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ScienceDirect
Materials Chemistry and Physics 107 (2008) 200–207
MATERIALS CHEMISTRY AND PHYSICS
www.elsevier.com/locate/matchemphys

Studies on kinetics and mechanism of thermal decomposition of yttrium tartrate trihydrate crystals

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Received 16 December 2006; received in revised form 23 June 2007; accepted 28 June 2007

Abstract

Thermogravimetric and differential thermal studies have been used for kinetics and mechanism of thermal decomposition of gel grown crystals of yttrium tartrate trihydrate. Studies have been carried under non-isothermal conditions ranging from 25 to 1000 °C. The material is stable up to 218 °C and becomes anhydrous at 275 °C. The decomposition process occurs in four stages until a complex of yttrium oxide-carbonate is formed at 700 °C. The energies of the reactions involved and the mechanism of decomposition at each stage have been examined. The values of kinetic parameters, viz., order of reaction, activation energy and the frequency factor have been evaluated by using the relations Horowitz–Metzger, Coats–Redfern and Piloyan–Novikova. The proposed model for thermal decomposition of the material for all the stages of decomposition is random nucleation model and the order of reaction is one. The final product, that is, yttrium oxide-carbonate has been confirmed by energy dispersive X-ray (EDAX) studies carried on the sample-heated up to 1000 °C for thermal analysis.

Keywords: Differential thermal analysis (DTA); Thermogravimetric analysis (TGA); Thermal properties; Organometallic compounds

1. Introduction

Single crystals of tartrate compounds exhibit ferroelectric, dielectric, optical and other interesting physical properties [1–5]. They are used in transducers and many linear and non-linear mechanical devices [6]. Practical application of any material is also dependent on its thermal stability. A lot of attention has been devoted to the thermal studies of metal tartrates due to their interesting properties [7–11]. Kotru et al. [12–14] has reported thermal parameters and probable reaction mechanisms for some of the rare earth tartrates. Jain et al. [15] have reported the growth of spherulites of pure and mixed samarium and yttrium tartrates in silica gel. The same authors have reported the thermal behaviour of these spherulites [16]. It has been reported [16] that the spherulites of yttrium tartrate grown in silica gel have stoichiometry as $[Y_2(C_4H_4O_6)_3{\cdot}8H_2O]$ and are thermally stable only up to 45 °C. These crystals then start decomposing leading to the formation of anhydrous yttrium tartrate at 160 °C. Thermal kinetics has been reported only for the first stage of decomposition and contracting cylindrical model was proposed for the thermal decomposition of those materials. In this paper, we are reporting the kinetics and mechanism of thermal decomposition of another phase of yttrium tartrate crystals grown in silica and agar gel under different conditions. The details regarding growth conditions, viz., variation of lower reactant concentration, upper reactant concentration, effect of gel concentration, etc., for silica and agar gel along with their characterization using X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray (EDAX) analysis, carbon–hydrogen–nitrogen (CHN) analysis, infra-red (IR) analysis will be published elsewhere [17]. The grown crystals are single, having stoichiometry $[Y(C_4H_4O_6)(C_4H_5O_6){\cdot}3H_2O]$, and this stoichiometry is further supported by various techniques like XRD, IR, CHN, EDAX and thermal analysis. Yttrium tartrate trihydrate grown as single crystals are thermally stable up to 218 °C. Thus, this new phase of yttrium tartrate crystals is more stable than the spherulites reported by Jain et al. [16]. The present work is the first ever report entailing the reaction mechanism of thermal decomposition and application of the theories, viz., Horowitz–Metzger [18], Coats–Redfern [19] and Piloyan–Novikova [20] for all the four stages of decomposition of the material.

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doi:10.1016/j.matchemphys.2007.06.059

Table 1
Summary of experiments for the growth of yttrium tartrate crystals in silica gel

Experiment	Constant parameters	Variable parameters	Results
Variation in upper reactant concentration	Lower reactant (tartaric acid) concentration: 0.5 M; gel pH: 3.25; gel aging time: 96 h; gel column length: 12 cm	Upper reactant YCl_3 concentration: 0.25 M, 0.5 M, 1 M, 1.5 M, 2 M	Morphology: good quality single crystals were obtained up to 1 M and spherulitic growth takes place above 1 M
Variation in lower reactant (tartaric acid) concentration	Upper reactant (YCl_3) concentration: 0.5 M; gel pH: 3.25; gel aging time: 96 h; gel column length: 12 cm	Lower reactant (tartaric acid) concentration: 0.25 M, 0.5 M, 0.75 M, 1 M, 1.5 M, 2 M	Morphology: single crystals were obtained at 0.5 M, and spherulites were obtained at 1.5 M
Variation in gel aging	Upper reactant (YCl_3) concentration, 0.5 M; lower reactant (tartaric acid) concentration, 0.5 M; gel pH, 3.25; gel column length, 12 cm	Gel aging time: 48 h, 72 h, 96 h, 120 h, 144 h	Nucleation density maximum for 72 h and minimum for 144 h, however, crystallization takes place for all gel aging
Variation in gel pH	Upper reactant (YCl_3) concentration: 0.5 M; lower reactant (tartaric acid) concentration: 0.5 M; gel aging time: 96 h; gel column length: 12 cm	(i) Gel pH: 4.0, 4.25, 4.5, 4.75, 5.0	(i) Morphology: spherulitic growth, maximum size: 6 mm at pH 4.25, nucleation density: maximum at pH 5.0 and min. at pH 4.25
		(ii) Gel pH: 2, 2.5, 2.75, 3.0, 3.25, 3.5, 3.75	(ii) At pH 3.75 and 4, single as well as spherulites were observed. At pH 3.25 and 3.0, well-defined single crystals were obtained. At pH 2.5 and 2.0, the gel does not set at all

2. Experimental

Single crystals of yttrium tartrate trihydrate are grown by using single gel single tube (SGST) diffusion method in silica and agar gel medium [17]. The reactants used for the growth of single crystals in silica gel are L-tartaric acid ($C_4H_4O_6$) as the lower reactant and yttrium chloride (YCl_3) as the upper reactant. Initially, silica gel solution of desired molarity (0.25–1 M) is prepared by dissolving sodium metasilicate powder in distilled water. The silica gel solution is then impregnated with a solution of tartaric acid of desired molarity (0.25–2 M). The pH of the gel medium is adjusted as per the requirement by adjusting the volume of tartaric acid. After setting of the gel for a certain time period, a pure solution of YCl_3 of desired molarity (0.25–2 M) is poured along the inner walls of the tube to prevent the gel medium from breaking. The slow diffusion of upper reactants into gel medium results into reaction of rare earth ions with tartaric acid ions already present in the gel medium.

The crystals have been grown in agar gel also. Agar gel is prepared by dissolving (0.5–1.5 M) wt.% agar in water as per the requirement. The agar gel solution is then mixed with L-tartaric acid of different molarity (0.25–1 M) in various proportions by volume. The pH of the mixed solution is kept at a value of 2 by adding few drops of dilute HNO_3. The solution is then transferred to several glass tubes. After gel setting, an aqueous solution of YCl_3 of desired molarity (0.5–2 M) is carefully poured over it. After about 15–20 days, small single crystals of yttrium tartrate appeared in the whole gel column.

Using different physico-chemical techniques, viz., EDAX, XRD, IR, CHN and thermal analysis, the stoichiometry of the grown crystals has been established as $[Y(C_4H_4O_6)(C_4H_5O_6)\cdot 3H_2O]$. The crystals grow as tetragonal with cell parameters as: $a = 6.010(1)$ Å; $c = 36.421(4)$ Å; with space group $P4_12_12$. Same cell parameters have been reported by Almond et al. [21] for yttrium tartrate hydrate grown by slow evaporation solution growth technique. Thermal behaviour of the material has been investigated using TGA, DTA, and DSC. TGA and DTA curves have been recorded simultaneously on a thermal analyzer (Shimadzu make DTG-60) over the temperature range from 25 to 1000 °C at a heating rate of 10 °C min^{-1} in the N_2 atmosphere at a flow rate of 30 ml min^{-1}. The DSC measurements have been carried out on a DSC thermal analyzer (DSC-60, Shimadzu make) over a temperature range from 25 to 500 °C at a heating rate of 10 °C min^{-1} in the N_2 atmosphere at a flow rate of 30 ml min^{-1}. The EDAX studies of the final product have been carried out on INCA ENERGY EDAX attached to SEM (JEOL 840).

3. Results and discussion

3.1. Growth of yttrium tartrate trihydrate single crystals

A number of experiments have been carried out to establish the conditions conducive for the growth of better quality single crystals of yttrium tartrate trihydrate in silica and agar gel. In case of growth in silica gel, the experiments have been performed under varying conditions of different growth parameters, which include concentration of upper and lower reactants, gel pH, gel aging, gel molarity and effect of surrounding temperature. Table 1 gives the complete summary of experiments performed and results obtained in case of growth of single crystals in silica gel. From Table 1, it is clear that the best conditions for growth of single crystals in silica gel are: lower reactant concentration, 0.5 M; upper reactant concentration, 0.5 M; gel pH, 3.25; gel age, 96 h; surrounding temperature, 30–40 °C.

In order to establish the conditions favorable for the growth of single crystals in agar gel, experiments have been performed by varying different parameters, which include variation in gel concentration, variation in agar gel and tartaric acid ratio, variation in lower and upper reactant concentration. The summary of experiments conducted for growth of single crystals in agar gel is given in Table 2. From Table 2, it is clear that the best conditions for the growth of single crystals in agar gel have been found as: lower reactant concentration, 1 M; upper reactant concentration, 1.5 M; gel concentration, 1.2% (w/v) and agar:tartaric acid ratio as 4:1.

3.2. Mechanism of thermal decomposition

Fig. 1(a) shows the recorded thermogram for yttrium tartrate grown in silica gel, hereafter denoted by YT(S). Fig. 2(a) is the thermogram for yttrium tartrate grown in agar gel, hereafter denoted by YT(A). These thermograms are almost similar.