JOURNAL OF MATERIALS PROCESSING TECHNOLOGY 208 (2008) 415–422

journal homepage: www.elsevier.com/locate/jmatprotec

Combustion synthesis of Y_2O_3 and Yb–Y_2O_3
Part I. Nanopowders and their characterization

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ARTICLE INFO

Article history:
Received 3 August 2007
Received in revised form
24 November 2007
Accepted 5 January 2008

Keywords:
Synthesis
Combustion
Nanocrystalline powders
Ytterbium doped yttrium oxide

ABSTRACT

Nanosized yttrium oxide and ytterbium doped yttrium oxide powders were prepared by ceramic combustion techniques such as flash combustion, citrate gel decomposition and glycine combustion using urea, citric acid and glycine respectively as fuels. As synthesized precursors and calcined powders were characterized for their structural, particle size and morphology, and the optimization of calcination process by differential scanning calorimetry and thermal gravimetry. The thermal analyses together with XRD results demonstrate the effectiveness of the combustion process for the synthesis of pure phase nanocrystalline powders. Nanocrystalline pure yttria powders were obtained by the calcination of as-prepared precursors at 1100 °C for 4 h.

1. Introduction

Yttrium oxide is an excellent ceramic material that is used for various applications, since its properties include chemically stability, high melting point, high thermal stability, low thermal expansion, high thermal conductivity and good transparency to infrared radiation (Saito et al., 1998; Dasgupta et al., 2001; Micheli et al., 1992; Dupont et al., 2003; Ikegami et al., 2002; Senthilkumar et al., 2004). The applications of yttrium oxide are chemically stable substrates, crucible material for melting reactive metals, nozzle material for jet casting of molten rare earth-iron magnetic alloys, cutting tools, IR windows (Dasgupta et al., 2001; Micheli et al., 1992; Dupont et al., 2003; Ikegami et al., 2002; Senthilkumar et al., 2004). Ytterbium doped yttrium oxide is a promising material for solid-state lasers since ytterbium is an efficient dopant for diode-pumped solid-state lasers. Yb^{3+} activator ion possesses many advantages because of its simple electronic structure (Deloach et al., 1994; Baney et al., 1996). Ytterbium doped materials show optimum quantum efficiency and no concentration quenching, since the Yb^{3+} ion has only two manifolds, the ground state $F^{7/2}$ and upper level $F^{5/2}$. Moreover, it shows weak non-radioactive transition, large crystal-field splitting, millisecond-lifetime of the metastable $F^{5/2}$ state, and intense inter-stark $F^{5/2} \rightarrow F^{7/2}$ transitions (Boulon et al., 2003; Pires et al., 2005; Redmond et al., 2004; Noginor et al., 2002; Anh et al., 2003). Polycrystalline ytterbium doped yttrium oxide ceramic can be a potential candidate material for laser applications. In order to manufacture a transparent polycrystalline ceramic by sintering for laser application, there are several requirements like small particle size and its distribution, purity and dopant distribution that the starting powder must meet.

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0924-0136/$ – see front matter © 2008 Published by Elsevier B.V.
doi:10.1016/j.jmatprotec.2008.01.023

The chemical methods such as spray drying, hydrothermal precipitation, co-precipitation and sol–gel techniques offer fine ceramic powders. However, these methods require longer processing time, expensive chemicals and special equipment. The wet chemical combustion methods of preparing ceramic nanopowders offer an alternate route to overcome the drawbacks of chemical methods. As well, these combustion methods of synthesis for ceramic powders enable precursor powders with different morphologies, which are good candidates to improve densification on sintering. The present investigation is focussed on the synthesis of pure yttria and ytterbium doped yttria using novel ceramic combustion techniques. These techniques are modified solid-state techniques: the constituent precursor salts are mixed thoroughly to ensure a molecular level of mixing and heated to form oxides. These processes yield reactive powders with high purity, more homogeneous, fine particle size and low temperature sinterability compared to the powders prepared by conventional method (Mckittrick et al., 1999; Kingsley and Pederson, 1993). Moreover, these combustion techniques are simple, inexpensive and less time consuming in comparison with other methods. The present investigation reports the synthesis of pure yttria and ytterbium doped yttria nanopowders by ceramic combustion techniques such as flash combustion (Mangalaraja et al., 2003, 2002, 2004), citrate–gel decomposition technique (Dupont et al., 2003; Mangalaraja et al., 2000) and glycine combustion (Ekambaram and Patil, 1995; Ye et al., 1997) using the organic fuels urea, citric acid and glycine, respectively.

2. Experimental

Pure and ytterbium doped yttria nanopowders were prepared by three different combustion techniques. The starting materials used in the preparation were yttrium nitrate, ytterbium nitrate, urea, citric acid and glycine. In this work 25 mol% of ytterbium doped yttria powders were prepared to test dopant distribution in the prepared powder.

2.1. *Flash combustion technique*

Flash combustion technique is a modified solid-state combustion technique, the metal nitrates react with urea to form precursor oxides. The metal nitrates (as oxidisers) were weighed according to the required proportion and mixed. Required amount of double distilled water was used in the experiments for homogenous mixing of metal nitrates. Urea (as fuel) was added to the mixture and mixed thoroughly. The oxidiser to fuel ratio (O/F) plays a crucial role in determining the exothermicity of combustion product. The equivalence ratio, i.e., the ratio of the oxidising valency to fuel was maintained at unity (O/F = 1). The valency of nitrogen was not considered because of its conversion to molecular nitrogen (N_2) during combustion. The chemical reactions for the two mixtures assuming complete combustion can be written as

$$2Y(NO_3)_3 + 5NH_2CONH_2 \rightarrow Y_2O_3 + 5CO_2 + 10H_2O + 8N_2$$

$$2[Y(NO_3)_3]_{0.75} + 2[Yb(NO_3)_3]_{0.25} + 5NH_2CONH_2 \rightarrow (Yb_{0.25}Y_{0.75})_2O_3 + 5CO_2 + 10H_2O + 8N_2$$

The mixture was transferred to a platinum crucible and introduced into an electric furnace, which was preheated at 500 °C. At this temperature, the mixture reacted leading to a flashed combustion and thus reaction was complete in 3–5 min, by forming a white coloured highly porous foamy solid precursor. The collected foam was crushed to powder by mortar and pestle, and then calcined at 1100 °C (Micheli et al., 1992; Dupont et al., 2003; Wen et al., 2005; Huang et al., 2004) for 4 h soaking in an oxygen atmosphere to get pure crystalline powder.

2.2. *Citrate–gel decomposition technique*

Citrate–gel decomposition technique is a modified sol–gel technique in which the gel is decomposed by a self-propagating high temperature synthesis (SHS) process. It is a combination of sol–gel and SHS reaction processes. The metal nitrates were weighed according to the required proportion and mixed. Double distilled water was used in the experiments for homogenous mixing of metal nitrates. Citric acid was added to the mixture as a fuel and mixed thoroughly followed by a clear solution was obtained. Similar to the flash combustion technique, the equivalence ratio was maintained at unity (O/F = 1). The assumed complete combustion reactions can be written as

$$6Y(NO_3)_3 + 5CH_2COOHCOHCOOHCH_2COOH \rightarrow 3Y_2O_3 + 30CO_2 + 20H_2O + 9N_2$$

$$6[Y(NO_3)_3]_{0.75} + 6[Yb(NO_3)_3]_{0.25} + 5CH_2COOHCOHCOOHCH_2COOH \rightarrow 3(Yb_{0.25}Y_{0.75})_2O_3 + 30CO_2 + 20H_2O + 9N_2$$

The process was carried out in a glass cylindrical beaker. The beaker was kept on a hot plate and continuously stirred while monitoring the temperature. The sol was heated to 80 °C and stirred constantly until it transformed into honey like consistency and then to a transparent sticky gel. This gel was rapidly heated to 200 °C and at this stage an auto combustion process occurred accompanied by the evolution of a brown fume, and finally yielded a fluffy precursor. The precursor was crushed and then heat treated at 1100 °C (Micheli et al., 1992; Dupont et al., 2003; Wen et al., 2005; Huang et al., 2004) for 4 h in an oxygen atmosphere.

2.3. *Glycine-combustion technique*

The glycine-combustion technique is similar to flash combustion technique in which glycine is used as a fuel, and in our synthesis, the equivalence O/F ratio was maintained at unity. The assumed synthesis reaction is described in the way:

$$6Y(NO_3)_3 + 10NH_2CH_2COOH \rightarrow 3Y_2O_3 + 20CO_2 + 25H_2O + 14N_2$$

$$6[Y(NO_3)_3]_{0.75} + 6[Yb(NO_3)_3]_{0.25} + 10NH_2CH_2COOH \rightarrow 3(Yb_{0.25}Y_{0.75})_2O_3 + 20CO_2 + 25H_2O + 14N_2$$