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Photo Absorption in Gel Grown Strontium Oxalate Single Crystals

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Abstract

Strontium oxalate crystals have been grown by simple gel technique using agar gel as the growth medium at ambient temperature. The slow and controlled reaction between strontium chloride and oxalic acid in agar gel has formed strontium oxalate. Optical absorption spectra of these grown crystals are recorded in the wavelength region from 200 to 800 nm. The particular range 200 to 350 nm is important because it only yields the necessary information. 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. The forbidden indirect transitions in crystals are found to be 0.058eV and 0.078eV, and these correspond to 262.8 nm and 326 nm respectively as internal vibrations. Different segment of a1/3 vs hn graph were used to distinguish individual contribution of phonons and scattering of charge carriers in the lattice and it is found due to acoustic phonons.

Keywords: Strontium oxalate single crystal, Agar-agar gel, X-ray diffraction, Photo-absorption, Photon energy

1. Introduction

Strontium oxalate shows great promise in pyrotechnic and high temperature electronic applications. This material is used in pyro-techniques[1], tanning process [2] and as a catalyst [3].

The high dielectric constant and melting point of strontium oxalate is an advantage to improve hardness of strontium titanate in capacitor industries [4].

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It is also used with magnesium powder as a pyrotechnic colorant to produce yellow color in firecrackers [5].

Oxalates have poor solubility in water and decompose before melting [6]. 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 [7-8] and found unique place due to its characteristics to suppress the nucleation centers [9]. Many investigators have taken efforts to find photo-absorption of many materials [10-13], however, little work is reported on the characteristic data of strontium oxalate. Hence, an attempt is made to report the optical absorption characteristic of this material.

2. Experimental

The growth of strontium oxalate crystal was carried out in agar gel [14]. The growth process in single diffusion involves the diffusion of oxalic acid into a gel in which strontium chloride is already impregnated at the time of setting of gel, while in double diffusion strontium chloride and oxalic acid were poured from the two limbs of the Utube after setting the gel.

The reaction, which leads to the growth of crystal, can be expressed as-

$$SrCl2 + H2C2O4 = SrC2O4 + 2HCl$$

The optimum conditions for the growth of strontium oxalate single crystals were: concentration of gel 1.5%, concentration of strontium chloride 1M, concentration of oxalic acid 1M, gel setting period 3 days in single diffusion and 6 days in double diffusion, gel aging 24h, period of growth 60 days in single diffusion and 80 days in double diffusion. Transparent, prismatic and bi-pyramidal crystals with maximum size 6 x 6 x 3 mm3 in single diffusion while opaque and spherullite crystals with 4 mm in diameter in double diffusion were obtained. 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 figure 2. Measurements were taken in accordance with the process mentioned [15] on as-grown crystal of thickness 0.347 cm. One can see from figure 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 262.8 nm is assigned to that of the oxalate group [16].

3. Results and Discussion

Strontium oxalate crystals were grown by gel method as reported earlier [14]. The perfect crystallinity of the grown crystal was confirmed from the powder X-ray diffraction analysis as shown in figure 1. From the powder X-ray diffraction data, it is found that the system is monoclinic(P) and the lattice parameters computed are a = 9.67628Ao ; b = 6.7175Ao ; c = 8.6812Ao ; β = 113.566o ; V = 521.84Ao 3 . Figure 2 displays the variation of optical absorbance with wavelength of the as-grown strontium oxalate crystals. Optical absorption coefficient (a) has been calculated in the wavelength region 200-800 nm. The values of absorption coefficient a versus photon energy hn are plotted as shown in figure 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 data, which cover a limited energy range (3.9 to 4.2 eV) below the band gap in which a(E) increases exponentially and can be expressed as-

$$a(E) = ao \exp[E/Eo] \quad \ldots\ldots (1)$$

This equation helps to determine the characteristic energy Eo (inset of figure 3), which comes out to be 5.42 eV. The value of Eo, comes greater than kT is implied that there is some feeble disorder in the crystal [17]. The inter-band optical absorption theory described by Tauc and Menth [18] helps to determine the electronic transitions. These transitions further show dependence of absorption on energy [19] and represented in terms of power law equation as-

$$an = Ak(hn - Eg) \quad \ldots\ldots (2)$$

where Eg is the optical band gap, Ak is a constant nearly independent of photon energy hn, 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 [20]. For different set of values (n, Eg), graphs are plotted between lna Vs hn 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 its momentum is conserved by emission or absorption of phonons during transition due to electron-photon interaction [10]. Such indirect transitions in grown material at room temperature are analyzed here. Analysis of the three straight lines in the graph between a1/3 ® hn as shown in figure 4 is made to find the individual contribution of phonons.

Choyke and Patrick method [21] is adopted to make an accurate determination of discontinuities in the above graph. First, partial absorption coefficient a1 is found by extrapolating dotted segments marked '1', the total absorption coefficient a=(a1+a2) is obtained by taking six different values of energy hn from the segment CB, then a2 are calculated as a2

1/3= (a-a1)1/3 as shown in figure 5(a). Now the segment CB marked '2' is treated as a1, which are then substracted from the six different values (a) of segment BA marked '3' and are represented by a3, then graph is plotted between a3 1/3= (a-a1)1/3 as shown in figure 5(b). Likewise, using for the last segment marked '4', the values a4 1/3=(a-a1)1/3 are found and thus represented in figure 5(c). From these graphs, three estimated energy gaps are obtained and listed in table 1. Bardeen's equation [22] was used to estimate energy gaps for indirect transitions. The threshold photon energies for absorption and emission are given by the equations,

$$(h\nu_{thr})_a = (E_g - E_p) \; ; \quad \ldots\ldots (3)$$

$$\text{and } (h\nu_{thr})_e = (E_g + E_p) \quad \ldots\ldots (4)$$

The knee points A, B and C indicated by the arrows in figure 4, give the threshold energies. According to equations (3) and (4), the energy interval B-A and C-B between threshold energies are obtained, which equals to twice of phonon energy Ep. Thus, the values of phonon energy involved in the forbidden indirect transitions in crystals are found to be 0.029 eV and 0.039 eV, and these energies correspond to 262.8 nm may be involved due to internal vibrations of oxalate ion [16] and 326 nm respectively may be due to internal vibration of metal ion. Further, the extrapolation of steps CB, BA and A… on energy axis give the fitted energy gaps as shown in table 1.

As the free carrier absorption af is a weight sum [23,24] of scattering by acoustic phonon, optical phonons and ionized impurity, therefore it is represented by the equation as-

$$af = AI^{1.5} + BI^{2.5} + CI^{3.5}$$

where A, B and C are constants and $I^{1.5}$, $I^{2.5}$ and $I^{3.5}$ are dependent factor of acoustic phonons, optical phonons and ionized impurity respectively. In our case, the graph between logaf vs. logI(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 strontium oxalate crystal is transparent in the region 500 to 800 nm. The phonon assisting indirect transitions correspond to internal vibrations at 262.8 and 326 nm. The indirect transition predominantly occurs due to scattering by acoustic phonons.

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Table 1: The Calculated 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)
4.07	A	4.099	A-B	0.058	4.03
4.05	B	4.041	B-C	0.078	3.94
3.96	C	3.964			3.78

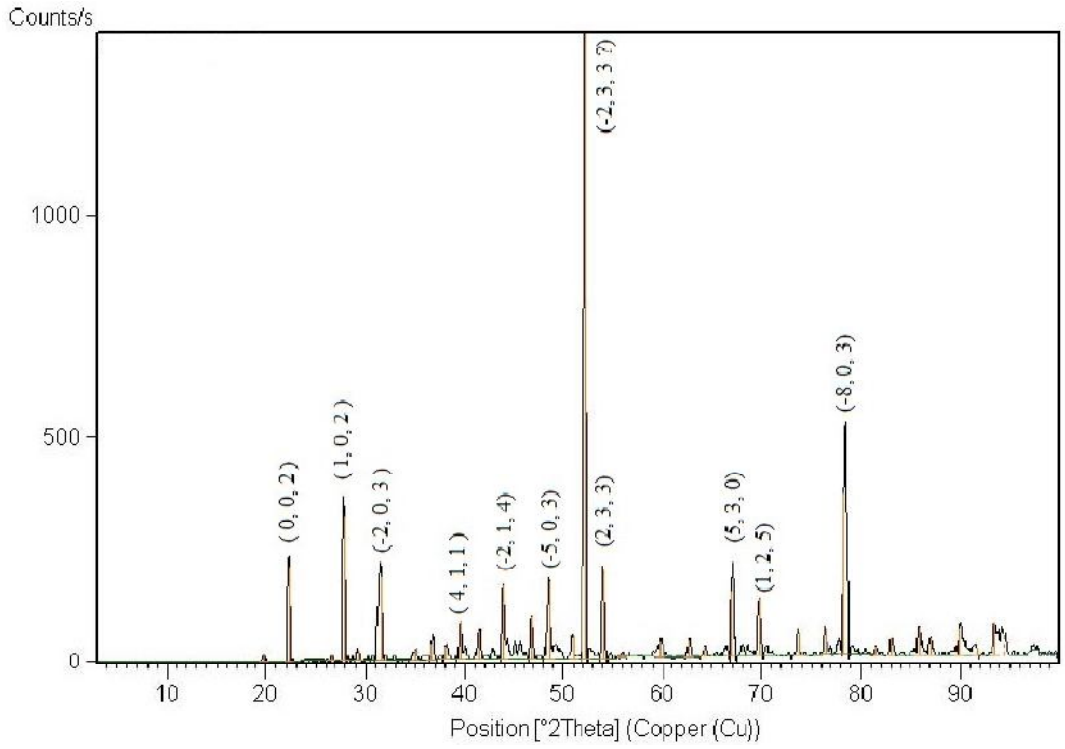

Figure1: X-ray Diffraction Pattern of Strontium Oxalate

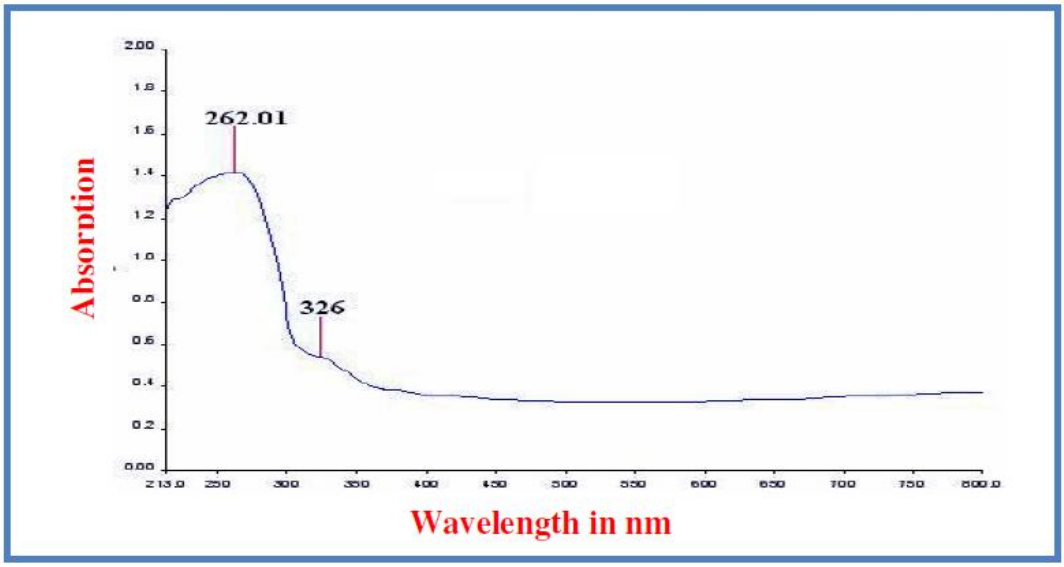

Figure 2: Plot of Optical Absorbance (A) versus Wavelength (l)

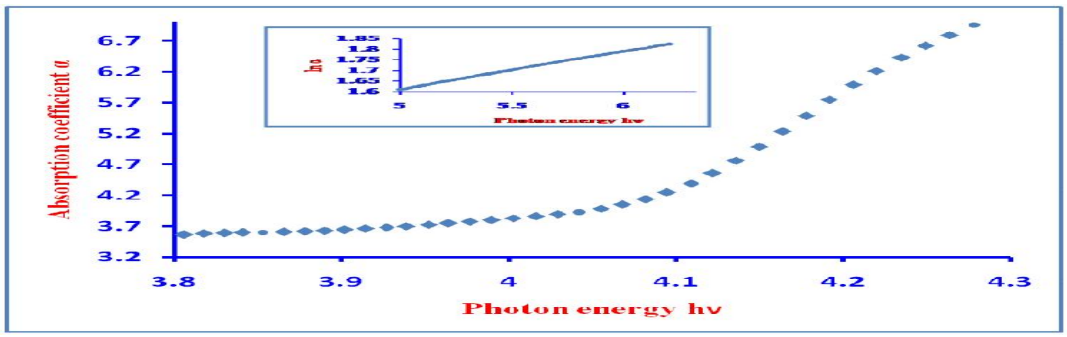

Figure 3: Graph of Absorption Coefficient (a) versus Photon Energy (hn)

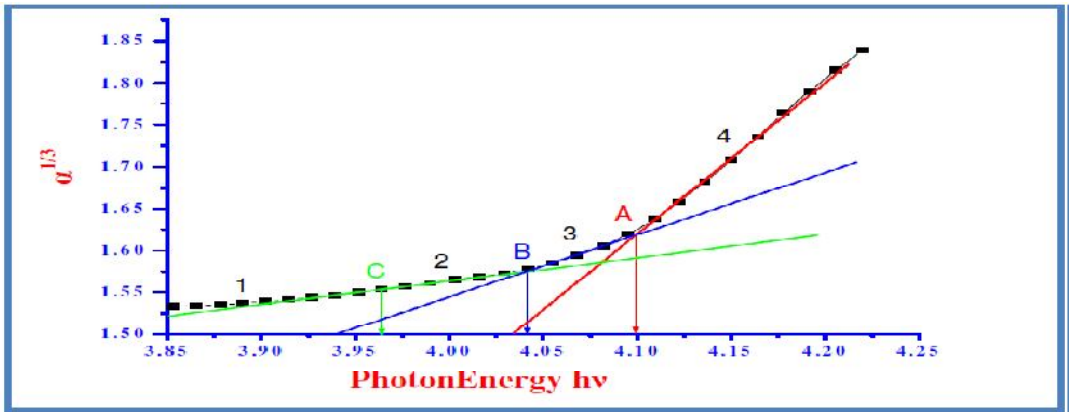

Figure4: Plot of $a^{1/3}$ Versus Photon Energy (hn)

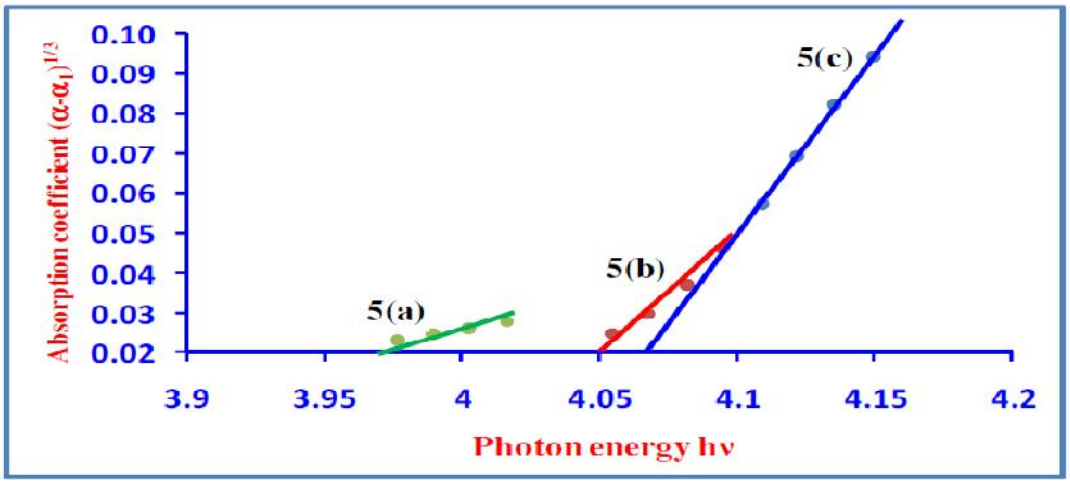

Figure 5: Plot of $(a-a1)^{1/3}$ Versus Photon Energy (hn)