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Ceramics International 38 (2012) 5453–5459

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Synthesis of $Lu_2Ti_2O_7$ nano-powders by salt modified sol–gel process

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Received 30 January 2012; received in revised form 23 March 2012; accepted 23 March 2012
Available online 7 April 2012

Abstract

Nano-sized $Lu_2Ti_2O_7$ powders have been prepared successfully by a chloride salt modified sol–gel process, by using tetrabutyl titanate and lutecium nitrate as precursors. The results indicate that salt precipitated during the synthesis process can form a thin layer of salt crust on the surface of the newly formed nano-particles and prevent re-agglomeration and hinder the particle growth resulting in well-dispersed $Lu_2Ti_2O_7$ nano-crystals. However, the increased salt contents can also lead to the significant size increase of the formed particles. Meanwhile, different types of salt species differently affect on the particle morphologies. Based on the above observation, well-dispersed spherical $Lu_2Ti_2O_7$ nano-crystals with an average particle size of about 50 nm can be obtained at 850 °C by the modified sol–gel process with precursor to NaCl ratio of 1:15.

Keywords: A. Powders: chemical preparation; A. Sol–gel processes; C. Thermal properties

1. Introduction

$A_{2+x}B_{2-x}O_{7-\delta}$ (A = Sm–Lu; B = Ti, Zr, Hf; x = 0–0.67) pyrochlores have attracted considerable attention because some of them are comparable in high-temperature oxygen ion conductivity to the well-known solid electrolytes ZrO_2–8–12 mol% Y_2O_3. Of particular interest are the $A_{2+x}Ti_{2-x}O_{7-\delta}$ (A = Er–Lu, x = 0–0.096) and $Ho_{2+x}Ti_{2-x}O_{7-\delta}$ (x = 0.48–0.67) pyrochlore-like titanates, which offer the highest oxygen ion conductivity in this family of materials, up to $\sim 1.4 \times 10^{-2}$ S/cm at 800 °C. Among these materials, $Lu_2Ti_2O_7$ with a pyrochlore structure can offer the highest ionic conductivity and is particularly suitable for application in an optical imaging system due to its high refractive index and high density [1,2]. Traditionally, $Lu_2Ti_2O_7$ is prepared by solid-state reaction [3,4], namely the metal oxides are used as precursors and the reaction reagents have to be sintered at higher temperature (>1100 °C) for a long time. Moreover, the products by solid-state reaction are usually non-uniform in part in chemical component and have large particle size, which is not favorable for their properties. Recently molten salt synthesis (MSS) method was employed successfully to synthesize the $Lu_2Ti_2O_7$ powders using TiO_2 and Lu_2O_3 as precursors. Especially two step calcinations technique was proved to be a novel method for fabrication of pure $Lu_2Ti_2O_7$ nano-particles [5,6]. In spite of this, one shortcoming of MSS is its multi-step washing for eliminating the salt. Moreover, different degrees of aggregation are usually presented in the final product. The solution-based soft chemical method is one of the typical strategies to synthesize nano-crystalline materials with perfect fine particles. Due to its unique features, a number of chemical methods have been used for synthesizing nano-powders, such as co-precipitation, the sol–gel method, hydrothermal synthesis, combustion and micro-wave-assisted synthesis [7–11]. Among these methods, sol–gel processing has gained an increasing importance in a variety of applications and has been the subject of intense study for last two decades. Sol–gel chemistry is an attractive alternative to other synthetic methods for many reasons. This method is low temperature, low cost, and can generally be done under room conditions with general lab equipment, all of which make processing convenient and inexpensive. So, based on the sol–gel process a large number of sophisticated materials have been prepared and studied and the corresponding theories elaborated. However, in all the cases discussed above the products obtained by sol–gel reaction had relatively large particle sizes caused by the high reaction temperatures. The molten salt-assisted chemical method of synthesizing nano-structured ceramic powders was recently employed [12–14]. It is based on the use of various inorganic salt additives (e.g. NaCl, KCl) as inert diluents to control the particle

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0272-8842/$36.00
http://dx.doi.org/10.1016/j.ceramint.2012.03.057

size. Alkali metal halide aids in transportation of the reactant species and prevents products grain growth by forming a protective layer around the particles. All these facilitate synthesis at low temperature, and positively affect the formation of fine grain products. To the best of our knowledge, there have been no prior reports of similar attempts to fabricate $Lu_2Ti_2O_7$ nano-powders up till the present. So, the emphasis of this work is to prepare and characterize well-dispersed $Lu_2Ti_2O_7$ nano-crystals synthesized via salt-assisted sol–gel method (SASG).

2. Experimental procedure

In the present study commercial tetrabutyl titanate, lutecium nitrate were used as the raw materials. All reagents were of analytical grade and used without further purification. Firstly, the deionized water was dropped into the mixture of lutecium nitrate and ethanol until lutecium nitrate was solved completely. Secondly, tetrabutyl titanate was dissolved in ethanol. The molar ratio of tetrabutyl titanate:lutecium nitrate is 1:1. The above two solutions were mixed together and the obtained solution was vigorously stirred for 15 h at 60 °C and further evaporated at 110 °C. Then, the as-prepared precursor was added to NaCl, ground for 20 min in an agate mortar. The ratio of the precursor to NaCl was chosen as 1:1, 1:5, 1:15, and 1:50. The mixture was then placed in a corundum crucible and annealed in a muffle furnace with heating rate of 10 °C/min. After heat treatment, the products were washed using hot deionized water to remove the residual salt. The products were then dried and characterized using an X-ray diffractometer (XRD, D/max-RB, Japan) for phase composition and a scanning electron microscopy (SEM, Model JSM-7401, Japan) for product morphology. Differential scanning calorimetry (DSC) measurements were made with the use of a liquid-nitrogen cooling accessory (DSC 404 F3 Pegasus).

3. Results and discussion

3.1. Sol–gel process

Fig. 1 illustrates the XRD patterns of $Lu_2Ti_2O_7$ nano-crystals calcined at 700–900 °C. It is easily found that Lu_2O_3, TiO_2 and $Lu_2Ti_2O_7$ coexist at 700 °C. TiO_2 tends to disappear gradually with temperature increasing. Almost no obvious TiO_2 can be detected at temperature higher than 750 °C. This indicates a large amount of $Lu_2Ti_2O_7$ phase can be synthesized at temperature higher than 700 °C by the sol–gel synthesis process.

With increasing of the calcinations temperature, the full width half-maximum (FWHM) decreases to some degree and the peaks become sharper. This implies that the calcinations temperature plays an important role on the control of the crystalline phase. When the sample is heated at 900 °C, all the intense diffraction peaks can be perfectly indexed to the cubic structure crystalline (JCPDS: 23-0375) indicating that the fluorite structure appears. In spite of these observations, the impure peaks, which are attributed to the residual Lu_2O_3, are still observed. This indicates that pure $Lu_2Ti_2O_7$ with fluorite structure cannot be synthesized by sol–gel method at

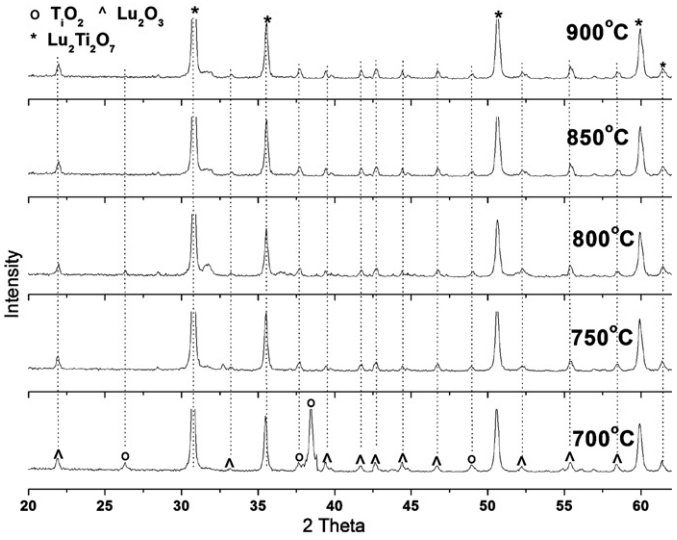

Fig. 1. XRD patterns of $Lu_2Ti_2O_7$ powders synthesized at various temperatures by sol–gel process without salt addition.

temperature lower than 900 °C. It was reported that conventional solid-state synthesis of pure $Lu_2Ti_2O_7$ phase was virtually impossible at a temperature < 1000 °C. Moreover, TiO_2 and Lu_2O_3 phase were reported to present with formation of $Lu_2Ti_2O_7$ [3,4]. When the molten salt route was applied to synthesize $Lu_2Ti_2O_7$, the similar results were obtained although two step calcinations technique (TSS) was reported to be a successful route for pure $Lu_2Ti_2O_7$ [5]. The similar results are also found in the sol–gel process.

In order to understand effects of the calcinations temperatures on the particle morphology, SEM micrographs of $Lu_2Ti_2O_7$ powders synthesized at different temperatures are shown in Fig. 2. When the calcinations temperature is as low as 750 °C, large blocks with pores and voids can be observed (Fig. 2(a)). The formed nano-particles agglomerate together and interconnect with each other forming a sponge-like mesostructure so that the average particle size cannot be distinguished very clearly. The presented pores and voids in the sponge-like mesostructure are probably due to the evolution of gases during synthesis reaction. With temperature increasing up to 800 °C, the pore size becomes enlarged obviously and at the same time the sponge-like mesostructure starts to disappear. The powders are mainly composed of sphere particles with an average size of about 30–40 nm at this temperature. Obvious change in the particles shape is observed when the temperature is increased to 850 °C, at which larger amounts of sphere particles start to be developed into ones with a relatively regular shape. Further increasing the calcinations temperature higher than 900 °C, no obvious change in particle morphology is found except the obvious duplex microstructure, as shown in Fig. 2(d), in which the small particles are less than 100 nm while the large particles size is increased to 300–400 nm.

3.2. Chloride salt modified sol–gel process

Fig. 3 shows the XRD patterns of the $Lu_2Ti_2O_7$ powders obtained through salt modified sol–gel process. The peaks to