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Effect of seeding on the formation of lanthanum hexaaluminates synthesized through advanced sol gel process

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ABSTRACT

Advanced sol gel processing was used to synthesize high purity lanthanum hexaaluminate powders. The effect of seeding on the formation of lanthanum hexaaluminate was also studied by seeding the gel. Dry gel was calcined at various temperatures starting from 1100 °C to 1600 °C for 2 h to study the phase evolution. The combine effects of advanced sol gel processing and the presence of seeds promoted the formation of lanthanum hexaaluminate phase at lower temperature than the conventional routes. Lanthanum hexaaluminate phase was detected at 1201 °C and 1300 °C in seeded and un-seeded gels, respectively. The presence of seed decreases the temperature of formation of lanthanum hexaaluminate by 99 °C. Single phase lanthanum hexaaluminate was formed at 1600 °C in seeded gel whereas trace of lanthanum monoaluminate phase still present in un-seeded gel even at 1600 °C.

1. Introduction

Lanthanum hexaaluminate (LHA, $LaAl_{11}O_{18}$) is a versatile material due to its superior microstructure and structure property relationship. The major properties of LHA are structural and thermochemical stabilities at high temperature up to 1400 °C [1], low thermal conductivity (0.8 to 2.6 $W\,m^{-1}\,K^{-1}$), high thermal expansion coefficient (9.5 to $10.7\times10^{-6}\,K^{-1}$) [2], low sintering rate at service temperature [3], low oxygen diffusivity [4], etc. Microstructure of LHA can be tailored suitably to meet the requirement of desired end applications [5]. Over last few decades, numerous applications of LHA have been tried out and several of them are established [2,6–9], Usage of LHA powders as coating for thermal insulation and oxidation resistance [2,4], catalyst and catalytic convertor [8,10], tuneable laser [9,11], nuclear waste immobilization [7], reinforcement phase in ceramic matrix composite [6,12], etc., have shown promising results and growing rapidly. Therefore, the demand of high purity, chemically homogeneous lanthanum hexaaluminate powder with superior microstructure is of greater extent.

The major processing routes for LHA synthesis used by researchers are solid state reaction of precursor oxides [13], co-precipitation of hydroxide from their respective salt solutions [14], micro emulsion of two or more immiscible liquids/solutions [8], combustion synthesis of metal nitrates with suitable fuels [15], sol gel processing starting from metal salts or alkoxides [13,16,17], etc. Each process has its advantages as well as some limitations. The formation of LHA is a sluggish process and needs much higher temperature (more than 1650 °C) with soaking time greater than 90 h to obtain a single phase LHA [15,18]. LHA formation takes place through formation of intermediate phases such as lanthanum monoaluminate (LMA, $LaAlO_3$) and Al_2O_3. These intermediate phases react to form LHA, but the rate of reaction is very slow [17,18]. Other processes like co-precipitation, [14] combustion synthesis [15] and sol gel processing [17] have faster kinetics of LHA formation. The yield of LHA phase increased at 1450 °C with 2 h of soaking, but the trace of LMA remains there [17]. Pure LHA phase synthesized at lower temperature (~1300 °C) in alumina rich formulation [16]. Saruhan et al. [19] reported that the alkoxide based precursors and electrostatically absorbed LHA seeds on oxide fibers promote the crystallization of sol gel derived lanthanum hexaaluminate even at 1200 °C. Various divalent cations (dopants) like MgO, MnO_2, etc., have been added to stabilize the magnetoplumbite structure and also to find out the effect on formation temperature [20]. Although synthesis of pure $LaMnAl_{11}O_{19}$ powders at 1000 °C without formation of intermediated perovskite phase was there [20], synthesis of pure phase LHA (without doping) is observed at temperature greater than 1450 °C with soaking time more than 2 h [17,20].

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Last few decades, many scientists and researchers have worked on the seeded boehmite gel to form alpha alumina based ceramics [21–24]. The small amount of alpha alumina seed addition significantly lowers the transformation temperature of boehmite gel/γ-alumina to α-alumina compared to the parent system [24,25]. Seeds, which are iso-structural with the final phase, provide the sites for growth and thus lower the activation energy required for nucleation [26–28]. But, seeding does not significantly influence the activation energy requirement for growth stage, as growth takes place by coalescence of α-alumina nuclei [25]. Seeds in the matrix of transition alumina influence the grain growth and alter the pore morphology which in turn refines the final microstructure [22].

The main objective of this present work is to synthesize single phase, high purity lanthanum hexaaluminate through advanced sol gel processing from economical precursors. The formation of lanthanum hexaaluminate at low temperature as well as obtaining single phase LHA is investigated. Effect of this processing technique and effect of seeding are also studied.

2. Experimental procedure

2.1. Synthesis of sol gel derived powders

Lanthanum hexaaluminate samples were prepared by advanced sol gel processing route. Boehmite (purity 99.9%) and lanthanum nitrate (purity 99.99%) were used as sources of alumina and lanthanum oxide, respectively. These precursor materials are commercially available in the market and used as such without any purification.

Boehmite powder was dispersed in hot demineralized water using high speed disperser and peptized the dispersion by slow addition of 4 M HNO_3 solution [29]. The concentration of the hydrosol was about 8%. The pH of the solution was maintained at 2.5. Required amount of lanthanum nitrate was dissolved in demineralized water separately and then added to the boehmite solution. Small amount of poly ethylene glycol (PEG) was finally added to the solution and stirred for 10 min to obtain a homogeneous dispersion. PEG acts as a crosslinking agent and increases the green strength of monolithic gel [30,31]. In case of seeding, 2 wt% of lanthanum hexaaluminate seed (particle size ~0.6 μm) was added to the solution after addition of lanthanum nitrate solution. The homogeneous solution is called sol and gets transformed into gel within 10 min once mechanical stirring was stopped. This gel was then dried at 90 °C for 24 h. Dry gel was crushed into fine powders using agate mortar & pestle and subsequently sieved through ASTM 270 mesh (<53 μm size). This powder sample was calcined at various temperatures starting from 1100 °C to 1600 °C for 2 h. Lanthanum hexaaluminate sample without and with 2 wt% seed are designated as SGL and SGLS, respectively. These abbreviated forms are used throughout this text.

2.2. Methods of characterization

Thermal decomposition behavior of the dry gel powder was done using simultaneous thermo gravimetric (TG) and differential thermal analysis (DTA) (Netzsch, Germany) from room temperature to 1500 °C in air. Alumina crucible was used as a sample holder and alpha alumina was used as reference sample. The heating rate was kept at 10 °C/min.

Crystal phases of the samples were determined by Bruker AXS, D8 Advance X-ray diffractometer (XRD) using Ni filtered CuK_α ($\lambda=0.154$ nm) radiation. The samples were scanned continuously from 10° to 80° (2θ) with a step size of 0.02° and scan rate 3°/min.

FTIR spectra of calcined powders were recorded on Thermo Nicolet, Avatar, FTIR spectrometer using KBr pellets. Samples were scanned in the wave number range 400–4000 cm^{-1} at resolution of 4 cm^{-1}.

Microstructural features of calcined powders were investigated on the gold coated surface using scanning electron microscope (JEOL, JSM, Japan).

3. Results and discussion

3.1. Thermal behaviour

TG–DTA curves of dried gel powder of SGL and SGLS are shown in Figs. 1 and 2, respectively. TG curves of both the samples show three stages of weight loss. The divisions are made based on the temperature range for the convenience of discussion as well as comparative evaluation. The first stage of weight loss in SGL and SGLS are about 8% and 10% respectively which is observed in the temperature range of 40–200 °C. This weight loss is mainly due to the evaporation of absorbed water. Second stage of weight loss is about 24% and occurred between 200 and 500 °C. This weight loss corresponds to the de-hydroxylation of structural water, decomposition of lanthanum nitrate, nitric acid and burning of PEG [32–34]. Finally, in the third stage (500–1500 °C), 3% and 5% weight losses were observed for SGL and SGLS, respectively. These weight losses are attributed primarily due to further removal of residual hydroxyl group [35].

DTA curve of SGL sample shows four exothermic peaks at 236 °C, 254 °C, 436 °C and 1300 °C. Exothermic peaks at 236 °C and

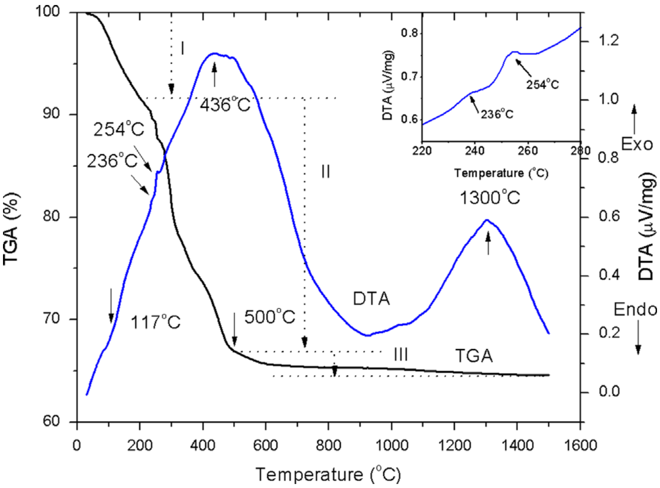

Fig. 1. TG-DTA curve of dry gel of SGL sample.

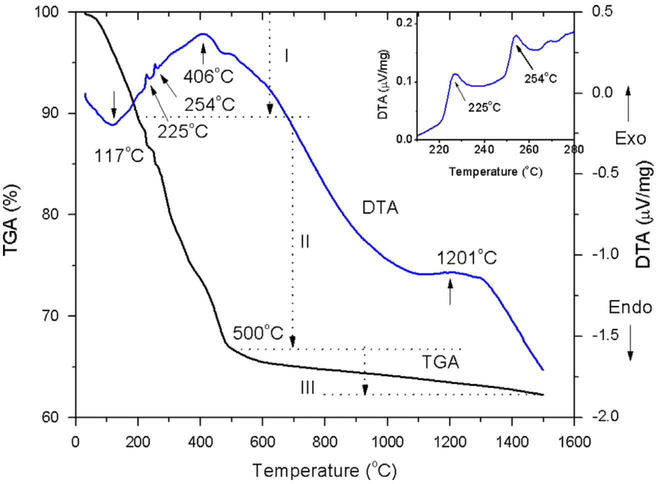

Fig. 2. TG-DTA curve of dry gel of SGLS Sample.