XRD, EDAX and UV-Vis Absorption Spectroscopy of Gel Grown Cerium Tartrate Crystals

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Abstract

The growth of cerium tartrate crystals is achieved in inorganic (silica) gels by single gel diffusion method. Cerium tartrate crystals were grown from sodium metasilicate gel and water solutions of tartaric acid and cerium chloride as the reactants. Crystals grown were spherulitic in size. The principle objective of this investigation is to study XRD, EDAX and UV-Vis absorption Spectroscopy on CeT crystals.

Powder X-ray diffraction (XRD) studies indicate that the crystals belong to monoclinic with the unit cell parameters a= 7.1095Å, b= 5.1838 Å, c = 3.4016 Å and $\alpha=90^0$, beta = 92.474°, γ =90°, and unit cell volume is 125.25 Å^3. The presence of C, O and Ce in the cerium tartrate crystals is evident from the characteristics K_α, L_α, and L_β peaks of these elements. From UV-Vis Spectroscopic studies the band gap energy calculated for CeT was found to 3.936eV.

Keywords: Gel Method, Cerium Tartrate, UV-Vis, XRD, EDAX, Band gap

1. Introduction

The salts of tartaric acid are found to exhibit a range of interesting physical properties such as ferroelectricity, piezoelectricity and optical second harmonic generation (SHG) [1-7]. Consequently, they are used in transducers and several linear and nonlinear mechanical devices [1-3]. This has led many investigators to grow single crystals of tartrate compounds and study their characteristics [8-11]. Many investigators have grown rare earth tartrates bearing the general formula $R_2 (C_4H_4O_6)_3 \cdot H_2O$ (R=Nd, Dy, Gd, La, Di, Pr, Sm and Y) by gel method [12-17]. Cerium is a promising rare earth metal with only a single electron in the 4f shell when it is in ionic state. Its optical, luminescent and magnetic properties are studied widely. Cerium (Ce^{3+}) is used as a co-dopant in certain photo refractive crystals like $LiNbO_3$, $KNbO_3$ and $Sr_xBa_{1-x}Nb_2O_6$ [18] and laser crystals like $Y_3Al_5O_{12}$:Nd and $YAlO_3$ [19]. Several compounds containing cerium are under study for their ferromagnetic, antiferromagnetic and superconducting properties. Optical and luminescent properties of laser scintillator crystals like YAG and YAP doped with Ce^{3+} ions are studied [20]. Studies on cerium oxalate crystals grown in hydro-silica gel have been reported [21]. Growth and characterization of several oxalates and mixed rare earth oxalates in silica gel also have been reported [22-24]. No report has been noticed on the study of UV-Vis absorption Spectroscopy of CeT sample. Hence growth of these crystals is attempted. Optical absorption studies in the region of UV-visible find widespread applications in the quantitative and qualitative determination of the molecular species present in the sample [25]. This is one of the most important analytical methods in many chemical, biological and chemical laboratories.

Most organic compounds and many inorganic ions and complexes absorb radiation in the UV-visible region. From the observed spectra one could identify the presence of particular element in the spectra. The energy absorbed in this region corresponds to the excitation of the valence electron from an occupied molecular orbit. Absorption measures transitions from the ground state to the excited state [26].

The spectrum obtained in this case is a plot of wavelength of absorption versus the absorption intensity. The position of absorption peaks corresponds to the wavelength of radiation whose energy is equal to that required for an electronic transition.

2. Experimental

The growth of cerium tartrate crystals was accomplished using single gel diffusion technique described by Henisch [13]. The crystals were grown in a single glass tube of length 200 mm and diameter 25 mm. Silica gel was prepared by adding a solution of sodium metasilicate of molarity (0.5-1.5 M) to tartaric acid of a particular molarity (0.25-2 M), drop by drop with continuous stirring. The solution with the desired value of pH (3-6) was then transferred to several glass tubes. Once gelled, an aqueous solution of cerium chloride was added as top solution. In silica gel, a gel pH of 3, 3.5, 3.75, 4.2 yields distinct types of spherulites, just below the gel/solution interface and in the lower half of the gel column.

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The spherulites grown were recognized as verium tartrate crystals. A strong precipitation was observed to occur at the gel/solution interface just after pouring of upper reactant. All experiments were carried out at room temperature. The grown crystals were characterized by Powder x-ray diffractometry (XRD), EDAX and UV-Vis absorption Spectroscopy.

3. Results and Discussion

XRD: X-ray powder diffractogram of the lanthanum sample was recorded using Reguka Miniflex, Japan, diffractometer with CuKα radiations of wavelength 1.54051 Å at 30kV and 15mA with a step of 0.01º and a step time of 0.2s. The powder XRD pattern of lanthanum tartrate is shown in Fig. 1. The diffractogram was indexed using POWD (an Interactive Powder Diffraction Data Interpretation and Indexing Program, Version 2.2) software. The revelation of well-defined peaks at specific 2θ angle suggests that the grown crystals are polycrystalline. The diffraction peaks are indexed and the crystal system is found to be monoclinic. The unit cell parameters are a= 7.1095Å, b= 5.1838 Å, c = 3.4016 Å and α=90º, beta = 92.474º, γ =90º, and unit cell volume is 125.25 Å³.
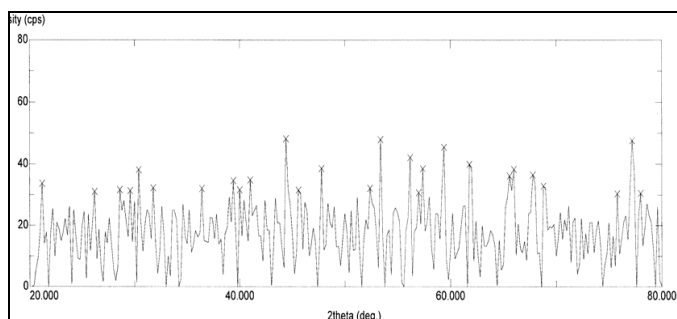

Fig 1: X-ray diffractogram of cerium tartrate

EDAX

The output of EDAX analysis is an EDAX spectrum as shown in Fig. 2. Using EDAX the amount of C, O, and Ce present in the sample could be well understood.
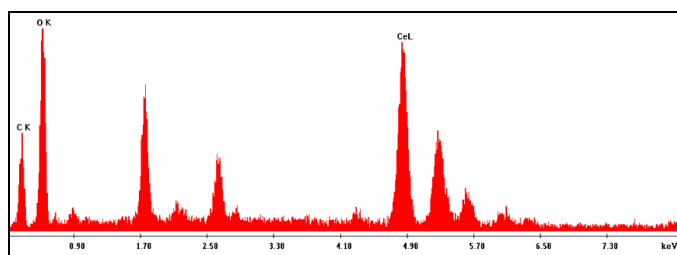

Fig 2: EDAX spectrum of neodymium tartrate

The two dominant peaks at 280eV and 487eV correspond quite well with the $K_α$ energies of carbon and oxygen in the crystal. These energy values are in good agreement with standard values 277 and 525eV respectively [27-28]. The intense peak at 4.8484keV corresponds to $L_{α1}$ energy of cerium giving a clue that the amount of cerium is in the detectable range of the instrument. This energy value is in good agreement with standard value 4.840keV. The lesser intense peaks at 5.2613 and 5.6226keV well corresponds to $L_{β1}$ and $L_{β2}$ energies of cerium which are in good agreement with the standard energy values 5.262 and 5.6134keV respectively. The two peaks present at 1.756 and 2.60keV may correspond to impurities present. The intense peak at 4.8484keV suggests the strong transition of $L_{α1}$ while lesser intense peaks at

5.2613 and 5.6226keV suggest that $L_{β1}$ and $L_{β2}$ transition are weak. Thus the presence of C, O and Ce in the cerium tartrate crystals is evident from the characteristics $K_α$, $L_α$, and $L_β$ peaks of these elements.

UV-Vis Absorption Spectroscopy

In a crystalline material the region of transparency to electromagnetic radiation defines the intrinsic loss mechanisms and also theoretical transmittance achievable within this region. For practical UV-vis spectrophotometry, the effective working range of wavelength is 200~800nm [29]. The UV-Visible spectrum of cerium tartrate crystal scanned between 200 and 800nm using SHIMADZU UV-2450 UV-Vis spectrophotometer at National Chemical Laboratory, Pune, is shown in Fig.3. The spectrum has no absorption band between 315 and 800 nm, hence the cerium tartrate crystal is expected to be transparent to all the UV-Visible radiations in between these two wavelengths. The UV cut off wavelength of cerium tartrate crystal is found to be 315nm. The absorption peak is observed at 283nm in the UV-B (280-315nm, middle wave) region of the UV spectrum. The sample is not transparent for far UV radiations (200-300nm). However it is transparent for near UV (300-400nm) radiations. Absorption in the far and near ultraviolet region arises from the electronic transitions associated within the sample. Using the formula E_g = hc/λ, where h is Plank's constant and c is velocity of light, the band gap energy can be found out by converting above formula to its simple conversion form 1240/λ. The band gap energy calculated from this simple conversion formula was found to 3.936eV.
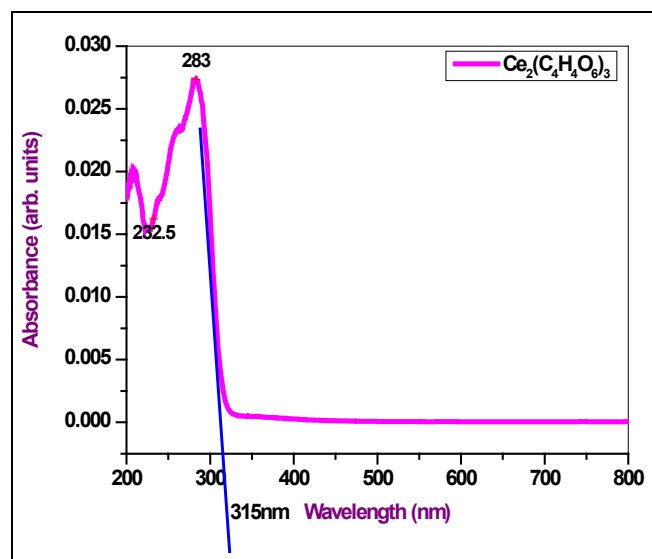

Fig 3: UV-Vis spectra of cerium tartrate crystal

Conclusions

In view of the above observations, we may conclude the following;

i). The gel growth system can be successfully used for the growth of pure cerium tartrate crystals.

ii). The diffusion of Ce^{3+} ions through the narrow pores of the silica lead to reaction between these ions and the $C_4H_4O_6^{-2}$ ions present in the gel as lower reactant. A good crop of crystals are obtained with the optimized parameters such as; Gel pH = 4.2; gel density = 1.05gcm⁻³; gel ageing for 72h; concentration of lower reactant = 1M; Concentration of upper reactant =0.5M.

iii). The diffraction peaks are indexed and the crystal system is found to be monoclinic. The unit cell parameters are a=

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7.1095Å, b= 5.1838 Å, c = 3.4016 Å and α=90^0, beta = 92.474º, γ =90^0, and unit cell volume is 125.25 Å^3

iv). The presence of C, O and Ce in the cerium tartrate crystals is evident from the characteristics K_α, L_α, and L_β peaks of these elements. From UV-Vis Spectroscopic studies the band gap energy calculated for CeT was found to 3.936eV.

v). The UV cut off wavelength of cerium tartrate crystal is found to be 315nm. The band gap energy calculated from simple conversion formula $E_g=1240/\lambda$, was found to 3.936eV.

Acknowledgements

References

1. M.E. Torres *et al. n*J. Crystal Growth. (1995)
2. M.E. Torres *et al*. J. Solid State Chem. (2002)
3. S.K. Arora *et al* J. Crystal Growth (2005)
4. K. Suryanarayana *et al*. Mater. Lett. (2000)
5. Jain *et al*. Mater. Sci. Eng. B (1991)
6. Jain *et al*. Mater. Chem. Phys. (1996)
7. A.R. Patel *et al*. J. Crystal Growth (1978)
8. R.A. Judge *et al*. Biophys. J. (1999)
9. M.E. Torres *et al*. J. Appl. Phys. (1998)
10. M.H. Rahimkutty *et al*. Bull. Mater. Sci. (2001)
11. J. Fousek *et al*. Ferroelectrics (1970)
12. N.R. Ivanov Ferroelectrics Lett. (1984)
13. F. Jona *et al*. Ferroelectric Crystals (1993)
14. S.K. Arora *et al*. Cryst. Growth Des. (2004)
15. K. Suryanarayana *et al*. Mater. Chem. Phys. (2002)
16. P.N. Kotru *et al*. Cryst. Res. Technol. (1987)
17. P.N. Kotru *et al*. Cryst. Res. Tech. (1986)
18. Shedam, M.R. and Venkateswara Rao, A., Bull. Mater. Sci., 16 (1993) 309.
19. Cyriac Joseph, George Varghese and Ittyachen, M.A., Cryst. Res. Technol., 30 (1995) 159.
20. Cyriac Joseph, Ittyachen, M.A., and Raju, K.S., Bull. Mater. Sci., 20 (1997) 37.
21. Bunn, C.W. and Alcock, T.C., Trans. Faraday Sci., 41 (1945) 317.
22. Keller, A., Polym. J. Sci., 17 (1955) 291.
23. Bhat, S., Kotru, P.N. and Koul, M.L., Mater. Sci. Engg., B34 (1995) 138.
24. Kotru, P.N. and Raina, K.K., J. Mater. Sci. Lett., 5 (1986) 760.
25. Jaffe, H.H. and Milton, O., *Theory and Application of Ultraviolet Spectroscopy*, Wiley, New York, 1962.
26. Skoog, *et al*., Principles of Instrumental Analysis, 6th ed. Thomson Brooks/Cole. 2007, 169-173
27. www.edax.com
28. http://xdb.lbl.gov/Section1/Periodic_Table/X-ray_Elements.html
29. Scott, A. J. *Interpretation of UV spectra of natural products*, Pergamon Press, London, 1964.

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