Surface Characterization Gel Grown Cerium Tartrate Crystals

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Abstract: 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 determine the surface area, pore volume and pore size of CeT sample. BET surface area was calculated from the BET plot; pore size distributions were calculated using BJH model. The pore volume was measured at the single point of $p/p_0 = 0.05$. The Adsorption / Desorption Isotherm for cerium tartrate, Pore Size Distribution by BJH Method, Pore Size Distribution by DFT method and Volume Histogram By DFT Method was studied respectively for the CeT sample. The isotherm obtained for the sample demonstrates that it belongs to the type II isotherm.

Keywords: Gel Method, Cerium Tartrate, Adsorption / Desorption Isotherm, BET, BJH, DFT method

I. INTRODUCTION

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 $Sr_xBa_{1-x}Nb_2O_6$ [1] and laser crystals like $Y_3Al_5O_{12}$:Nd and $YAlO_3$ [2]. 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 [3]. Studies on cerium oxalate crystals grown in hydro-silica gel have been reported [4]. Growth and characterization of several oxalates and mixed rare earth oxalates in silica gel also have been reported [5-7]. No report has been noticed on the study of surface area, pore volume and pore size of CeT sample. Hence growth of these crystals is attempted. The surface area of a powder can critically affects its behaviour in many applications. [8,9] The technique is referenced by several standard organizations such as ISO, and ASTM. Pharmaceuticals, catalysts, activated carbons, gas sensors, ceramics, paint & surface coating, pigments and numerous other materials exhibits varying physical properties and effectiveness depending on their surface area.

The surface area of a powder is determined by the physical adsorption of a gas (normally Nitrogen or Krypton) onto the surface of the sample at liquid nitrogen temperatures [10]. The choice of gas to be used is dependent on the expected surface area and the properties of the sample. Once the amount of adsorbate gas has been measured (either by a volumetric or continuous flow technique), calculations which assume a monomolecular layer of the known gas are applied.

The BET [11] (Brunauer, Emmett and Teller) theory is commonly used to evaluate the gas adsorption data and generate a Specific Surface Area result expressed in units of area per mass of sample (m^2/g) [12]. The data from certain sample types such as zeolites, activated carbon, catalysts and various nanoparticles often use an alternative theory referred to as the Langmuir equation for the data reduction process. Additional data processing can provide information on mean pore size and pore size distribution of the substrate if sufficient data points are collected.

II. EXPERIMENTAL

Cerium tartrate crystals were grown from sodium metasilicate gel and water solutions of tartaric acid and cerium chloride. The growth of cerium tartrate crystals were accomplished by the controlled diffusion of Ce^{+3} ions through the silica gel impregnated with tartaric acid. A stock solution for the gel formation was prepared according to Henisch [13] by taking 22gm $Na_2SiO_3.9H_2O$ and 250 ml water. All experiments were carried out by single tube diffusion method. The grown crystals were characterized by Surface Characterization. The density functional theory (DFT) based method for the calculation of pore size distribution (PSD) of activated carbon from nitrogen adsorption isotherms has become a standard characterization procedure in recent years. [14-16].

Nitrogen adsorption isotherms were measured at 77.40 K using Quantachrome Autosorb Automated Gas Sorption System [12] at NCL, Pune. BET surface area, pore volume, pore size of CeT sample are calculate using Autosorb System Software for Windows, Version 1.24.

The adsorption experiments were performed in static mode which allowed for sufficient time to reach equlibrium. The surface area was determined usign standard BET method applied to the nitrogen adsorption-desorption isotherm over a relative pressure range of 0.02 to 0.99

III. RESULTS AND DISCUSSION ON SURFACE CHARACTERIZATION OF CERIUM TARTRATE CRYSTALS

The present study is primarily concerned with the adsorption and desorption of nitrogen by CeT sample. The principle objective of this investigation is to determine the surface area, pore volume and pore size of CeT sample.
BET surface area was calculated from the BET plot; pore size distributions were calculated using BJH model. The pore volume was measured at the single point of $p/p_0 = 0.05$.
Figures 1, 2, 3 and 4 shows the Adsorption / Desorption Isotherm for cerium tartrate, Pore Size Distribution by BJH Method, Pore Size Distribution by DFT method and Volume Histogram By DFT Method respectively for the CeT sample. The isotherm obtained for the sample demonstrates that it belongs to the type II isotherm.

Quantachrome Autosorb Automated Gas Sorption System Report

Autosorb for Windows® Version 1.24

Sample: $Ce_2C_4H_4O_6$ Sample Weight: 0.0450 g
Adsorbate: NITROGEN, Outgas Temp: 110 °C,
Cross-Sec Area: 16.2 Å²/molec, Outgas Time: 12.0 hrs.,
Analysis Time: 92.0min
NonIdeality: 6.580E-05, P/Po Toler: 0.05 End of Run:
Molecular Wt: 28.0134 g/mol, Equil Time: 1.00
Bath Temp. 77.40

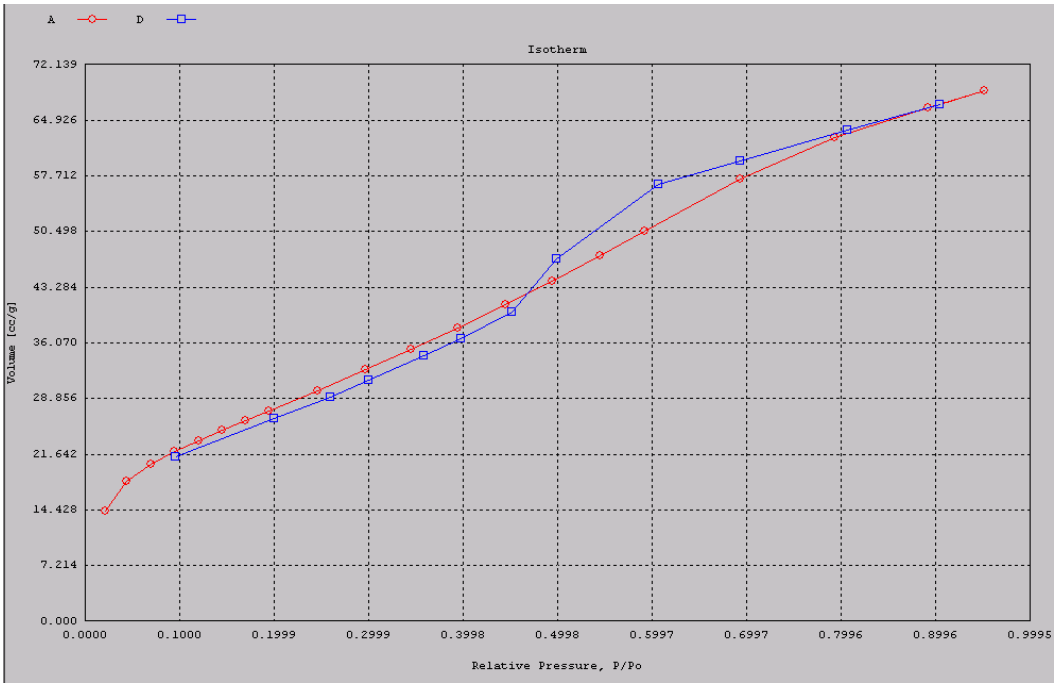

Figure 1. Adsorption / Desorption Isotherm for cerium tartrate

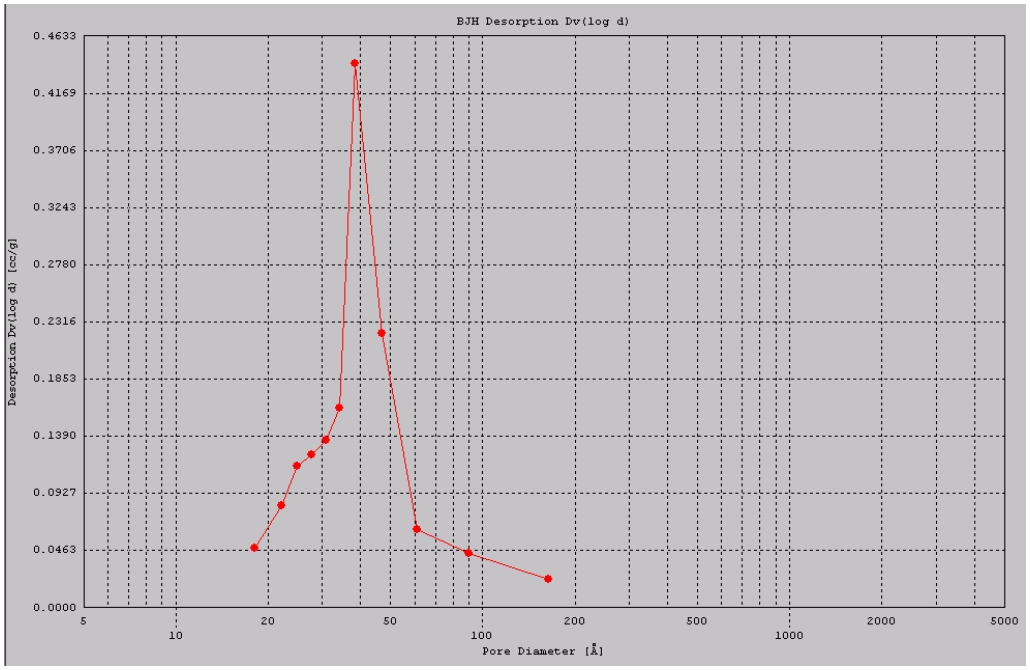

Figure 2. Pore Size Distribution by BJH Method

Pore Size Distribution by DFT method

Pore Volume = 0.0999 cc/g
Pore Width (Mode) = 8.4623E+01 Å

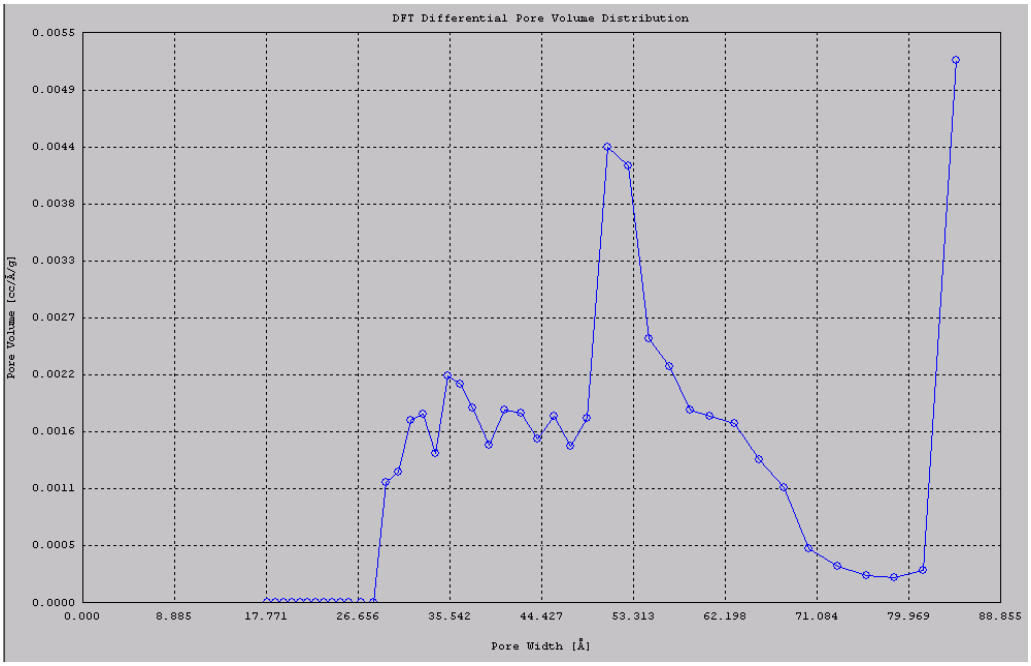

Figure 3. Pore Size Distribution by DFT method

Volume Histogram By DFT Method: Tabular Data

Pore Width [Å]		Pore Volume [cc/g]	Surface Area [m²/g]
31.62278 -	39.81072	4.66246E-03	6.07969E+00
39.81072 -	50.11872	1.47785E-02	1.63365E+01
50.11872 -	63.09573	2.09848E-02	1.81343E+01
63.09573 -	79.43282	3.23626E-02	2.30865E+01

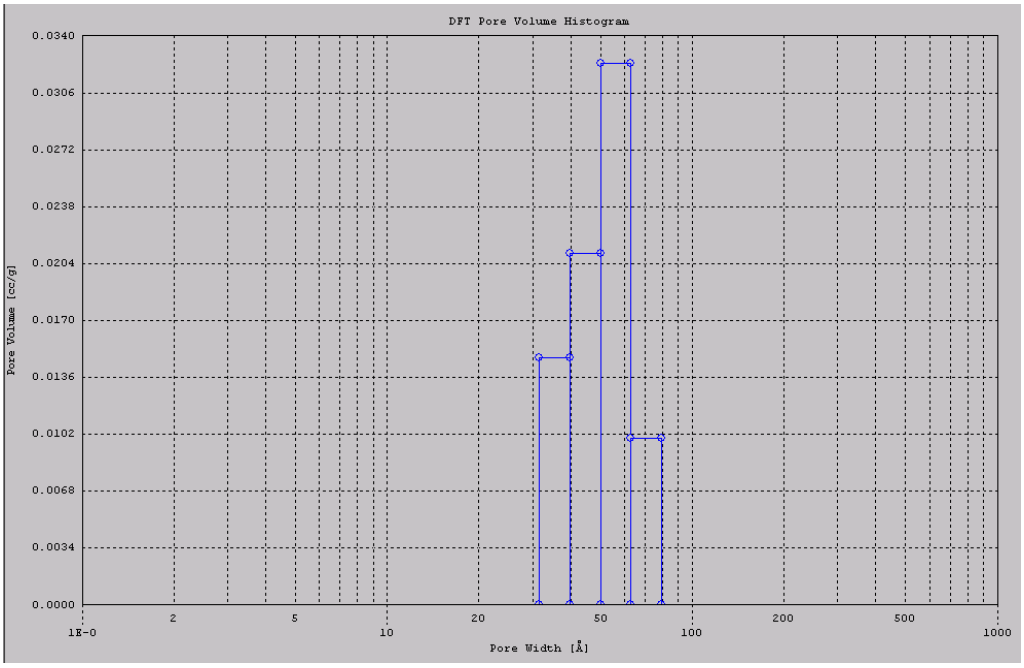

Figure 4. Volume Histogram By DFT Method

Result Summary

Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows® Version 1.24
Sample: $CeC_4H_4O_6$
Sample Weight: 0.0450 g
Adsorbate: NITROGEN, Outgas Temp: 110 °C,
Cross-Sec Area: 16.2 Å²/molec, Outgas Time: 12.0 hrs.,
Analysis Time: 92.0min
NonIdeality: 6.580E-05, P/Po Toler: 0.05 End of Run:
Molecular Wt: 28.0134 g/mol, Equil Time: 1.00
Bath Temp. 77.40

AREA-VOLUME-PORE SIZE SUMMARY

SURFACE AREA DATA

Multipoint BET.....	9.768E+01 m²/g
BJH Method Cumulative Desorption Surface Area.....	1.114E+02 m²/g
DH Method Cumulative Desorption Surface Area.....	1.151E+02 m²/g
t-Method External Surface Area.....	4.998E+01 m²/g
t-Method Micro Pore Surface Area.....	4.770E+01 m²/g
DR Method Micro Pore Area..... ……..	1.251E+02 m²/g

PORE VOLUME DATA

Total Pore Volume for pores with Diameter

less than 419.0 Å at P/Po = 0.95191.....	1.063E-01 cc/g
BJH Method Cumulative Desorption Pore Volume.....	1.066E-01 cc/g
DH Method Cumulative Desorption Pore Volume.....	1.064E-01 cc/g
t-Method Micro Pore Volume.....	4.605E-02 cc/g
DR Method Micro Pore Volume.....	4.444E-02 cc/g
HK Method Cumulative Pore Volume.....	6.608E-02 cc/g
SF Method Cumulative Pore Volume.....	6.653E-02 cc/g

PORE SIZE DATA

Average Pore Diameter.....	4.352E+01 Å
BJH Method Desorption Pore Diameter (Mode).....	3.827E+01 Å
DH Method Desorption Pore Diameter (Mode).....	3.827E+01 Å
DR Method Micro Pore Width	1.091E+02 Å
DA Method Pore Diameter (Mode).....	1.920E+01 Å
HK Method Pore Width (Mode).....	6.265E+00 Å
SF Method Pore Diameter (Mode).....	1.080E+01 Å
DFT Method Pore Width (Mode).....	8.462E+01 Å

Conclusions

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

1. The gel growth system can be successfully used for the growth of pure cerium tartrate crystals.
2. 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.

3. The data obtained by details of the calculations provide detailed representation of the porosity in the range of micro and mesopores.
4. The nitrogen adsorption-desorption isotherm obtained for the sample demonstrates that it belongs to the type II isotherm.

ACKNOWLEDGEMENTS

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