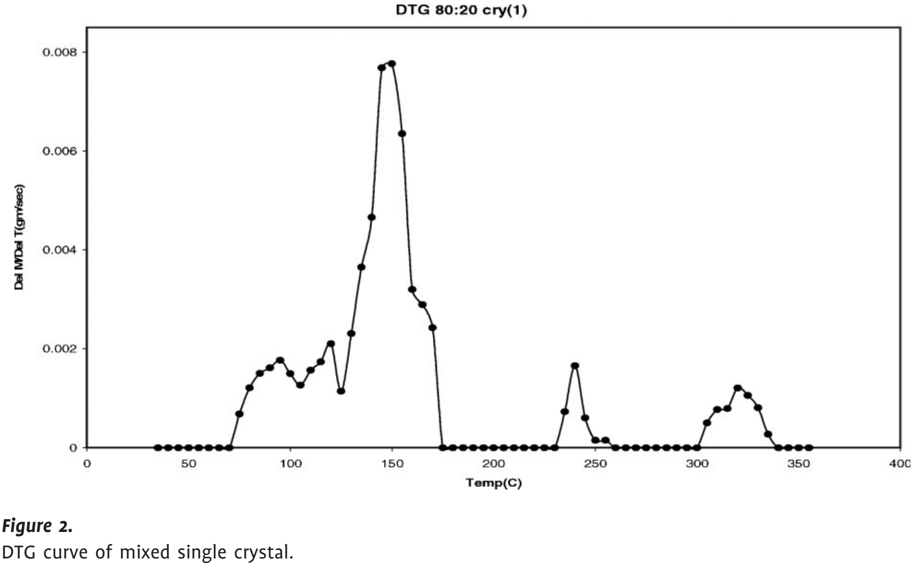

Figure 2.
DTG curve of mixed single crystal.

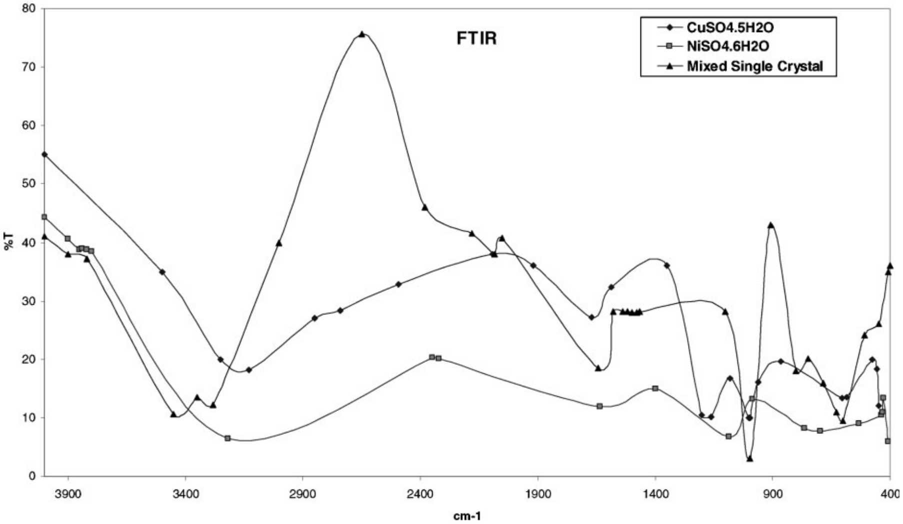

Figure 3.
FTIR of pure and mixed single crystal.

mixed crystal showing some new peaks and some shift in peaks. This observation confirms formation of new crystal. Peak observed between 1635-1680 cm^{-1} shows symmetric and asymmetric O-H stretching which established the presence of water of crystallization.

UV-VIS Spectroscopy
Figure 4 shows the UV-visible spectrum recorded for mixed single crystal. It is observed that absorption maxima of mixed single crystal obtained in between the range of pure salts, which is tabulated in Table 1.

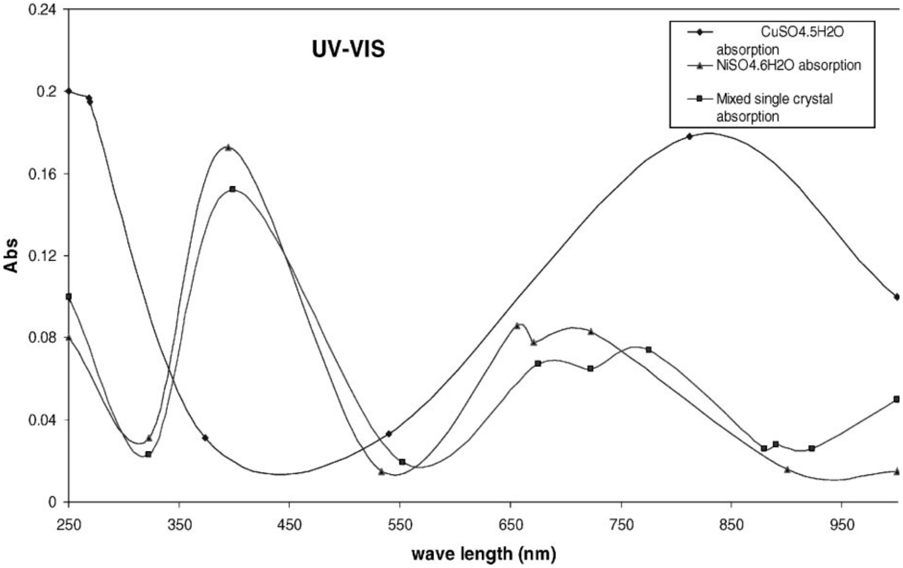

Figure 4.
UV-VISIBLE of pure and mixed single crystals.

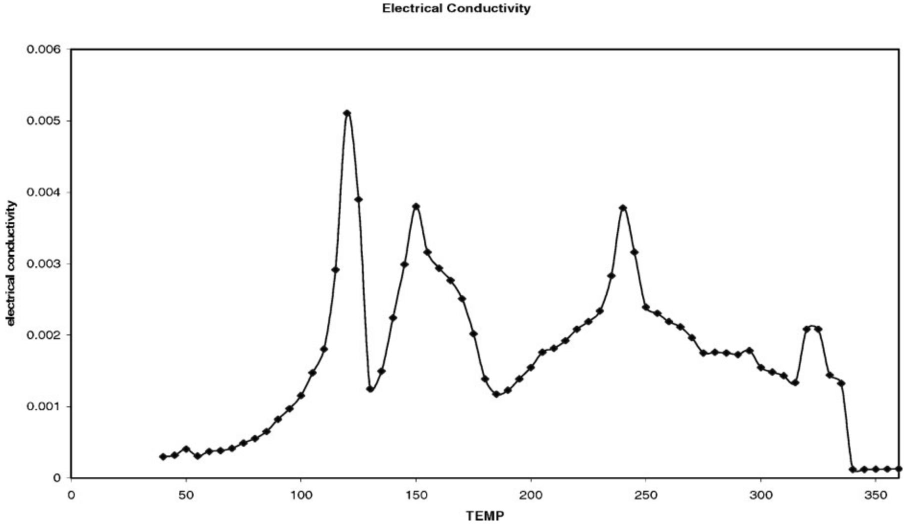

Figure 5.
Temperature verses Electrical conductivity (σ) of mixed single crystal.

Second peak of mixed single crystal is obtained at 398.50 nm with absorption value at 0.152. Thus, from UV-Visible spectra it can be observed that $CuSO_4.5H_2O$ crystal show blue color and $NiSO_4.6H_2O$ crystal show green color but mixed single crystal show bluish green color which confirms new crystal is formed having different color with different properties. As the crystals are made by mixing saturated solutions of pure salts by volume they show result as shown in Figure 4. We have confirmed this by taking UV-Visible spectrum of simple physical mixing of two saturated solutions but they do not show such nature. The reason behind this is mixed single crystal contains slightly different weight of parent salts as they are made up from the solution which was mixed by volume only.

XRD

The values of lattice parameters a, b, c in (Å) with the crystal axes α, β, γ in (°) and cell volume CV in (Å) with crystal type were obtained from single crystal XRD pattern which is also shown in Table 2.From this study it can be conclude that new crystal was formed of new structure.

Electrical Conductivity

To confirm these dehydration steps electrical conductivity measurements are done. It was observed from the graph that there are four peaks of different height. These peaks are sharper than the DTG peaks. Peaks could be explained on the basis of the fact that small fraction of water molecule that is liberated gets dissociated into H^+ and OH^- ions. The ions move towards the respective electrodes giving rise to the conducting peaks.

Table 1.
Xxx

$NiSO_4.6H_2O$		$CuSO_4.5H_2O$		Mixed single crystal	
Wavelength nm	Absorption	Wavelength nm	Absorption	Wavelength nm	Absorption
722.5	0.077	812	0.496	775.5	0.074
656	0.066	539.5	0.033	675.5	0.067
394.5	0.173	373.5	0.031	398.5	0.152

Table 2.
Xxx

	Single crystal XRD							
	a (Å)	b (Å)	c (Å)	α	β	γ	C.V. (Å)	Type
$NiSO_4.6H_2O$	6.2435	9.1954	12.447	90.155	89.99	106.98	683.43	Monoclinic
$CuSO_4.5H_2O$	5.945	6.1089	10.696	77.47	82.4072	72.75	361.25	Triclinic
Mixed single crystal	6.7817	6.7892	18.309	90.1516	89.9664	90.0795	843.016	Tetragonal

The large increase in conductivity at the transition temperature at 115 °C, 150 °C, 240 °C and 325 °C indicates a sudden and enormous increase in the concentration of mobile charge carriers in the samples. It is therefore, assumed here that a very small fraction of one of the water molecules that are detached from the structure at 115 °C gets dissociated into H^+ and OH^- ions. Four peaks of electrical conductivity obtained are at 115 °C, 150 °C, 240 °C and 325 °C. The height of the peak indicates that the conductivity of crystal should correspond to the dehydration process. The rapid rise and fall in conductivity of the crystal during heating indicates that free charge carriers are available for the conduction during dehydration. Kher and Nandi[7,8] while studying the electrical behavior of $CuSO_4 \cdot 5H_2O$ and $NiSO_4 \cdot 6H_2O$ crystals have shown that the electrical conductivity and dehydration steps are intimately linked and the conductivity changes at the corresponding dehydration temperatures are due to the dissociation of small fraction of the water molecule that are detached from the structure and dissociated into H^+ and OH^- ions. All the water molecules released and dissociated are not able to escape from the crystal immediately and many of them remain trapped in the interstitial space. The dissociated and trapped H^+ and OH^- ions are made mobile driven by the forces of the electric field. This increases the concentration of mobile charge carriers causing the observed large increase in conductivity. As the temperature crosses the dehydration temperature, the number of trapped ions increases at a high rate as they are driven by the applied field and collected by the respective electrodes, while the trapped water molecules can come out relatively slowly by the diffusion process.

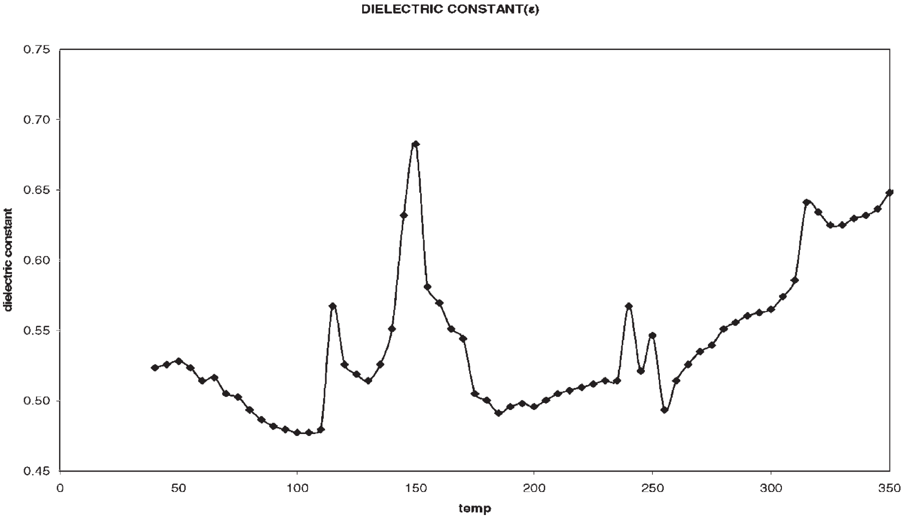

Figure 6.
Temperature verses Dielectric constant of mixed single crystal.

Dielectric Constant

The Dielectric constant of mixed single crystals was studied by measuring capacitance *c*. Graph was plotted between dielectric constant ε and temperature *T*, as shown in Figure 6. In Figure 6 there are four different peaks at 115 °C, 150 °C, 240 °C and 325 °C, respectively. These temperatures correspond to the dehydration steps as discussed earlier. The large increase in ε at 115 °C, 150 °C, 240 °C and 325 °C is due to orientation of permanent dipoles of the water molecules released from the crystal structure but trapped within the material and space charge polarization produced by trapped positive and negative charges generated after dissociation of water molecules.

As the number of free detached molecules and dissociated water molecule decreases, the value of ε also decreases. The dielectric constant again shows a gradual increase at 150 °C and onwards there is again increase at 240 °C and 325 °C .Beyond this region the value of (ε) again decreases.

Conclusions

Mixed single crystal exhibit variation in color than the pure single crystals. FTIR spectroscopic study suggests that mixed single crystal shows some new bands and some shifts in peaks. XRD suggests tetragonal crystal structure. The crystal is thermally unstable; on heating they become anhydrous. The amount of water of hydration is determined. From above all these studies at can be concluded that new crystal is formed having different color, different shape and different properties than the parent crystals. At the deaquation temperature, H_2O gets detached and get splitted into H^+ and OH^- ions causes an increase in dc electrical conductivity and these H^+ and OH^- ions get trapped within the material then space charge polarization will produced which results in increase in the value of dielectric constant. Therefore, dc electrical conductivity and dielectric constant show close agreement with the dehydration steps of thermo gravimetric study. It can be concluded from the above result that there is a correlation between DTG, dc electrical conductivity and dielectric constant properties.

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