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Optical absorption in gel grown barium oxalate single crystals

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Single crystals of barium oxalate have been grown by simple gel technique using agar gel as the growth medium at ambient temperature. The slow and controlled reaction between barium chloride and oxalic acid in agar gel has formed barium oxalate. Optical absorption spectra of this grown crystal is recorded in the wavelength region from 200 to 800 nm. The absorption spectra reveal transitions involving absorption and emission of phonons and also show that the crystal is transparent in the region 500 to 800 nm. The detail study supports the existence of forbidden indirect transition in the material. Different segment of $\alpha^{1/3}$ vs hν graph were used to distinguish individual contribution of phonons and scattering of charge carriers in the lattice is found due to acoustic phonons.

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1. Introduction

Barium oxalate is a pyro-nature material that shows great promise in pyrotechnic and high temperature electronic applications. The high dielectric constant and melting point of barium oxalate is an advantage to improve hardness of barium titanate in capacitor industries [1]. Hydrated barium oxalate has been shown to be more suitable absorbents and hence to be used to fabricate effective sensor to monitor sulphur trioxide [2]. It is also used with magnesium powder as a pyrotechnic colorant to produce green color in firecrackers [3]. Barium oxalate has poor solubility in water (0.0093 g/100 ml of H_2O) and decomposes before melting [4]. Therefore, single crystals of these materials cannot be grown by either slow solvent evaporation or melt techniques but they can be suitably grown by gel method. The gel growth technique has attracted much attention because of its simplicity [5-6] and found unique place due to its characteristics to suppress the nucleation centers [7]. Many investigators have taken efforts to find photo-absorption of many materials [8-10], however, little work is reported on the characteristic data of barium oxalate. Hence, an attempt is made to report the optical absorption characteristic of this material.

2. Experimental

The growth of barium oxalate crystal was carried out in agar gel [11-12]. The growth process in single diffusion involves the diffusion of oxalic acid into a gel in which barium chloride is already impregnated at the time of setting of gel, while in double diffusion barium chloride and oxalic acid were poured from the two limbs of the U-tube after setting the gel. The reaction, which leads to the growth of crystals can be, expressed as

$$BaCl_2 + H_2C_2O_4 = BaC_2O_4 + 2HCl$$

The optimum conditions for the growth of barium oxalate single crystals were: concentration of gel 1.5%, concentration of barium chloride 1M, concentration of oxalic acid 1M, gel setting period 4 days in single diffusion and 6 days in double diffusion, gel aging 48h, period of growth 60 days in single diffusion and 80 days in double diffusion. Prismatic, platy shaped crystals were obtained with maximum size 12 × 4 × 2 mm^3 in single diffusion and 8 × 4 × 2 mm^3 in double diffusion. Optical absorption spectra at room temperature were recorded using UV-VIS-NIR Perkin Elmer (USA) Lembda-19 spectrometer in the range 200 – 800 nm, which are shown in Fig. 2. Measurements were taken in accordance with the process mentioned by Arora [10] on as-grown crystal of thickness 0.290 cm. One can see from Fig. 2 that the crystal is transparent in the range 500 to 800 nm and the transmittivity is greater than 80%. The strong absorption peak at 256.68 nm is assigned to that of the oxalate group [13].

3. Results and discussion

Barium oxalate crystals were grown by gel method as reported earlier [12]. The perfect crystallinity of the grown crystals was confirmed from the powder X-ray diffraction analysis as shown in Fig. 1. From the powder X-ray diffraction data, it is found that the system is

Monoclinic(P) and the lattice parameters computed are a = 6.6562 A^o ; b = 8.0464 A^o ; c = 2.8090 A^o ; β = 96.832^o ; V = 149.38 A$^{o\,3}$. Fig. 2 displays the variation of optical absorbance with wavelength of the as-grown barium oxalate crystals. Optical absorption coefficient (α) has been calculated in the wavelength region 200-800 nm. The values of absorption coefficient α versus photon energy hν are plotted as shown in Fig. 3. In the high absorption energies, crystals seems to exhibit sharp absorption edge while at low energies, the relationship is represented by long vary Urbach's tail. The absorption coefficient at 3.93 to 4.06 eV below the band gap increases exponentially and can be expressed as

$$\alpha(E) = \alpha_o \exp[E/E_o]$$

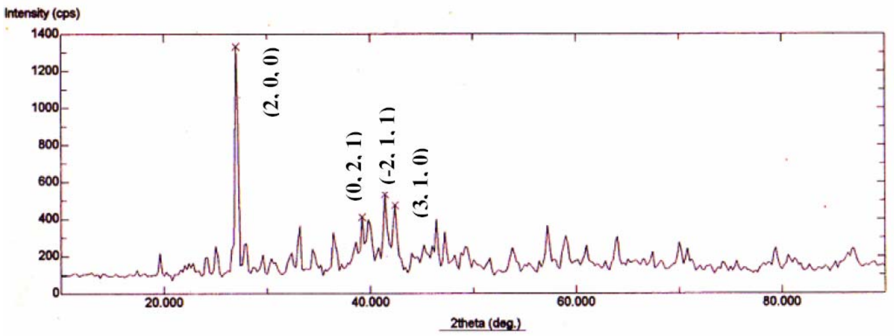

Fig. 1. X-ray diffractogram of barium oxalate sample.

This equation helps to determine the characteristic energy E_o (inset of Fig. 3), which comes out to be 5.6 eV. The value of E_o, comes greater than kT is implied that there is some feeble disorder in the crystal [14]. The inter-band optical absorption theory described by Tauc and Menth [15] helps to determine the electronic transitions. These transitions further show dependence of absorption on energy [16] and represented in terms of power law equation as

$$\alpha^n = A_k(h\nu - E_g)$$

where E_g is the optical band gap, A_k is a constant nearly independent of photon energy hν, and the value of index n characterizes the optical absorption process; n=2 and ½ for the direct and indirect allowed transition respectively and n = 2/3 and 1/3 for the direct and indirect forbidden transitions respectively. For different set of values (n, E_g), graphs are plotted between lnα Vs hν and best linear fits are obtained. In our case, the best fit is obtained with n=1/3, implying that the material is having indirect band gap. As for indirect transition, wave-vector of the photon cannot compensate for the change in crystal momentum of the electronic state, while it's momentum is conserved by emission or absorption of phonons during transition due to electron- photon interaction [8]. Such indirect transitions in grown material at room temperature are analyzed here. Analysis of the three straight lines in the graph between $\alpha^{1/3} \rightarrow h\nu$ as shown in Fig. 4 is made to find the individual contribution of phonons.

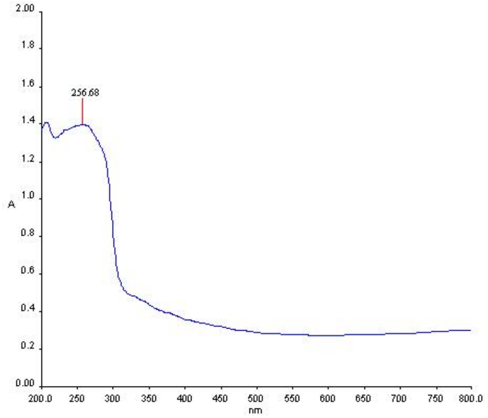

Fig. 2. Plot of optical absorbance(A) versus wavelength (λ).

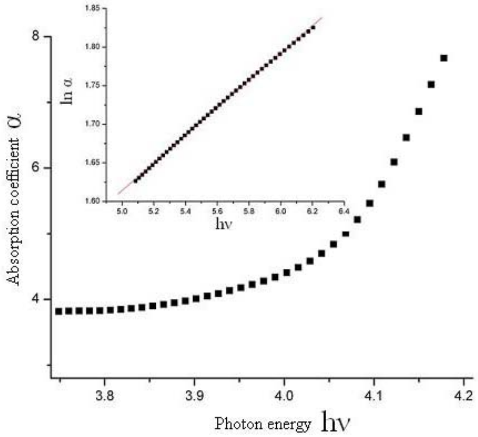

Fig. 3. Graph of absorption coefficient (α) versus photon energy (hν).

Choyke and Patrick method [17] is adopted to make an accurate determination of discontinuities in the above graph. First, partial absorption coefficient α_1 is found by extrapolating the first segments BA, the total absorption coefficient $\alpha=(\alpha_1+\alpha_2)$ is obtained by taking six different values of energy hν from the segment CB, then α_2 are calculated as $\alpha_2^{1/3}= (\alpha-\alpha_1)^{1/3}$ as shown in Fig. 5(a). These selected six values from the segment CB are now treated as $\alpha_{1,}$ which are then substracted from the six different values (α) of segment DC and are represented by $\alpha_{3,}$ then graph is plotted between $\alpha_3^{1/3}= (\alpha-\alpha_1)^{1/3}$ as shown in Fig. 5(b). From these graphs we obtained two estimated energy gaps for indirect transitions [18], which are given in Table 1. The absorption coefficient for phonon absorption and emission are given by the equations,

$$A(h\nu - E_g + E_p)^2\, \mathbf{a_a} = h\nu \quad \rule{3cm}{2pt} \quad ; \; h\nu > (E_g - E_p)$$

and

$$A(h\nu - E_g - E_p)^2\, \mathbf{a_e} = h\nu \quad \rule{3cm}{2pt} \quad ; \; h\nu > (E_g + E_p)$$

where A and B are constants. The threshold energies obtained from above equations are represented by the equations [19]

$$(h\nu_{thr})_a = (E_g - E_p) \;;$$

and

$$(h\nu_{thr})_e = (E_g + E_p)$$

Table 1. The values of estimated, threshold and fitted energies.

Estimated E_g (eV)	Knee point	Threshold E_g (eV)	Interval	Threshold interval (eV)	Fitted E_g (eV)
4.04	C	4.09	C-B	0.06	3.90
4.02	B	4.03			3.98

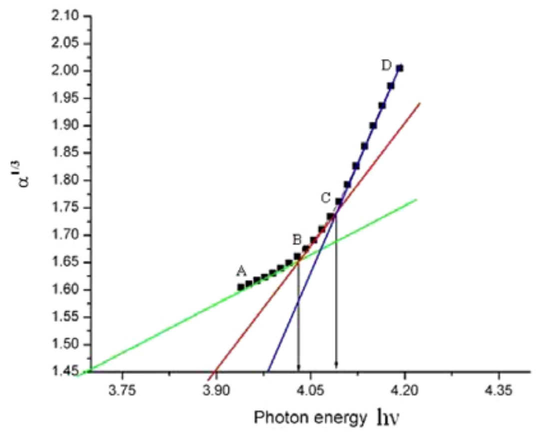

Fig. 4. Plot of $\alpha^{1/3}$ versus photon energy (hν).

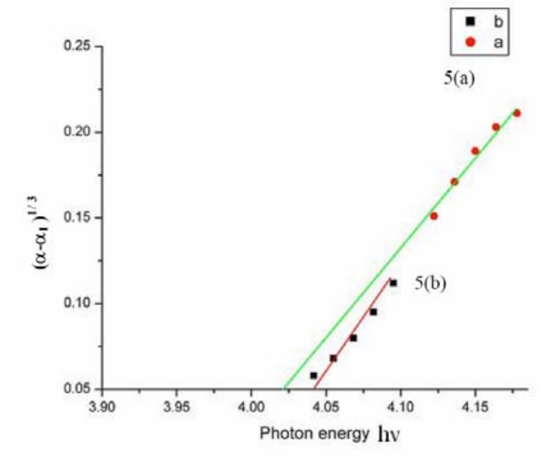

Fig. 5. Plot of $(\alpha-\alpha_1)^{1/3}$ versus photon energy(hν).

Different graphs were analyzed [20] to find individual contribution of phonons. The knee points B, C indicated by the arrows in Fig. 4, give the threshold energies. The interval of threshold energies, tabulated in Table 1 are twice of phonon energy $E_{p.}$ The values of phonon energy involved in the indirect transitions are found to be 0.03 eV. These energies may be involved due to internal vibrations at 256.68 cm^{-1}. Further, the extrapolation of curve DC and CB on energy axis gives the fitted energy gaps as shown in Table 1. As the free carrier absorption α_f is a weight sum [21,22] of scattering by acoustic phonon, optical phonons and ionized impurity, therefore it is represented by the equation as

$$\alpha_f = A\lambda^{1.5} + B\lambda^{2.5} + C\lambda^{3.5}$$

where A, B and C are constants and $\lambda^{1.5}$, $\lambda^{2.5}$ and $\lambda^{3.5}$ are dependent factor of acoustic phonons, optical phonons and ionized impurity respectively. In our case, the graph between $\log\alpha_f$ vs. $\log\lambda$(graph not shown) gives the slope of magnitude 1.5 which indicates that the transition predominantly occurs due to scattering by acoustic phonons.

4. Conclusion

The absorption spectra show that the gel grown barium oxalate crystal is transparent in the region 500 to 800 nm. The phonon assisting indirect transitions correspond to internal vibration at 256.68 cm^{-1}. The indirect transition predominantly occurs due to scattering by acoustic phonons.

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