

# Preparation, characterization, photoactivity and XPS studies of $\text{Ln}_2\text{ZrTiO}_7$ (Ln = Sm and Nd)

B. Vijaya Kumar<sup>a</sup>, Radha Velchuri<sup>a</sup>, G. Prasad<sup>b</sup>, B. Sreedhar<sup>c</sup>, K. Ravikumar<sup>d</sup>, M. Vithal<sup>a,\*</sup>

<sup>a</sup>Department of Chemistry, Osmania University, Hyderabad-500 007, India

<sup>b</sup>Department of Physics, Osmania University, Hyderabad-500 007, India

<sup>c</sup>Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad-500 007, India

<sup>d</sup>Laboratory of X-ray Crystallography, Indian Institute of Chemical Technology, Hyderabad-500 007, India

Received 15 October 2009; received in revised form 4 December 2009; accepted 4 January 2010

Available online 1 February 2010

## Abstract

Oxides of composition  $\text{Ln}_2\text{ZrTiO}_7$  (Ln = Sm and Nd) were prepared by sol–gel method and characterized by powder X-ray diffraction (XRD), energy dispersive spectra (EDS), Raman, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). These compounds were crystallized in the disordered pyrochlore structure in cubic lattice with  $Fd\bar{3}m$  space group. The TEM images of  $\text{Sm}_2\text{ZrTiO}_7$  and  $\text{Nd}_2\text{ZrTiO}_7$  prepared at 600 °C gave the particle size of 13 and 21 nm respectively. The photocatalytic activity of products was studied using photodegradation of methyl orange under UV light irradiation. The photocatalytic activity of these oxides was found to be less than that of  $\text{La}_2\text{Zr}_2\text{O}_7$  and  $\text{Nd}_2\text{Zr}_2\text{O}_7$ . The 3d profile of  $\text{Nd}_2\text{ZrTiO}_7$  gave satellite peaks on the low binding energy side in the XPS spectrum which were absent in the XPS spectrum of  $\text{Sm}_2\text{ZrTiO}_7$ . The reasons for the observation of satellite peaks were given.

© 2010 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

**Keywords:** Sol–gel; Transmission electron microscopy; Powder XRD; Photocatalytic activity

## 1. Introduction

Oxide materials exhibiting pyrochlore structure have attracted scientific and industrial community due to their interesting properties and potential applications. These compounds have high photocatalytic activity, piezoelectric behavior, ferro- and ferrimagnetisms, order/disorder transformations, high thermal expansion coefficient, range of electrical and ionic conductivities that include metallic, semiconducting and superconductivity [1–7]. Due to these combinations of properties they are used as magnetic materials [8,9], as fast ion conductors [10–13], as thermal barrier coating materials in gas turbines [7] and in the immobilization and treatment of nuclear waste [14,15]. The general formula of pyrochlore oxides is  $\text{A}_2\text{B}_2\text{O}_7$  or  $\text{A}_2\text{B}_2\text{O}_6\text{O}'$  or  $\text{B}_2\text{O}_6\text{A}_2\text{O}'$ . The structure is characterized by corner shared  $\text{BO}_6$  octahedra forming a  $\text{B}_2\text{O}_6$  network which intersects with A–O' chains of formula  $\text{A}_2\text{O}'$  [1]. Further, defects can occur in the  $\text{A}_2\text{O}'$

network. The site A can be occupied by trivalent rare earth or divalent alkaline earth or monovalent alkali ions. Tetra, penta or hexavalent transition metal ions occupy the site B. Thus the structure is flexible for substitution at A or B sites giving rise to a large family of materials.

The studies on materials containing rare earth ions are interesting. The 4f levels in rare earth ions (except Ce) are strongly localized within the ion and does not contribute significantly to chemical bonding although Mott-type phase transition of Pr in metallic systems under pressure is an exception [16,17]. The coupling of 4f states with delocalized electrons, the number of electrons present in 4f orbitals (the so called *f* count) and the possibility of hybridization has been the subject of many investigations [18–25]. The observation of satellite peaks for 3d core level in the XPS spectra of some rare earth ions, their origin and variation of their intensity with respect to main peaks has made these rare earth materials attractive both from experimental and theoretical points of view. The present investigation is aimed at the preparation, characterization, XPS and photocatalytic studies of new nano sized  $\text{Sm}_2\text{ZrTiO}_7$  and  $\text{Nd}_2\text{ZrTiO}_7$ .

\* Corresponding author. Tel.: +91 40 27682337; fax: +91 40 27090020.

E-mail address: [muga\\_vithal@osmania.ac.in](mailto:muga_vithal@osmania.ac.in) (M. Vithal).

## 2. Experimental

Rare earth oxide ( $\text{Ln}_2\text{O}_3$ , Ln = Sm and Nd) (Indian Rare Earths Ltd., purity 99%), zirconyl nitrate (Wilson Laboratories, Bombay), Ti (100 mesh, Aldrich 99.7%),  $\text{H}_2\text{O}_2$  (30%, SD Fine) and ammonia solution (25%, AR grade, SD Fine) were used as received.

*Solution “A”.* Stoichiometric amount of  $\text{Ln}_2\text{O}_3$  was dissolved in excess of concentrated nitric acid to form rare earth nitrate. Excess nitric acid was removed by slow heating. About 25 ml of distilled water was added. This solution contains 11.12 mmol of  $\text{Ln}^{3+}$  ions.

*Solution “B”.* Calculated amount of zirconyl nitrate was dissolved in hot water. The solution contains 5.56 mmol of  $\text{Zr}^{4+}$  ions.

*Solution “C”.* Calculated amount of Ti powder was added to a solution containing 60 ml of  $\text{H}_2\text{O}_2$  and 10 ml of ammonia at 0–10 °C under constant stirring. A yellow gel was obtained after 6 h. The solution contains 5.56 mmol of  $\text{Ti}^{4+}$  ions.

Solution “A” was mixed with solution “B”. To this resultant solution, solution “C” was added. Then citric acid was added to this solution such that the molar ratio of citric acid:metal ion is 2:1. At this stage metal citrates are believed to be formed. The total volume of the solution was about 300 ml. The pH of the resultant metal citrate solution was adjusted to 6–7 by adding dilute ammonia solution drop wise. The solution was then slowly evaporated on a water bath till a viscous liquid was obtained. At this stage ethylene glycol (gelating reagent) was added such that the molar ratio of citric acid to ethylene glycol was 1:1.2. This mixture was heated on a hot plate/stirrer at 100 °C for 2–3 h with constant stirring. The temperature was increased to 160–180 °C at the onset of solidification. The ensuing porous solid mass was ground in an agate mortar using spectral grade acetone and heated to about 400 °C in small amounts in an electric burner to remove the organic matter completely. The resultant ash colored solid (named as “precursor”) was mixed with solid NaCl in the weight ratio of 1:1 and divided into several parts.

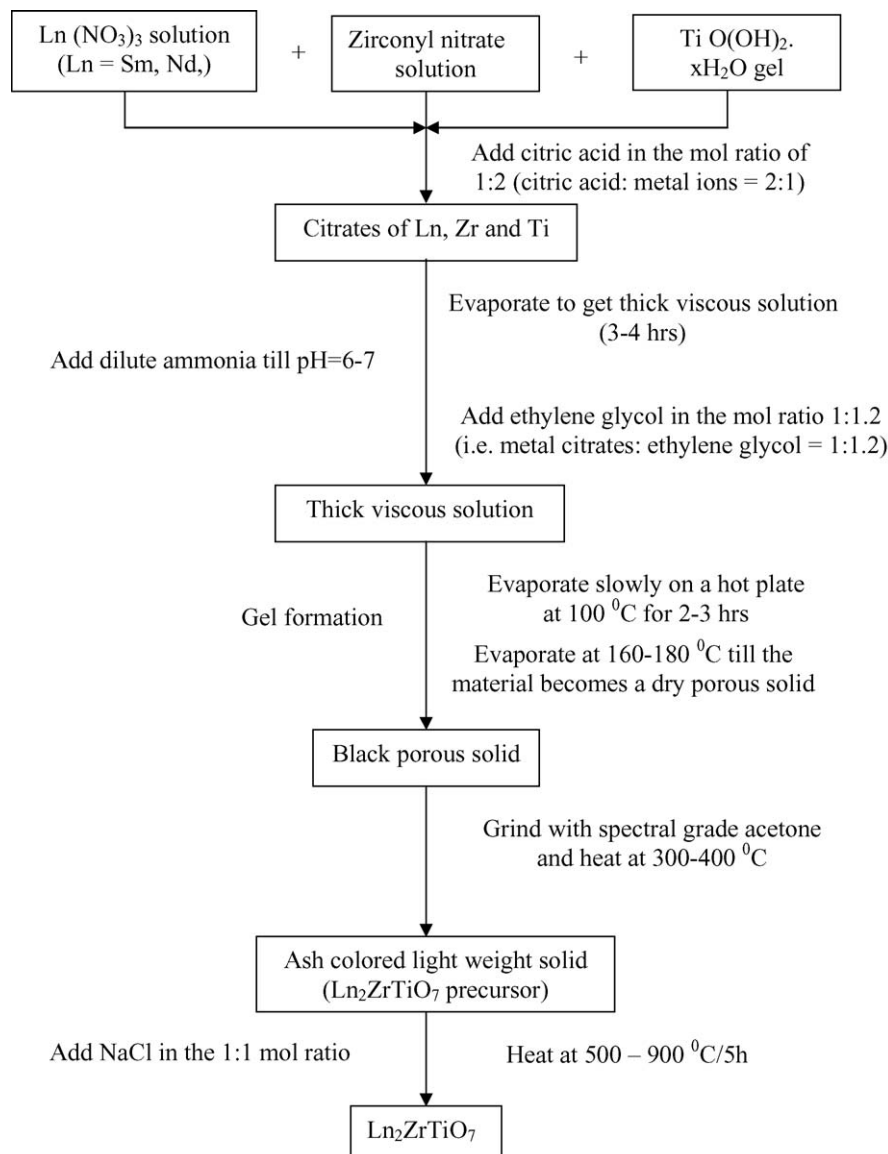


Fig. 1. Flow chart showing the sol-gel method of preparation of  $\text{Ln}_2\text{ZrTiO}_7$ .

Download English Version:

<https://daneshyari.com/en/article/1463930>

Download Persian Version:

<https://daneshyari.com/article/1463930>

[Daneshyari.com](https://daneshyari.com)