



THE VARIATIONS IN DIELECTRIC PROPERTIES OF CALCIUM OXALATE MONOHYDRATE SINGLE CRYSTALS DUE TO DOPING OF IMPURITIES

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ABSTRACT

Pure and doped single crystals of calcium oxalate monohydrate were grown by gel technique using silica gel. Two (Nickel and cobalt) impurities were used as dopants. Some variations in their dielectric properties were observed due to doping of impurities.

Key words: Gel growth, Silica gel, Nucleation, Calcium oxalate, Doping, Dielectric studies.

INTRODUCTION

Kidney stones consist of various organic and inorganic compounds¹. Calcium oxalate (CaC_2O_4) is one of the major components of renal stones. It is found to be present in almost kidney and bladder stones². About 40% of the total composition of the kidney stones is found to contain purely calcium oxalate³. There are three types of hydrated forms of calcium oxalate, such as calcium oxalate monohydrate, calcium oxalate dihydrate and calcium oxalate trihydrate. Among these, calcium oxalate monohydrate is found to be thermodynamically stable⁴. The study of calcium oxalate monohydrate is intensively interested, because crystalline diseases has lead to the *in vitro* investigations of the crystalline components present in the stones. Oxalate is a major component of urinary stones and its urinary concentration plays an important role in stone formation. Even a small increase in urinary oxalate has a significant impact on calcium oxalate saturation.

Clinical experiences with the fragmentation methods have shown that calcium oxalate monohydrate is the hardest stone having low fragility. The difference in fragility between calcium oxalate monohydrate and calcium oxalate dihydrate was observed⁵. The knowledge of mechanical and dielectric properties of the stone is essential in optimizing the

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parameters such as frequencies, intensities and dielectric constant needed for stone fragmentation. There is a previous report on the growth of calcium oxalate monohydrate (pure and doped) in gel method⁶. It has shown that urinary stones grow in a gelatinous medium that is probably one of the reasons for the oriented striated growth of the crystals specifically encountered in the urinary calculi⁷. Crystallization using gel medium is popular in the study of urinary crystal formation⁸. Gel acts as an inert medium during the growth of many crystalline compounds and it acts as an ideal medium in the study of crystallization of biomolecules *in vitro*⁹.

The micro hardness values of pure calcium oxalate monohydrate single crystals (gel grown) were measured by Girija et al.,⁶ but the variations of dielectric properties of calcium oxalate monohydrate crystals due to doping of impurities such as cobalt and nickel were not reported in the literature. The observed variations in dielectric properties are reported in the present communication.

EXPERIMENTAL

The Analar grade chemicals were used for the growth of crystals. Double diffusion (U-tube) growth technique was employed. The gel was set by mixing sodium metasilicate solution of density 1.04 g cm^{-3} with 5% acetic acid. The pH value was adjusted to 5.5. and kept at room temperature (30°C). After the gel was set, 1M calcium chloride solution was added to one limb of the U-tube and 1M oxalic acid was added to the other limb simultaneously without disturbing the gel surface. After one week, small crystals were seen as a disc on the bent portion of the U-tube. For nickel doped crystals, 0.01M nickel chloride solution was mixed with 1M calcium chloride solution and for cobalt doped crystals; 0.01M cobalt chloride solution was mixed with 1M calcium chloride solution in this procedure. Nickel doped calcium oxalate (light green) and cobalt doped calcium oxalate (pink) crystals were obtained. Fifty five days were taken for complete growth of pure and doped crystals of calcium oxalate monohydrate. The size of the crystals obtained was $2 \times 2 \times 1.5 \text{ mm}^3$ approximately. The crystals were harvested and then subjected for dielectric properties studies.

Experiments were repeated for pH values ranging from 4 to 6 in steps of 0.5 and for densities 1.03 , 1.04 and 1.05 g cm^{-3} . The crystals obtained at pH 6 were not good in quality. Crystals at 4 and 4.5 were very small in size. The density variation does not make any significant changes in their size. Characteristic studies such as XRD, FTIR and thermal analysis on grown crystals were reported earlier¹⁰.

Dielectric properties of pure and doped crystals were studied and the variations on the values due to doping of nickel and cobalt (impurities) on pure calcium oxalate were analyzed. The grown crystal faces were polished and were made in the form of rectangles. Area and thickness of the crystals were measured. Silver paste was applied on the experimental faces and silver electrodes are attached to them. The capacitance and the dielectric loss were measured using an hp 4192 ALF impedance analyzer (5 Hz – 13 MHz) at different temperatures and at different frequencies ranging from 100 Hz to 1 MHz. (Measurements were made at Research Center, Department of Physics, S.T. Hindu College, Nagarcoil, T.N). The relation connecting capacitance (C) and permittivity (ϵ) of the sample could be represented by, $C = \frac{\epsilon A}{d}$, where d is the thickness and A is the area of the faces in contact with the electrodes. The dielectric constant of the crystals was calculated using the formula, $\epsilon = \epsilon_r \epsilon_0$, where ϵ_r is the relative permittivity or relative dielectric constant of the sample and ϵ_0 is the permittivity of free space (8.854×10^{-12} F/m). The a.c. conductivity was calculated using the equation, $\sigma_{ac} = 2\pi f \epsilon \tan \delta$, where ' f ' is the frequency and ' $\tan \delta$ ' is the loss tangent. The values C , ϵ , σ_{ac} and $\tan \delta$ of grown crystals at different frequencies and at different temperatures were tabulated. Three sets of graphs were plotted for all grown crystals as Fig. 3: (1-3). Dielectric constant vs log f , (Figs. 4-6) a.c. Conductivity vs log f and (Figs. 7-9) loss tangent vs log f .

RESULTS AND DISCUSSION

The characteristic studies revealed that the grown crystals are pure calcium oxalate monohydrate and their doped (cobalt and nickel) crystals.

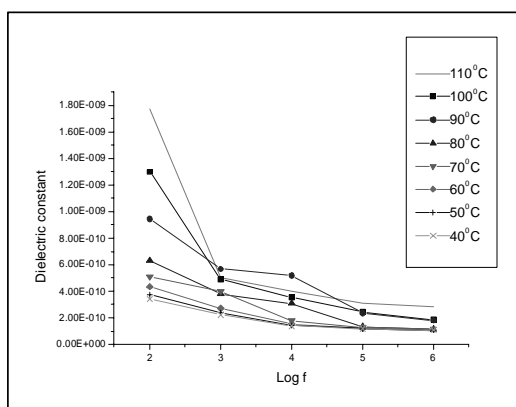


Fig. 1: Pure calcium oxalate

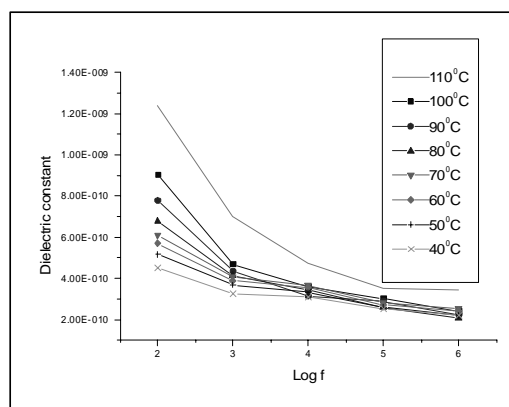


Fig. 2: Nickel doped calcium oxalate

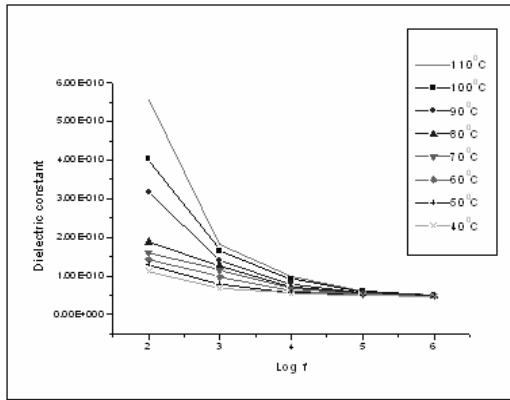


Fig. 3: Cobalt doped calcium oxalate

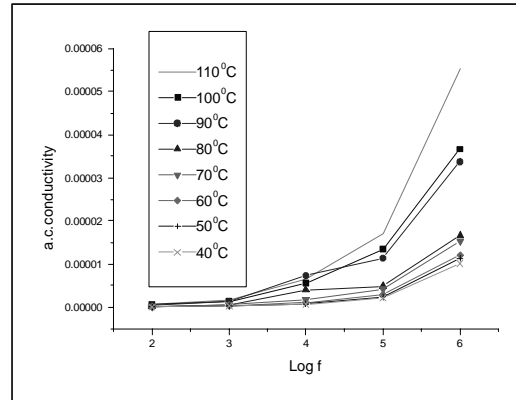


Fig. 4: Pure calcium oxalate

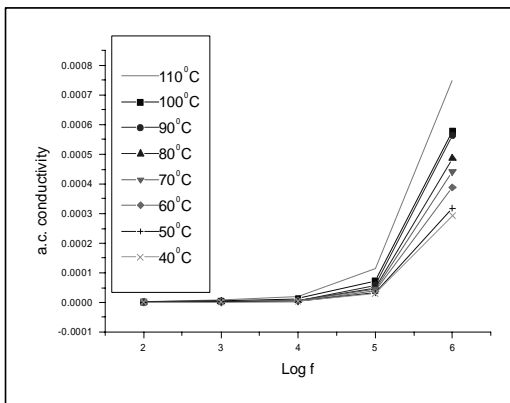


Fig. 5: Nickel doped calcium oxalate

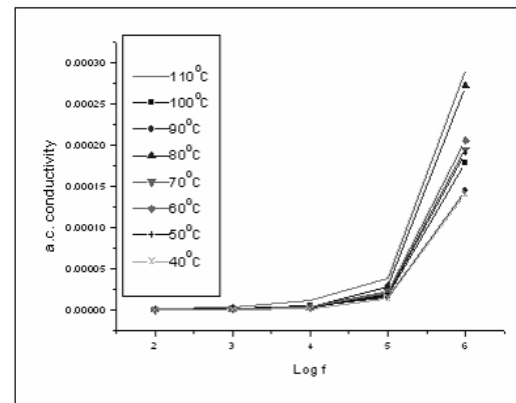


Fig. 6: Cobalt doped calcium oxalate

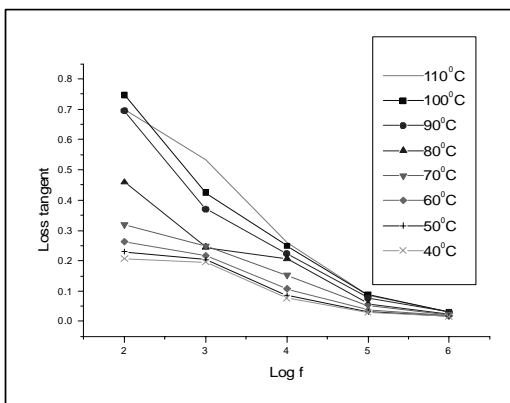


Fig. 7: Pure calcium oxalate

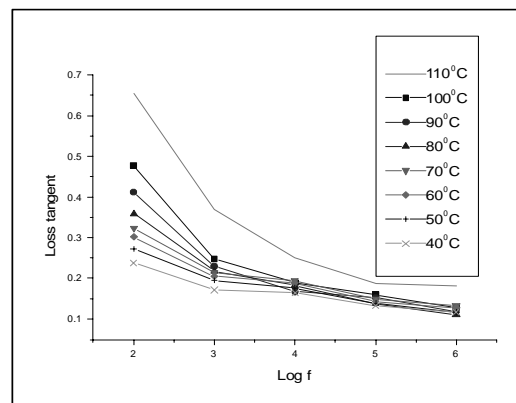


Fig. 8: Nickel doped calcium oxalate

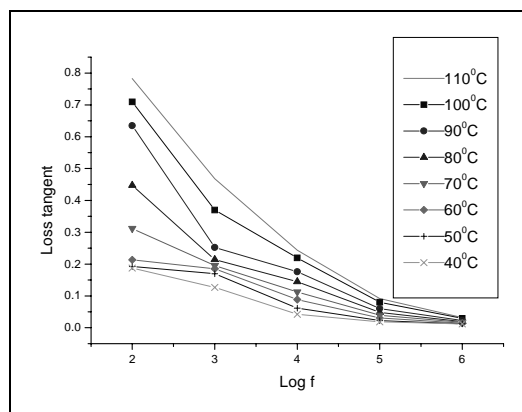


Fig. 9: Cobalt doped calcium oxalate

The values of relative dielectric constants (ϵ_r), capacitance (C), loss tangent ($\tan \delta$) and the a.c. conductivity of all grown crystals were determined. The first set of plots with Dielectric constant (ϵ_r, ϵ_0) vs log f of all grown crystals were seen in Figs. 1-3. From the plot, it is seen that the dielectric constant initially decreased with increase in frequency. It was also found that the doping changes the dielectric behavior of all the crystals. In normal dielectric behavior, the dielectric constant decreases with increase in frequency reaching a constant value depending on the fact that beyond a certain frequency of electric field, the electron exchange does not follow the alternating field. The variation of a.c. conductivity with log f of grown crystals is clear from the second set of plots shown in Figs. 4-6. The variation of loss tangent ($\tan \delta$) with frequency was studied from the third set of graphs plotted with log f vs $\tan \delta$, shown in Figs. 7-9. All variations were studied for different temperatures ranging from 40°C to 110°C, in steps of 10°C. Variations of capacitance, dielectric constant, loss tangent and a.c. conductivity with temperature were observed.

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Revised : 05.11.2010

Accepted : 08.11.2010