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Electrical properties of MTC single crystals doped with Zinc Chloride

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Abstract

In recent years organic-inorganic hybrid materials have attracted considerable attention. Non linear optical (NLO) materials play vital role in various fields of science and technological developments. The semi organic crystals bring the advantages such as high resistance to optical damage, multifaceted application and enhancement in the mechanical and thermal properties of the crystals. MTC is one such promising semi organic materials belongs to ZTC family crystals. Limited work has been done on MTC crystals. In the present study, Pure and Zinc doped magnesium thiourea chloride single crystals have been grown by slow evaporation method in the dopant concentration 1:0.01, 1:0.02, 1:0.03, 1:0.04, 1:0.05 and 1:0.05. Grown crystals were characterized electrically by measuring the capacitance and loss factor of the crystals at various temperatures ranging from 40 to 120°C at different frequencies viz. 5kHz, 10kHz, 50kHz, 100kHz, 150kHz and 200kHz using LCR meter. Electrical parameters like dielectric constant, AC conductivity, activation energy were determined. The dielectric constants found to increases with temperature and decreases with frequency.

Keywords: MTC, dielectric constant, loss factor, AC conductivity

1. Introduction

The field of molecular non linear optics has benefited from both upstream rejuvenation and downstream application oriented breakthroughs, aiding to bring the field closer to industrial developments [1]. Engineering of new nonlinear optical (NLO) materials, structures and devices with enhanced figures of merit has developed over the last two decades as a major force to drive nonlinear optics from the laboratory to real applications[2].In recent years, second order nonlinear optical materials have attracted many researchers because of their potential applications in various emerging technological fields[3-9].In the last decade, organic nonlinear optical crystals with aromatic rings have attracted much attention because of their high nonlinearity, fast response and tailor made flexibility. However, the short comings of aromatic crystal, such as poor physic-chemical stability, low hardness and cleavage tendency hinder their device application. In order to keep the merits and overcome the shortcomings of organic materials, some new classes of NLO crystals such as metal organic or semi organic crystals have been developed[10,11]. In semi-organic crystals, the organic ligand is ionically bonded with inorganics. These crystals have higher mechanical strength, chemical stability, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness [12-14].

2. Experimental Details:

MTC was synthesized using AR Grade(Magnesium Chloride Hexahydrate ($MgCl_2.6H_2O$ of molecular weight 203.3 g/mol) and Thiourea (molecular weight of 76.12 g/mol) in the molar ratio 1:3 from the following reaction

$$MgCl_2.6H2O+3[CS(NH_2)_2] \rightarrow Mg[CS(NH_2)_2]_3Cl_2.6H_2O$$

Magnesium Chloride and Thiourea were taken in 1:3 molar ratio in a beaker. The solution was continuously stirred at 50°C about one hour using magnetic stirrer to avoid nucleation and the mixture is kept in a undisturbed place. The product obtained in the reaction was collected and dried, then used for the preparation of the sample.

The capacitance and dielectric loss factor of all the grown crystals were measured using LCRZ meter (Model TH2816A) . The crystal was cut in the rectangular shape and polished. The sample was kept in between the two electrodes of two probe setup. The dimension of the sample was determined by using travelling microscope of least count 0.001 cm. The opposite faces of the sample were coated with good quality graphite for good conduction. The sample was annealed for about 120°C to eliminate the moisture if any present in the sample. The measurements were carried out while cooling the sample. The capacitance and the loss factor of all the samples were measured at various temperatures ranging from 40-120°C at different fixed frequencies viz. 1, 10, 50, 100, 150 and 200 kHz in identical conditions.

The dielectric constant was calculated using the simple formula

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A}$$

where

C – measured capacitance
d – thickness of the crystal
A – area of the crystal
ε_0 – permittivity of free space ($8.85 \times 10^{-12}\ C^2 N^{-1} m^{-2}$)

Electrical conductivity is the measure of the amount of electrical current a material can carry or its ability to carry a current.

The ac conductivity (σ_{ac}) was calculated from dielectric constant and dielectric loss (tanδ) using the simple relation

$$\sigma_{ac} = \varepsilon_o \varepsilon_r \omega \tan\delta$$

where, ω is the angular frequency ($\omega = 2\pi f$)

f is the applied ac frequency.

The obtained values of σ_{ac} were fitted into the Arrhenius equation,

$$\sigma_{ac} = \sigma_0 exp(-\frac{E_{ac}}{kT})$$

where, σ_0 is a constant depending on the material.

k is the Boltzmann's constant

T is the absolute temperature

The activation energy which is used to initiate the electrical conduction was calculated from the slope of the best fit of the curve drawn between 1/T vs ln σ_{ac} .

3. Results and Discussion

The temperature dependence of the dielectric constants of the grown crystals at 1kHz in the present study is shown in fig. 1 and the frequency dependence of the dielectric constant of all the grown crystals at 40°C is shown in the fig.2.