FTIR and thermal studies on gel grown neodymium tartrate crystals

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Received: 20 March 2011/Accepted: 14 April 2011/Published online: 3 May 2011 © Akadémiai Kiadó, Budapest, Hungary 2011

Abstract The growth of neodymium tartrate crystals was achieved in silica gel by single diffusion method. Optimum conditions were established for the growth of good quality crystals. Fourier transform infrared (FT-IR) spectroscopic study indicates the presence of water molecules and tartrate ligands and suggests that tartrate ions are doubly ionised. The thermal behaviour of the material was studied using thermogravimetry (TG), differential thermal analysis (DTA), derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC). Thermogravimetric analysis support the suggested chemical formula of the grown crystal to be Nd₂(C₄H₄O₆)₃·7H₂O, and the presence of seven water molecules as water of hydration. It is shown that the material is thermally stable up 45 °C beyond which it decomposes through many stages till the formation of

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Department of Physics, S.V.S.'s Arts and Science College, Dondaicha 425408, Maharshtra, India e-mail: kdgirase_1964@rediffmail.com neodymium oxide (Nd_2O_3) at 995 °C. The decomposition pattern is reported to be typical of a hydrated metal tartrate.

Keywords Gel growth · Neodymium tartrate · Spherulitic crystals · FT-IR · Thermal stability

Introduction

Tartaric acid, a common byproduct of the wine industry, may serve as a base for the development of new class of materials. The presence of the two hydroxyl as well as two carbonyl groups in this compound permits the ready incorporation of monovalent, divalent or trivalent metal ions as well as incorporation of phosphorus-containing moieties. For most applications, these materials must be dielectric, ferroelectric and piezoelectric or show non-linear optical properties [1-3]. These characteristics of tartrate compounds are utilised for their use in transducers, linear and non-linear mechanical devices [2]. Sodium tartrate dihydrate is commonly used as primary standards for methods that determine water contents [4]. Lanthanides form a series of compounds with properties that change regularly with increasing atomic number of lanthanide [5]. For the materials which shows poor solubility in water and which decomposes before melting and does not vapourise or sublime on heating, the gel method offers an attractive advantage for their synthetic crystallization [6]. Several researchers have grown materials of great interest from both solid state sciences as well as technological point of view in single crystal and polycrystalline form by gel technique [7] and modified such materials by suitable substitution to determine the effect of modification of composition on their characteristics [8–10]. Thermal stability of phosphinated diethyl tartrate which is flame retardant has been reported [11]. Thermal behaviour of three polynuclear co-ordination compounds of Nd(II) and Co(II) or Fe(III) with tryptophan have been reported [12]. Studies on thermal decomposition of lanthanum tartrate decahydrate have been reported, which shows the material to be unstable even at room temperature [13]. Rareearth materials have attracted considerable attention on account of their luminescent and magnetic properties [14]. Rare-earth tartrates bearing the general formula $R_2(C_4H_4O_6)_3 \cdot xH_20$ (R = Pr, Dy, Gd, Ho) have also been grown by the gel method and characterised by thermoanalytical techniques [15-18]. The studies on crystals of lanthanum tartrate grown in silica gel medium in pure form have already been reported [19]. But in the literature survey, to the best of our knowledge, there is no report on the systematic study on the thermal characterisation of neodymium tartrate crystals.

In these investigations, the authors have grown spherulitic crystals of neodymium tartrate crystals in silica gel. The results obtained by powder X-ray diffraction (XRD) studies, Fourier transform infra-red spectroscopy (FT-IR) and thermogravimetric analysis (TG, DTA, DTG, DSC) of neodymium tartrate crystals studied in grater detail considering the onset and step inflection temperature and a typical pattern of decomposition is established.

Experimental

Spherulitic crystals of neodymium tartrate hydrate were grown by single gel diffusion method. The details of various experiments on the growth of these crystals have been published elsewhere [20]. The experiments pertaining to the growth of neodymium tartrate crystals were conducted in borosilicate glass tubes of 2.5 cm diameter and 20 cm length. Gel was prepared by mixing sodium metasilicate solution of specific gravity 1.05 g cm^{-3} with the desired concentration of tartaric acid (0.5-1.5 M) which acted as a lower reactant. The solution was continuously stirred to avoid local ion concentration, which may cause premature local gelling and make the final solution inhomogeneous. The pH of the gel medium was adjusted between values of 3 to 5. The solution with the desired value of pH was then transferred to several glass tubes and left for gelling. After confirming the gel setting, an aqueous solution of neodymium chloride (0.25-1.5 M) was carefully poured along the walls of the tube with the help of pipette over the set gel, in order to avoid any gel breakage. The Nd⁺³ ions diffuse through the narrow pores of the gel to react with the tartrate ions $(C_4H_4O_6^{-2})$ present in the gel as lower reactant, giving rise to the formation of neodymium tartrate crystals.

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

 $NdCl_3 + 3(C_4H_6O_6) \rightarrow Nd_2(C_4H_4O_6)_3 \cdot 7H_2O + 6HCl$

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 neodymium tartrate crystals are given as: gel pH = 4.2; gel density = 1.05 g cm^{-3} ; gel ageing for 72 h; concentration of lower reactant = 1 M; concentration of upper reactant = 0.75 M; temperature = 30 °C. The crystals were harvested in a month.

The powder X-ray diffraction pattern of neodymium tartrate hydrate was recorded using Reguka Miniflex diffractometer with $CuK\alpha$ radiations of wavelength 1.54051 Å. The FT-IR spectra of the material were recorded in the wave number range 450–4000 cm^{-1} using KBr pellet technique. The thermal decomposition behaviour of the grown crystal was studied by simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) using a Perkin-Elmer thermal analyzer, with a heating rate of 10 °C/min from 30 to 100 °C in a nitrogen environment. The gas flow was maintained at 50 ml/min. The initial mass taken for simultaneous recording of TG and DTA was 25.319 mg. The reference substance for DTA was α -Al₂O₃. DSC curve was recorded in the temperature range 30 to 400 °C with a heating rate of 10 °C/min. The sample was hold for 1 min at 400 °C and cooled from 30 to 100 °C with a cooling rate of 10 °C/min.

Results and discussion

X-ray diffraction

The powder X-ray diffractogram for pure neodymium tartrate crystals is shown in Fig. 1. From the diffractogram it is clear that neodymium 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 neodymium 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 = 5.2275 Å, b = 3.9352 Å, c = 2.9180 Å, $\alpha = 90^{\circ}$, $\beta = 94.80^{\circ}$, $\gamma = 90^{\circ}$ and unit cell volume is 59.82 Å³. The experimental *d* values are in good agreement with the calculated ones for the above cell parameters.

FT-IR analysis

The FTIR spectra obtained for the grown crystals of neodymium tartrate is shown in Fig. 2. The infrared spectrum

Fig. 1 Powder diffraction pattern of neodymium tartrate crystals

Fig. 2 FT-IR spectrum

of neodymium tartrate



was recorded in the wave number range 450 to 4000 cm^{-1} using the KBr pellet technique. The details of band assignments are given in Table 1. The characteristics infrared spectrum recorded here shows all the bands expected from metal tartrate crystals with water of crystallization.

A free tartrate ion has two hydroxyl groups, so two bands can be expected for the stretching vibration of the hydroxyl group. A broad band centered on 3405.25 cm¹ has been observed. This is because the bands due to stretching vibrations of hydroxyl, water and C-H groups are overlapping and appears as broader ones. Thus, broad and strong peak at 3405.25 cm¹ is due to water and OH stretching mode of vibration. A narrow band at 2920 cm¹ is assigned to strong C-H stretching vibrations. As compared with the authentic data of tartaric acid, bands in the range 1700 to 2900 cm¹ are absent in the IR spectrum of neodymium tartrate. This suggests the replacement of acidic hydrogen of COOH group by metal cations. A band centered at 1599.10 cm^1 is due to the C=O asymmetric stretching of coordinated carbonyl group. The absorption at 1463.58 cm¹ is attributed to C=O symmetric vibration. The value $\Delta v = 135.52 \text{ cm}^{-1}$, the difference between the two numbers $v_{as}(COO^{-})$ and $v_s(COO^{-})$, indicates the bridging mode of the carboxylate group [21]. The strong and sharp band near 1377.47 cm^{-1} may be attributed to OH in plane

Table 1 Assignment of some selected FTIR wave numbers/ cm^{-1} of neodymium tartrate hydrate

IR band/cm ⁻¹	Assignment of peaks per band		
3405.25	$v_{s}(OH)$ and $v_{s}(OH)$ of water and OH of carboxylic acid.		
2920.00	C-H stretching		
1599.10	Asymmetric COO ^{$-$} vibrations (v_{as})		
1463.58	Symmetric COO ^{$-$} vibrations (v_s)		
1377.47	O-H in plane bending		
1076.11	C–OH stretching vibration, δ (C–H), π (C–H)		
967.09	C-C symmetric stretching vibrations		
721.46	Crystal water		

bending. The absorption band at 1076.11 cm⁻¹ is assigned to v(C-O-H) stretching vibration. The absorption band at 97.09 cm⁻¹ is attributed to symmetric C-C stretching vibrations. A significant band is observed at 721.46 cm⁻¹ which is attributed to the presence of crystal water. Besides, there are some peaks below 500 cm⁻¹ indicating the metal oxygen bond.

It is thus clear that the FTIR spectroscopic results of neodymium tartrate hydrate crystals confirms the presence of water of crystallization, tartrate ligands and establishes that tartrate ions are doubly ionized.

Thermal analysis

The TG curve gives useful information regarding the thermal stability and composition of the sample under investigation. The recorded curve is first analyzed for obtaining the percentage mass loss at different temperatures and hence about the thermal stability and dissociation of the compound.

TG/DTA curves of neodymium tartrate hydrate in the temperature range 30 to 1000 °C are shown in Fig. 3, whereas Fig. 4 shows TG/DTG curves in the temperature range 30 to 1000 °C. As indicated, the material remains stable up to a temperature 45 °C and starts decomposing at about 45 °C and process continue up to 995 °C, after which it is reduced to its oxide. Some of the decomposing steps in the TG show considerable overlapping but are very much distinct in the DTG curve. A combined study of TG, DTA and DTG indicates a decomposition pattern as given in Table 2.



Fig. 3 TG/DTA curves of neodymium tartrate hydrate



Fig. 4 TG/DTG curves of neodymium tartrate hydrate

The first stage of decomposition $(45-55 \ ^{\circ}\text{C})$ results in the elimination of five water molecules. The calculated and observed mass losses corresponding to this are 10.49 and 10.61% of the total mass taken, respectively. The second stage between 155 and 275 $^{\circ}\text{C}$ corresponds to the loss of two water molecules and results in the formation of anhydrous neodymium tartrate. The measured and theoretical values of mass losses in the process are 14.83 and 14.68% of the total mass taken, respectively.

A close look at the DTG curve of Fig. 4 revels that the first stage of decomposition actually consists of two sub-stages. The first sub-stage (45-155 °C) is due to dehydration resulting in the elimination of five water molecules from the material. This dehydration occurring at low temperature (45-155 °C) range suggests the presence of water of crystallization. The next sub-stage (155-275 °C) corresponds to the loss of two water molecules. The dehydration temperature 155–275 °C which is quite high, suggest the presence of coordinated water in the compound [22]. Corresponding to these sub-stages, there are two endothermic peaks in the DTA curve at about 130 and 215 °C which also correspond to DTG peaks. A strong endothermic peak at 130 °C is attributed to loss of five water molecules and a weak endothermic peak at 215 is attributed to loss of further two water molecules, thereby suggesting a phase transition in the material. The total loss of seven water molecules in the temperature range 45 to 275 °C includes five molecules of water of crystallization and two coordinated water molecules in the compound. Thus, the possibility of presence of intermolecular water molecules is ruled out.

In the second stage of decomposition between 275 and 400 °C, there occurs a loss of $6H_2O$ and 2C, thereby reducing the anhydrous neodymium tartrate to neodymium oxalate. The measured and theoretical values of mass losses at this stage are 35.63 and 35.66% of the total mass taken. Corresponding to these losses there is an endothermic peak in DTA at about 310 °C and exothermic peak at 385 °C. This suggest that the loss of six water molecules takes place at about temperature 310 °C and results an endothermic reaction, while loss of carbon takes place about temperature 385 °C and shows exothermic type of reaction. Simultaneous loss of $6H_2O$ and 2C can be confirmed from the peak observed in DTG at 320 °C since only one peak is observed in DTG curve corresponding to the two peaks in DTA curve.

In the third stage of decomposition in the temperature range from 400 to 490 °C, the material losses 3CO molecules, leading to the formation of neodymium carbonate. The measured and theoretical values of mass loss at this stage are 45.44 and 45.45% of the total mass taken. Corresponding to this mass loss there is an endothermic peak in DTA at about 450 °C, suggesting a further crystallographic phase transition in the material (Table 3).

Table 2 Result of decomposition process of Nd₂(C₄H₄O₆)₃·7H₂O

Decomposition step	Temperature range/°C	Observed mass loss/%	Calculated mass loss/%	Loss of molecules in the step	Corresponding peak in DTG/°C
I	45–155	10.61	10.49	5H ₂ O	125
II	155-275	14.83	14.68	$2H_2O$	220 (small)
III	275-400	35.63	35.66	$6H_2O + 6C$	320
IV	400-490	45.44	45.45	3CO	435
V	490-855	55.69	55.70	$2CO_2$	820 (small)
VI	855-995	58.12	60.81	CO ₂	_
	>995	39.18	41.72	Nd ₂ O ₃ (residual neodymium oxide)	

Table 3 DTA data of neodymium tartrate

Peak temperature/°C	Nature of reaction		
130	Endothermic		
215	Endothermic		
270	Exothermic		
310	Endothermic		
385	Exothermic		
450	Endothermic		
745	Endothermic		

In the fourth step, between 490 and 885 $^{\circ}$ C, the resulting intermediate decomposes further giving a stable intermediate as neodymium carbonate (basic). The last step between 885 and 995 $^{\circ}$ C, results in the further decomposition and the material is reduced to Nd₂O₃.

The thermal decomposition reactions are usually endothermic. However, some of the DTA peaks are exothermic. This is due to the concomitant oxidation reactions taking place along with decomposition reactions. The final solid products of thermal decompositions of those investigated are oxides [23].

From the extrapolated decomposition onset temperatures obtained from the TG curve, it can be seen that an anhydrous neodymium tartrate presents a thermal stability between 126 and 298 °C. The second onset temperature corresponding to the decomposition of anhydrous neodymium tartrate to neodymium oxalate is 298 °C. This suggests that the neodymium oxalate is stable in the temperature range 298–410 °C. Further onset temperature 410 °C corresponds to the turning of neodymium oxalate to neodymium carbonate.

In order to confirm that the final product was Nd₂O₃, the parent material was heated in a ceramic crucible in an oven to 1000 °C and kept at that temperature for an hour. The difference between the initial and final masses gave the mass loss due to loss of seven water molecules and decomposition of the anhydrous neodymium compound to the final product Nd₂O₃. The mass of the end product thus formed confirms the presence of seven water molecules and corresponds very well to the stoichiometry of the compound viz., Nd₂(C₄H₄O₆)₃·7H₂O.

Figure 5 shows the DSC profile of neodymium tartrate in nitrogen at 10 °C min⁻¹. The profile displayed three endothermic peaks (Table 4). The peak observed at 133.047 °C, is accounted for the dehydration step. The peak at 218.047 °C, is due to reduction of anhydrous neodymium tartrate to oxalate and the peak at 318.04 °C, is due to the reduction of oxalate to basic carbonate. The DTA portion of the thermal curve is consistent with description of DSC results. Critical examination of the TG and DSC curves indicates that the decomposition pattern is typical of a hydrated metal tartrate [19] and transformations are associated with mass changes and there are no physical (crystallographic) transformations independent of mass change or decomposition of the material.

Following is the stoichiometry of the different intermediates involved in the decomposition process of neodymium tartrate hydrate.

Table 4 DSC data of neodymium tartrate

Peak no.	Onset temperature/°C	Peak temperature/°C	Peak area/mJ	$\Delta H/\mathrm{Jg}^{-1}$	$\Delta H_{\rm f}/{\rm kJ}~{\rm mol}^{-1}$	Reaction
1	100.34	133	3679.43	285.23	0.2852	Dehydration
2	190.30	218	411.27	31.88	0.0319	Decomposition
3	286.76	318	1141.4	88.48	0.0885	Decomposition



Fig. 5 DSC curve of neodymium tartrate hydrate

- 1. $Nd_2(C_4H_4O_6)_3 \cdot 7H_2O$ (neodymium tartrate hydrate) $\xrightarrow{-7H_2O} Nd_2(C_4H_4O_6)_3$ (neodymium tartrate anhydrous)
- 2. $Nd_2(C_4H_4O_6)_3$ (neodymium tartrate anhydrous) $\xrightarrow{-(6H_2O+6C)} Nd_2(C_2O_4)_3$ (neodymium oxalate)
- 3. $Nd_2(C_2O_4)_3$ (neodymium oxalate) $\xrightarrow{-3CO}$ $Nd_2(CO_3)_3$ (neodymium carbonate)
- 4. $Nd_2(CO_3)_3$ (neodymium carbonate) $\xrightarrow{-2CO_2}$ 2NdO(CO₃)_{1/2} (neodymium carbonate basic)
- 5. $2NdO(CO_3)_{1/2}$ (neodymium carbonate basic) $\xrightarrow{-CO_2}$ Nd₂O₃ (neodymium oxide)

Conclusions

- Growth of neodymium tartrate crystals was accomplished by allowing diffusion of neodymium chloride solution through silica gel impregnated with tartaric acid in single gel tube system. With all growth conditions, Neodymium tartrate crystals assume spherulitic morphology.
- The thermogravimetric analysis suggests that the grown neodymium tartrate is associated with seven molecules of water of hydration. Out of which five water molecules are of water of crystallization and remaining two are coordinated water molecules.
- 3. The results of thermal analysis suggest that the gelgrown neodymium tartrate is thermally unstable even at low energies. Decomposition starts at about 45 °C and process continues up to 995 °C, after which it reduces to its oxide. Neodymium tartrate decomposes to neodymium oxide through oxalate and basic carbonate.

- 4. Infrared spectrum shows the presence of carbon, hydrogen, oxygen and water of crystallization in the material.
- 5. Infrared spectrum also shows the presence of tartrate ligands and establishes that the tartrate ions are doubly ionized.
- 6. Comparison of TG and DSC curves suggest that the transformations are associated with mass changes and there is no physical (crystallographic) transformation independent of mass change.
- 7. The stoichiometric composition of the crystals is established to be $Nd_2(C_4H_4O_6)_3$.7H₂O.

Acknowledgements Authors are thankful to the Principal, Pratap College, Amalner, NCL Pune, Department of Chemical Technology, NMU, Jalgaon and Principal, JES's Arts, Science and Commerce College, Nandurbar for providing necessary facilities to carry out this work.

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