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Electrical conductivity studies on pure and barium added strontium tartrate trihydrate crystals

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Abstract

Pure and barium added strontium tartrate trihydrate single crystals were grown using silica gel by chemical reaction method at room temperature. The DC conductivity measurements were carried out on the crystals. The Arrhenius plots show that two types of conduction exists in these crystals-one at low temperature and the other at high temperature in the form of extrinsic and intrinsic conduction, respectively. Within the temperature range considered in the present study these crystals do not exhibit ferroelectric transitions.

Keywords: Crystal growth; strontium tartrate trihydrate; DC conductivity; electrical properties.

Introduction

Tartrate crystals have attracted the attention of many workers due to their interesting physical properties. Some crystals of this family are ferroelectric, some others are piezoelectric and few others are used in the control of laser emission (Yadava & Padmanabhan, 1973; Desai & Patel, 1987; Gon, 1990; Jesu Rethinam *et al*., 1994). Considerable attention has been devoted recently to grow these crystals and study their properties (Sahaya Shajan & Mahadevan, 2004; Firdous *et al*., 2009: Emanuel C Rodriguesa *et al*., 2009: Jochan Joseph *et al*., 2009). They are sparingly soluble in water and decompose before melting. Therefore the only viable method to grow these crystals is gel method. In dielectrics, the electrical conduction is mainly a defect controlled process in the low temperature region. The presence of impurities and vacancies mainly determines the conduction in this region. The energy needed to form the defect is much larger than the energy needed for its drift. The conductivity of the crystalline material in the higher temperature region is determined by the intrinsic defects caused by the thermal fluctuations in the crystal. As the temperature increases, more and more defects are produced and the conductivity is increased. It was reported that strontium tartrate trihydrate (STT) crystals are monoclinic with lattice parameters: a = 7.55±0.02 Å, b = 10.06±0.02 Å, c = 6.47±0.02 Å and space group $P2_1$ (Ambady, 1968). So far no systematic study is available in the literature on the conductivity mechanism of Ba^{2+} added STT crystals. The present work is aimed at understanding the conduction mechanism in pure and impurity (Ba^{2+}) added STT crystals.

Experimental

Crystal growth

The growth of STT was achieved by controlled diffusion of strontium ions through silica gel impregnated with tartaric acid. The gel solution was prepared by mixing 1 M tartaric acid with silica gel, made from sodium metasilicate, of density 1.05 g/cc. The titration was continued till the contents attain the pH 4. The gel was set in about 48 h. After the gel aging of one day, 1 M strontium chloride was added above it without causing any damage. The tube was kept undisturbed at room temperature. Crystals appeared near the gel solution within two days and at the middle of the gel column within four days. All the crystals were harvested after 30 days. The experimental temperature was 32±2°C. The expected chemical reaction is,

$$SrCl_2 + C_4H_6O_6 \rightarrow SrC_4H_4O_6 + 2HCl$$

Barium added STT crystals were grown in five different impurity concentrations, viz., 0.02, 0.04, 0.06, 0.08, 0.10 M. Barium (II) chloride was mixed with the supernatant solution and allowed to diffuse into the gel medium containing tartaric acid. For pure crystals, the maximum size is 8 x 4 x 4mm^3 and in the case of doped crystals the maximum size is 6 x 4 x 3 mm^3.

D.C. conductivity studies

The grown crystals were powdered and made into pellets (polycrystalline) of diameter 10 mm and thickness 3 mm. The pellets were prepared using a hydraulic press ('LYNX', Lawrence and Mayo, India) and the pressure applied was about 4 tonnes. The surfaces of the pellet in contact with the electrode were coated with good quality graphite paste. The pellet was then placed between the electrodes of the experimental cell. The experimental cell consists of two electrodes made up of stainless steel coated with silver and has a diameter same as the pellet. This experimental cell was electrically shielded and placed in an electric oven for temperature variation. The electrodes of the experimental cell were connected to a Galvanostat (Autolab make) to measure the resistance of the sample. Before the measurements were carried out, at each temperature the sample was kept for about 20 min to ensure proper sample thermal equilibrium. The temperature range was 40 to 100°C.

Results and discussion

Crystal Growth

It was observed that when the pH of the gel was between 3.8 to 4.2 and the concentration of the reactants was equal (1 M), good quality STT crystals were grown. A change in the pH of the gel solution other than this range resulted in poor quality crystals. It was further observed that the crystals appearing near the gel solution interface were smaller in size and the crystals grown down the gel column (2 to 3 cm from the gel solution interface) were well shaped and highly transparent. Similar observations have been reported for Cu^{2+} doped STT crystals (Gowri and Sahaya Shajan, 2006).

The atomic absorption spectroscopic analysis was carried out using Varian Model Spectraa 620 to determine the atomic concentrations of the impurity atom in the crystal. The atomic concentrations in the grown crystals were 0.0082, 0.021, 0.038, 0.053 and 0.061 M for 0.02, 0.04, 0.06, 0.08, 0.10 M respectively. The powder X-ray diffraction data was also collected using PANalytical make Model X'per PRO X-ray diffractometer. The XRD pattern was then indexed and compared with the JCPDS data. The data matches very well with the JCPDS data for strontium tartrate trihydate crystals. The results are presented in Table 1.

Table 1. Indexed XRD data for strontium tartrate trihydrate crystals

hkl	From present work		from JCPDS file (file no. 23-0551)	
	2θ (°)	I/I_o	2θ(°)	I/I_o
110	11.71	100	11.806	100
111	14.92	87	15.185	60
020	15.97	74	16.402	60
120	19.23	61	19.195	60
202	27.12	54	26.997	40
301	30.11	63	30.378	80
023	31.89	64	32.054	80
203	34.78	52	34.061	60
252	48.67	58	48.929	60

Table 2. Activation energies (in eV) obtained from the Arrhenius plots

Crystal	Activation energy E_A (in eV)	
	Extrinsic region	Intrinsic region
Pure STT	0.783	0.324
0.02M Ba^{2+} doped STT	0.369	0.081
0.04M Ba^{2+} doped STT	0.408	0.178
0.06M Ba^{2+} doped STT	0.527	0.094
0.08M Ba^{2+} doped STT	0.737	0.126
0.10M Ba^{2+} doped STT	0.789	0.102

D.C Conductivity

The variation of D.C conductivity with temperature is illustrated in Fig. 1. The conductivity is found to increase with impurity concentration. The order of D.C. conductivity observed in the present study is comparable with the conductivity ($10^{-9}\ \Omega^{-1}m^{-1}$) reported in the literature for other tartrate crystals. Pure and impurity added STT pellets were taken up for conductivity studies. As the pellets are polycrystalline, grain boundaries are present and therefore when an electric field is applied some of the charge carriers will be trapped at grain boundaries. This give rises to interfacial polarization resulting in lower conductivity. However in the case of tartrate crystals it was reported that the value of conductivity of the crystal was slightly higher than the conductivity of the pellet, but the order ($10^{-9}\ \Omega^{-1}m^{-1}$) remained the same in both the cases (Sahaya Shajan and Mahadevan, 2005; Gowri and Sahaya Shajan, 2006).

To understand the conduction mechanism in these crystals, the DC conductivity data are plotted as 1000/T versus $\ln\sigma_{dc}$ in fig. 2. All the crystals grown in the present study show Arrhenius type behaviour described by,

$$\sigma_{dc} = \sigma_o \exp(-E_A/kT)$$

where σ_o is the pre-exponential factor and k is the Boltzmann's constant. From these plots we observe that there are two activation energies in the temperature range considered.

These plots are similar to intrinsic-to-extrinsic transition found in electronic semiconductor. The presence of protons to be exchanged between and hence able to diffuse through interspaces makes these materials protonic conductors (Sahaya Shajan and Mahadevan, 2005). The variation in electrical conductivity yields two straight lines of different slopes showing that there exist two types of conduction in these crystals. The one at low temperature is extrinsic and the other at high temperature is intrinsic. It has been already reported that no phase change was observed by Thermo-gravimetric analysis (TGA) in the temperature region considered in the present study (Gowri & Sahaya Shajan, 2006). This further confirms that there exist two types of conduction in these crystals. The activation energies in the extrinsic and intrinsic ranges were calculated and are presented in Table 2. The low activation energies in the intrinsic region show that the conductivity is predominantly due to the movement of defects produced by thermal activation.

Fig. 1. Variation of DC conductivity with temperature

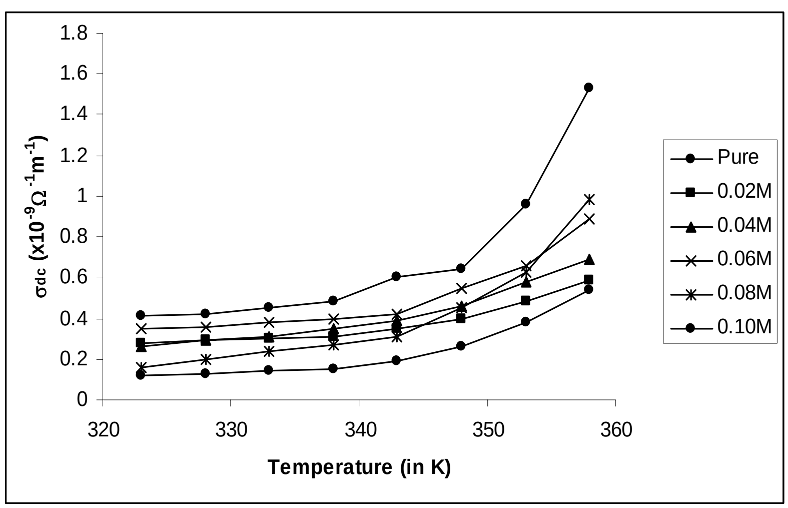
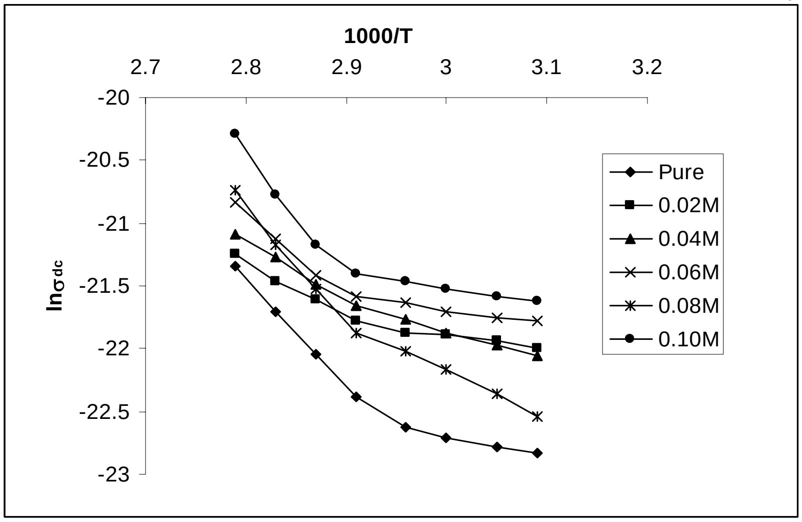


Fig. 2. Arrhenius plots of the grown crystals



Conclusions

Pure and impurity (Ba^{2+}) added STT single crystals were grown by the gel method and DC conductivities were measured at various temperatures. The present study indicates that the conductivity increases with impurity addition and these crystals exhibit two types of conduction by the way of intrinsic and extrinsic conduction. No ferroelectric transition was observed in Ba^{2+} added STT crystals within the temperature range considered in the present study.

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