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Microwave Studies on Gadoliniium Barium Coppr Oxalate Crystals

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Abstract

Rare earth compounds are recognized for outstanding physical, magnetic, electrical and optical properties. Using cavity perturbation technique dielectric parameters of the sample such as complex permittivity and conductivity at microwave frequency were determined. Using X-ray diffraction study the crystalline nature of the sample was established. Photoconductivity studies of the Gadolinium Barium Copper Oxalate (GdBaCuOx) crystals revealed the negative photo conducting nature.

Keywords: Gadolinium Barium Copper Oxalate crystals, Cavity perturbation technique, Microwave frequency, Photoconductivity

Introduction

Rare earth compounds have a significant place among the technologically important materials. They have their importance for the luminescent, photoconductive, photorefractive, electric, magnetic and superconducting properties [1]. Synthesis of superconducting compounds by the controlled precipitation of oxalates followed by calcinations has been reported [2]. The ferroelectric and ferro elastic properties of rare earth molybdates and oxalates find application in electro and acousto optical device [3]. The rare earth oxalates evoked greater attention because of their ionic conduction and due to their easy conversion into their corresponding oxides [4,5]. The rare earth doped lasers quite suitable for pulse generation with Q- switching [6].

Experimental Procedure

The gel was prepared by mixing Sodium Meta silicate (density=1.03 g/cc) with

Oxalic acid to obtain the desired pH value. A mixed solution of Gadolinium Chloride, Barium chloride, Cuprous Nitrate and Nitric acid was used as the outer electrolyte. The outer electrolyte diffused into the gel to form a colloidal precipitate and it was dissolved by nitric acid, which enhanced crystallization.

$$2GdCl_3.6H_2O + Cu\ (NO_3)_2\ 3H_2O + Ba\ Cl_2.2H_2O \quad + 5H_2C_2O_4.2H_2O$$
$$\rightarrow \quad Gd_2\ Ba\ Cu\ (C_2O_4)_5.\ 13H_2O + 8\ HCl + 14H_2O. + 2HNO_3$$

Results and discussion

X –ray analysis

In order to estimate the crystal data, X-ray diffraction was carried out using Bruker AXS D8 Advance X-ray Diffractometer. The GdBaCuOx crystals were indexed in tetragonal symmetry using a computer program. The lattice parameters are a=b=9.75 and c=15 for wavelength λ (CuKα) = 1.54180 Å

Photoconductivity

Photoconductivity refers to the difference of electrical conductivity of a device with and without illumination. Photoconductivity measurements were carried out on the pellet sample of the GdBaCuOx crystals by fixing it onto a microscope slide. The sample was connected in series with a DC power supply and KEITHLEY123 Pico ammeter. The sample was covered with a black cloth and the voltage applied was increased from 0 to 5 volts. The dark current was recorded. The sample was illuminated by the radiation from 100 mW halogen lamp containing iodine vapour and tungsten filament. The photocurrent was recorded for the same values of the applied voltage. Field dependence of dark and photocurrents of GdBaCuOx crystals are shown in figure.1. The photocurrent was found to be less than the dark current at every applied electric field. This represents negative photoconductivity of GdBaCuOx crystals. Generally, this may be attributed to the loss of water molecules in the crystal [7]. However, the negative photoconductivity in this case may be due to the reduction in the number of charge carriers or their lifetime in the presence of radiation [8].

Decrease in lifetime with illumination, could be due to trapping process and increase in carrier velocity according to the relation:

$$\tau = (vsN)^{-1}$$

Where v is the thermal velocity of the carriers, s is the capture cross-section of the recombination centers and N is the carrier concentration. As intense light falls on the sample, the lifetime decreases [9]. In Stockmann model, a two level scheme is proposed to explain negative photoconductivity [10]. The upper energy level is situated between the Fermi level and the conduction band, whereas the other one is located in the neighbourhood of the valance band. The lower level has high capture cross-section for electrons from the conduction band and holes from the valance band. As a result, no sooner the sample is kept under exposure to light, the recombination of electrons and holes take place, resulting in decrease in the number of mobile charge carriers, giving rise to negative photoconductivity.

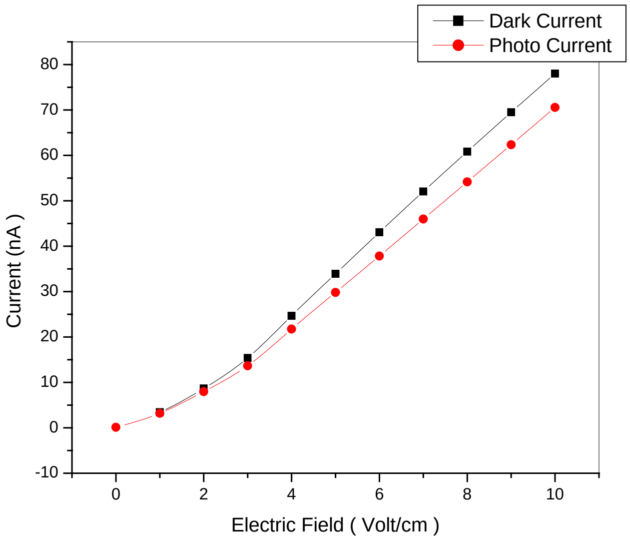

Figure 1 : Field dependence of photo and dark conductivity of GdBaCuOx crystals

Microwave Dielectric Studies on GdBaCuOx Crystals

A rectangular wave-guide resonator in the S-band was designed to measure the dielectric constant of solid-state materials. The dielectric properties of GdBaCuOx crystals had been studied by the cavity perturbation technique at microwave frequency.

Theory of cavity perturbation

When a material is introduced into a resonator cavity, the cavity field distribution and resonant frequency are changed, depending on the geometry, electromagnetic properties and the position of the sample in the fields of the cavity. Dielectric material interacts only with electric field in the cavity. When the sample is introduced into the cavity, Waldron [11] gives the relative complex frequency shift on the resonator

$$d\Omega / \Omega = \frac{(\varepsilon' - 1)\varepsilon_0 \int_{vs} E E_0 dV + (\mu' - 1)\mu_0 \int_{vs} H_0 . H dV}{\int_{vo} D_0 E_0 dV + \int_{vo} H_0 B_0 dV} \qquad (1)$$

Where ‘E_0’ is the electric field in the unperturbed cavity, ‘E’ the electric field in the perturbed cavity and ‘D’ the displacement current density. ‘H_0’,‘H’ and ‘B’ are the respective magnetic quantities. ε’ is the relative complex permittivity of the sample. But $\varepsilon' = \varepsilon_r' - j\varepsilon_r''$ where ε_r' is the real part of complex permittivity and ε_r'' is the imaginary part of complex permittivity. ‘μ’ is the magnetic parameter. The numerator of Eq. (1) represents the total energy stored in the sample and the denominator represents the total energy stored in the cavity. When a dielectric material is introduced in a cavity resonator at the position of maximum electric field, the contribution of magnetic field for the perturbation is minimum.

Mathew et al. [12] related the field perturbation due to the introduction of dielectric sample at the position of maximum electric field

$$d\Omega \,/\, \Omega = \frac{(\varepsilon' - 1)\varepsilon_0 \int_{vs} E E_{0max} dV}{2 \int_{vs} |E0|^2 dV} \qquad (2)$$

Where ‘dΩ’ is the complex frequency shift. V_s and V_c are the volumes of the sample and cavity resonator respectively. The complex frequency shift is related to the quality factor as

$$\frac{d\Omega}{\Omega} = \frac{d\omega}{\omega} + (j/2)\ [(1/Q_s) - (1/Q_0)] \qquad (3)$$

Where Q_s, Q_0 are the quality factors of cavity resonator with and without the sample.

Quality factor Q is given by, $Q = \frac{f}{\Delta f}$

Where ‘f ’ is the resonant frequency and Δf the corresponding 3dB bandwidth. For small sample, we assume that $E=E_0$ which is one of the assumptions taken in the theory of perturbation.

For dominant TE_{10p} mode in rectangular wave guide

$$E_0 = E_{0max} \operatorname{Sin}\{\pi x/a\} \operatorname{Sin}\{p\pi z/d\} \quad p = 1, 2.\ 3 \qquad (4)$$

$E_{0\ max}$ is the peak value of E_0, ‘a’ is the broader dimension and ‘d’ is the length of the wave-guide cavity resonator.

From Eqs. (2)& (3)

$$\varepsilon_r' - 1 = \frac{f_0 - f_s}{2f_s}\left(\frac{V_0}{V_s}\right) \qquad (5)$$

$$\varepsilon_r'' = \frac{V_0}{4V_s}\left(\frac{Q - Q_s}{Q_0\, Q_s}\right) \qquad (6)$$

The real part ε_r', of the complex permittivity is usually known as dielectric constant. The imaginary part ε_r'', of the complex permittivity is associated with dielectric loss of the material. The effective conductivity σ is given by

$$\sigma = \omega\varepsilon'' = 2\pi f \varepsilon_0 \varepsilon_r'' \qquad (7)$$

The dielectric loss of a material will be usually expressed by a term loss tangent or tan δ.

$$\tan\delta = \frac{\varepsilon_r''}{\varepsilon_r'} \qquad (8)$$

Experimental Procedure

The cavity was made from a S-band wave-guide with both ends closed**.** Fig. 2 shows the schematic diagram of the cavity resonator. The length of the resonator determined the number of resonant frequencies. The resonator was excited in the TE_{10p} mode. The resonant frequency ‘f_0’ and the corresponding quality factor ‘Q_0’ of each resonant peak of the cavity resonator, without sample placed at the maximum of the electric field, were noted. The sample was introduced into the cavity resonator through the non-radiating slot. The resonant frequencies of the sample - loaded cavity were selected and the position of the sample was adjusted for maximum perturbation (that is, maximum shift of resonant frequency with minimum amplitude for the peak). The new resonant frequency f_s and quality factor Q_s were determined. The procedure was repeated for other resonant frequencies. The microwave frequency dependence of dielectric constant, effective conductivity and dielectric loss were plotted in Fig.3, Fig.4 and Fig.5 respectively.

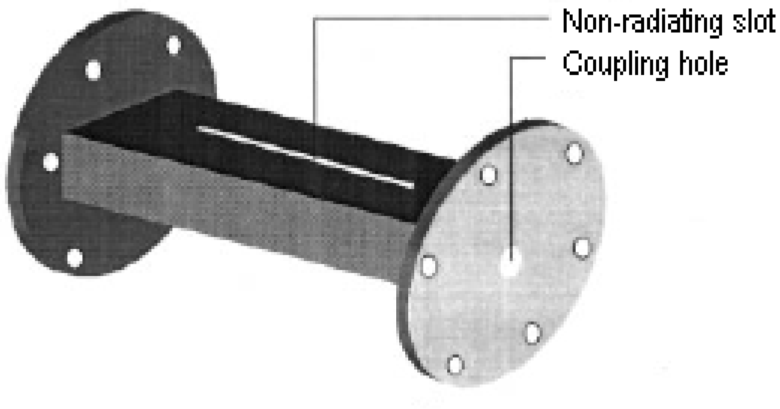

Figure 2 : The schematic diagram of the cavity resonator.

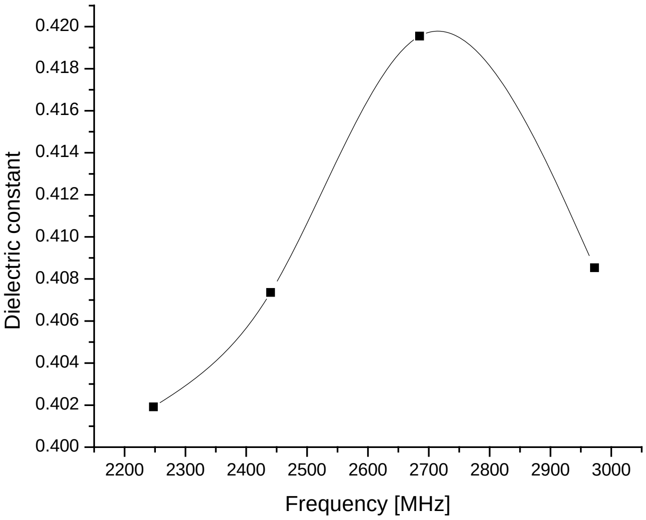

Figure 3 : Frequency vs. Dielectric constant

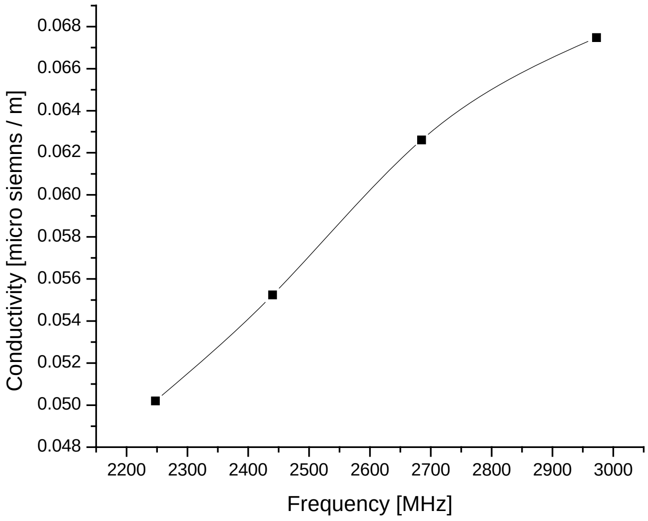

Figure 4 : Frequency vs. conductivity

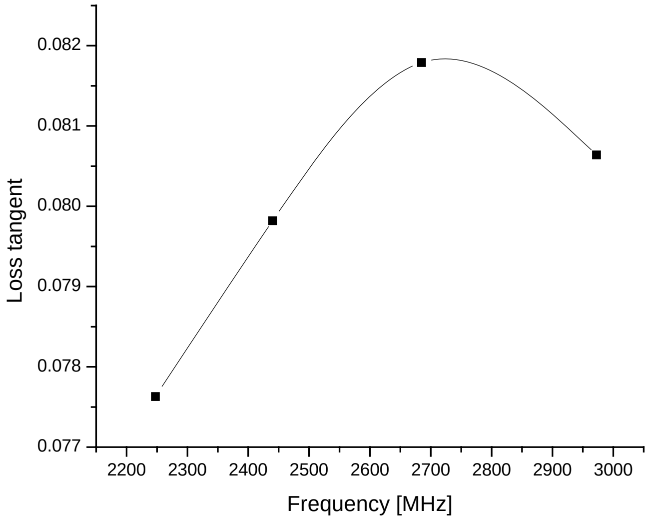

Figure 5 : Frequency vs. Loss tangent

Conclusions

Precipitation-cum-dissolution control mechanism of the growth of rare earth mixed crystals is no doubt a useful method for growing good quality crystals. Photoconductivity studies of GdBaCuOx crystals revealed the negative photoconducting nature. From the microwave studies it had been observed that GdBaCuOx exhibit considerable dielectric loss. This sample can be used for the preparation of microwave absorbing materials for electro magnetic shielding.

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