Quim. Nova, Vol. 25, No. 6, 897-901, 2002

OXOCHLOROALKOXIDE OF THE CERIUM (IV) AND TITANIUM (IV) AS OXIDES PRECURSOR

Luiz Carlos Machado*, Milton Koiti Morigaki, Antonio Augusto Lopes Marins e Emanuel José Bassani Muri
Departamento de Química, Universidade Federal do Espírito Santo, Av. Fernando Ferrari s/n, 29060-900 Vitória - ES
Jair Carlos Checon de Freitas
Departamento de Física, Universidade Federal do Espírito Santo, Av. Fernando Ferrari s/n, 29060-900 Vitória - ES

Recebido em 11/6/01; aceito em 19/3/02

OXOCHLOROALKOXIDE OF THE CERIUM (IV) AND TITANIUM (IV) AS OXIDES PRECURSOR. The Cerium (IV) and Titanium (IV) oxides mixture (CeO_2-$3TiO_2$) was prepared by thermal treatment of the oxochloroisopropoxide of Cerium (IV) and Titanium (IV). The chemical route utilizing the Cerium (III) chloride alcoholic complex and Titanium (IV) isopropoxide is presented. The compound $Ce_5Ti_{15}Cl_{16}O_{30}(^iOPr)_4(OH\text{-}Et)_{15}$ was characterized by elemental analysis, FTIR and TG/DTG. The X-ray diffraction patterns of the oxides resulting from the thermal decomposition of the precursor at 1000 °C for 36 h indicated the formation of cubic cerianite ($a = 5.417$Å) and tetragonal rutile ($a = 4.592$Å) and ($c = 2.962$ Å), with apparent crystallite sizes around 38 and 55nm, respectively.

Keywords: chemical synthesis; oxide; thin film.

INTRODUCTION

Multicomponent oxide films are of interest to several technical applications, as well as to the fundamental science. Thin films of various inorganic materials exhibit potential applications in electronic and optelectronics devices, catalysis and corrosion protection[1-3]. Recently, cerium-titanium oxide films have been investigated by many techniques, especially motivated by use these materials in electrochromic devices. However, these applications are conditioned to the oxides stoichiometry and coating thickness[4-7].

Thin films of CeO_2-TiO_2 were prepared by Deroo *et al*[4] applying the sol-gel process to the product of the reaction involving two alkoxides, $Ce(OBu)_4$ and $Ti(OBu)_4$ in BuOH. The films, deposited by spin coating method, presented a homogeneous, transparent, and colorless appearance, with composition varying from the pure TiO_2 to the CeO_2. The authors established a model where the films are supposedly constituted by amorphous matrix of titanium oxide embedding nanocrystallites of cerium oxide, which size increased strongly for compositions that contain higher than 50% of the CeO_2.

A detailed interpretation for influence of lanthanide addition on the electrochromic properties of Ce-Ti oxide films deposited by reactive dc magnetron sputtering and containing electrochemically intercalated Li was given by Granqvist *et al*[5]. The authors found that the oxide films presenting Ce/Ti ratios varying between 0.3 and 0.6 were almost fully transparent irrespective of their lithiation; while further Ce addition was found to cause a decrease in their electrochromism. The Ce-Ti sputtered oxide films presented low crystallinity, with grain sizes around 5-10 nm, as estimated from X-ray diffraction (XRD) spectra. This behavior was found for the Ce/Ti ratios up to 1.25.

Von Rottkay *et al*[6] studied the influence of the stoichiometry on the electrochromic properties of Ce-Ti oxide thin films deposited by dc sputtering, in a wide range of compositions. Mixed CeO_2-TiO_2 films showed that the roughness was lower for intermediate compositions than for pure components. This could point to a more pronounced amorphous character in the compound material. The typical grain size varied from about 100 nm, for the mixed compound, to 150 nm for the pure components. The authors also demonstrated that the charge capacity of CeO_2-TiO_2 films is more intense for intermediate compositions of the cerium oxides.

Alves *et al*[8] have investigated the effect of the CeO_2 addition on the mixed compound IrO_2-TiO_2. The samples were synthesized in both powder and film forms. The catalytic activity and electrochemical stability of the electrocatalytic oxide are largely influenced by microstructure. The titanium supported electrode films of nominal composition $Ir_{0.3}Ti_{(0.7-x)}Ce_xO_2$, x = 0, 0.3, 0.5 and 0.7, as well as the oxides mixture IrO_2-TiO_2-CeO_2, in the same composition range, were investigated by means of XRD. The results indicate the formation of a rutile phase with mixed composition $(Ir,Ti)O_2$, besides the pure oxides IrO_2, TiO_2, CeO_2, and Ce_2O_3. The crystallite sizes of the IrO_2 and $(Ir,Ti)O_2$ phases are increased (up to 9 nm for the Ir-Ti mixed oxide), when CeO_2 is added to the oxides mixture (30 and 50 % of mol CeO_2), as evidenced by the narrowing of the correspondent diffraction lines. The CeO_2 crystallite size is the lowest when compared to the values obtained for the other component of the mixture (4-6 nm, compared to 7-8 nm for TiO_2 and 10-13 nm for IrO_2). The XRD patterns of the films prepared with the same oxide composition are characterized, depending on the CeO_2 contents, by a variable amorphousness degree that indicate an opposite trend, when compared to previous results.

Metal alkoxides and oxochloroalkoxides are versatile precursors to the oxides. The attractive properties of the alkoxides, concerning their use as precursor materials, are the solubility, sublimation facility and thermal stability[2, 9-11]. The M-O-C bond polarity and the polymerization degree mainly govern their solubility and volatility. Alkoxides that display the highest nuclearity are often non-volatile and non-soluble, when compared to other alkoxides. These properties make the alkoxides appropriate to the oxide film preparation via chemical routes as hydrolysis and vapor deposition[10, 12, 13]. Unfortunately, the chemical synthesis of the lanthanide alkoxides presents several problems, such as pure metals requirements, excessive time consumption, uncertain reactional stoichiometry and normally leads to low yield. A simplification in the experimental

---

*e-mail: lmachado@verao.cce.ufes.br

synthesis procedure and in the reactional logistic is therefore necessary, for an opportune utilization of the lanthanide alkoxides in the routine chemical synthesis[2, 14-17].

In this paper, we present the reaction of the cerium (III) chloride alcoholic complexes and the titanium (IV) isopropoxide in benzene solvent as an access path to the lanthanide bimetallic alkoxides. These alkoxides are subsequently pyrolyzed to produce Ce-Ti oxides. A detailed study on the mechanism of thermal degradation of the precursor is carried out, along with a comparative structural investigation of the materials produced at different temperatures.

EXPERIMENTAL

All the experimental procedures for the precursor preparation were performed under pure argon atmosphere using Schlenk, glove box and vacuum line apparatus. Petroleum ether (refers to the fraction b. p. 40-60 °C), ethyl ether and benzene were treated with sulfuric acid solution. In the sequence, they went dry with metallic sodium and finally purified by distillation under O_2-free argon.

Titanium alkoxide $Ti(^iOPr)_4$ and triethylortoformate $CH(OC_2H_5)_3$ were commercial products (Sigma, Fluka respectively) and they were distilled before use. The cerium (III) chloride alcoholic complex was obtained by reaction of cerium (III) chloride hydrated with triethylortoformate as previously described[18]. The oxoalkoxide precursor compound was synthesized by reaction of cerium (III) chloride alcoholic complex (2.0417g, 0.004743 moles) with titanium isopropoxide (2.6960g, 0.009486 moles) in benzene medium. The cerium (III) chloride complex excess was filtered and the precursor was obtained by concentrated solution crystallization.

Elemental analysis of Ce and Ti was executed on a Spectroflame Plasma Atomic Absorption spectrophotometer, employing the methodology of internal standard. Elemental analysis (CHN) was performed on a Perkin Elmer 2400 microanalytical analyzer instrument. IR spectra were obtained on Jasco IR-700 and Midac Prospect FTIR instruments (scan number = 16, smooth = 60% and uncorrected baseline) using nujol mulls and KBr pellets.

Thermogravimetric (TG) curve was recorded using a Shimadzu TGA-50H thermoanalyser system. The sample (with initial mass around 12 mg) was heated in alumina crucible under argon flow (at a rate of 20.0 ml/min) at a heating rate of 2.0 ºC/min. The differential thermogravimetric (DTG) curve was computationally derived from the TG curve.

X-ray diffraction (XRD) powder patterns were recorded with a Rigaku 4053A3 diffractometer equipped with a proportional counter and pulse height discriminator and using CuKa radiation (λ = 1.5418Å). The patterns were recorded from $2\theta = 10$ up to 100°. Powdered silicon (< 200 Mesh) was used as an external reference standard.

The apparent crystallite sizes were estimated from the inverse linewidth of the most intense XRD peaks for each identified phase by using the Scherrer formula[19]:

$$t = \frac{0.9\lambda}{B\cos\theta} \tag{1}$$

In this expression, t is the estimated crystallite size, λ is the X-ray wavelength, B is the extra broadening of the diffraction line due to the crystallite-size effect alone, and θ is the corresponding diffraction angle. The parameter B is obtained from the expression below[19]:

$$B = \sqrt{B_M^2 - B_S^2}\ , \tag{2}$$

where B_M is the experimentally observed broadening (measured at half maximum intensity, in radians) for the analyzed sample and B_S is the broadening obtained with a standard (which is attributed to instrumental broadening). The parameter B_S was obtained from the XRD pattern recorded for powdered silicon by measuring the full width at half maximum intensity of a diffraction line near the most intense line corresponding to each identified phase of the sample under analysis[19].

The thermal treatment of the precursor was performed under argon atmosphere in a horizontal resistive furnace equipped with an alumina tube and using alumina crucibles. The heating rate was 2.0°C/min and the samples were kept at the final temperatures of 700, 1000 or 1250ºC for varying times (up to 36 h).

RESULTS AND DISCUSSION

The formation, under anidrous atmosphere and room temperature, of a species between $CeCl_3.4ROH$ and $Ti(^iOPr)_4$ was evidenced by partial dissolution of the cerium complex in the benzene solution of titanium (IV) isopropoxide with a simultaneous solution color change. The characteristics absorption bands of the titanium (IV) isopropoxide were not detected in the IR spectrum of the excess of cerium alcoholic complex samples. The titanium isopropoxide insertion in the cerium alcoholic complex molecule was verified applying the IR spectral interpretation to the synthesized compound[11, 15, 20]. The occurrence of the typical values of the stretching frequencies of the titanium isopropoxide (1028 and 1115cm^{-1}) constitute the foremost indication of the intermetallic compound formation (see Table 2).

The well-defined heterometallic species containing cerium and titanium was isolated as a yellow-brown solid in good yield (68%). The depolymerization of $Ti(^iOPr)_4$ in non-polar media was not observed either with a large excess of the cerium complex or by the solution reflux. Considering this behavior and also the low solubility demonstrated by the heterometallic species in many solvents tested, a polymeric arrangement could be expected for the compound. Normally, the monometallic and bimetallic alkoxides are soluble in the organic solvents, although their nuclearities are significantly low[9, 11]. The compound does not reveal any hygroscope characteristic, when isolated in the Schlenk tube, under argon atmosphere and at room temperature. However, if the flask is open the compound absorbs the air constituents and, in a few minutes, changes to a gel form.

Based on the elemental and TG analysis the molecular formula of the compound corresponds to $Ce_5Ti_{15}Cl_{16}O_{30}(^iOPr)_4(OH\text{-}Et)_{15}$. The results of elemental analysis and the theoretical values computed from this proposed formula are presented in Table 1, as well as the Ce and Ti contents derived from the residual weight in TG analysis (to be discussed later).

Table 1. Analytical and thermoanalytical results for elemental composition of the Ce(IV)/Ti(IV) oxochloroisopropoxide (wt. %)

	Ce	Ti	Cl	C	H
Theoretical	20.52	21.04	17.26	14.76	3.46
Elemental Analysis	21.00	20.00	17.60	14.40	3.64
TG	20.32	20.83			

The lanthanide chloride used in the synthesis corresponds to the alcoholic complex resultant of the dehydration process employing the triethylortoformate[18]. The presence of oxo-groups in lanthanide alkoxides molecules, after water isolation, is due to the oxidation induced by traces of O_2 dissolved in the alcohols or present in the gas phase. This reaction is characteristic of the molecules with considerable polarization of M-OR bonds being dependent of physical properties of reaction solvent[9].

The cerium (IV) and titanium (IV) oxochloroisopropoxide has been further characterized by infrared spectroscopy. The IR frequency values of the compound are presented in Table 2. The literature assignments to ν(C-O) and ν(M-O) stretching frequencies for Ti(^{i}OPr)$_4$ and Sm-Ti oxoisopropoxide compounds were also given for comparison[11, 15, 20].

The frequencies positioned in the wavenumber range from 1328 to 1006cm^{-1} are shifted by 20-30cm^{-1} in the lanthanide oxo and oxochlorocompound spectra, in comparison with the same frequencies of titanium (IV) isopropoxide. However, the most notable changing is the splitting of bands centered on the 960cm^{-1} (2 bands), 850cm^{-1} (3 and 4 bands) and 620cm^{-1} (1 and 3 bands) of the oxo and oxochlorocompounds comparatively to the isopropoxide bands. These changes are associated with lanthanide compounds perturbation in the titanium (IV) isopropoxide ν(M-O), as previously noticed[11, 20].

The band value at 753cm^{-1} can be recognized with ν(M-Cl) stretching frequency and both the low intensity and the shift of this band to lower frequencies, compared to other lanthanide chloride complexes[21, 22], are consequence of the intensive electronic demand imposed by the highly charged titanium (IV) and cerium (IV) ions onto the oxygen and chlorine atoms.

Table 2. IR data for the Ce(IV)/Ti(IV) oxochloroisopropoxide (this work), Sm(III)/Ti(IV) oxoisopropoxide[15] and ligand Ti(^{i}OPr)$_4$[11,20]

Ce/Ti ν(C-O) (cm^{-1})	**Sm/Ti ν(C-O) (cm^{-1})**	**Ti(^{i}OPr)$_4$ ν(C-O) (cm^{-1})**
1307w	1333m	1328vs
1160sh	1162vs	1140sh
1115vs	1128vs	1127vs
ν(M-O) (cm^{-1})	**ν(M-O) (cm^{-1})**	**ν(M-O) (cm^{-1})**
1028vs	1001vs	1006vs
950sh	966s	960sh
932m	654m	—
860sh	851w	850s
830sh	936m	—
807w	830w	—
—	824w	—
753w	—	—
640w	—	—
620m	625s	620s
607m	—	—
595w	—	583m
545m	555m	533m
504m	528m	520w
458m	474m	463m
428m	445m	425w

w = weak, s = strong, sh = shoulder, m = media and vs = very strong

It was pointed out previously by Zucchini *et al*[16, 17] that in the reaction of the anidrous magnesium chloride and titanium isopropoxide, the occurrence of the chlorine atom bridge is essential to the isopropoxide bimetallic formation. The chlorine bridge is responsible for the maintenance of two monometallic species – the magnesium chloride and titanium isopropoxide – bonded into the chloroalkoxide structure. The chloroalkoxides structural characterization and the chemical bonding considerations, as related by Caulton *et al*[23], can support the idea of a polymer constituted of the alkoxi units and connected via chlorine atom bridge. In this polymeric arrangement the chlorine atoms act as donors toward the metallic ion. The development of the capabilities as chloroalkoxide sublimation and hydrolytic reactional ability are allowed by maximization of the isopropoxide units bonded to metallic cations[9]. The chlorine bridge in the chloroalkoxides plays therefore an essential role in the adjustment of the suitable characteristics of the precursors destined for the ceramic material[16, 17, 23].

The results of TG/DTG analysis under argon atmosphere for the oxochlorocompound are presented in Table 3 and Figure 1. The removal of various light residues is responsible for the initial weight loss observed from room temperature to 480 ºC, whereas the elimination of more tightly bonded groups take place between 540 and 680 ºC, yielding a residue composed by mixture of the Ce and Ti oxides (see Figure 2 and related discussion). From the value of the residual weight obtained after the complete decomposition of the oxochlorocompound (59.73%) and considering that a mixture of CeO_2 and TiO_2 in the molar ratio of 1:3 composes the residue, it is possible to estimate the Ce and Ti contents of the oxochloroisopropoxide. The results are presented in Table 1 and show a reasonable agreement with the results of elemental analysis, which accords with the chemical formula proposed for this precursor.

The first weight loss step in the oxochlorocompound TG analysis can be accounted for the loss of 5 moles of ethanol, 4 moles of isopropanol, 10 moles of hydrochloric acid, 3 moles of chlorine and 4 moles of methane. These results sum a total weight loss of 32.78% that in reasonable accordance with the experimental value of 32.91% (Table 3). In this simulation, the chlorine atoms participants of the oxochloroalkoxide molecule are totally released up to the final temperature of the first loss. The second weight loss can be attributed to the liberation of hydrocarbons molecules only[24]. The weight loss corresponding to this second reaction should comprise 6.56%, which is lower than the experimental value of 7.36%.

The structure of the residue of the TG experiment obtained at 1000 °C was analyzed by XRD (Figure 2). Also one shows the XRD patterns for some heat-treated samples at the temperatures of 750 °C (during 30 min) and 1000 °C (during 36h). The aim of these treatments was, first, to reproduce the thermal decomposition observed in the TG experiments for large mass samples. Thus, the treatment at 750 °C for 30 min just corresponds to the weight loss terminal stage. Further treatments at 1000 °C (and higher temperatures) were performed in the oxide mixture of the CeO_2 and TiO_2 to investigate the possibility of growing of mixed compositions for these oxides[8, 25].

Table 3. Results of TG/DTG experiments for the Ce(IV) and Ti(IV) oxochloroisopropoxide under argon atmosphere

	First weight-loss	Second weight-loss	Residual weight (%)
T_{onset} (°C)	30	540	
T_{peak} (°C)	58	640	
T_{end} (°C)	480	680	
Weight-loss (%)	32.91	7.36	
			59.73

T_{onset} and T_{end} from TG curves; T_{peak} from DTG curve

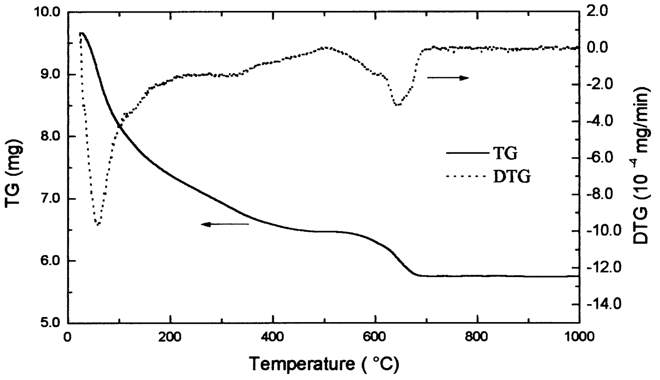

***Figure 1.** TG/DTG curves for the Ce(IV) and Ti(IV) oxochloroisopropoxide under argon atmosphere*

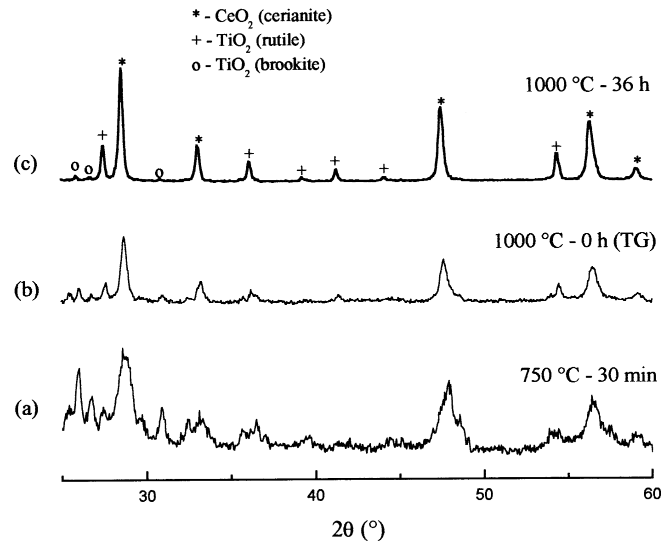

***Figure 2.** XRD powder patterns of the TG residue and some heat-treated samples*

The XRD spectrum attained for the 750 °C heat-treated sample (Figure 2a) shows the existence of broad lines, at positions nearly corresponding to the cerianite phase of CeO_2 and to rutile and brookite mixed phases for TiO_2, as indicated in the figure. The pattern suggests a poorly crystalline ordered sample, which is related to the relatively low heat treatment temperature[8]. Increasing the time at 750 °C up to 12 h does not cause any substantial change in the XRD pattern. The TG decomposition product obtained at 1000 °C (under argon atmosphere) without any residence time presents a much more ordered structure, as can be seen in the XRD spectrum of Figure 2b. The reflections are narrower and the peaks positions are little changed when compared to the 750 °C heat-treated sample. The predominant phases are the cerianite and rutile, identified by the main peaks at $2\theta = 28.67$ and 27.62°, respectively. The brookite peaks are still observable, around 25.9, 26.6, and 30.8°. The TiO_2 brookite and anatase phases are known to be unstable for temperatures above 700 °C, what explains the progressive increase in the rutile phase fraction in the heat-treated samples[26].

The treatment at 1000 °C for 36 h leads to the attainment of a well-organized crystalline arrangement (Figure 2c), with cerianite and rutile narrower peaks and just small residual signals due to brookite. From the peaks positions one can determine (by standard calculation procedures[19, 27]) the cell parameters for cubic cerianite $a = 5.417(4)$ Å and for tetragonal rutile $a = 4.592(2)$ Å and $c = 2.962(3)$ Å, values that are coherent with previously reported results: 5.411 Å for cerianite, 4.593 and 2.959 Å for rutile[26]. Further thermal treatments at temperatures up to 1250 °C do not lead to any appreciable change in the XRD pattern presented in Figure 2c.

Concerning the XRD investigation and respective conclusion elaborated separately by Roginskaya and Morozova[28] and by Alves *et al*[8], the parameters a and c of the pure phase are constant, under the modification of the CeO_2 oxide amount, contrasting with the values revealed by the solid solution. The expanded reticular parameters a and c of the solid solution approximate of the reference value in the presence of the higher CeO_2 amounts or when the equilibrium system is attained at temperature of 800 °C. The crystallite size of the pure phase of TiO_2 and IrO_2 and of the solid solution $(Ir, Ti)O_2$ are also enhanced, after the addition of CeO_2 to the oxide mixture, as confirmed by the intensity of the XRD peak's height. In spite of this, the intensification of the crystallite size of the additive CeO_2 is less evident than the others components. To the films corresponding to the same compositions of the oxides and titanium supported, the XRD signals of the pure phase and the solid solution are unobserved to the samples containing the $CeO_2 > 30\%$ mol. The only observed signal is attributed to cerianite phase. The XRD of the oxide mixture film corresponds to the isolated phase dispersed in the CeO_2 oxide matrix. The hindrance verified in the solid solution formation arises from the difference in the crystalline structure of the cerianite oxide phase (cubic) and the others components of the oxide mixture.

From Figure 2 it is apparent the progressive increase in crystallinity due to the increase in heat treatment temperature/time, which is manifested as a progressive narrowing of all XRD reflections. The crystallite sizes corresponding to these reflections were estimated by the procedure previously described. For cerianite, we obtained an increase from 8 to 38 nm between 750 and 1000 °C (36 h). For rutile, the sample held at 1000 °C for 36 h showed an apparent crystallite size around 55nm.

The large values obtained, in this paper, for the crystallite sizes of CeO_2 and TiO_2 oxides are indicative of the formation of an intimate mixture of CeO_2-TiO_2 performing the high degree of crystalline order. The expressive increase detected in the values of the crystalline size of the cerianite, in the interval of the 750-1000 ºC, seems to confirm this conclusion. The CeO_2 oxide participation, as an authentic phase, in the CeO_2 and TiO_2 oxide mixture may be derived of the oxides structural characteristics, as already commented. However, the most reliable argument available to explain the predominance of the pure phase in the oxide mixture is attributed to nonexistence of the hydrolysis reaction of the precursor solution. The difference in the phase composition and in the microstructure of the solid solution can be encountered in reaction of the components of the oxide mixture at the hydrolysis stage[29].

CONCLUSION

The Ce(IV)/Ti(IV) oxochloroalkoxide has been prepared as a precursor for the production of high purity CeO_2/TiO_2 mixed powders. The synthesis route followed in this work has made use of the practical effectiveness showed by the chlorine bridge in the formation and stabilization of intermetallic compounds. The dehydration of the cerium (III) chloride employing the trietilortoformate avoided the hydrolysis of the ligand (Ti(IV) isopropoxide). In these conditions, the interaction between the dehydrated lanthanide chloride and the ligand, via chlorine bridge, showed effective. The reactional stoichiometry (1:2) allowed the exhaustion of the ligand, giving rise at the end of the reaction to an excess constituted only by the ethanolic compound of Ce (III) chloride. The thermal decompostion of the Ce(IV)/Ti(IV) oxocloroalkoxide lead to the formation of an intimate mixture of CeO_2 and TiO_2. The development of well crystallized phases cubic cerianite and tetragonal rutile was verified after heat-treatment of the powders at 1000 ºC for 36 h, with apparent crystallite sizes around 38 nm and 55 nm for CeO_2 and TiO_2, respectively. In this form the oxides mixture is appropriate to be tested and employed in electrochromic applications.

ACKNOWLEDGEMENTS

The authors are grateful to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Pró-Reitoria de Pesquisa e Pós-Graduação (PRPPG-UFES).

REFERENCES

1. Swartz, S. L.; Wood, V. E.; *Condensed Mat. News* **1992**, *1*, 4.
2. Hubert-Pfalzgraf, L. G.; *New J. Chem.* **1987**, *11*, 663.
3. Lebrun, A.; Namy, J. L.; Kagan, H. B.; *Tetrahedron Lett.* **1991**, *32*, 2355.
4. Keomany, D.; Poinsignon, C.; Deroo, D.; *Sol. Energy Mater. Sol. Cells* **1994**, *33*, 429.
5. Kullman, L.; Azens, A.; Granqvist, C. G.; *J. Appl. Phys.* **1997**, *81*, 8002.
6. Von Rotkay, K.; Richardson, T.; Rubin, M.; Slack, J.; Kullman, L.; *Solid State Ionics* **1998**, *113*, 425.
7. Stangar; U. L.; Orel, B.; Grabec, I.; Agoreve, B.; Kalcher, K.; *Sol. Energy Mater. Sol. Cells* **1993**, *31*, 171.
8. Alves, V. A.; Da Silva , L. A. ; Coleta , J. F. B.; *Quim. Nova* **2000,** *23,*608.
9. Turova, N. Y. A.; Turevskaya, E. P.; Kessler, V. G.; Yanovskaya, M. L.*; J. Sol-Gel Sci. Technol.* **1994,** *2*, 17.
10. Hubert-Pfalzgraf, L. G.*; Appl. Organomet. Chem.* **1992**, *6*, 627.
11. Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P.; *Metal Alkoxides*, Academic Press: London, 1978, p. 118.
12. Sanchez, C.; Livage, J.; *New J. Chem.* **1990**, *14*, 513.
13. Livage, J.; Henry, M.; Sanchez, C.; *Prog. Solid State Chem.* **1988**, *18*, 259.
14. Hubert-Pfalzgraf, L. G.; Sirio, C.; Abada, V.; Bois, C.; Vaissermann, J.; *Abstr. Pap. Am. Chem. Soc.* **1995**, *1*, 20.
15. Daniele, S.; Hubert-Pfalzgraf, L.G.; Daran, J.-C.; *Polyhedron* **1994**, *13*, 927.
16. Zucchini, U.; Dall'Occo, T.; Angelini, A.; *J. Mol. Catal.* **1993**, *82*, 45
17. Malpezzi, L.; Zucchini, V.; Dall'Occo, T.; *Inorg. Chem. Acta* **1991**, *180*, 245.
18. Merbach, A.; Pitteloud, M. N.; Jaccard, P.; *Helv. Chim. Acta* **1972**, *55*, 44.
19. Cullity, B. D.; *Elements of X-Ray Diffraction*; Addison-Wesley: Massachussetts, 1967, p. 262.
20. Bradley, D. C.; Chudzinska, H.; Frigo, D. M.; Hammond, M. E.; Hursthouse, M. B.; Mazid, M. A.; *Polyhedron* **1990**, *9*, 719.
21. Imai, T.; Shimoi, M.; Ouchi, A.; *Bull. Chem. Soc. Jpn.* **1987**, *60*, 159.
22. Krishnamurthy, S. S.; Soudararajan, S.; *J. Less- Common Metals* **1987**, *16*, 1.
23. Caulton, K. G.; Hubert-Pfalzgraf, L. G.; *Chem. Rev.* **1990**, *90,* 969.
24. Miyano, M. H.; Melios, C. B.; Ribeiro, C. A.; Redigolo, H.; Ionashiro, M.; *Thermochim. Acta* **1993**, *221*, 53.
25. Preuss, A.; Green, R.; *J. Solid State Chem.* **1994,** *110*, 363.
26. JCPDS – International Centre for Diffraction Data **1996**, cards numbers 21-1276 (rutile) and 34-0394 (cerianite).
27. Guinier, A.; *X-ray Diffraction in Crystals, Imperfect Crystals, and Amourphous Bodies*, Dover Publications: New York, 1994, p. 121.
28. Roginskaia, Y. E.; Morozova, O.V.; Loubnin, E. N.; Popov, A. V.; Ulitina, Y. I.; Zhurov, V. V.; Ivanov, S. A.; Trasatti, S.; *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1707.
29. Roginskaia, Y. E.; Morozova, O.V.; *Electrochim. Acta* **1995**, *40*, 817.