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GROWTH AND CHARACTERISATION OF SEMICARBAZONE CRYSTALS

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ABSTRACT

Semicarbazone crystals have been grown by gel technique. The grown crystals have been characterized using X–ray diffraction, micro hardness and FT–IR studies. The X–ray diffraction analysis reveals that the crystal belongs to the triclinic crystal system and space group P1. The FT–IR studies reveal that the compound possess both; the free and hydrogen bonded N–H stretching modes. The micro hardness studies show the dislocations etch pits and these are temperature dependent.

Key words: X–ray diffraction, Gel growth, Nonlinear optic materials

INTRODUCTION

In recent years, the interest of growing organic materials for nonlinear optical (NLO) applications has increased because of their high potential, i.e. use in devices such as second harmonic generators, electro optic modulators etc. Organic and polymeric materials have shown great interest in NLO applications[1,2]. These materials work because they exhibit strong nonlinear polarization in the presence of high intensity electromagnetic fields. The properties and performance of nonlinear optical and photonic materials depend critically on their composition, micro hardness and purity. Convection and sedimentation can cause variations in processing conditions of such materials, which in turn, can affect the morphology and microstructure of the materials, and thereby, also optical properties[3,4].

The large nonlinear optical effect found in some organic crystals makes the materials attractive for applications in frequency conversion[5]. NLO materials play an important role in the field of fiber optic communication and optical signal processing. Optoelectronics and NLO are expected to play a major role in photo electronics, which is emerging as a multidisciplinary new frontier area of science and technology. The organic molecular materials have emerged as a new class of superior quality over inorganic systems. Among the nonlinear phenomena, frequency mixing and electro optic modulation are important in the field of optical image storage and optical communacations[1, 6,7]

Crystal growth from gel is a powerful purification process and the purity of the crystal obtained is higher than the corresponding starting reactives. This is an advantage with respect to

high temperature growth methods, where much more care should be taken in the impurity contents of the starting materials. Also the low temperature involved in growth from gel makes it easier to obtain crystals with fewer defects than in high temperature growth techniques[8].

Crystal growth in gel technique has gained considerable importance due to simplicity and effectiveness in growing single crystals. Here, we present the details of the growth of semicarbazone crystals by gel technique at room temperature. The grown crystals have been characterized by XRD, microhardness and FT–IR studies.

EXPERIMENTAL

Sodium meta silicate gel solution of density 1.04 g cm^{-3} was prepared. 5 mL of H_2S solution was mixed with the gel solution. For gelation, 1N acetic acid was used. After gelation, solution of semicarbazone dissolved in HCl of concentration 10 N was used as the outer reactant. The outer reactant was allowed to diffuse into the gel medium and according to the principle involved in this growth technique, at ordinary temperature in the presence of H_2S, crystallization of semicarbazone pronounced.

But, the amount of H_2S solution added with the gel solution before acidification is very meagre. Though crystallization of semicarbazone was possible without H_2S, the presence of H_2S improves the size of the crystals. The experiment was also repeated by using semicarbazone dissolved in HCl directly as the outer reactant instead of H_2S dissolved in HCl of concentration 6 N. The different stages taking place during the process of crystallization of semicarbazone were also observed. The grown crystals are harvested after 30 days. The methods of growing semicarbazone in the form of single crystal in gel under ambient conditions were tried. Further, the effects due to the variation of growth parameters like the concentration of the reactants, the pH of the gel solution and density of the gel solution have been investigated.

RESULTS AND DISCUSSION

X–ray diffraction

In order to confirm the grown crystals of semicarbazone, the powder X–ray diffraction pattern was taken (Model : Rich Seiffart Powder diffractometer). Then the single crystal X–ray diffraction studies of the grown semicarbazone crystals were obtained using single crystal X–ray diffractometer (Model : ENRAF NONIUS CAD4). The crystallographic data are given in Table 1. The powder X–ray diffraction data was analyzed using Celn software package.

Table 1. Crystallographic data of semicarbazone

a	b	c	α	β	τ	Volume
10.520(2)Å	10.954(2)Å	12.608(3)Å	66.89(2)°	76.01(2)°	71.02(2)°	1252.7510Å^3

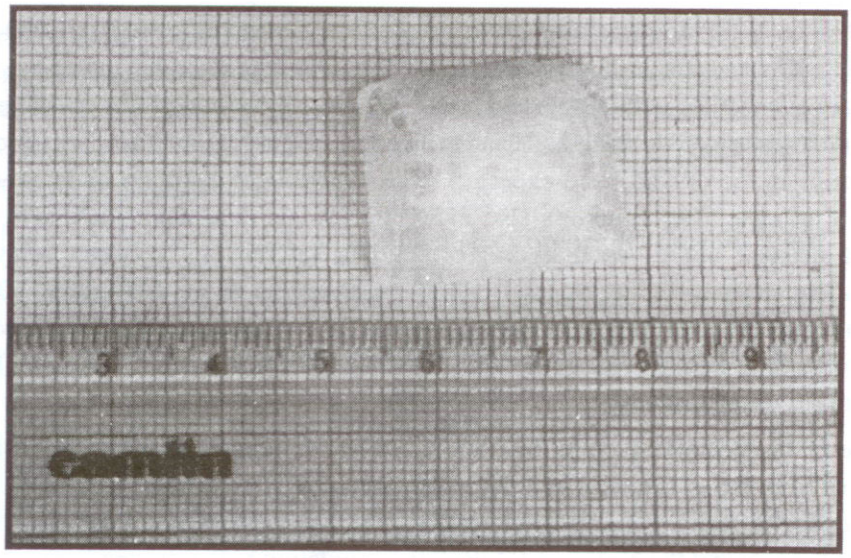

Figure 1 Crystal

The recorded X–ray spectra (Fig. 2) will have the intensity peaks and it was increasing with 2θ values. This indicates that there was no impurity content in the crystal. The lattice parameters derived from the diffraction pattern were found to be in good agreement with the available literature values.

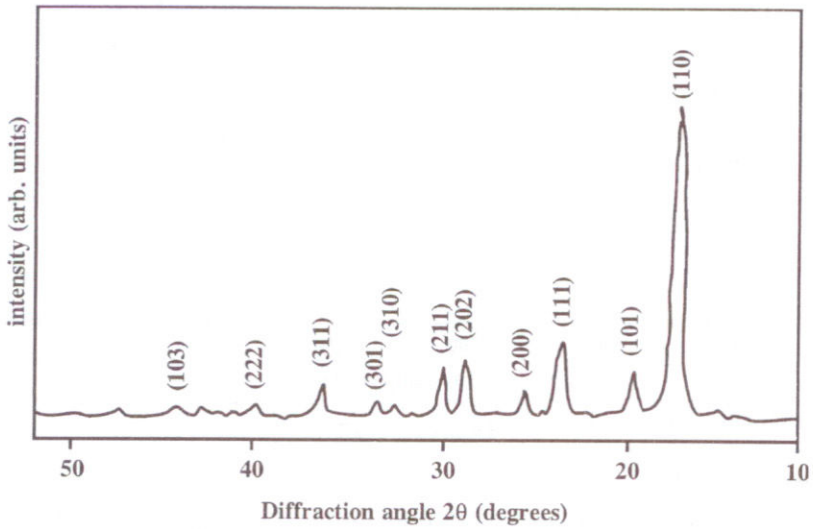

Fig. 2 XRD

FT–IR spectra

In order to absorb infrared radiation, a molecule must undergo a net change in dipole moment as a consequence of its vibrational motion. The FT–IR spectrometer (Model :

BRUKER IFS 66 V FT–IR) was used to record the IR spectrum in the region 4000–400 cm^{-1} and the middle IR spectrum is shown in the Fig. 3. The intense peaks lying just above and below 3500 cm^{-1} are due to NH_2 asymmetric and symmetric stretching modes. The sharp peak at 3300 cm^{-1} was due to hydrogen–bonded N–H and aromatic C–H stretch. As it was very broad, nearly all NH_2 groups in the crystal were expected to be in hydrogen bonding interaction with the neighbouring groups. The broadness also indirectly reveals that major packing force in the crystal was derived out of such hydrogen bonding interactions between semicarbazone molecules. The aromatic ring skeletal vibration is observed at 1450 cm^{-1}. The mono substitution in the aromatic ring is evidenced by the C–H out of plane bending modes of five adjacent hydrogen in each aromatic ring; they occur at 700 and 725 cm^{-1}. The C = O stretch of amide was observed at 1700 cm^{-1}.

It is intense but it is not much broad, so its contribution to molecular packing in the crystal is not as much as the previously said hydrogen–bonded NH_2 groups. The C=N stretch of semicarbazone is seen as a well–resolved peak at 1600 cm^{-1}. The peaks lying below 1500 cm^{-1} could be due to C=N and the N–H bond[11]. But its conjugation with nitrogen lone pair electrons is clearly evident by the shift of C = O stretching to lower value in this material.

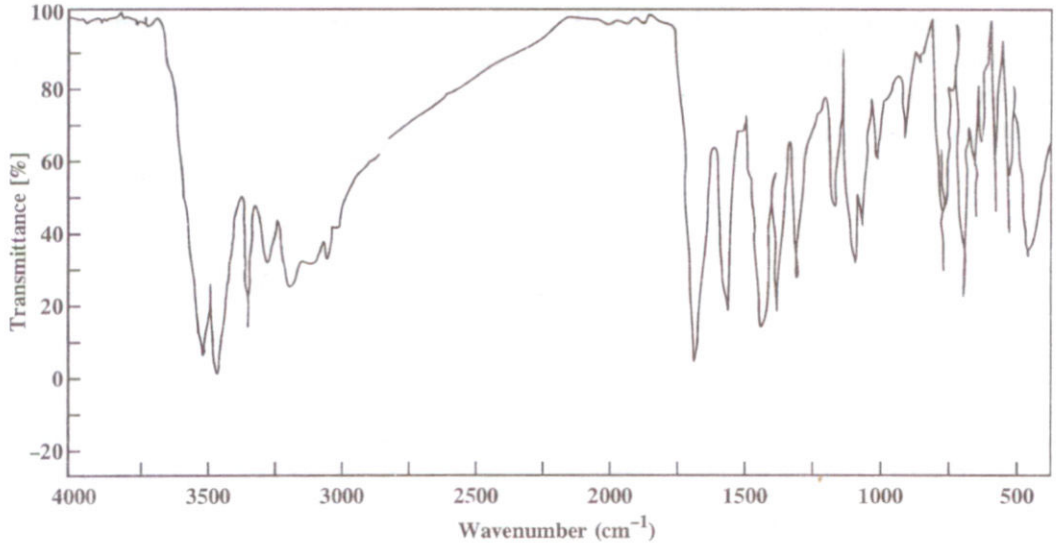

Figure 3 FT–IR

Microhardness studies

Hardness of a material is the resistance it offers to indentation by a much harder body. Hardness test is a method of subjecting crystal surface to relatively high pressure within a localized area. The method of measuring hardness depends on the elastic and plastic deformation characteristics of the crystal and the results obtained depend on the factors like yield point, elastic limit, elastic modulus, brittleness, etc.

Selected smooth surfaces of the crystal were subjected to static indentation test at room temperature to make microhardness measurements on the grown crystal. A Leitz–Wetzlar hardness tester fitted with diamond pyramidal intender attached to an incident light microscope was used. The load peak was varied from 2 to 100 g and the time of indentation is kept constant at 10 seconds for all the trials.

Table 2. The Diagonal length and michrohardness number for various loads

Load (**P**) (g)	Diagonal length (**d**) (μm)	H_v (Kg/mm^2)
5	10.98	76.89
10	16.12	71.35
25	26.80	64.53
50	38.30	63.19
100	54.90	61.51

Table 2 shows the diagonal lengths of the intended impressions obtained at various loads measured by a micrometer eyepiece. Several indentation trials at each load were carried out and the average value of the diagonal length of the indentation mark in each trial was calculated. The micrometer value H_v is calculated using the following relation,

$$H_v = 1.854\ P/d^2\ kg.mm^{-2}.$$

Where, H_v = Michrohardness number

P = Applied load on kg.

d = Average diagonal length in mm.

The composition of hardness is a nonlinear function and the value starts decreasing, when the load was increased (Fig.4). This is attributed to difference in the sizes of two mixing ions and the intermediate composition depends on the pure and end members.

The hardness decreases slowly with composition rising to a maximum value in the equimolar region, which is about 20 to 30% of the value of the end members.

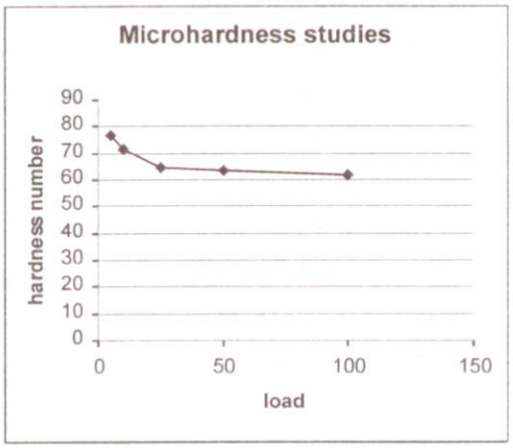

Figure 4. Showing the relation between load and hardness number

From the graph, it was seen that the coexistence of two ions of different sizes in a mixed crystal in a place of single ion would produce dislocation density in mixed crystals. The lattice contribution due to disorder was dependent on the product of concentration of the two mixing ions. Thus the proposed hardness depends on the time also.

CONCLUSION

Semicarbazone single crystals have been grown by gel technique. From the X–ray diffraction analysis, it is found that the crystal belongs to triclinic crystal system and space group P1. The functional group of semicarbazone crystals have been confirmed by FT–IR studies. The hardness studies have carried out on the grown crystals and dislocation density and mechanical parameters show the dependence on the load and time.

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