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Synthesis and characterization of YAG precursor powder in the hydroxyhydrogel form

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Abstract

Powder precursor in the form of hydroxyhydrogel was prepared from yttrium nitrate and aluminium nitrate, using ammonium hydroxide as precipitant by flash polycondensation technique. Precursor powder obtained in the hydroxyhydrogel form was characterized by TG/DTA, FTIR, SEM and XRD analysis. This method produced material which could be transformed into YAG at comparatively lower temperature (800 °C) and was phase pure.

Keywords: Hydroxyhydrogel; Flash polycondensation; Powder precursor; YAG

1. Introduction

There are three reported congruent phases in the pseudo-binary Y_2O_3–Al_2O_3 system, maintaining Y_2O_3:Al_2O_3 ratios of 3:5 (YAG), 1:1 (YAP) and 2:1 (YAM). YAG adopts the cubic garnet structure and is the only stable phase in the system [1].

Yttrium aluminium garnet (YAG) finds frequent application because of its good optical properties [2]. Recent works show that it also has a great potential as a high temperature engineering material due to its high temperature strength coupled with low creep rate [3]. Unfortunately single crystal YAG is expensive and is technically difficult to produce in desired sizes. One potential alternative is sintered polycrystalline YAG that can be made economically and is also found to exhibit good high temperature properties [3].

Crystalline $Y_3Al_5O_{12}$ normally exist in a cubic form with the garnet structure and is commonly known as ‘‘yttrium aluminium garnet’’ (YAG) [4]. A high temperature tetragonal polymorph has also been reported [5]. Crystalline $YAlO_3$, ‘‘yttrium aluminium perovskite (YAP) has orthorhombic [6] and hexagonal [7] polymorphs. Crystalline $Y_4Al_2O_9$ is monoclinic and is referred to as YAM [8]. These terms have been used to signify both composition and structure of the compound.

YAG powder can be synthesized by many methods, such as solid-state reaction, co-precipitation, sol–gel process, spray thermal decomposition, etc. The solid-state reaction method is a simple process suitable for large-scale production but it requires high temperature >1700 °C and a long reaction time [9]. The particle size of the YAG precursor powder synthesized by the solid-state method was very large, normally larger than 1 μm and the composition of the powder was not homogeneous. The sintereblity of this non-homogeneous powder was also very low [10]. Although YAG powder synthesized by chemical methods has general advantages like high purity, homogeneity and finer grain sizes, but preparation process were complicated and they also require a long preparation time. Additional thermal treatment at high temperature [11] is also an essential step resulting hard agglomerates. YAG powder can be obtained at lower temperature and pressure by using organic solvothermal synthesis [12]. However, the powders synthesized by this method consist of aggregates of irregular shapes, which is not beneficial to ceramic sintering process. Some of the organic solvents used in this process like ethylene glycol, butanediol, etc., increases the cost of production and even may pollute the environment [10].

The above difficulties may be overcome by synthesizing a novel intermediate molecule, consisting of a network of Al^{3+} and Y^{3+} bonded by hydro, hydroxy and oxo bonds of different energies. The molecule was formed by following a typical and a new processing route, i.e. flash polycondensation technique

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[13] and was termed by a generic name ‘‘hydroxyhydrogel’’ as it has a large number of similarities with the conventional ‘‘organic hydroxyhydrogel’’ compounds.

In the present study initially a powder precursor was prepared in the hydroxyhydrogel form by a new technique named as flash polycondensation [13–18] followed by heat treatment to transform the powder material into YAG. Both the powder precursor and the transformed material were characterized.

2. Experimental

Three samples were prepared by varying Y_2O_3:Al_2O_3 ratio in such a way that the ultimate heat-treated materials maintained the ratio as, sample-1 3:5, sample-2 2:1 and sample-3 1:1. The yttrium and aluminium sources for synthesis of samples-1–3 were 99.9% $Y(NO_3)_3$, $6H_2O$ and 99.997% $Al(NO_3)_3$, $9H_2O$. As precipitant 25% ammonia water was used (analytical grade). Two stock solutions of mother salt were prepared by dissolving yttrium and aluminium nitrate in distill water, respectively. Chemical precipitation was done by reverse strike [13] (adding salt solution to the precipitant solution) using flash polycondensation technique. The gel like masses so obtained were aged overnight for equilibration. The extraneous insoluble impurities were removed by washing the gel like mass obtained above with hot water and the solid mass left was dried at 110 ± 10 °C. The characteristic of the powder precursor were examined by DTA, TG, XRD, FTIR and SEM analysis. Throughout the precipitation process pH was maintained at 9–11.

3. Results and discussion

Thermal analysis was done using Libratherm TGA instrument (no-PID-300/25). FTIR analysis and phase analysis were carried out by FTIR spectrometer (Perkin-Elmer model no. 1615) and X-ray diffractometer (PW 1730, Phillips, Holland), respectively. Microstructures were studied by using a scanning electron microscope (SEM Model-LEO S430 LEO UK). Precursor powders were then heat treated at different temperature, all the heat-treated powders were subjected to XRD and IR analysis.

3.1. TG–DTA

Thermal decomposition of the precursor powder for three samples was studied by TG–DTA analysis. Results of the TG–DTA analysis were given in Table 1 and curves were shown in Fig. 1a–c for samples-1–3, respectively. For samples-1 and 3 complete thermal decomposition of the precursor into oxides were noted at around 800 °C with weight loss value 39.91% and 42.07%, respectively. For sample-2 the decomposition temperature was slightly higher (900 °C) with weight loss 37.88%. For all these three compounds the weight loss value was much higher than the weight loss of pure hydroxides. This observation indicated that the compounds were not merely hydroxide rather they were in the hydroxyhydrogel form. Though sample-2 contain less amount of water but the bonding were strong enough requiring higher temperature for its complete conversion to oxide. All the three compounds exhibited a broad endothermic peak at around 149–150 °C which indicated the removal of adsorbed water. Endothermic peak at around 429–439 °C were attributed to the decomposition of hydroxide group. Exothermic peak in the range 924–929 °C indicated crystallization of different phases as for example sample-1 is crystallized in cubic system corresponding to YAG, sample-2 crystallized into monoclinic system corresponding to YAM. But for sample-3 formation of perovskite (YAP), hexagonal (YAH) and monoclinic (YAM) was indicated. DTA–TG graph of $Y(OH)_3$ and $Al(OH)_3$ show that total water content of $Y(OH)_3$ was higher than $Al(OH)_3$. In the first zone, weight loss was higher for $Al(OH)_3$. In the second zone weight loss was comparable but in the third zone weight loss was high for $Y(OH)_3$ [14]. These indicate that hydroxy groups were strongly bonded to Y^{3+} and higher temperature was required for breaking this structure. In sample-2 Y_2O_3 content was highest, so it also exhibited highest loss in third zone.

3.2. FTIR

IR spectra of the precursor powders of samples-1–3 were shown in Fig. 2a–c, respectively. The wide band around 3450 cm^{-1} can be assigned to O–H stretching. Bands around 1530 cm^{-1} and 1385 cm^{-1} represented NH_4 and NO_3 stretching mode. The IR spectra of these three material heat treated at 1200 °C was represented in Fig. 3a–c. Sample-1 contain only Y–O and Al–O stretching band without any detectable O–H bond, but samples-2 and 3 contain Al–O and Y–O bond along with some O–H implying presence of some hydroxy group even after heat treatment at 1200 °C. Presence of O–H at higher temperature in the bulk ceramic system synthesized in the solution phase reaction is not uncommon [19]. Precursor powder of sample-1 exhibited Al–O stretching mode for

Table 1
TG–DTA results

Composition	% Alumina	Net weight loss (%)	Weight loss for pure hydroxide	% Weight loss (0–390 °C) first zone	% Weight loss (390–490 °C) second zone	% Weight loss (490–1200 °C) third zone
Al_2O_3	100	27.48	27.48	35.2	44.28	20.25
YAG (3:5)	63	39.91	31.17	65.82	19.44	14.73
YAM (2:1)	50	37.88	34.03	53.64	23.25	23.09
YAP (1:1)	33	42.07	32.39	66.10	16.25	17.63
Y_2O_3	0	37.3	37.3	30.43	45.12	24.45

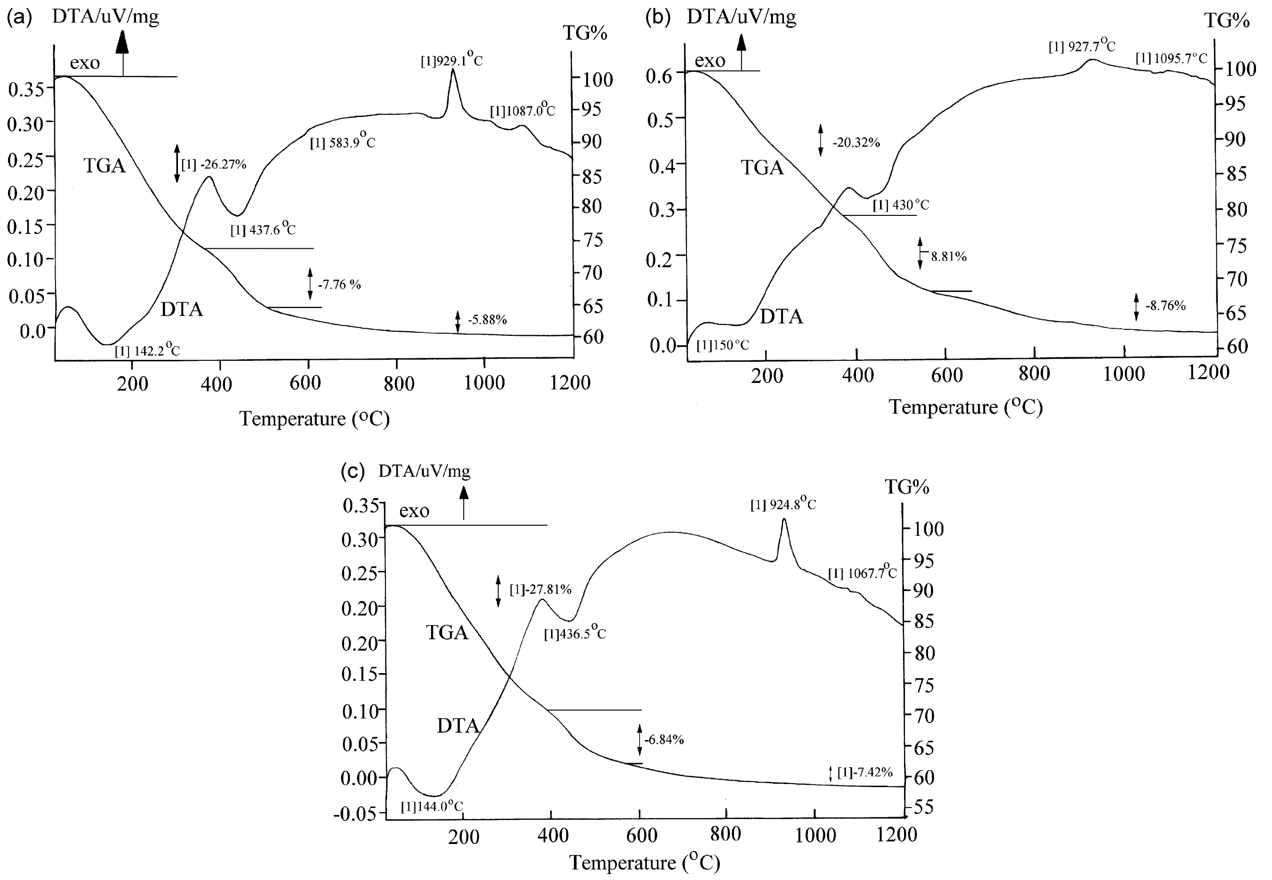

Fig. 1. (a) TG–DTA study of sample-1; (b) TG–DTA study of sample-2; (c) TG–DTA study of sample-3.

octahedral co-ordination before heat treatment but when the sample was heat treated at 1200 °C Al–O stretching mode both for octahedral and tetrahedral co-ordination were noticed. From literature it was found that [8] Al is hexa coordinated in aqua complex and in Al_2O_3, but in YAG, Al exhibited both tetra and hexa co-ordination. Before the addition of NH_4OH, Al^{3+} in the salt solution remain octahedral coordinated but as it came in contact with NH_4OH its co-ordination changed from octahedral to tetrahedral. On calcinations the tetrahedral Al cation

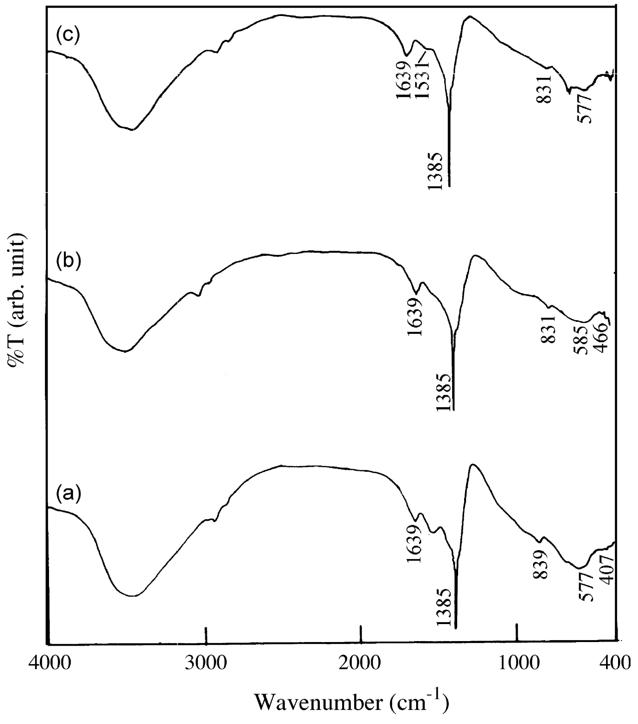

Fig. 2. IR spectra of precursor powders.

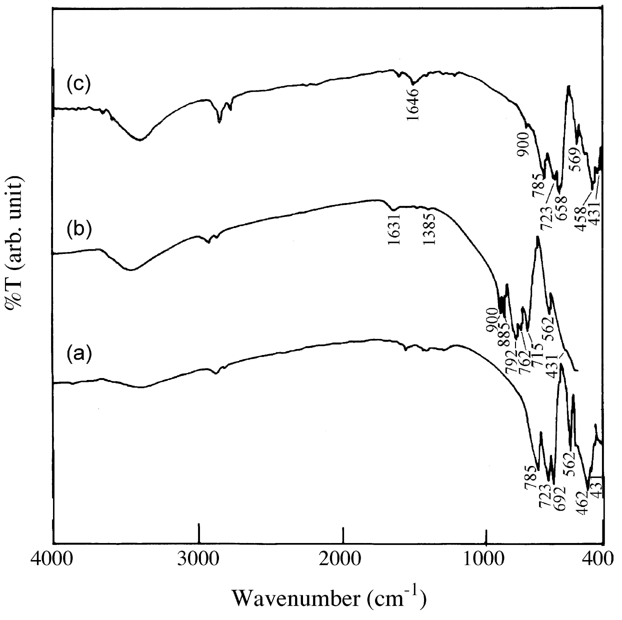

Fig. 3. IR spectra of 1200 °C heat-treated sample.

normally changes to octahedral co-ordination. However in flash polycondensation technique, salt solution was added to NH_4OH in such a way that cations polymerized into gel form maintaining its co-ordination partially in octahedral and partly in tetrahedral form. Therefore, on calcination this gel was converted to the powder containing Al in both tetrahedral and octahedral co-ordination as is in YAG. This was probably the reason of early bulk conversion of precursor powder to YAG

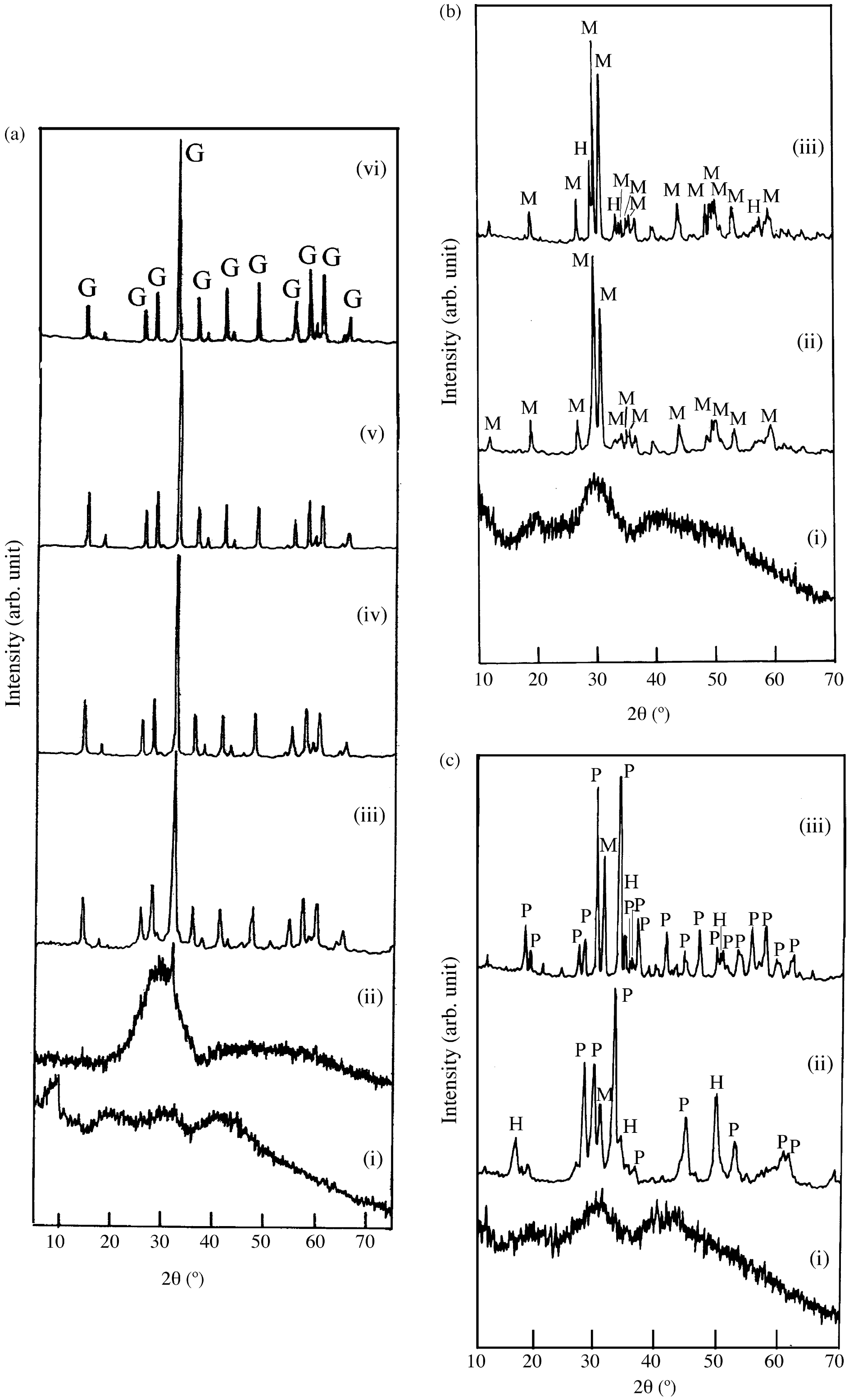

Fig. 4. (a) XRD study of sample-1: (i) powder precursor; (ii) 800 °C heat-treated sample; (iii) 900 °C heat-treated sample; (iv) 1000 °C heat-treated sample; (v) 1100 °C heat-treated sample; (vi) 1200 °C heat-treated sample. (b) XRD study of sample-2: (i) powder precursor; (ii) 900 °C heat-treated sample; (iii) 1200 °C heat-treated sample. (c) XRD study of sample-3: (i) powder precursor; (ii) 900 °C heat-treated sample; (iii) 1200 °C heat-treated sample.

phase at comparatively lower temperature. This phenomenon was also observed in other cases [14–18].

3.3. XRD

The result of XRD analysis of powder precursor for all the samples (Fig. 4a–c) indicated diffused band. From DTA analysis the first exothermic peak for all the samples were found around 930 °C. All the samples were heat treated at 930 °C and XRD analysis was performed on those heat-treated materials. Sample-1 was found to crystallize into a cubic phase corresponding to YAG without any unreacted Y_2O_3 and Al_2O_3 in the system. Sample-2 crystallized into monoclinic system corresponding to YAM. But sample-3, on heat treatment, crystallized into three systems, i.e. hexagonal (YAH), perovskite (YAP) and monoclinic (YAM). When the heat treatment temperature was raised to 1200 °C there was no change in the crystallization behavior in sample-1 excepting in better crystallization, and sample-2 produced YAM phase along with hexagonal phase. For sample-3 phases were YAP and YAM. Therefore, it may be said that the present method though suitable for producing YAG in the phase pure form at lower temperature, it is not suitable for preparing phase pure YAM and YAP under similar conditions.

As it was found that the method of preparing powder precursor by flash polycondensation technique was suitable for sample-1 a detail analysis of sample-1 was carried out by heat treating the powder at different temperature such as from 800 °C to 1200 °C. The results were shown in Fig. 4a. From the figure it appear that the gel remains amorphous as indicated by XRD up to 750 °C, and the first peak appeared at 800 °C indicating the beginning of crystallization of the pure garnet phase $Y_3Al_5O_{12}$. Further heating of the gel up to 1200 °C showed no change in phase composition except for an increase in the intensity of the peaks. Here the crystallization temperature 800 °C was lower than as reported by DTA analysis, which showed the crystallization temperature of cubic garnet phase at about 929 °C (Fig. 1a). This difference may be due to the exothermic peak in the DTA curve which often lags behind crystallization because of hysterisis of temperature [20].

Some reports [21–24] found that cubic garnet phase was the result of phase transformation from the intermediate phase that usually could be perovskite, hexagonal and monoclinic. In our experiment monoclinic and perovskite phase was not detected and cubic garnet was the only crystalline phase that could be detected at relatively lower temperature (800 °C) for sample-1.

X-ray diffraction pattern for sample-2 heat treated at 930 °C showed only pure monoclinic phase. Further heat treatment of the samples at 1200 °C showed the formation of some new hexagonal peak which can be explained from the work of Hess et al. [24]. They showed that on low temperature (1200 °C) heat treatment of 2:1 Y_2O_3:Al_2O_3 composition resulted in an assemblage consisting of YAM and YAH. Further heat treatment at 1500 °C, resulted pure phase YAM. The crystallization sequence suggested is

$$\text{amorphous YAM} \rightarrow \text{YAH} \rightarrow \text{amorphous YAP} \rightarrow \text{YAM}$$

It was reported [25] that though heat treatment of 1:1 Y_2O_3:Al_2O_3 gel at 900 °C yielded a mixture of garnet and monoclinic phase, increasing amount of perovskite phase $YAlO_3$ appeared with increasing temperature of heat treatment. A highly idealized reaction for the crystallization of $YAlO_3$ from 1:1 Y_2O_3:Al_2O_3 gel as suggested [24].

$$\text{amorphous YAlO}_3 \rightarrow \text{YAM} \rightarrow \text{YAH} \rightarrow \text{YAG} \rightarrow \text{orthorhombic YAP}$$

In the above case YAP, YAG and YAM phases were identified, but in present investigation predominantly YAP phase along with small amount of YAM and hexagonal YAP were found to be formed at 930 °C, and all the phases were stable up to 1200 °C. These results indicate that pure phase YAG powder can be obtained by the flash polycondensation method at comparatively lower temperature than other techniques. The YAG crystallized directly from amorphous phase at 800 °C. The lowering of reaction temperature was attributed to the shorter diffusion distance for the reactants,

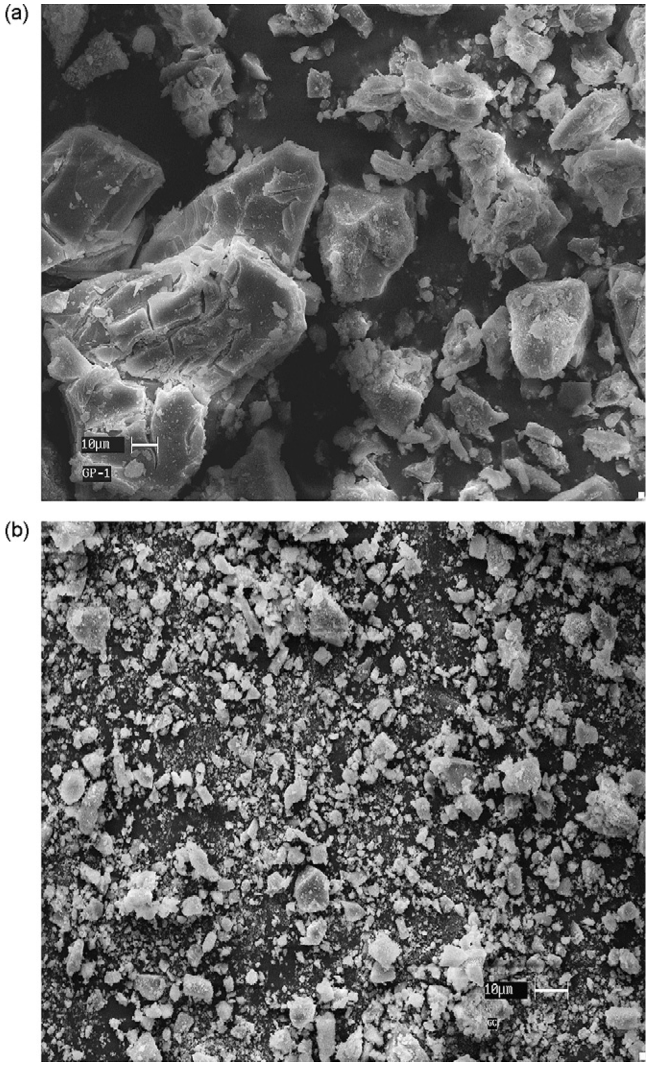

Fig. 5. Scanning electron micrograph of (a) precursor powder and (b) calcined powder.

resulting from the fine grain size of the precipitated hydroxyhydrogel precursor in addition to the proximity of molecular stage of element in precursor and formed compound. It is likely that this methods offer molecular or nano-level mixing of the constituent leading to chemical homogeneity [11].

3.4. SEM

Fig. 5a and b shows scanning electron micrographs of the precursor powder and calcined powder, respectively. The hydroxyhydrogel precursor mainly contains micron (5–30 μm) size dense aggregates of nano-sized primary particles. The gel remains in agglomerated state maintaining geometrical shapes. When it was calcined agglomerates get finer, but the overall morphology remains the same to that of the precursor powder.

4. Conclusion

Flash polycondensation technique was found to be an effective method, for producing phase pure YAG. Phase pure YAP and YAM could not be prepared by this technique due to inherent thermal instability of those two phases which undergoes decomposition during thermal treatment. Flash polycondensation technique found an excellent alternative for producing several materials as mentioned in Refs. [14–18] is found to be also suitable for making YAG expectedly economically.

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References

[1] J.S. Abell, R. Harris, B. Cockayne, B. Lent, An investigation of phase stability in the Y_2O_3–Al_2O_3 system, J. Mater. Sci. 9 (1974) 527–537.

[2] G. De With, H.J.A. Van Dijk, Translucent $Y_3Al_5O_{12}$ ceramics, Mater. Res. Bull. 29 (12) (1984) 1669–1674.

[3] I. Shoji, S. Jurimura, Y. Sato, T. Taira, A. Ikesue, K. Yoshida, Optical properties and laser characteristics of highly Nd^{3+} doped $Y_3Al_5O_{12}$ ceramics, Appl. Phys. Lett. 77 (7) (2000) 939–941.

[4] H.S. Yoder, M.L. Keith, Complete substitution of aluminium for silicon: the system $3MnO{\cdot}Al_2O_3{\cdot}3SiO_2$–$3Y_2O_3{\cdot}5Al_2O_3$, Am. Mineral. 36 (7/8) (1951) 519–533.

[5] M.L. Keith, R. Roy, Structural relations among double oxides of trivalent elements, Am. Mineral. 39 (1/2) (1954) 1–23.

[6] S. Geller, E.A. Wood, Crystallographic studies of perovskite-like compounds: rare earth orthoferrites and $YFeO_3$, $YCrO_3$, $YAlO_3$, Acta Crystallogr. 9 (1956) 563–568.

[7] F. Bartaut, J. Mareschal, C.R. Hebd, A new type hexagonal structure: AlTO, 3 (T. Y, Eu, Gd, Tb, Dy, Ho, Er), Seances Acad. Sci. 257 (1963) 867.

[8] I. Warshaw, R. Ray, Stable and metastable equilibria in the systems Y_2O_3–Al_2O_3 and Gd_2O_3–Fe_2O_3, J. Am. Ceram. Soc. 42 (1959) 434–438.

[9] A. Ikesue, I. Furusato, K. Kamata, Fabrication of polycrystalline transparent YAG ceramics by a solid state reaction method, J. Am. Ceram. Soc. 78 (1) (1995) 225–228.

[10] L.B. Kong, J. Ma, H. Huang, Low temperature formation of yttrium aluminium garnet from oxides via a high energy ball milling process, Mater. Lett. 56 (2002) 344–348.

[11] X. Li, Q. Li, J. Wang, S. Yang, H. Liu, Synthesis of Nd^{3+} doped nano-crystalline yttrium aluminum garnet (YAG) powders leading to transparent ceramic, Opt. Mater. 29 (5) (2007) 528–531.

[12] X. Zhang, H. Liu, W. He, J. Wang, X. Li, R.I. Boughton, Novel synthesis of YAG by solvothermal method, J. Cryst. Growth 275 (2005) 1913–1917.

[13] Patent application no. 149/DEL/00.

[14] A.K. Samanta, Studies on the consolidation characteristics of silicon carbide in presence of sol–gel derived oxide additives, PhD Thesis, University of Calcutta, 2000.

[15] A.K. Basu, A. Mitra, S. Ghatak, Synthesis of a powder precursor in the form of hydroxyhydrogel for reaction sintering of BN–mullite composite, Ceram. Int. 32 (2) (2000) 213–219.

[16] S. Mandal, S. Chakrabarti, S. Ghatak, Preparation and characterization of a powder precursor, consisting of oxides of Li–Al–Si in the form of hydroxyhydrogel for synthesis of β-spodumene, Ceram. Int. 30 (3) (2004) 357–367.

[17] S. Mandal, S. Chakrabarti, S. Das, S. Ghatak, Sintering characteristics of in situ formed low expansion ceramics from a powder precursor in the form of hydroxyhydrogel, Ceram. Int. 30 (8) (2004) 2147–2155.

[18] A.K. Samanta, K.K. Dhargupta, A.K. De, S. Ghatak, SiC–YAG sintered composites from hydroxyhydrogel powder precursors, Ceram. Int. 26 (8) (2000) 831–838.

[19] J. Li, Y. Pan, F. Qiu, Y. Wu, W. Liu, J. Guo, Synthesis of nanosized Nd:YAG powders via gel combustion, Ceram. Int. 33 (2007) 1047–1052.

[20] J. Su, Q.L. Zhang, C.J. Gu, D.L. Sun, Z.B. Wang, H.L. Qiu, A.H. Wang, S.T. Yin, Preparation and characterization of $Y_3Al_5O_{12}$ (YAG) nano-powder by co-precipitation method, Mater. Res. Bull. 40 (2005) 1279–1285.

[21] J.G. Li, T. Ikegami, J.H. Lee, T. Mori, Y. Yajima, Co-precipitation synthesis and sintering of yttrium aluminum garnet (YAG) powders: the effect of precipitant, J. Eur. Ceram. Soc. 20 (2000) 2395–2405.

[22] T. Tachiwaki, M. Yoshinaka, K. Hirota, T. Ikegami, O. Yamaguchi, Novel synthesis of $Y_3Al_5O_{12}$ (YAG) leading to transparent ceramic, Solid State Commun. 119 (2001) 603–606.

[23] L. Wen, X.D. Sun, Z.M. Xiu, S.W. Chen, C.T. Tsai, Synthesis of nanocrystalline yttria powder and fabrication of transparent YAG ceramics, J. Eur. Ceram. Soc. 24 (2004) 2681–2688.

[24] N.J. Hess, G.D. Maupin, L.A. Chick, D.S. Sunberg, D.E. Mccreedy, Synthesis and characterization of yttrium aluminium garnet and related compounds, J. Mater. Sci. 29 (1994) 1873–1878.

[25] G. Gowda, Synthesis of yttrium aluminates by the sol–gel process, J. Mater. Sci. Lett. 5 (1986) 1029–1032.