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Growth, optical, thermal, mechanical and electrical properties of anhydrous sodium formate single crystals

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ABSTRACT

Anhydrous sodium formate single crystals were grown by the solvent evaporation method at 40 °C. Etching study was carried out to assess the crystalline perfection. X-ray diffraction and FTIR spectral analyses were performed for the identification of the material and the crystal structure. Suitability of the crystal for photonic applications was studied by the optical transmittance, SHG efficiency and Z-scan measurements. The thermal and mechanical stabilities of the grown crystal were also investigated. Thermal decomposition and load dependence of various mechanical parameters viz. H_v, K_c, B, σ_v and C_{11} have been understood. AC (with various frequencies ranging from 20 Hz to 200 kHz) and DC electrical measurements were carried out at various temperatures ranging from 30 to 150 °C. Temperature and frequency dependences of important electrical parameters have been understood. Results obtained indicate that the grown crystal exhibits higher crystallinity, good optical transmittance, third order optical nonlinearity, good thermal stability (up to 318 °C), higher dielectric constant and normal mechanical behaviour.

1. Introduction

The metal formate crystals have gained much interest due to their potential applications and interesting physical properties [1]. The formates of group I and II metals in periodic system exhibit strong nonlinear optical properties [2]. Crystal structures have been reported for several metal formates such as lithium formate [3], sodium formate [4], ammonium formate [5], strontium formate [6], barium formate [6], calcium formate [6], cupric formate [7] and gadolinium formate [8]. However, reports on physico-chemical properties are limited. Studies on amino acid formates such as L-threonine formate [9–12], L-alanine formate [13,14], L-valinium formate [15] L-arginine formate [16] and L-argininium formate [17] have also been reported. Among the metal formate crystals, lithium formate [18] and strontium formate [19] crystals have been studied, to some extent. However, the literature shows very little about the other metal formate crystals.

Among all the alkali metals, sodium has been widely used due to its higher charge density. In semi-organic crystals, sodium has the ability to combine with organic ligands. Sodium formate has been used in many industries and its aqueous solutions are used to absorb SO_2 in thermoelectric power plants. The structure determination and vibrational spectral analysis for sodium formate crystal have already been reported in the literature [20–22]. Crystals of sodium formate have monoclinic-holohedral symmetry with the centro-symmetric space group C2/c. The crystal has four molecules in a unit cell and each sodium atom is linked to six oxygen atoms belonging to five different formate radicals. The formate anion lies on a twofold axis and has C_{2v} symmetry. The density of this crystal is 1.91–1.93 g/cc.

Sodium formate (hydrous/anhydrous) is a representative of hydrogen bonded crystals and the crystal is expected to be highly useful for device applications. In hydrous sodium formate, the water molecule may increase the elastic and NLO properties but reduces the thermal stability of the crystal. But, it is essential for the crystal to possess reasonably good thermal stability for their suitability in practical applications. So, we have made an attempt in the present study to grow single crystals of anhydrous sodium formate for device applications. In the present study, we have grown the anhydrous sodium formate (SF) single crystals by using the simple solvent evaporation method and characterized chemically, structurally, optically, thermally, mechanically and electrically. The results obtained are reported and discussed herein.

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2. Experimental

2.1. Material synthesis

Sodium formate was synthesized by mixing high purity sodium hydroxide (obtained from Merck) and formic acid (obtained from Rankem) taken in equimolar ratio and dissolving completely in millipore water of resistivity 18.2 MΩcm at room temperature (30 °C) using a magnetic stirrer. The purity of the crystalline product was further improved by repeated recrystallization process. The sodium formate formation can be represented by the following chemical reaction:

$$NaOH + CH_2O_2 \rightarrow NaHCOO + H_2O$$

2.2. Crystal growth

Solvent evaporation solution growth technique was employed to grow single crystals of sodium formate. Saturated solution of sodium formate was prepared and allowed to equilibrate in a beaker (crystal growth cell). The cell was covered with a perforated sheet and kept undisturbed in a constant temperature bath maintained at 40 °C to avoid forming the dihydrate [22]. After a period of one month, evaporation of the solvent gives thin transparent plate-like crystals with the maximum size of $14 \times 9 \times 1$ mm^3. The grown crystals were harvested and used for the characterization experiments. Two-dimensional nucleation may be considered as the mechanism behind the formation of single crystals.

2.3. Characterization

In order to understand the surface features of the grown crystals, good quality crystals (macroscopically free from defects) with flat and smooth surface of thickness 0.7 mm were selected and subjected to etching study with water as the etchant. The crystal was dipped in the etchant from 10 to 60 s with an interval of 10 s and then wiped with a tissue paper. The etch patterns were observed and photographed with an Olympus-BX51M optical microscope in the reflection mode. Powder X-ray diffraction (PXRD) analysis of the crystal was carried out using a PANalytical EMPYREAN diffractometer with Cu Kα radiation of wavelength 1.5405 Å. The data were collected in the 2θ range of 5–80° with a step size of 0.026°. The Fourier transform infrared (FTIR) spectrum was recorded for the as-grown crystal using a JASCO FT/IR-4100 spectrophotometer by the ATR technique at room temperature (30 °C) in the wave number region 4000–550 cm^{-1}.

The linear, second order nonlinear and third order nonlinear optical properties of the grown SF crystal were understood by measuring its optical transmittance in the UV–vis–NIR region (200–1200 nm), second harmonic generation (SHG) efficiency and Z-scan measurements respectively. The optical transmittance of the crystal was measured using a Shimadzu UV-2600 UV–vis–NIR spectrometer by placing the crystal of thickness 0.7 mm directly on the path of the source. The Kurtz and Perry powder method [23] was employed to measure the SHG efficiency. The input Q-switched Nd-YAG laser beam of wavelength 1064 nm with energy 1 mJ/pulse, pulse width 10 ns and repetition rate 10 Hz was made to fall on the powder form of the crystal filled in the micro capillary tube. The second harmonic output (emission of green light) generated by the crystal was detected by the photomultiplier tube. The third-order nonlinear refractive index (n_2) and absorption coefficient (β) were evaluated by using the single beam Z–scan technique [24,25]. The laser beam from 635 nm continuous wave (CW) diode laser was focused by a convex lens with focal length of 5 cm, which produces a beam waist ω_o of 23.57 μm and the Raleigh length, Z_R of 2.7 mm in the sample. A 1 mm thickness of cuvette containing the aqueous solution (0.4 g dissolved in 5 ml water) of SF crystal placed on a translational stage was moved across the focal region (+Z to −Z) along the axial direction, which is the direction of propagation of laser beam.

The thermogravimetric (TG/DTG) analysis was performed on the SF crystal in powder form from 24 to 700 °C with a heating rate of 10 °C/min using a TGA Q500 V6.7 Build 203 instrument with pin-holed platinum crucible under nitrogen atmosphere. The mechanical stability analysis was done by a Shimadzu HMV-2T Vickers microhardness tester with diamond pyramidal indenter at room temperature. The crystals were selected by the same procedure followed for the etching studies and it was indented by applying a load varying from 25 to 100 g with a dwell time of 5 s on the large surface area of the crystal.

The AC electrical (dielectric) measurements were carried out by the parallel plate capacitor method with an accuracy of ±2% by varying the frequency from 200 Hz to 200 kHz at various temperatures ranging from 30 to 150 °C using a HIOKI IM3528 LCR meter. The DC electrical measurements were also made to an accuracy of ±2% at various temperatures ranging from 30 to 150 °C by the conventional two-probe method using the same LCR meter. In both the cases, the temperature was controlled to an accuracy of ±0.01 °C and the measurements were made while cooling the sample crystal. An as grown (fresh) crystal was polished with an emery paper to get a perfect shape and the dimensions were measured using a travelling microscope (least count = 0.001 mm). Opposite faces of the crystal were coated with good quality silver paste to obtain a good conductive surface layer. The measurements were carried out along the direction perpendicular to the large area surfaces of the crystal. Dielectric loss factor (tan δ) and capacitances with the crystal (C_{crys}) and without the crystal (C_{air}) were considered in the case of dielectric measurements and resistance (R) was considered in the case of DC electrical measurement. The other AC and DC electrical parameters were determined using the above measured values.

3. Results and discussion

3.1. General features

Fig. 1 shows the photograph of a sample SF crystal grown in the present study. The crystals grown are found to be well shaped, colourless and transparent. However, it exhibits some hygroscopic

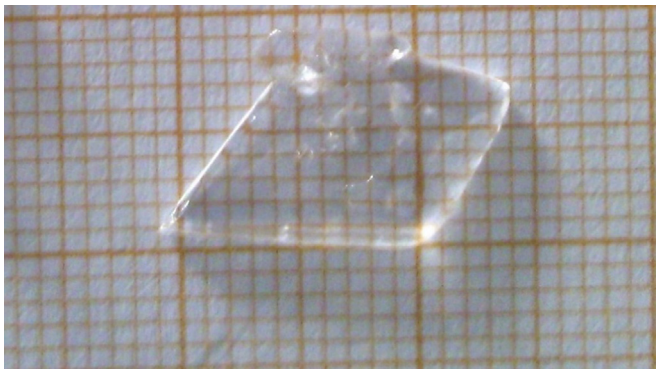

Fig. 1. Photograph of sample SF crystal grown.