XRD,FTIR and Elemental Analysis of Single Crystal Mercury Tartrate Grown by Gel Method

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Abstract:

Crystal growth is a heterogeneous chemical process that involves changing a compound's phase from one to another.The gel used in the crystal formation approach study has gained popularity and is employed by several investigators. In this research paper, we have developed high-quality Mercury Tartrate crystals using a simple gel diffusion method and determined the optimal growth conditions byvarying parameters such as pH of the gel solution, gel setting time, reactant concentrations, the density of a solution of sodium meta silicate, mercury chloride volume and temperature, etc.A few of the developed crystals were translucent, while others were opaque. XRD was used to analyze the crystalstructure and confirm crystalline perfection at various optimal conditions. EDAX was used to verify the chemicalcomposition and elemental analysis. FTIR confirms the material's design and structural analysis. This investigation aimed to examine the factors governing Mercury Tartrate crystals' formationin silica gels. Gel methods have been widely utilized compared to other techniques due to their low cost sensitivity and ease of use.

Keywords: Gel method, Mercury Tartrate, XRD, FTIR and EDAX

1. Introduction

In recent years crystal growth in gel medium has attracted the attention of many investigators. Most of the tartrate compounds are soluble in water and decompose before melting. Hence single crystals of such compounds cannot be grown by either slow evaporation or melt technique. In this situation, the gel method is appropriate for their growth. Tartrate has several applications in medicine, optics etc. and hence; it was thought work to undertake an investigation on the development of crystals of mercury tartrate and their characterization by different methods. The current paper's goal is to provide a first-time report. (to the best of our knowledge) the growth of single crystalsof mercury tartrate in silica gel at ambient temperature. Mercury Tartrate crystals have developed in silica gel.

This research used a powder X-ray diffraction (XRD) investigation; Fourier transforms infrared spectroscopy (FT-IR), and EDAX analysis to achievethe results. This study aims to talk about the variables influencing the gel method for making mercurous chloride.

2. LiteratureReview

Tartrates (Aroraetal., 2004), malates (Jinietal., 2006) (Jinietal., 2007) and malonates (Lincyetal., 2010) (Doreswamyetal., 2005) (Mathewetal., 2011) (Natarajanetal., 2011) exhibit properties like piezoelectricity, photoconductivity, and ferro electricity and have become technologically important (Mukherjeeetal., 2003) (Mahalakshmi, 2013) due to their use in many medicinal related applications,

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pharmacological, and industrial applications, several tartrate compounds require special consideration(Joshi et al., 2006)A typical byproduct of the wine industry called tartaric acid may be used as the base for the development of new types of materials. This compound's two hydroxyl and two carbonyl groups make it possible to easily include phosphorus-containing moieties and monovalent, divalent, or trivalent metal ions. These materials must possess nonlinear optical characteristics or be dielectric, ferroelectric, and piezoelectric for most uses. (Torres et al., 2002)These characteristics of tartrate compounds are used to make linear and nonlinear mechanical devices, such as

2012)The gel method offers a seductive advantage for the synthetic crystallization of materials that have poor water solubility, deteriorate before melting, and do not vapourize or sublime when heated. (Korah et al., 2010)The gel approach offers an alluring advantage for the synthetic crystallization of materials that exhibit poor water solubility, decompose before melting, and do not vaporize or sublime on heating. (Freeda et al., 2013)The typical formula of tartrates is $A_2C_4H_4O_6$ for monovalent alkali metals and $BC_4H_4O_6$ for bivalent alkali metals, respectively. Two, three, or more water molecules may also be present in some tartrate molecules, making them hydrated. Tartrates are less soluble in water and decompose before melting; it has been discovered that the gel development approach in an environment with air temperature is ideal for these substances. (Structures, n.d.)Mercurous chloride is a substance with great potential for use in acousto-optic devices. (Singh et al., 1987)Mercurous chloride is typically grown as a single crystal utilizing physical vapour transfer in sealed ampoules. The industrial application process is still limited, however. The complexity of transport events in the vapour phase and the challenge of obtaining a high-quality starting material are the causes. (Awitor et al., 2001)

3. Research Methodology

They titrated sodium meta silicate solution ($Na_2Sio_3.9H_2O$) against tartaric acid ($C_4\ H_6\ O_6$). They added a few drops of diluted acetic acid and potassium iodide until the necessary pH was reached, creating gel matrice in straight glass tubes. The tubes were hermetically sealed, stored at room temperature, and gently poured with mercury chloride solution to ensure good gelation. The gel method generates single crystals of pure and modified mercury tartrate. The apparatus for this process consists of two borosil glass tubes, each measuring 20 cm in length and 2.5 cm in diameter. Numerous studies were carried out at medium pH levels (4-7, in steps of 0.1) and gel densities (1.02gm/cc-1.07gm/cc). In various tests, the inner and supernatant reactants' strengths were changed from 0.25 M to 2 M. To prevent the gel from breaking, an exact molar concentration of an aqueous Mercury chloride solution was carefully poured over the gel along the test tube walls. In our experiment, tiny needles that are primarily white and yellow with red spots are formed into crystals that are all plate-like in shape. The gel's body is a translucent pale yellow-brown colour. The supernatant liquor and the gel body are colorless when too much $HgCl_2$ is applied as the external reactant. (Kurtz, 1966)when the reaction has finished. It was developed after 40 to 42 days; size, perfection, and colour appear around 1 cm below the gel-solution interface. About 1.5 months were needed to complete the growth process. Only under the following conditions were high-quality crystals possible to obtain: Table 5.1(a) lists the many circumstances discovered suitable for crystal growth.The following reaction should occur, resulting in the creation of mercury tartrate crystal:

$$HgCl_2 + C_4\ H_6\ O_6 \Rightarrow HgC_4\ H_4\ O_6 + 2HCl$$

This Mercury chloride is expected to react with Tartaric acid, creating crystals of Mercury tartrate ($HgC_4H_4O_6$) that diffuse in a gel from the supernatant solution. Used the gel to develop various morphologies, including tiny, plate-like crystals with primarily white, yellow, and red needles. Show below fig.5.2 (a).

4. Results and Discussion

Various apparatuses were used to characterize the produced crystals. Recorded the powder XRD pattern on the D2 (PHASER) BRUKER system with Detector SSD160-2 (1D model). The FTIR spectra were recorded on the SHIMADZU FTIR -8100 S System spectrometer in the range of 400 cm^{-1} to 4000 cm^{-1}. Advanced microanalysis solution instruments provided by AMETEK were used for the elemental composition

and material identification.

X-ray diffraction studies on grown mercury tartrate crystals

X-ray powder diffraction was carried out on powdered samples to evaluate the degree ofcrystalline perfection of $HgC_4H_4O_6$Figure 5.1(b) shows the strong, mighty peaks in the powder X-ray pattern of the $HgC_4H_4O_6$ samples confirming that the produced crystals have a high crystallinity of 86.5%. Powder-X software was used to estimate the crystal plane orientations, or (h, k, l) values, and the greater interplane distance, or "d," utilizing the cell parameters a=4.325, b=12.73, and c=5.963. It demonstrates the orthorhombic nature of the structure. And $\alpha= \beta= \gamma= 90^0$. This formula is used to determine the orthorhombicity:

Orthorhimbicity = [b – a / b + a] x 100(Crystals et al.2016)

The lattice parameters are a and b, the Orthorhimbicity is 49.28 after calculation, and the Cell volume $(A^0)^3$ = 328.31 after single crystal X-ray diffraction. The values of (h, k, l) 004 and "d" values were found to coincide with those of mercury tartrate (JCPDS- 02-0255).

Analysis of the grown Mercury tartrate crystal using FTIR spectroscopy

Fig 5.1(c)shows FTIR Spectra of Mercury tartrate Shevchenkoi looked at the infrared (IR) spectra of various tartrates, both regular and partially deuterated, and found absorptions at 600 cm^{-1} and 400 cm^{-1} that could be attributed to the COO^-group in metal tartrates. (Bridle & Lomer, 1965). The FTIR examination of materials offers information about their chemical bonding or molecular structure. The absorption peaks correspond to chemical group vibrations, and Infrared spectral theories were given the link between chemical group vibrations and unique absorption bands. (Joshi et al., 2010) The current study looked at theIR absorption of Mercury tartrate compounds from 400 cm^{-1} to 4000 cm^{-1}. Infrared spectroscopy probes molecular vibrations. Functional groups can be associated with characteristic infrared absorption bands, which correspond to the fundamental vibrations of the functional groups(Berthomieu & Hienerwadel, 2009).Each of the two halves of the tartrate ion comprises a carboxyl group, a tetrahedral carbon atom, anda hydroxyl oxygen atom. The C = C bond between these two halves binds them together. Therefore, it is expected that the hydroxyl and C-H groups will vibrate in a stretched state. The two hydroxyl groups presentin a free tartrate ion may result in two bands of stretching vibrations of the hydroxyl group. The wave number range for the FTIR spectra is 400 to 4000 cm^{-1}. O-H stretching mode causes strong absorption bands between 2500cm^{-1} and 3550cm^{-1}. TheC-H stretching method causes absorptions between 2990 $cm^{-1}$to 2850 cm^{-1}. The C=O stretch of the carbonyl group is responsible for the bands about 1685 cm^{-1} and 1800cm^{-1}(Freeda et al., 2013). The stretching of the C = C atoms causes the absorption at 1626.05 cm^{-1}. N-H bending is the cause of the absorption at 1583.61 cm^{-1}. N-H bending is the cause of the peak at 1539.25 cm^{-1}. Because of out-of-plane O-H bending, the N-O stretching at 1539.25cm^{-1} has significant intensity peaks. The FTIR spectra produced in this work are comparable to the IR spectrum of crystals of mercury tartrate shown in table 5.1(b). The presence of O-H, C=O, C=C, N-O, and N-H bonds is confirmed in all samples, including the crystals, crystalline mass, and precipitates of mercury tartrate, according to the FTIR spectra.

Energy dispersive X-ray analysis -

Performed an Energy Dispersive X-ray analysis on the sample of produced crystals to verify the elements' existence in the $HgC_4H_4O_6$ crystals analyzed using an energy-dispersive X-ray spectrometer named by an advanced microanalysis solution instrument provided by AMETEK. The obtained spectrum Fig. 5.1(d) confirms the presence of Mercury. It verified the presence of sodium, chlorine, and silicon in low concentrations ranging from 1% to 4.32%, respectively, and significant amounts of carbon, oxygen, and Mercury. C, O, and Hg had atomic percentages of (60.95%), (34.50%), and (00.87%), respectively, and apparent concentrations of (02.91%), (00.55%), and (00.22%), according to the energy dispersive X-ray spectra. EDAX research determined the molecule's Tartrate nature. To put it another way, mercury tartrate ($HgC_4H_4O_6$) could develop. Additionally, it shows all of a growing crystal's fundamental characteristics. The EDAX investigation also demonstrated ideal stoichiometry for $HgC_4 H_4 O_6$. Fig.(5.6) depicts the material's component structure. This diagram displays the distribution of specific

material elements over a given area. To confirm the creation of the HgC_4 H_4 O_6 compound, an EDX study was conducted. The significant peaks from the EDX measurement, which covered several places, are displayed in the figure. The generated composite nanostructure can be seen in the EDX spectrum as Synthesis and Characterization studies of IB transition metal mercury tartrate single crystals ($HgC_4H_4O_6$). C, O, Hg, and Cl each had atomic percentages of 47.26% and 35.63%. 00.50 per cent and 11.28%, respectively. Details of the EDX spectra of the electro-spam ($HgC_4H_4O_6$) levels, expressed in atomic and weight percentages, are provided in table 5.1(c).

5. Figures and Tables

Figures

Conditions	Mercury Tartrate
The density of sodium meta-silicate solution	1.04 gm/cm^3
The concentration of tartaric acid	1 M
The volume of tartaric acid	5 ml
The volume of sodium meta-silicate solution	16 ml
The pH of the gel	4.4
Concentration of $Hgcl_2$	1M
Volume of $Hgcl_2$	5ml
Temperature	Room temperature up (30^0C)
Period	40 to 42 days
Quality	Transparent

Table 5.1 (a) Optimal conditions for crystal formation of Mercury tartrate.

Fig. 5.1 a) spotted with red needles plate-like colored crystal b) White needles crystals c) Growth crystals.

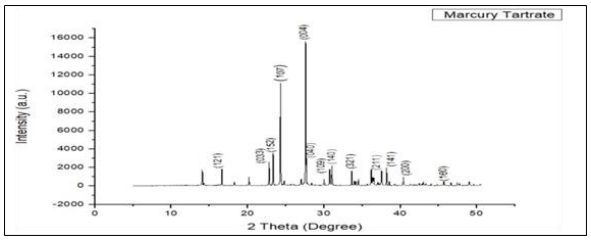


Fig. 5.1(b)X-ray diffraction pattern of Mercury tartrate

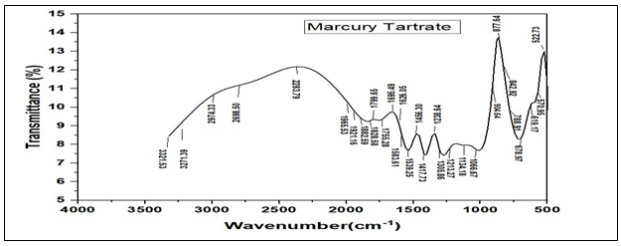
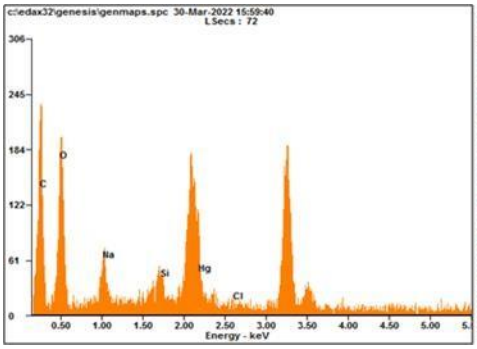


Fig. 5.1(c)Shows FTIR Spectra of Mercury tartrate

FTIR Peaks (cm^{-1})	Intensity	Functional group	Assignments
3321.53	Strong, broad	Alcohol	O-H Stretching
3271.38	Strong, broad	Alcohol	O-H Stretching
2974.33	Medium	Alkane	C-H Stretching
2698.5	Strong, broad	Carboxylic acid	O-H Stretching
1799.65	Strong	anhydride	C=O Stretching
1695.49	Strong	Conjugate acid	C=O Stretching
1626.05	medium	Alkene	C=C
1583.61	medium	Amine	N-H bending
1539.25	Strong	Nitro compound	N-O Stretching
1417.73	Medium	Alcohol	O-H bending

Table 5.1(b) Shows Identified bands of FT-IR investigation of the tartrate crystals



Element	Wt%	At%
CK	47.26	60.95
OK	35.63	34.50
NaK	04.32	02.91
SiK	01.00	00.55
HgM	11.28	00.87
ClK	00.50	00.22
Matrix	Correction	ZAF

Fig: 5.1(d) EDAX spectrum of different radiation Table 5.1(c) The elemental composition weight ratio.

6. Conclusion

The experiments on the growth of mercury tartrate crystals in the system allow us to draw the conclusions like in silica gel, high-quality single crystals of mercury tartrate were produced. Structural characterization of the grown crystals was completed using single crystal and powder X-ray diffraction examinations, and the lattice parameters were assessed. The FTIR spectrum shows the presence of various functional groups in the mercury tartrate crystals. Optical studies show that the formed crystal is transparent over the visible range. Mercury is present, according to qualitative elemental analysis (EDAX).

7. Acknowledgements

A special thanks to Dr. Meera Ramrakhani, Department of Physics, Rani Durgawati University, Jabalpur for her valuable suggestions, Dr. Anand Yadav, Scientific Officer, SFSL, Sagar, for his keen interest in Data analysis and Adnano Technologies Pvt. Ltd, Karnataka for providing the facilities for characterization like XRD, FTIR and EDAX spectrum.

References

[1] Arora, S. K., Patel, V., Patel, R. G., Amin, B., & Kothari, A. (2004). Electrical characterization of strontium tartrate single crystals. Journal of Physics and Chemistry of Solids, 65(5), 965–973. https://doi.org/10.1016/j.jpcs.2003.10.058

[2] Awitor, K. O., Bernard, L., Bonnin, O., Coupat, B., Fournier, J. P., & Verdier, P. (1999). Préparation du chlorure mercureux et mesure de sa pression de vapeur. Canadian Journal of Chemistry, 77(2), 243–248. https://doi.org/10.1139/v98-237

[3] Berthomieu, C., & Hienerwadel, R. (2009). Fourier transforms infrared (FTIR) spectroscopy. Photosynthesis Research, 101(2–3), 157–170. https://doi.org/10.1007/s11120-009-9439-x

[4] Bridle, C., & Lomer, T. R. (1965). The development of crystals in silica gel and the sizes of the unit cells of copper tartrate and cadmium oxalate. Acta Crystallographica, 19(3), 483–484. https://doi.org/10.1107/s0365110x65003699

[5] Crystals, C. D., Jethva, H. O., Dabhi, R. M., & Joshi, M. J. (2016). Structural, Spectroscopic, Magnetic and Thermal Studies of GelGrown Copper Structural, Spectroscopic, Magnetic and Thermal Studies of Gel- Grown Copper Levo-Tartrate and Copper Dextro-Tartrate Crystals. June. https://doi.org/10.9790/4861- 0803033342

[6] Dalal, P. V., & Saraf, K. B. (2006). Study and growth of barium oxalate single crystals in agar gel. Bulletin of Materials Science, 29(5), 421–425. https://doi.org/10.1007/BF02914071

[7] Doreswamy, B. H., Mahendra, M., Sridhar, M. A., Prasad, J. S., Varughese, P. A., George, J., & Varghese, G. (2005). A new crystalline neodymium malonate hydrate three-dimensional polymeric structure. Materials Letters, 59(10), 1206–1213. https://doi.org/10.1016/j.matlet.2004.12.029

[8] Freeda, M. M., Freeda, T. H., & Delphine, S. M. (2013). Growth, structural, spectral, optical and mechanical studies of calcium mixed strontium tartrate single crystals. Asian Journal of Chemistry, 25(4), 1863–1865. https://doi.org/10.14233/ajchem.2013.13196

[9] Henisch, H. K. (1970). I 6 i 5. 66.

[10] Jini, T., Saban, K. V., & Varghese, G. (2006). The growth, spectral and thermal properties of the

coordination compound crystal - Strontium malate. Crystal Research and Technology, 41(3), 250–254. https://doi.org/10.1002/crat.200510569

[11] Jini, T., Saban, K. V., Varghese, G., Naveen, S., Sridhar, M. A., & Prasad, J. S. (2007). Growth, crystal structure and thermal properties of calcium bis(malate) dihydrate. Journal of Alloys and Compounds, 433(1– 2), 211–215. https://doi.org/10.1016/j.jallcom.2006.06.035

[12] Joshi, S. J., Parekh, B. B., Vohra, K. D., & Joshi, M. J. (2006). Growth and characterization of gel-grown pure and mixed iron-manganese Levo-tartrate crystals. Bulletin of Materials Science, 29(3),307–312. https://doi.org/10.1007/BF02706501

[13] Joshi, S. J., Tank, K. P., Parekh, B. B., & Joshi, M. J. (2010). Characterization of gel-grown iron-manganese- cobalt ternary Levo-tartrate crystals. Crystal Research and Technology, 45(3), 303–310. https://doi.org/10.1002/crat.200900152

[14] Korah, I., Joseph, C., & Ittyachen, M. A. (2010). GelGrowth and Structural Characterization of Gadolinium Neodymium Oxalate Crystals Grown in Hydro-Silica. Journal of Minerals and Materials Characterization and Engineering, 09(12),1081–1086. https://doi.org/10.4236/jmmce.2010.912078

[15] Kurz, P. F. (1966). Some Chemical Reactions in Silica Gels : III. Formation of Potassium Acid Tartrate Crystals. The Ohio Journal of Science, 66(2), 296–304.

[16] Lincy, A., Mahalakshmi, V., Tinto, A. J., Thomas, J., & Saban, K. V. (2010). Structural, thermal and dielectric properties of cobaltous malonate single crystals grown in limited diffusion media. Physica B: Condensed Matter,405(22),4673–4677. https://doi.org/10.1016/j.physb.2010.08.059

[17] Mahalakshmi, V. (2013). Growth, Structure and Physical Properties of Tetraaqua Bismaleatocobalt (II) Crystals. IOSR Journal of Applied Physics, 4(1), 67– 74. https://doi.org/10.9790/4861-0416774

[18] Mathew, V., Xavier, L., Mahadevan, C. K., & Abraham, K. E. (2011). Thermal and dielectric properties of gel-grown cobalt malonate dihydrate single crystals. Physica Scripta, 83(3). https://doi.org/10.1088/0031- 8949/83/03/035801

[19] Mukherjee, P. S., Konar, S., Zangrando, E., Mallah, T., Ribas, J., & Chaudhuri, N. R. (2003). Structural analyses and magnetic properties of 3D coordination polymeric networks of nickel(II) maleate and manganese(II) adipate with the flexible 1,2-bis(4-pyridyl)ethane ligand. Inorganic Chemistry, 42(8), 2695– 2703. https://doi.org/10.1021/ic026150n

[20] Natarajan, B., Mithira, S., & Sambasiva Rao, P. (2011). Single-crystal electron paramagnetic resonance study of the interstitial position of Mn(II) in dipotassium diaquabis zincate(II) dihydrate. Physica Scripta, 83(6). https://doi.org/10.1088/0031-8949/83/06/065704

[21] Patil, H. M., Sawant, D. K., Bhavsar, D. S., Patil, J. H., & Girase, K. D. (2012). FTIR and thermal studies ongel-grown neodymium tartrate crystals. Journal of Thermal Analysis and Calorimetry, 107(3),1031–1037. https://doi.org/10.1007/s10973-011-1599-1

[22] Rejeena, I., Thomas, V., Mathew, S., Elizabeth, A., Radhakrishnan, P., & Mujeeb, A. (2019). Nonlinear optical studies of calcium tartrate crystals. Journal of Taibah University for Science,13(1),611–615. https://doi.org/10.1080/16583655.2019.1612978

[23] Singh, N. B., Gottlieb, M., & Goutzoulis, A. (1987). Devices made from vapour-phase-grown mercurous chloride crystals. Journal of Crystal Growth,82(3),274–278. https://doi.org/10.1016/0022-0248(87)90314-9

[24] Torres, M. E., López, T., Stockel, J., Solans, X., García-Vallés, M., Rodríguez-Castellón, E., & González- Silgo, C. (2002). Structural characterization of doped calcium tartrate tetrahydrate. Journal of Solid State Chemistry, 163(2),491–497. https://doi.org/10.1006/jssc.2001.9435.