

Scholars Research Library

Archives of Physics Research, 2011, 2 (1): 239-245 (http://scholarsresearchlibrary.com/archive.html)



Crystallographic and FT-IR Characteristics of Gel Grown Cerium Tartrate Crystals

H. M. Patil^{1*}, D.K. Sawant², D.S. Bhavsar³, J.H. Patil⁴, K.D. Girase⁵

 ^{1,2}Department of Physics, JES's Arts, Science and Commerce College, Nandurbar (MS), India
 ³Department of Physics, Pratap College, Amalner (MS), India
 ⁴Department of Electronics and Telecommunication, PSGVP Mandals College of Engineering, Shahada (MS), India
 ⁵Department of Physics, SVS's Arts, and Science College, Dondaicha (MS), India

ABSTRACT

Crystals of cerium tartrate hydrate bearing the formula $Ce_2 (C_4H_6O_6)_3 xH_2O$ were grown in silica gel in pure form. The optimum conditions required for the growth of these crystals are worked out. With all growth conditions crystals attain spherulitic morphology. The results were obtained from x-ray powder diffractogram, Fourier transform infrared spectroscopy and quantitative elemental analysis by EDAX. Powder XRD results indicate the polycrystalline nature of this material. Calculation of cell parameters using POWD software suggests that the pure cerium tartrae crystals belong to monoclinic system. The cell parameters and (hkl) values are reported for the first time. FT-IR for these crystals show all the bands expected from the metal tartrate with water of crystallization. Further the presence of cerium, carbon and oxygen is confirmed by EDAX.

Keyword: Gel growth, Cerium tartrate, Spherulitic crystals, XRD, FT-IR, EDAX..

INTRODUCTION

Tartaric acid is a principal by-product of the conversion of grape stock to wine by fermentation. The presence of the reactive hydroxyl groups in tartrate ions allows the introduction of a variety of metal elements. Recently considerable attention has been devoted to tartrate salts due to their interesting physical properties. Some members of this family are dielectric, ferroelectric, and piezoelectric and are used for transducers and many linear and non-linear devices[1-3]. Of particular interest are the investigations about the calorimetric and electric behaviour of rubidium hydrogen tartrate[4] and ammonium tartrate[5].

Rare-earth tartrates bearing the general formula $R_2(C_4H_6O_6)_{3.}xH_20$ (R= Nd, Dy, Gd, La, Di, Pr, Sm, Y) have also been grown by the gel method using silica hydrogel as a medium of growth [6-12]. Amongst the metal tartrates, copper tartrate is visualized to be of great interest.

This work is a part of our research program concerning the investigation of various properties of tartrate salts with trivalent cations as related to their crystalline structure [13-14]. The purpose of such a studies is establish their identity so that other physical properties can be fully investigated. To the best of author knowledge, no systematic study has been conducted on the growth of cerium tartrate crystals by the gel method. As a result, details on their characteristics are also not found in the literature. Practically no information on characteristics of pure cerium tartrate by silica gel technique is available.

MATERIALS AND METHODS

Cerium tartrate crystals have been grown in silica gel medium using the technique described by Henisch [15-16]. Cerium tartrate shows poor solubility in water hence it was thought worthwhile to grow such a kind of material by chemical reaction at controlled rate using gel method. The crystals were grown in single glass tubes of length 200m and diameter 25mm. Silica gel was prepared by adding a solution of sodium metasilicate of molarity (0.5 to 1.5) to tartaric acid of particular molarity (0.25 to 2.0M), drop by drop with continuous stirring. The solution with desired value of pH (3.5 to 5) was then transferred to several glass tubes. Once gelled, an aqueous solution of cerium tartrate (0.25 to 1.5M) was carefully poured with the help of pipette along the walls of the tubes over the set gel. The Ca⁺³ ions diffuse through the narrow pores of the gel to react with the tartrate ions (C₄H₄O₆⁻²) present in the gel as lower reactant, giving rise to the formation of cerium tartrate hydrate crystals.

The following reaction is expected to take place in the gel medium.

$$CeCl_3 + 3(C_4H_6O_6) \rightarrow Ce_2 (C_4H_6O_6)_3 xH_2O + 6HCl$$

Based on the various experiments conducted leading to pH of gel, gel density, concentration of upper reactant, concentration of lower reactant, gel ageing etc., the best controlling parameters which lead to the growth of good spherulitic cerium tartrate crystals are; Gel pH = 4.5; gel density = 1.06gcm⁻³; gel ageing for 78h; concentration of lower reactant = 1M; Concentration of upper reactant =1M. The crystals were harvested in a month. Spherulitic crystals growing in the silica gel are shown in figure 1. The maximum diameter of spherulitic crystals is found to be 6mm.

The powder X-ray diffraction pattern of neodymium tartarte hydrate was recorded using Reguka Miniflex diffractometer with CuK α radiations of wavelength 1.54051A° at 30kV and 15mA. Measurements were made from 2theta = 20-80°. The FT-IR spectra of the material was recorded in the wave number range 450-4000cm⁻¹ on a Perkin Elemer spectrometer using KBr pellet technique.



Figure 1 Formation of spherulitic crystals out of precipitate in silica gel

RESULTS AND DISCUSSION

The powder x-ray diffractogram for pure cerium tartrate crystals is shown in figure 2. From the diffractogram it is clear that cerium tartrate is polycrystalline in nature. The diffractogram was indexed using POWD (an Interactive Powder Diffraction Data Interpretation and Indexing Program, Version 2.2) software. The cell parameters of pure cerium tartrate crystals were obtained by selecting 27 intense peaks. Calculations of cell parameters reveals that the pure crystal belongs to monoclinic crystal system, with unit cell parameters a = 7.1095Å⁰, b = 5.1838Å⁰, c = 3.4016Å⁰, α =90⁰, β =92.47⁰, γ =90⁰ and unit cell volume is 125.25 Å⁰³ The experimental 'd' values are in good agreement with the calculated ones for the above cell parameters. The powder x-ray diffraction data for cerium tartrate are listed in table 1. To the best of author's knowledge, x-ray diffraction data on these crystals is limited only to the 20 values and intensity[17]. Cell parameters, (hkl) values and d-spacing are reported for the first time.



Figure 2 Powder XRD spectrum of cerium tartrate

Line	d-spac	cing A ^o	ng A ^o Intensity		2Theta Deg.		diff
No	obs.	calc.	Intensity	(h k l)	obs	calc.	unn.
1	4.1873	4.1873	34	1 1 0	21.20	21.20	.000
2	3.3984	3.3984	31	0 0 1	26.20	26.20	.000
3	3.1185	3.1185	32	-101	28.60	28.60	.000
4	3.0153	3.0153	31	1 0 1	29.60	29.60	.000
5	2.9378	2.9298	38	2 1 0	30.40	30.48	085
6	2.8116	2.8421	32	0 1 1	31.80	31.45	.351
7	2.4661	2.4349	32	1 2 0	36.40	36.88	484
8	2.2850		35		39.40		
9	2.2521	2.2592	32	-2 1 1	40.00	39.87	.131
10	2.1994	2.1809	35	2 1 1	41.00	41.36	363
11	2.0386	2.0609	48	0 2 1	44.40	43.89	.507
12	1.9877	1.9832	32	-301	45.60	45.71	108
13	1.9012	1.9045	39	3 0 1	47.80	47.71	.088
14	1.7446	1.7481	32	3 2 0	52.40	52.29	.112
15	1.7143	1.7279	48	030	53.40	52.94	.456
16	1.6353	1.6367	42	1 0 2	56.20	56.15	.050
17	1.6143	1.6147	31	0 1 2	57.00	56.98	.016
18	1.6040	1.6025	38	-401	57.40	57.46	058
19	1.5546	1.5538	45	2 3 0	59.40	59.44	035
20	1.4999	1.4992	40	1 3 1	61.80	61.83	030
21	1.4219	1.4211	36	0 2 2	65.60	65.64	044
22	1.4142	1.4096	38	-302	66.00	66.25	245
23	1.3810	1.3839	36	1 2 2	67.80	67.64	.158
24	1.3634	1.3630	33	-421	68.80	68.82	020
25	1.2539	1.2550	30	-402	75.80	75.72	.081
26	1.2346	1.2383	48	-322	77.20	76.93	.273
27	1.2239	1.2198	31	-412	78.00	78.32	316

Table 1. X-Ray Powder Data of Cerium tartrate

In order to confirm the presence of cerium, quantitative elemental analysis was performed on application of EDAX. The EDAX spectra shown in figure 3 reveals prominent peaks due to Ce L α , C K α and O K α . This confirms the formation of cerium tartrate crystals. The weight % and atomic weight % calculated from the peak height further confirms the expected proportion of carbon, oxygen and cerium in cerium tartrate crystals. (Table 2)



Figure 3 An EDAX spectra recorded for cerium tartrate

Table 2. EDAX Data

Element	Wt %	At. Wt.%	K-Ratio	Z	А	F
С	30.30	51.08	0.1141	1.0782	0.3492	1.0004
0	34.64	43.85	0.0856	1.0629	0.2326	1.0000
Ce	35.06	05.07	0.3288	0.8069	1.1623	1.0000

Figure 4 shows the characteristics FT-IR spectra for cerium tartrate. Table 3 gives the details of band assignments for these crystals. The very strong and broad peak at 3367.45 cm⁻¹ is due to stretching mode of O-H from water of crystallization. The very strong peak at 2929.70 represents v (OH) stretching due to other OH groups in the structure. A week shoulder at 2693.10 cm⁻¹ is due to overtones. The peaks at 1728.05 cm⁻¹ and 1602.69 cm⁻¹, respectively, represent asymmetric stretch of O-C-O (v_{as} (O-C-O)) while peaks at 1464.07 cm⁻¹ 1377.75 cm⁻¹ are due to v_s (O-C-O) stretch. The spectra shows doublet peaks at frequencies 1321.66 cm⁻¹ 1284.92 cm⁻¹, respectively, which are due to v(C-OH). The doublet show that the two are dissimilarly coordinated as has been reported earlier in some similar compounds [18-19]. Peaks at 1142.81 cm⁻¹ 1117.89 cm⁻¹ may be due to inclusion of gel during the crystal formation. Peaks at 1077.33 cm⁻¹ 1057.71 cm⁻¹ are due to C-H stretch in the plane deformation. vCH mode is indicated by the peaks at 882.04 cm⁻¹ 845.48 cm⁻¹. Peaks at 720.52 cm⁻¹ 594.69 cm⁻¹ 536.03 cm⁻¹, respectively, are due to metal oxygen bonding v(M-O). Thus the IR spectra for these crystals show all the important peaks as expected in metal tartrates with water of hydration as reported in literature.[20-23].



Figure 4 FT-IR spectrum of cerium tartrate

Table 5. F I-IR band Assignment					
Sr.No	Band cm ⁻¹	Assignment			
1	3367.45	v (OH) of water			
2	2929.70	ν (OH)			
3	2693.10	Overtones			
4	1602.69	$v_{as}(O-C-O)$			
5	1464.07	ν _s (O-C-O)			
6	1321.66	v(C-OH) doublet			
7	1077.33	C-H in plane deformation			
8	882.04	v (C-H)			
9	845.48	v (C-H)			
10	720.52	v (M-O)			

Table 3. FT-IR Band Assignment

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 XRD studies revels the polycrystallinity of cerium tartrate crystals.
- 3. 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 = 4.5; gel density = 1.06gcm⁻³; gel ageing for 74h; concentration of lower reactant = 1M; Concentration of upper reactant =1M.
- 4. Grown crystals exhibit spherulitic morphology for all growth conditions.
- 5. FT-IR spectroscopy reveals the presence of water of crystallization, expected functional groups and presence of metal oxygen bond in cerium tartate.
- 6. The quantitative elemental analysis confirms the presence of cerium, carbon and oxygen in grown material.

Acknowledgements

Authors are thankful to the Principal, Pratap College, Amalner and Principal, JES's Arts, Science and Commerce College, Nandurbar for providing necessary facilities to carry out this work.

REFERENCES

[1] M.E. Toress, T. Lopez, J. Peraza, J. Stockel, A.C. Yanes, C. Gonzalez-Silgo, C. Ruiz-Perez, P.A. Lorenzo-Luis, *J. Appli.Phys.*, **1998**, 84, 5729.

[2] M.E. Toress, T. Lopez, J.F. Peraza, J. Stockel, A.C. Yanes, J. Cryst. Growth., 1995, 156, 421.

[3] M.E. Toress, T. Lopez, J. Peraza, J. Stockel, A.C. Yanes, C. Gonzalez-Silgo, X. Solan, M.

Garcia-Valle's, E. Rodriguez-Castellon, J. Solid State Chem., 2002, 163, 491.

[4] C.C. Desai, A.H. Patel, M.S.V. Ramanna, Ferroelectrics, 1990, 102, 23.

[5] M.M. Abdel-Kader, F. El-Kabbany, S. Taha, A.M. Abosehly, K.k. Tahoon and A.A. El-Sharkawy, *J.Phy. Chem. Solids*, **1991**, 52, 655.

[6] P.N. Kotru, K.K. Raina, N.K. Gupta, Cryst. Res. Technol., 1987, 22, 177.

- [7] P.N. Kotru, N.K. Gupta, K.K. Raina, Cryst. Res. Technol., 1986, 21, 15.
- [8] P.N. Kotru, K.K. Raina, J. Mater. Sci. Lett., 1986, 05, 760.
- [9] P.N. Kotru, N.K. Gupta, K.K. Raina, J. Mater. Sci., 1986, 21, 90.
- [10] V. Mansotra, K.K. Raina, P.N. Kotru, J. Mater. Sci., 1991, 26, 3780.

[11] A. Jain, A.K. Razdan, P.N. Kotru, Mater. Sci. Eng., 1991, B8, 129.

- [12] A. Jain, A.K. Razdan, P.N. Kotru, Mater. Chem. Phys., 1996, 45, 180.
- [13] H.M. Patil, D.K. Sawant, J.H. Patil, D.S. Bhavsar, J. Scientific Review, 2010, 2, 2, 108.
- [14] H.M. Patil, D.K. Sawant, J.H. Patil, D.S. Bhavsar, Archives of Physics Research, 2010, 1, 4, 168.

[15] H.K. Henisch, Crystal Growth in Gels, Pennsylvania State University Press, University Park, PA 1973.

[16] H.K. Henisch, Crystals in Gels and Liesegang Rings, Cambridge University Press, Cambridge, **1988.**

- [17] PCPDF File No. 19-0298.
- [18] R.M. Sharma, M.L. Koul, J. Indian. Chem. Soc., 1987, 64, 459.
- [19] K.C. Satpathy, P. Herna, J. Indian. Chem. Soc., 1981, 58, 1002.
- [20] Aniama Jain, P.N. Kotru, M. L. Koul, Materials Chemistry and Physics, 1994, 38, 332.
- [21] P.N. Kotru, N.K. Gupta, K.K. Raina, I.B. Sharma, J. Mat. Sci., 1986, 21, 83.

[22] P.N. Kotru, K.K. Raina, M.L. Koul, J. Mat. Sci. Lett., 1987, 6, 711.
[23] V. Mansotra, K.K. Raina, P.N. Kotru, M.L. Koul, J. Mater. Sci., 1991, 26, 6729.