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Single crystal growth by gel technique and characterization of lithium hydrogen tartrate

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ABSTRACT

Single crystal growth of lithium hydrogen tartrate by gel encapsulation technique is reported. Dependence of crystal count on gel density, gel pH, reactant concentration and temperature are studied and the optimum conditions for these crystals are worked out. The stoichiometric composition of the grown crystals is determined using EDAX/AES and CH analysis. The grown crystals are characterized by X-ray diffraction, FTIR and Uv-Visible spectroscopy. It is established that crystal falls under orthorhombic system and space group P_{222} with the cell parameters as: $a=10.971$ Å, $b=13.125$ Å and $c=5.101$ Å; $\alpha=90.5^{o}$, $\beta=\gamma=90^{\circ}$. The morphology of the crystals as revealed by SEM is illustrated. Crystallite size, micro strain, dislocation density and distortion parameters are calculated from the powder XRD results of the crystal. UV–vis spectroscopy shows indirect allowed transition with an optical band gap of $\sim$4.83 eV. The crystals are also shown to have high transmittance in the entire visible region. Dependence of dielectric constant, dielectric loss and conductivity on frequency of the applied ac field is analyzed. The frequency-dependent real part of the complex ac conductivity is found to follow the universal dielectric response: $\sigma ac\ (\omega)\sim\omega s$. The trend in the variation of frequency exponent with frequency corroborates the fact that correlated barrier hopping is the dominant charge-transport mechanism in the present system.

1. Introduction

Materials exhibiting excellent second order non-linear optical (NLO) properties have been the focus of condensed matter community owing to their various potential applications in modern electronics such as optoelectronics, telecommunications and optical storage devices [1]. Non-linear optical processes are one of the key functions of frequency conversion and optical switching [2]. These useful applications depend upon various material features, such as transparency, birefringence, refractive index and photochemical stability. These requirements are though mostly met by various organic materials, yet their utility gets limited on account of their low physical strength and chemical stability. Semi organic materials possessing large optical nonlinearity may overcome these limitations without adversely affecting the optical characteristics that are essential for their potential application in telecommunication, optical computing, optical data storage and optical information processing [3,4]. In tartrate compounds, the metal ion is ionically bonded with the tartrate ion which, in their single crystal form, shows high optical non-linearity [5–7]. Such materials are presently receiving a large attention due to rapid development of laser diodes [8]. Presence of metal ions not only improves the charge carrier injection but also modifies the conductivity of the materials. Growth and characterization of some other tartrate compounds have been reported from this laboratory earlier [9–12]. In this article the authors describe single crystal growth of lithium hydrogen tartrate (LHT) by gel method and their characterization. The advantage of diffusion technique is that the crystals grow at ambient temperatures and, as such, there is least chance of equilibrium defects in them. The gel, being chemically inert, provides a three dimensional matrix and controls the rate of reaction between the reactants. Also, transparency of gel helps us to monitor the nucleation and growth of crystals regularly and as such enables one to make in situ observations and understand the growth kinetics of crystals. An attempt has been made to relate nucleation kinetics with the classical nucleation theory. It may be noted that, to the best of author's knowledge, the growth and characteristics of LHT single crystals are reported for the first time.

2. Experimental

Chemicals used in the present investigation include, Lithium chloride (99.998%) of Chengdu Haoxuan Technology Co. Ltd. China,

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Sodium meta silicate (99.9%) from Thomas Baker, Mumbai, India and L-Tartratic Acid (99.5%) from Loba-Chemie Indoaustranal Co; Mumbai, India.

2.1. Single crystal growth

Single crystals of lithium hydrogen tartrate were grown by gel encapsulation technique [13,14]. The crystallizer was a glass tube of length 200 mm and diameter 25 mm. Initially, the gel was prepared by adding a solution of sodium meta silicate (molarity ranging between 0.1–2.0 M) to L-tartaric acid (molarity ranging from 0.2–1.5 M) drop by drop with continuous stirring which may otherwise result in premature local gelling and make final solution inhomogeneous. The gel of given pH (2.0–5.0) was then allowed to set for a given time (20–196 h) at room temperature averaging around 25 °C. Once the gel got set, an aqueous solution of lithium chloride of a particular molarity was poured over the gel carefully along the walls of the crystallizer in order to avoid any gel breakage. The diffusion of Li^+ ions through narrow pores of the silica gel leads to reaction between these ions in LiCl, the upper reactant (abbreviated as UR) and tartaric acid ($HC_4H_4O_6$) ions present in the gel as lower reactant (abbreviated as LR). The controlled reaction between the reactants through the gel matrix was expected to take place as given below

$$LiCl + C_4H_6O_6 \rightarrow LiHC_4H_4O_6 + HCl$$

The reaction leading to the formation of lithium hydrogen tartrate (LHT) single crystals did proceed as expected. Several experiments were performed in order to optimize the conditions of growth viz, gel pH, gel molarity, upper and lower reactant concentrations and the temperature. The maximum size of LHT single crystals grown at the optimum conditions (gel pH 4, gel age 96 h, UR concentration 0.8 M and LR concentration 0.5 M) was 3 mm × 2.8 mm × 2.1 mm.

2.2. Characterization techniques

Morphology of the grown crystals was studied using scanning electron microscope (SEM, Model JEOL 840). The energy dispersive spectrometer (OXFORD ISIS-300 system) attached to the SEM was used to establish the chemical composition. CH analysis was carried out using Vario- EL-III CHNS analyzer. AES was recorded using model- IRIS INTREPID II XSP. Single crystal X-ray diffraction was carried out using single crystal Oxford X-ray diffractometer, whereas powder X-ray pattern was obtained using powder X-ray diffractometer (Rigaku Co. Ltd Japan) with CuK_α radiation (α=1.5406 Å) with a scanning rate of 2°/min. UV–vis spectrum was recorded employing Hitachi U3300 spectrophotometer in order to understand optical characteristics. Perkin-Elmer Paragon-1000 spectrophotometer Esquire 3000 spectrometer was used for recording FTIR spectra ranging from 450 to 4000 cm^{-1}, using KBr technique. In order to know about dielectric behavior of the material, the dielectric measurements were conducting on finely powdered crystalline material pressed into pellets of 6 mm diameter and 1.5 mm thickness at a pressure of 10 MPa by using a hydraulic press. The flat surfaces of the pellets so obtained were coated with a thin layer of silver paste for making good electrical contacts. Room temperature dielectric properties of this sample were recorded on application of ac field (in the frequency range 20 Hz-1 MHz), using Agilent 4285 A precision LCR meter. Having achieved the growth of LHT single crystals by gel technique, the above said characterization was carried out to establish stoichiometric composition (EDAX/AES/CH analysis/FTIR), optical characteristics (UV–vis spectroscopy) and dielectric behavior (LCR meter) and to obtain information on their external and internal crystallographic features (SEM & XRD).

3. Results and discussion

Fick's Law expressed as $R = Dt^{1/2}$ (where R stands for the rate of diffusion, t for time and D for diffusion coefficient/ Diffusivity) governs the growth of crystals in gel media [15].The diffusion coefficient is dependent on temperature, viscosity and size of the ions. To determine optimum conditions for the growth of LHT single crystals, a series of experiments were performed, particularly in regard to effect of gel density, gel pH, gel age, surrounding temperature of the crystallizer and concentration of UR (LiCl). Sodium meta silicate gel acidified with tartaric acid of a particular pH was allowed to set and then suitably aged in a number of crystallizers. The UR was then poured in the crystallizer as per the procedure described above. In order to conduct studies on effect of basic parameters of gel on nucleation and number of single crystals formed, the following experiments were performed:

3.1. Dependence of crystal count on gel density, pH & temperature

Preliminary experiments were conducted to determine appropriate conditions for the preparation of silica gel, which indicated that the specific gravity of 1.05 g/cm^3 is suitable. Fig. 1 shows the dependence of crystal count on concentration of gel. The crystal count decreases with increase in gel concentration. The density used in practice is a compromise. Greater gel density implies small pore sizes which does indeed diminish nucleation. However, greater gel density tends to increase contamination of the crystals by silicon and, thereby, to affect their perfection and shape adversely. On the other hand, gels of insufficient density take a long time to form and are mechanically unstable [13].

It is well known that gel is a loosely interlinked polymer. The principal role played by it is that of suppressing nucleation, thereby reducing the competitive nature of the growth. Nucleation control is the key to the ultimate success of the gel method. One operative parameter is the size of the diffusing particles, relative to the pore size in the gel. Another is the amount of interaction between solute and the internal gel surfaces. pH during gelling has significant influence on gel structure. As pH increases the gel structure changes from a distinctly box–like network to a structure consisting of loosely bound platelets which appear to lack cross-linkages and the cellular nature becomes less dinctint [13]. It may be noted that the time required for the gelation is very sensitive to pH. At very low pH values the tendency toward polymerization is diminished and chain formation is slowed. The gel structure affects the crystal growth characteristics, including growth rate and ultimate crystal size.

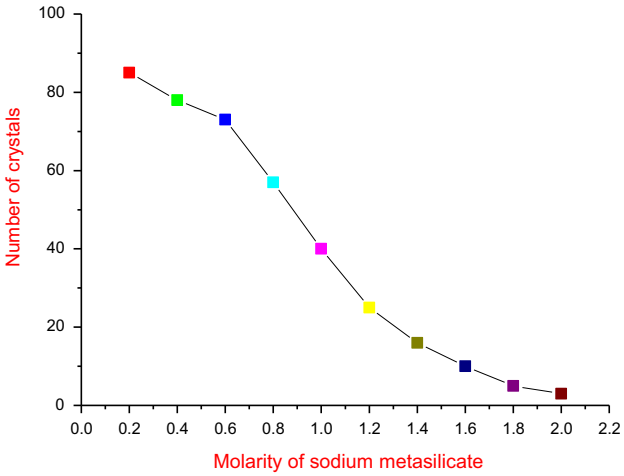

Fig.1. Variation of crystal count with gel molarity.