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Studies on the dehydration kinetics and rehydration of YAG precursor powder in the hydroxyhydrogel form

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Abstract

YAG precursor powder was prepared in the hydroxyhydrogel form. Dehydration kinetic study and rehydration experiment was carried out to know the behavior of water molecules and hydroxide bonds present in the hydroxyhydrogel network structure with temperature. Rate constants and activation energies for dehydration and dehydroxylation were evaluated by static thermogravimetry. Percent rehydration was determined at different heat treatment temperatures. The results obtained were explained, correlated to establish the thermal stability of hydroxyhydrogel network structure and finally supported by the FTIR analysis.

Keywords: Hydroxyhydrogel; Structural-stability; Dehydration-kinetics; Rehydration

1. Introduction

The nature of powder precursor is closely related to the synthesis route following which it is prepared. Synthesis route are broadly two types one is mechanical mixing of different ingredients and the other is chemical processing route. In chemical route depending on the type of chemical interaction as for example whether it is sol–gel route or hydroxide precipitation the property of produced precursor powder may vary. Hydroxyhydrogel is a new processing route by which reactive homogeneous precursor powder can be prepared [1–9]. Thermal treatment of the produced hydroxyhydrogel for the generation of a series of intermediate state is important for determining the reactivity and composition of the final synthetic material. This hydroxyhydrogel route is advantageous compared to other method because the precursor powder produced by this method has high surface area, good homogeneity and better reactivity which permit low temperature processing [1].

While making the powder precursor for the preparation of sintered transparent ceramic material, it is always essential to find the relationship of water molecules and OH bonding present in the precursor with temperature. A thorough characterization of the powder precursor by TG-DTA, XRD and FTIR spectroscopy is required to know the formation and deformation of the bonds with varying temperature in the resultant product.

The aim of the present work is to find out the behavior of water molecule and OH bonding present in the yttrium aluminium garnet (YAG) precursor powder with temperature and correlate these properties with structural stability of the network structure of powder precursor. This network structure, discussed in our earlier paper [1] is quite similar to the naturally occurring zeolite. The properties of the final ceramic material are strongly influenced by the crystallization path of the precursor powders therefore a detailed knowledge on the development of structure of powder precursor and its dependence on temperature is important. In this paper we are using a new method of characterization i.e. dehydration rehydration study along with isothermal dehydration kinetic study from which we

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get detail knowledge on the temperature dependent structural development of the precursor powder.

2. Experimental

The yttria and alumina sources for the synthesis of YAG hydroxyhydrogel were 99.9% $Y(NO_3)_3{,}6H_2O$ (Sigma Aldrich) and 99.997% $Al(NO_3)_3$, $9H_2O$ (Merck). As precipitant 25% ammonia water was used (analytical grade). The stock solutions of mother salts were made by dissolving yttrium and aluminium nitrate in distilled water. Chemical precipitation was done by reverse strike (adding salt solution to the precipitant solution) using flash polycondensation technique [1]. The gel like masses so obtained was aged overnight for completing the reaction. The extraneous soluble impurities were removed by washing with hot water and the solid mass left was dried at 110 °C ± 10 °C. The dried mass then calcined at 830 °C for 1 h. The contents of alumina and yttria in the corresponding stock solutions of mother nitrate salts were analyzed chemically and the amount of solutions required for the preparation of 50 g of calcined powder maintaining the stoichiometric ratio of yttria and alumina as 3:5 is given in Table 1. The process flow sheet for preparing the powder precursor of YAG in the hydroxyhydrogel form is shown in Fig. 1.

TG-DTA analysis of the dried powder precursor was carried out by NETZSCH Thermal analyzer STA409 instrument up to 1000 °C at a heating rate of 10 °C/min.

The dried powder precursor was heat treated at temperatures between 200 and 1000 °C with an interval of 100 °C and a soaking period of 1 h at each temperature. The percent weight loss after heat treatment was calculated from thermo gravimetric results. Isothermal dehydration kinetic study was conducted using Libratherm TGA instrument (no-PID-300/25).

The rehydration characteristics of the powder precursor, heat treated at different temperatures (300–600 °C) was studied at different humidity conditions in the range of relative humidity 20% to 100% using H_2SO_4 as a desiccant.

The IR study of the precursor powder and the heat treated powder in the range 4000–400 cm^{-1} was carried out on a Perkin-Elmer FTIR Spectrometer (Model No-1615) using KBr pellets.

3. Results and discussion

TG-DTA study on the YAG hydroxyhydrogel in the temperature range 100–1200 °C as shown in Fig. 2 revealed the existence of several peak indicating the presence of H_2O in the main network structure in the different form. The loss of water took place broadly in the four different stages. In the initial stage (temperature range 150 to 270 °C) the weight loss was maximum and the rate of weight loss was faster. It was followed by intermediate stages (300–360 °C and 390–500 °C). The final stage (550–650 °C) recorded minimum weight loss. Detail analysis on thermogravimetry was included in our earlier paper [1]. To understand

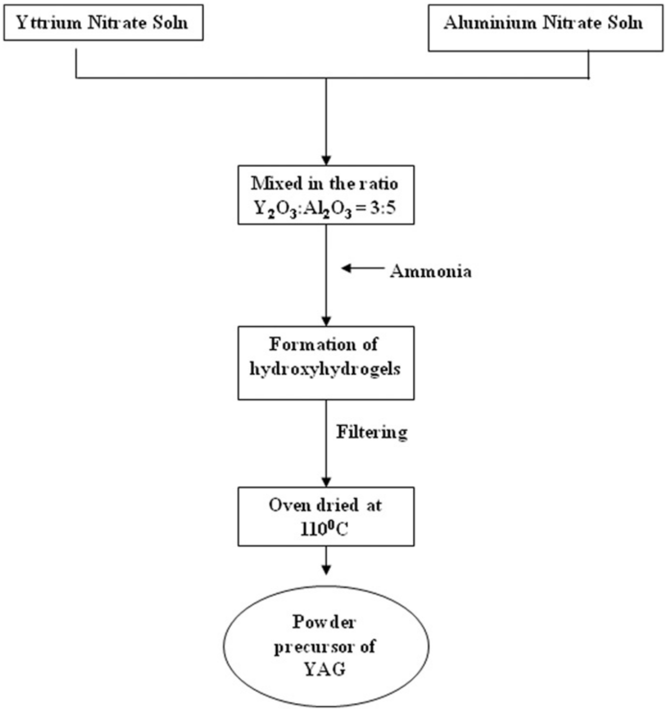

Fig. 1. Preparation process of YAG powder precursor.

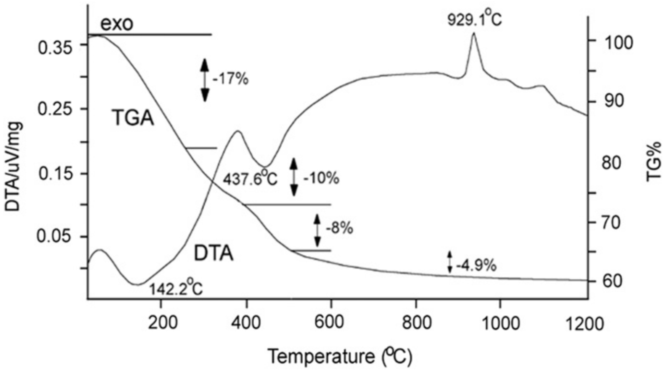

Fig. 2. TG-DTA study of YAG.

Table 1
Batch composition.

Stock solution	Amount of constituent present per cc	Amount of stock solution required for 50 g of calcined powder
Yttrium nitrate	0.162 g of Y_2O_3	128
Aluminium nitrate	0.042 g of Al_2O_3	372

about the stability of the prepared HHG network structure and nature of bonding present within, a detailed analysis through isothermal dehydration kinetic study and dehydration rehydration study was carried out. The exponential nature of the weight loss versus. time curve for all temperature as shown in Fig. 3 permits the application of 1st order kinetics. The range of validity of first order kinetics was calculated by considering the linearity of weight loss versus time curve, and the validity range of first order kinetics was in the acceptable level.

From the first-order kinetics it could be said that weight loss of water from the sample at any time could be proportional to the concentration of water present in the system at that time. The concentration of water in the sample could be replaced by the weight of the water present within the sample, which can be lost at the experimental temperature divided by the volume of the sample. Therefore, if the weight and hence the volume of the initial sample was kept constant, the weight loss may substitute concentration. Therefore, at a given temperature if L is the weight loss of the sample at time t and L_∞ is the total weight loss at infinite time, then L_∞ is equivalent to the initial concentration of water dehydratable at the experimental temperature. Therefore, $L_\infty - L$ is equivalent to the concentration of water remaining in the sample at time t.

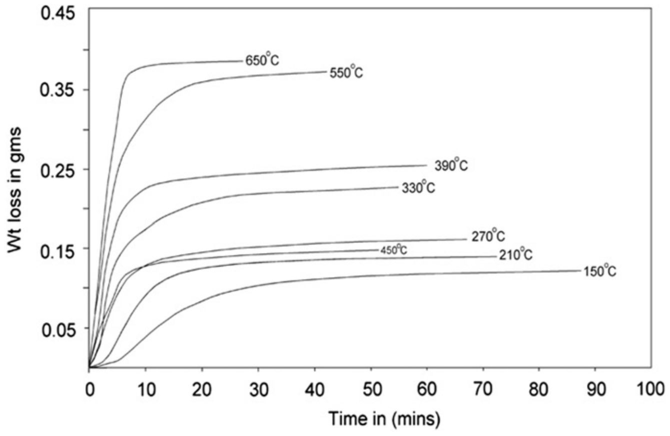

Fig. 3. Validity of first order kinetics.

Now, according to the first-order kinetics the rate of loss of water will be given by Eq. 1

$$dL/dt = k(L_\infty - L) \tag{1}$$

$$\log_{10}[(L_\infty - L)/L_\infty] = -kt/2.303 \tag{2}$$

If the value of L_∞ is known then using Eq. 1, the value of rate constants for dehydration can be easily found out from the slope of the line obtained by plotting $\log_{10}(L_\infty - L)/L_\infty$ versus t. But direct determination of L_∞ is not possible because theoretically the 1st order equation could never go to completion. Therefore, the method that was suggested by Guggenheim and later followed by Murray and White [10], Mitra et al. [11] and also by Bhattacharyya et al. [4], Meher at al [5], Maitra

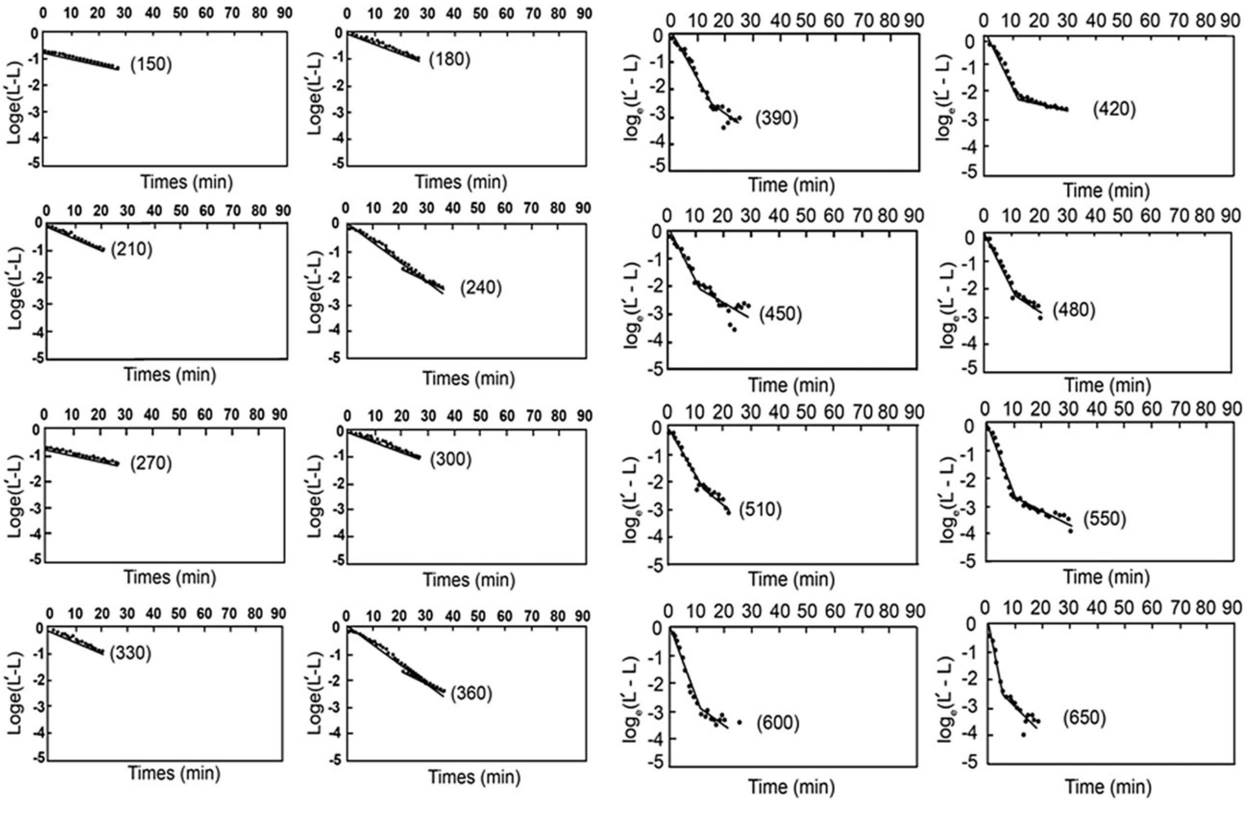

Fig. 4. Log ΔL versus Time curve for different temperatures.

et al. [12] was adopted for the evaluation of rate-constants.

Let L_t=Wt. loss in grams at any time t, and L_∞=Wt. loss at infinite time, then using Eq. 2 we may write

$L_\infty - L_t = L_\infty \ e^{-kt}$

Suppose L_1, L_2, …, L_n are the respective readings at t_1, t_2, …, t_n, without any restrictions as to the time intervals, and L'_1, L'_2, …, L'_n at times $t_1+\Delta t$, $t_2+\Delta t$, …, $t_n+\Delta t$ each at a constant time Δt after the previous set.

Then $L_\infty - L_1 = L_\infty \ e_1^{-kt}$

And $L_\infty - L_1' = L_\infty \ e_1^{-kt\Delta t}$

Subtracting,

$L_1' - L_1 = L_\infty \ e_1^{-kt} \ (1 - e^{-k\Delta t})$

Table 2
Activation energy at different temperature zones.

Stage	Activation energy R1	R2
1	7246	
2	2759	5124
3	2357	10957
4	9214	13830

Taking logarithms and expressing in general terms,

$\log_e(L' - L) = -kt + \log_e[L_\infty(1 - e^{-k\Delta t})]$

or

$\log_{10}(L' - L) = -kt/2.303 + \log_{10}[L_\infty(1 - e^{-k\Delta t})]$

or

$$\log_{10}\Delta L = -kt/2.303 + \log_{10}[L_\infty(1 - e^{-k\Delta t})] \quad (3)$$

$\log_{10}(\Delta L)$ was plotted against time for different experimental temperatures. Representative curves were shown in Fig. 4. It appears from figures that the process of dehydration at higher temperature followed two rate-constants; one for the initial stage (k_1) and another is for final stage (k_2). In the initial stages of dehydration a single value of rate-constant was found which maintains linearity with time of dehydration, however at higher temperature, from 300 to 650 °C rate-constant values changed abruptly after certain extent of dehydration and two values of rate-constant were observed. From these rate-constant values the activation energy in each stage was calculated by following the Arrhenius equation:

$D \ \ln(k)/dt = \Delta H/RT^2$i.e.

$\log_{10}K = \log_{10}PZ - \Delta H/4.575\text{T}$

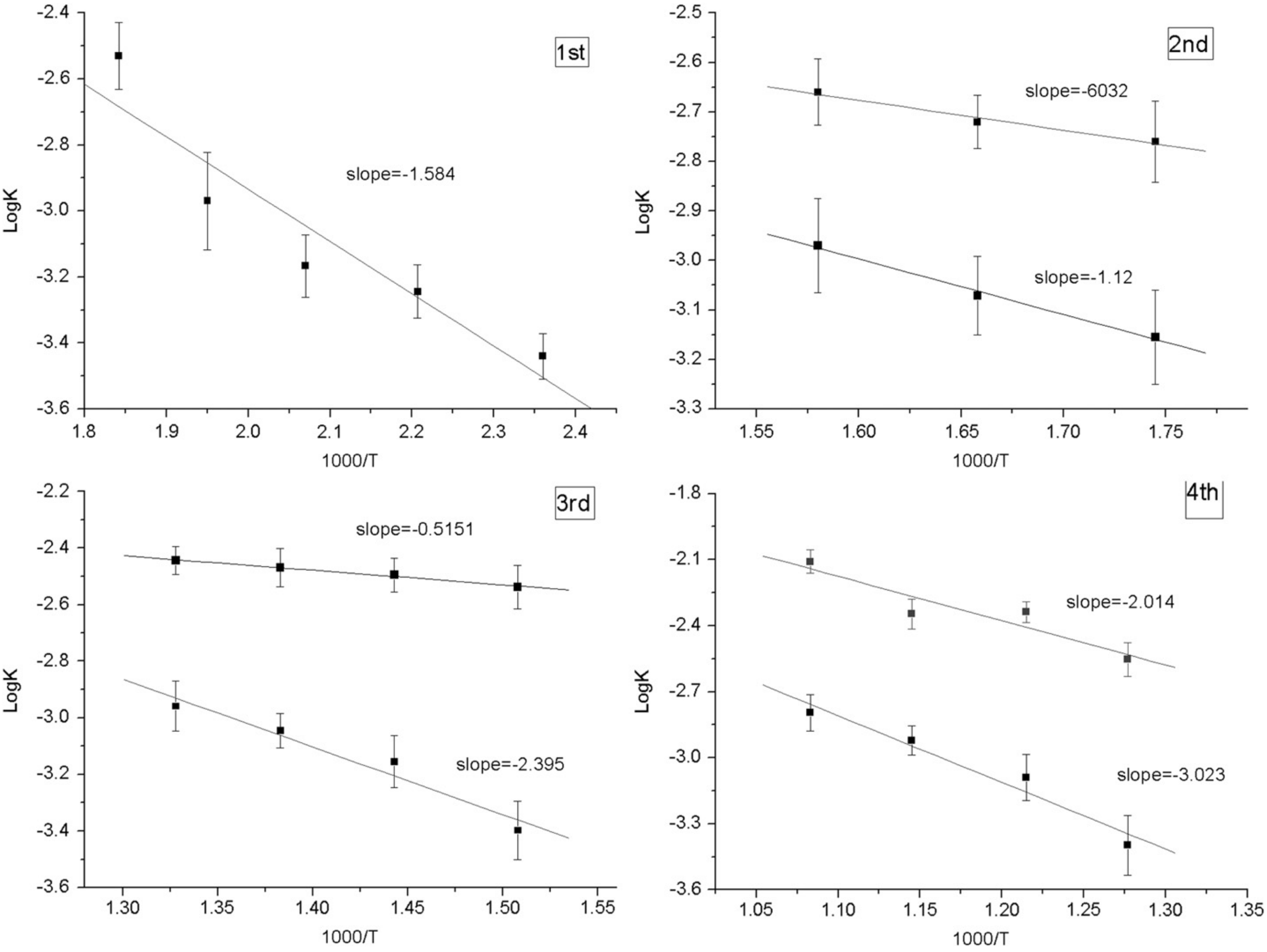

Fig. 5. (a, b, c and d) Log K versus. 1000/T plot for 1st, 2nd, 3rd and 4th stages of dehydration.

$\log_{10}K$ was plotted against $1/T$ to calculate the activation energy of the respective system, from the slope of the line activation energy was calculated and the results were given in Table 2 and plots were shown in Fig. 5(a–d).

In the temperature range of 150–270 °C dehydration followed a single rate-constant and single activation energy was obtained which indicated that during dehydration the network structure remained almost undisturbed. Water molecules come out from the surfaces, channels and cavities linked to the surface. Single activation energy was the indicative of removal of absorbed water but the numerical value of the activation energy was much higher due to staggering of molecules within. In the temperature range of 300–360 °C rate-constant abruptly changed after a certain time of dehydration indicating re-organization of the network structure. In this zone dehydration followed two different rate-constants and two different activation energies were obtained. The first activation energy was responsible for removal of remnant absorbed water whereas the second activation energy was due to the decomposition of hydroxide bonds. Presence of two different activation energies implied that structural reorientation was already started. Similar to the earlier case in the temperature range of 390–500 °C dehydration followed two different rate-constant and two different activation energies were obtained indicating bonds of OH– with different energies. Finally in the temperature range of 550–650 °C also two values of rate-constant and two different activation energies were observed. Both the activation energy values were very high indicating that they were the effective activation energy for the decomposition of hydroxide linkages of different energies. Thus it appeared that all the hydroxide bonds were not energetically equivalent.

From the structure of hydrargillite it was found that OH groups on the underside of one layer rested on the groups of the layer below. This unusual arrangement was due to, and in fact led to the idea of, directed bonds between OH groups of adjacent layers. Thus it was noticed that the hydrogen bonds in the planes of the OH groups were all longer than those between the layers [13]. This fact implied that in hydrargillite all the hydroxide linkages were not of same energy. Similarly in YAG powder precursor the central cations like Al^{3+}, Y^{3+} were bonded by hydroxyl groups of different energies for which the combined or effective activation energy in the intermediate stage-II and in final stage was high. Therefore, from the above discussion it could be said that the structural reorientation initiated in the intermediate stage and became prominent in the final stage. To support this phenomenon rehydration study was done

The dehydration of YAG precursor powder followed an exponential path as shown in Fig. 6. The curve indicated a steep rise in dehydration up to 500 °C followed by a zone of medium loss up to 800 °C then the dehydration became constant. From the nature of the curves it could be said that in the first zone the molecular water, that weakly bonded to the surface and in the open pores of the precursor leave the network. During heat treatment above 500 °C the thermal energy was high enough for dehydroxylation so the dehydroxylation takes place causing the ultimate collapse of network structure. The actual temperature range for structural break down can be obtained if percent rehydration of the dehydrated samples were plotted against temperature at different relative humidity.

It was found from the curve (Fig. 7) that the rehydration dropped abruptly with increasing heat treatment temperature from 300–400 °C. Beyond 400 °C the rehydration was insignificant. It implied that the structural collapse occurred in between 300 and 400 °C that is the intermediate temperature range of kinetic study. Actually heat treatment of specimens affected network structure that influenced the rehydration characteristics of the prepared samples. During thermal treatment the network structure

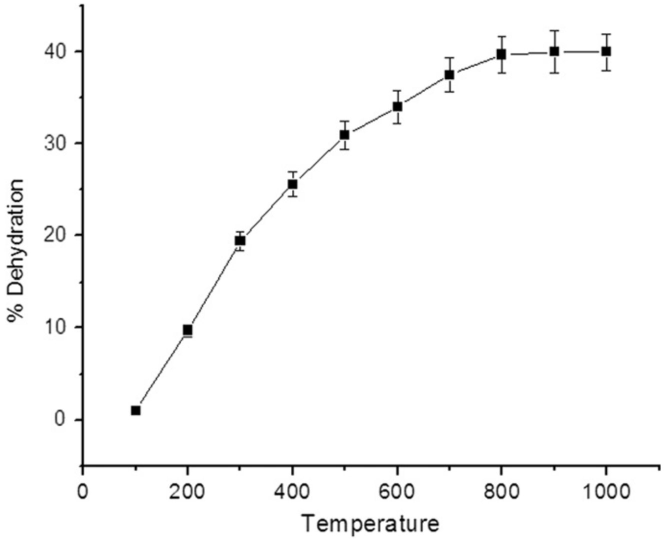

Fig. 6. Change of % dehydration of YAG with heat treatment temperature.

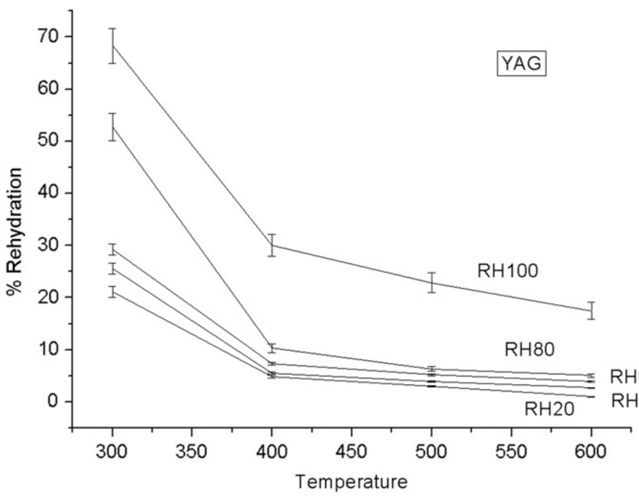

Fig. 7. Rehydration characteristics of YAG precursor powder with respect to heat treatment temperature at different relative humidity.

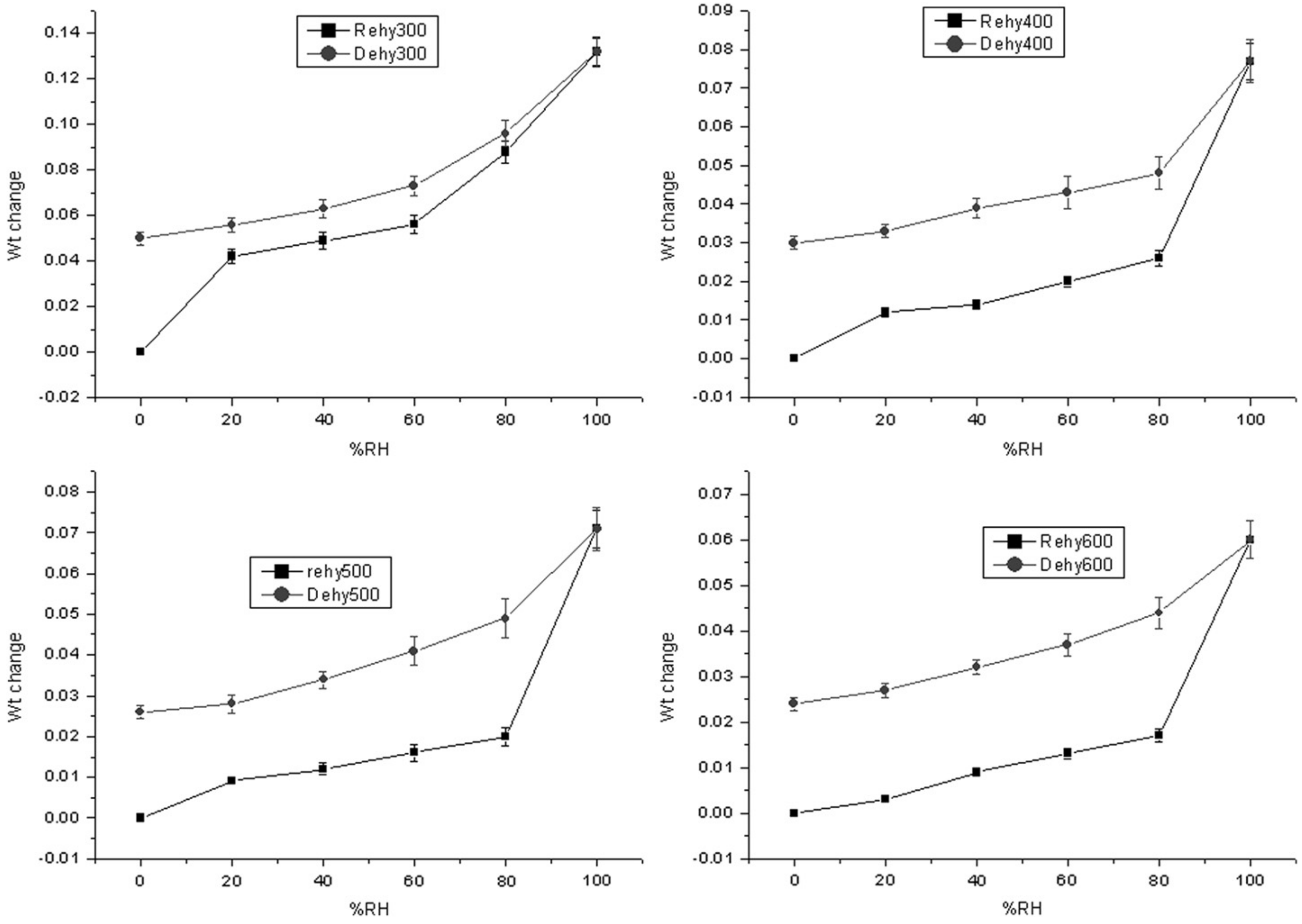

Fig. 8. Nature of rehydration with %RH at different temperatures.

might collapse. This type of behavior was found in geolite type of materials [12,14] where channels and cavities were present in the alumino silicate framework and they hold polar molecules like water and cation of suitable size. In the present experiment YAG precursor powder was prepared in the hydroxyhydrogel form in which Al^{3+} and Y^{3+} bonded by hydro, hydroxyl and oxo bonds of different energies forming a polynuclear network structure [15–16]. These network structures were open type and composed of cavities, pores and channels of different sizes which hold polar molecules like water. During dehydrations water molecules comes out from the system leaving the voids and the structure becomes unstable due to thermal vibration. In a destabilized structure the channels and pore volume would be contracted which was related with reduced rehydration with increasing heat treatment temperature. Thus it may be said that amount of degree of rehydration was an indirect indication of the structural collapse.

At the first stage of dehydration higher activation energy was required for the removal of absorbed water due to staggering of molecule but at the later stage as there would be gradual generation of pores which made the structure more open type, the removal of water molecules from channels and voids became easier and the activation energy decreased. In the final stage, first activation energy increased as here in the later stage irreversible structural reorientation occurred due to the decomposition of hydroxide group which ultimately eliminated the vacancy during dehydration/dehydroxylation blocking removal of remaining OH/H_2O. In all the stages the second activation energy was always higher than the first activation energy as the removal of absorbed water was much easier than the breaking of hydroxide linkages.

If the precursor powder is dehydrated at a particular temperature and then rehydrated by increasing relative humidity then it was found that the weight gain due to rehydration increased with increasing relative humidity (Fig. 8). The dehydration of the same rehydrated sample by decreasing relative humidity generated a hysteresis loop (Fig. 8). Therefore, it may be said that dehydration rehydration is not ideally reversible which further indicates gradual structural collapse.

If we assume that area of the hysteresis loop indicated the extent of irreversibility of rehydration then increase of this area with respect to increasing temperature of heat

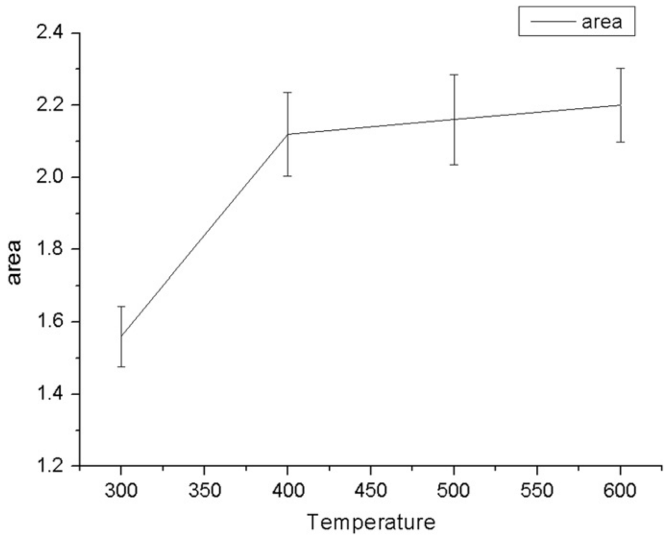

Fig. 9. Area versus temperature curve for rehydrated YAG.

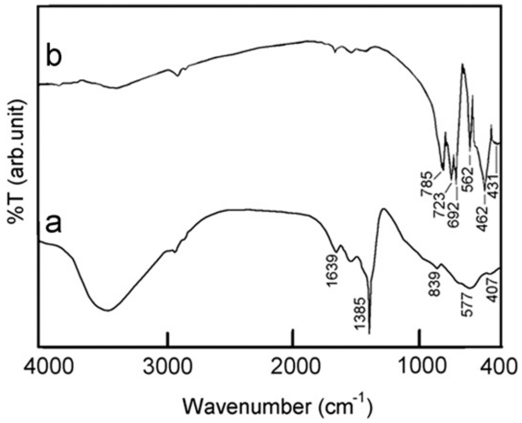

Fig. 10. IR study of YAG (a) powder precursor and (b) 1200 °C heat treated powder.

treatment of the powder may be an important guideline to understand structural re-orientation. For this purpose the areas were calculated and were plotted against heat treatment temperature. On the basis of results obtained as represented in Fig. 9, it appeared that area considerably increased with increasing heat treatment temperature from 300 to 400 °C i.e. irreversibility increased in this temperature range. Actually up to 400 °C irreversibility increased then it became constant. Thus, within 400 °C structural reorientation was almost started. This collapse occurs due to collapsing of the different bonds (OH/H_2O bonding) by which the central metal cation like yttrium or aluminium were connected to form a polynuclear hydrogel structure.

The IR spectra of the processed powder precursor dried at 110 °C and heat treated at 1200 °C are shown in Fig. 10. The presence of IR absorption band at around 3460 cm^{-1} (due to hydroxide stretching mode) and around 1366 cm^{-1} (due to bending moment of water) is in agreement with the presence of both H_2O and OH group in the powder precursor [17]. The IR spectra of 1200 °C heat treated powder revealed the elimination of H_2O and OH group from the heat treated powder. From this result it can be said that a gradual change of network structure during dehydration gives rise to a modified material that loses its rehydration abilities.

4. Conclusions

The methods of powder precursor characterization like isothermal kinetic analysis and dehydration–rehydration study was found to be effective to understand the temperature dependent behavior of removable water molecule and hydroxide bonds present in the precursor powder. These new methods of analysis clearly indicate that

- YAG powder precursor above 300 °C showed the presence of two rate constants and two different activation energies. The first activation energy was responsible for removal of absorbed water where as the second activation energy was due to the decomposition of hydroxide bond. This phenomenon clearly indicated the fact of structural collapse in this temperature range.
- The higher value of the second activation energy in the intermediate and final stage of dehydration indicated that, in YAG powder precursor the central cations like Al^{3+}, Y^{3+} were bonded by hydroxy groups of different energies for which the combined or effective activation energy was high.
- For YAG powder precursor the sharp fall in the percent rehydration value after dehydration was found in the temperature range of 300–400 °C indicating structural break down occurring within this temperature zone. This clearly supported the results obtained by kinetic study.

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