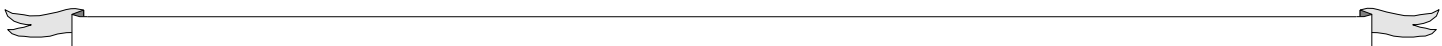


**Annals of the University of Craiova**  
**The Chemistry Series**  
**VOLUME XLII No 1, 2013**



# Annals of the University of Craiova The Chemistry Series

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**Cerium Titanates. Synthesis and Structural Investigations****Nicoleta Cioateră<sup>1\*</sup>, Elena-Adriana Voinea<sup>1</sup>, Aurelie Rolle<sup>2</sup>, Rose-Noelle Vannier<sup>2</sup>**<sup>1</sup>University of Craiova, Faculty of Mathematics and Natural Sciences, Department of Chemistry, Craiova, Romania<sup>2</sup>Unité de Catalyse et de Chimie du Solide, Equipe de Chimie du Solide, UMR CNRS 8181, ENSCL / UST Lille 1, BP 90 108, 59652 Villeneuve d'Ascq Cedex, France

Received: 07.03, 2013/ Accepted: 10.04, 2013

⊕ **ABSTRACT**

Ceria-titania mixed oxides with  $\text{CeTi}_2\text{O}_6$  and  $\text{CeTiO}_4$  compositions have been synthesized using two different methods: the sol-gel method and a modified Pechini method. By adequate thermal treatment of the resulted gel or solid resin, cerium oxidation state can be adjusted. XRD and FT-IR analysis of the solid oxides evidenced the formation of  $\text{CeTi}_2\text{O}_6$  and  $\text{CeTiO}_4$  crystalline phases.

**Keywords:** sol-gel synthesis; mixed oxide; ceria; titania.

**INTRODUCTION**

$\text{TiO}_2$  and  $\text{CeO}_2$  solid oxides were widely investigated mainly for photocatalytic and catalyst support applications, while titania-ceria mixed oxides exhibited interesting properties for gas sensors and electrochromic devices <sup>1</sup>. Different synthesis procedures were used for their preparation such as precipitation and sol-gel synthesis.

Depending on Ti : Ce ratio and cerium oxidation state, different cerium titanates can be obtained. Thus,  $\text{Ce}^{3+}$  is involved in  $\text{Ce}_2\text{TiO}_5$  (reddish-brown),  $\text{Ce}_2\text{Ti}_2\text{O}_7$  (reddish-brown) and  $\text{Ce}_4\text{Ti}_9\text{O}_{24}$  (chestnut), while  $\text{CeTi}_2\text{O}_6$  and  $\text{CeTiO}_4$  are yellow cerium titanates with  $\text{Ce}^{4+}$ . Cerium oxidation state can be tuned by controlling the thermal treatment atmosphere. The formation of cerium titanate phases with  $\text{Ce}^{3+}$  is favoured when the thermal treatment is performed in reducing environments. By thermal treatment in air,  $\text{Ce}^{4+}$  titanates are obtained; they exhibit higher photocatalytic activity than  $\text{Ce}^{3+}$  phases <sup>2</sup>.

Unlike many titanates with general formula  $\text{Ln}_2\text{Ti}_2\text{O}_7$  which possess a pyrochlore-type crystalline structure,  $\text{Ce}_2\text{Ti}_2\text{O}_7$  exhibits a layered perovskite structure. The isometric pyrochlore structure is favoured when  $r_{\text{Ln}^{3+}}/r_{\text{Ti}^{4+}}$  ratio falls in the range 1.46 – 1.78 <sup>3</sup>. For  $\text{Ce}_2\text{Ti}_2\text{O}_7$ , the ratio between ionic radii of octa-coordinated  $\text{Ce}^{3+}$  (1.143 Å) and hexa-coordinated  $\text{Ti}^{4+}$  (0.605 Å) ( $r_{\text{Ce}^{3+}}/r_{\text{Ti}^{4+}} = 1.89$ ) <sup>4</sup> is higher than the upper limit of the pyrochlore stability range and this compound has a monoclinic structure ( $P 2_1$  space group) (Fig. 1 and Table 1).

$\text{Ce}_2\text{TiO}_5$  has an orthorhombic structure (space group  $Pnma$ ), Ti is penta-coordinated with oxygen, while Ce is hepta-coordinated <sup>5</sup> (Fig. 2).

$\text{CeTi}_2\text{O}_6$  is a brannerite-type oxide with monoclinic structure (space group  $C2/m$ ). Its structure consists in layers of  $\text{TiO}_6$  octahedra, alternating with columns of  $\text{CeO}_6$  octahedra (Fig. 3) <sup>6</sup>. Thermal treatment and synthesis procedure have a strong impact on the oxygen stoichiometry in this oxide.

$\text{Ce}_4\text{Ti}_9\text{O}_{24}$  crystallizes in the orthorhombic space group  $Fddd$  (similar to  $\text{Nd}_4\text{Ti}_9\text{O}_{24}$ ), with  $\text{TiO}_6$  octahedra,  $\text{CeO}_6$  distorted square antiprisms and  $\text{CeO}_6$  octahedra <sup>7</sup>.

In this study, the preparation of  $\text{CeTi}_2\text{O}_6$  and  $\text{CeTiO}_4$  phases by sol-gel and modified Pechini methods, respectively, is presented.

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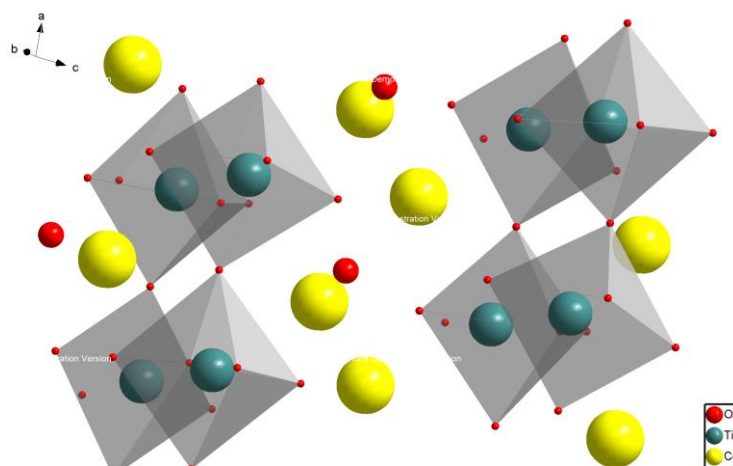


Figure 1. Crystal structure of Ce<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (1404676-ICSD) <sup>8</sup>

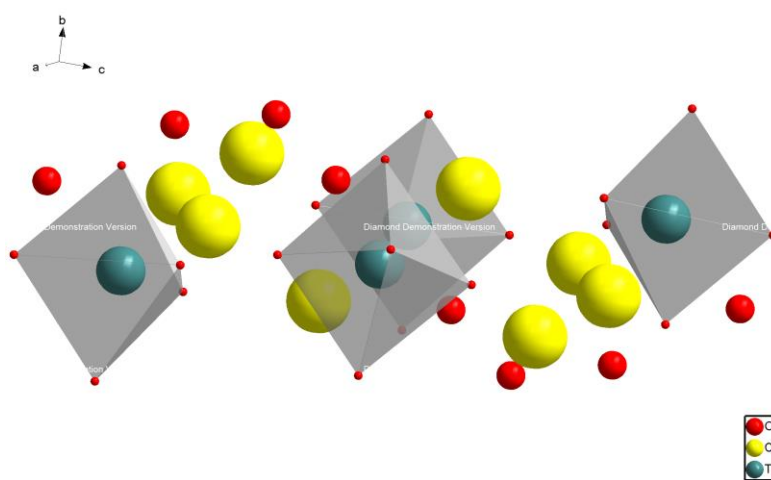


Figure 2. Crystal structure of Ce<sub>2</sub>TiO<sub>5</sub> (1404675-ICSD) <sup>8</sup>

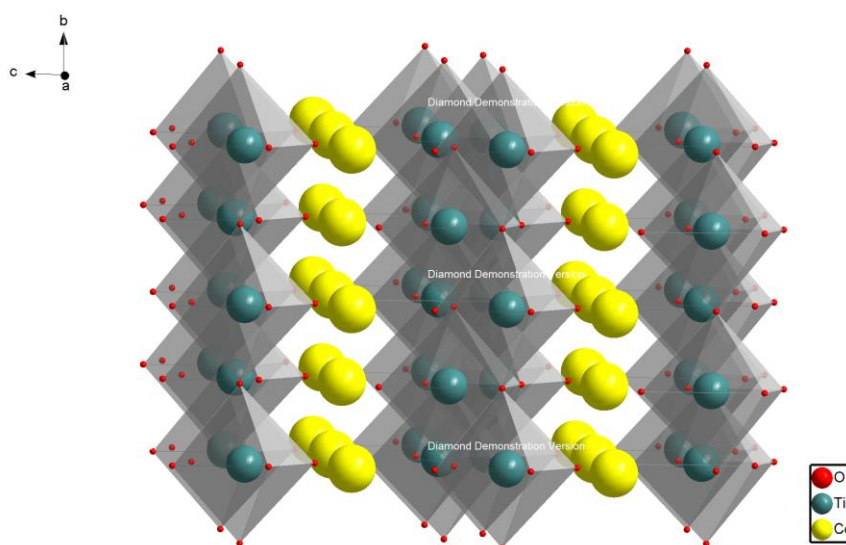


Figure 3. Crystal structure of CeTi<sub>2</sub>O<sub>6</sub> (308333-ICSD) <sup>9</sup>

Table 1. Structural parameters of different ceria-titania mixed oxides

Compound	Space group	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	<i>V</i> , Å <sup>3</sup>
Ce <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>	<i>P2<sub>1</sub></i>	7.776	5.515	12.999	551.53
Ce <sub>2</sub> TiO <sub>5</sub>	<i>Pnma</i>	10.877	3.893	11.389	482.26
Ce <sub>4</sub> Ti <sub>9</sub> O <sub>24</sub>	<i>Fddd</i>	14.082	14.516	35.419	7240.15
CeTi <sub>2</sub> O <sub>6</sub>	<i>C2/m</i>	9.840	3.750	6.910	222.47

## EXPERIMENTAL

Ceria-titania mixed oxides have been synthesized using two methods. As starting cation precursors, cerium (III) nitrate hexahydrate (Sigma-Aldrich, >99.9 %) and titanium (IV) propoxide (Sigma-Aldrich, >98 %) in stoichiometric proportion were used. In the first method (the sol-gel method), both salts were dissolved in isopropyl alcohol (i-PrOH). Acetylacetonate (acac) was added to moderate the alcoxide hydrolysis kinetics, thus preventing the precipitation of titanium oxyhydroxide. The molar ratio Me : H<sub>2</sub>O : i-PrOH : acac = 1 : 10 : 50 : 0.3 was used. After salts and acac dissolution in i-PrOH, the solutions were mixed together and continuously stirred for 2 h. Then distilled water was dropwise added into the reaction mixture. The mixture was allowed to gel for 24 h. The resulted gel was dried at 120 °C overnight and the thermal treatment of as-obtained powder was performed in four steps: (i) heating in air with a 2 °C/min rate from room temperature to 350 °C, (ii) holding at 350 °C for 2 h in air in order to remove the organics, (iii) heating in 3 % hydrogen – nitrogen mixture from 350 °C to 850 °C with a rate of 2 °C/min, (iv) holding at 850 °C for 6 h under reducing atmosphere. In the second method (a modified Pechini method), the cation salts and citric acid were dissolved in water. The pH was adjusted to 7 with ammonia. Triton X-100 was used as structuring agent. After removal of excess solvent, the resulted gel was dried at 120 °C overnight. The as-obtained solid resin was calcined in air at 950 °C for 5 h.

Ceria-titania mixed oxides were analysed by simultaneous TG/DTA measurements, FT-IR spectroscopy and X-ray diffraction (XRD). TG/DTA measurements were performed using a Diamond TG/DTA (PerkinElmer) in air FT-IR spectra were recorded on KBr pellets using a Bruker Alpha spectrometer. A D8 Bruker diffractometer equipped with Vantec1 linear detector was used for the analysis of powder in the range of  $2\theta = 10^\circ$ - $80^\circ$  with a  $0.0148^\circ$  step size.

## RESULTS AND DISCUSSIONS

TG/DTA curves corresponding to the precursor solid resin of ceria-titania mixed oxide prepared by modified Pechini method are shown in Fig. 4. The first endothermic wide peak from r.t. to about 230 °C can be ascribed to the removal of solvent (water), while the following three exothermic peaks centered at 270 °C, 350 °C, and 400 °C respectively can be attributed to the removal of organics.

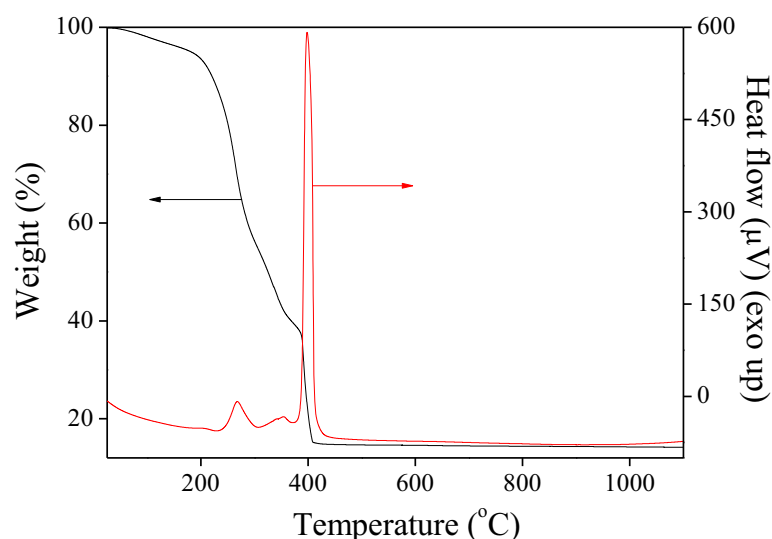


Figure 4. TG/DTA curves for the solid resin of ceria-titania mixed oxide

The X-ray diffraction pattern of the calcined powders (Fig. 5) evidenced a poor crystallization sample for the powder prepared by sol-gel method and thermal treated under reducing atmosphere (Fig. 5a). The characteristic peaks of monoclinic  $\text{CeTi}_2\text{O}_6$ , as well as the ones of cubic  $\text{CeO}_2$  and tetragonal  $\text{TiO}_2$  were identified in the XRD pattern. It is well known that  $\text{Ce}^{4+}$  is stable in solution and in air. By thermal treatment in hydrogen-nitrogen mixture, some of  $\text{Ce}^{4+}$  is reduced to  $\text{Ce}^{3+}$  and the formation of  $\text{CeTi}_2\text{O}_6$  phase is favoured<sup>10</sup>.

For the powder obtained by modified Pechini method, only the characteristic peaks of  $\text{CeTiO}_4$  could be evidenced in the XRD pattern (Fig. 5b). Unfortunately, the crystalline structure of  $\text{CeTiO}_4$  was not elucidated yet<sup>11</sup>.

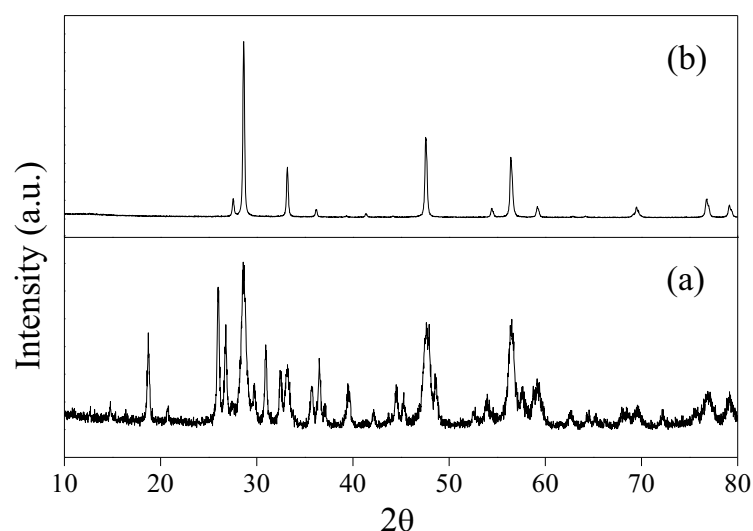
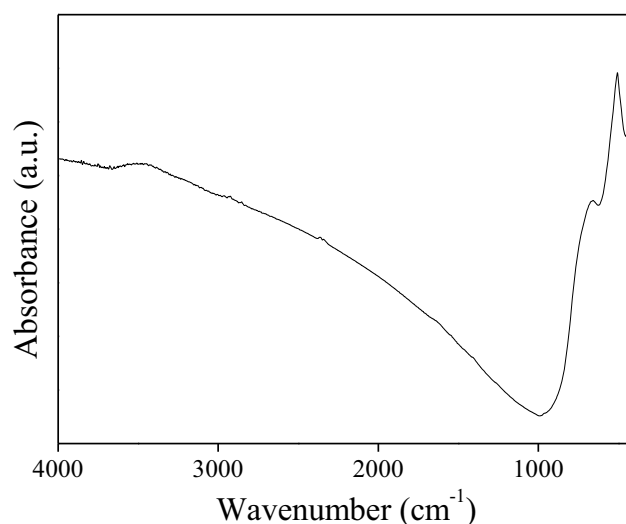


Figure 5. XRD patterns of ceria-titania mixed oxide powders prepared by sol-gel method (a) and by Pechini method (b)



**Figure 6.** FT-IR spectra of ceria-titania mixed oxide powder calcined at 950°C

Fig. 6 shows the FT-IR spectra of the calcined mixed oxide powder synthesized by modified Pechini method. The broad peak from about 3500  $\text{cm}^{-1}$  can be attributed to the hydroxyl group stretching vibration, while the weak peak from 2365  $\text{cm}^{-1}$  is characteristic to adsorbed  $\text{CO}_2$  from air. The strong band from about 500  $\text{cm}^{-1}$  is ascribed to Ti-O bond and the one from  $\sim 600 \text{ cm}^{-1}$  is due to the Ti-O-Ce bond vibration. This last band is very wide in pure titania, being modified in  $\text{TiO}_2\text{-CeO}_2$  mixed oxides by the presence of Ti-O-Ce bonds. The band from around 400  $\text{cm}^{-1}$  suggests the formation of Ce-O bond<sup>12, 13</sup>.

## CONCLUSIONS

$\text{CeTi}_2\text{O}_6$  and  $\text{CeTiO}_4$  mixed oxides have been obtained using two synthesis procedures. Sol-gel method was involved in the preparation of  $\text{CeTi}_2\text{O}_6$ , the thermal treatment of the gel being adjusted in order to reduce  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$ . Using a modified Pechini method, combined with thermal treatment in air for the resulted solid resin,  $\text{CeTiO}_4$  was obtained. XRD and FT-IR analysis of the solid oxides evidenced the formation of  $\text{CeTi}_2\text{O}_6$  and  $\text{CeTiO}_4$  crystalline structures.

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