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THERMAL AND CRYSTALOGRAPHIC STUDIES OF MIXTURE La_2O_3–SrO PREPARED VIA REACTION IN THE SOLID STATE

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Abstract

The compound obtained via state solid reaction of the La_2O_3 and SrO oxides and expose the room atmosphere shows the crystallographic data of the compound reported as La_2SrO_x. However, thermogravimetric, differential thermal analysis and XRD with controlled temperature indicated that the stoichiometry of the compound is $2La(OH)_3$–$SrCO_3$, which structural parameters were determined by using the Rietveld method. It was verified that when the compound exposed at room atmosphere, the mixture oxide absorbs H_2O and CO_2 producing hydroxide and carbonate of lanthanum and strontium, respectively, which thermal decomposition occurs by the same steps, producing the La_2O_3–SrO.

Keywords: lanthanum hydroxide, reversible thermal decomposition, strontium carbonate

Introduction

Lanthanum and strontium compounds are important precursors for alkaline earth doped lanthanum manganite preparation [1]. Besides this, there is considerable current interest in the use of alkaline earth and rare earth oxides as components in heterogeneous catalysis for the oxidative coupling of methane [2, 3].

Several investigations have been carried out on the synthesis of the ternary system Ln_2O_3–H_2O–CO_2 (*Ln*–lanthanides) [4, 5]. Wakita [6] has obtained $La_2(CO_3)_3 \cdot 8H_2O$ by the reaction between carbonates and rare-earth salts in sodium metasilicate gels. Sastry *et al.* [7] have prepared $Nd_2O_3 \cdot 2.5CO_2 \cdot 3.5H_2O$ by treating a neodymiun chloride solution with sodium carbonate solution at boiling temperature, and $Nd_2O_3 \cdot 2CO_2 \cdot 2H_2O$ by hydrolysis of the trichloroacetate. On the other hand, $SrCO_3$ is used as a high temperature standard for DTA [8, 9]. In the present work the mixture $2La(OH)_3$–$SrCO_3$ was obtained by exposure of the mixed oxides La_2O_3–SrO in the laboratory atmosphere and investigated by TG and DTA in a dynamic atmosphere and X-ray diffraction (XRD) under variable temperature to characterize the crystal structure of the samples.

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Experimental

Materials

High purity La_2O_3 (MERCK 99.5%) and SrO (Alfa AESAR 99%) were used in this work. Typically, $2La(OH)_3$–$SrCO_3$ was prepared by exposure of the mixture La_2O_3–SrO in the laboratory atmosphere. The oxide mixture was obtained by solid state reaction of the mixture thermally treated at 1593 K for 17 h.

Methods

TG and DTA curves were obtained employing simultaneous module of thermal analysis, SDT 2960 (TA Instruments), with air synthetic and CO_2 flux of 100 mL min^{-1}, heating rate of 10°C min^{-1} and samples weighting between 14 and 16 mg. An aluminium crucible was used in the thermoanalysis measurements. X-ray powder diffraction patterns, to structural refinement, were obtained by using synchrotron radiation with λ=1.533 Å at National Laboratory of Synchroton Light (LNLS) at DRX line. High temperature powder diffraction (Siemens - D5000) was obtained by using the HTK (high-temperature camera) mounted on an Ω goniometer operating at temperatures of up to 1573 K with a position sensitive detector (PSD-50M). The Rietveld structure analysis was performed using the program DBWS9411. Elemental analysis was carried out by using a CE instrument, model EA1110 CHNS O, by flash method.

Results and discussion

The resultant compound from mixture of the La_2O_3 and SrO oxides was submitted to XRD analysis. Interplane distances and relative intensities values are in agreement with those described in the literature for the La_2SrO_x compound [10]. However, when this compound was submitted to thermogravimetric and differential thermal analysis, the decomposition is observed in four stages of the mass loss, Fig. 1a. The first mass loss is due to elimination of adsorbed water. The two following stages are ascribed to dehydration, with loss of two and one water molecules, respectively. The last mass loss is ascribed to thermal decomposition of the strontium carbonate with CO_2 liberation. It is showed in DTA curve through endothermic events and presented below by the reactions:

$$2La(OH)_3\text{–}SrCO_3 \rightarrow 2LaO(OH)\text{–}SrCO_3 + 2H_2O \qquad \text{reaction 1}$$

$$2LaO(OH)\text{–}SrCO_3 \rightarrow La_2O_3\text{–}SrCO_3 + lH_2O \qquad \text{reaction 2}$$

$$La_2O_3\text{–}SrCO_3 \rightarrow La_2O_3\text{–}SrO + CO_2 \qquad \text{reaction 3}$$

As it is well known, lanthanum and strontium oxides absorb water and carbon dioxide from atmosphere with great easiness. Thus, lanthanum hydroxide and strontium carbonate formation is ascribed to the exposition of the resultant compound of

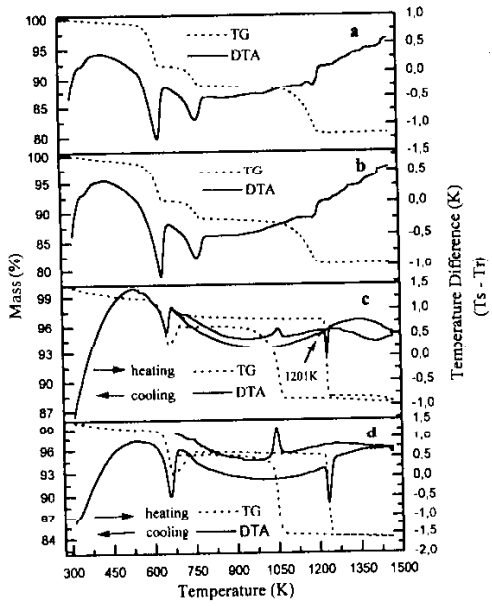

Fig. 1 TG and DTA curves of the $2La(OH)_3$–$SrCO_3$ compound obtained in synthetic air dynamic atmosphere: a – first heating, b – heating after 24 h; c – obtained in carbon dioxide dynamic atmosphere and d – TG and DTA curves of the $La(OH)_3$ obtained in carbon dioxide dynamic atmosphere

the oxide mixture in the atmosphere due to absorption of H_2O and CO_2. In order to check the absorption, the residue was exposed to room atmosphere for twenty-four h and analyzed again. TG and DTA, curves, Fig. 1b, shown the same thermal decomposition behavior indicating that the absorption mechanism of water and carbon dioxide were not altered by the thermal treatment to which the compound was submitted in the previous analysis. TG and DTA obtained data are showed in Table 1.

The compound was submitted to elementary analysis for determination of C, H and O and the results are showed in the Table 2. Obtained values from elementary analysis and those indicated by TG analysis are similar and in good agreement with the proposal stoichiometry. Figure 1c show TG and DTA curves of the mixed compound obtained in carbon dioxide atmosphere, which present different thermal behavior to the previously observed one. A mass loss between 320 and 586 K is ascribed to loss of adsorbed water, followed by a second stage of mass loss from 591 to 656 K, corresponding to compound dehydration. In the next stage, it was observed a continuous mass gain due to CO_2 absorption. Thus, occurred the substitution of the water by CO_2 molecules in the coordination site water, forming lanthanum carbonate. The compound remains stable until 1217 K followed by an abrupt mass loss corresponding to the strontium carbonate decomposition and CO_2 liberation. These steps are confirmed by endothermic peaks in the DTA curve. An endothermic peak

at 1201 K is observed and ascribed to rhombohedric-hexagonal phases transition of the strontium carbonate [11]. In the cooling curve was observed an exothermic peak at 1054 K due to CO_2 absorption indicated by mass gain in the TG curve, resulting in the lanthanum carbonate formation again. This behavior was related to lanthanum, based on TG and DTA curves of the La_2O_3, Fig. 1d, which presenting the similar thermal behavior.

X-ray diffraction patterns at several temperatures was carried out to accomplish the thermal decomposition indicated by thermoanalysis. Figure 2 show the X-ray diffraction patterns at different temperatures of (a) mixture La_2O_3–SrO obtained by grinding, (b) SrO and (c) La_2O_3, both exposed in the room atmosphere. The X-ray diffraction reflections of mixture La_2O_3–SrO turn up at 1413 K (Fig. 2a), while before 473 K there are reflections due to $2La(OH)_3$–$SrCO_3$, according to the results of the structural refinement. It indicates that sample absorb atmospheric water and carbon dioxide. As best form to interpret the phenomenon, measures were accomplished in the precursor oxides, after exposure in the laboratory atmosphere. The temperature range used was based on decomposition temperatures obtained by thermal analysis. The results suggest that SrO (Fig. 2b) absorbs carbon dioxide going to $SrCO_3$ and La_2O_3 (Fig. 2c) absorb atmospheric water transforming in lanthanum hydroxide. Both phases are decomposed by heating in the respective oxides.

Table 1 TG and DTA results from mixed compound curve analysis in synthetic air atmosphere (100 mL min^{-1}) and hetaing rate of 10°C min^{-1}

Analysis	Initial mass/mg	TG			DTA
		Δm/mg	ΔT/ K	residue/%	endo/K
First	16.16	−0.09	313– 544	99.44	359
		−1.11	544– 645	92.57	628
		−0.55	700– 792	89.17	765
		−1.34	1043–1225	80.88	1200
After 24 h	14.88	−0.18	313– 541	98.79	363
		−0.98	541– 651	92.20	633
		−0.47	694– 786	89.05	761
		−1.17	1028–1216	81.18	1187

Table 2 Obtained results from elementary analysis of the mixed compound

Elements	Elementary analysis/%	TG/%
C	2.39	2.28
H	1.16	1.15
O	15.69	27.30 (15.17)*

* O present in the initial compound remains in the residue, in the oxide form, was not detected

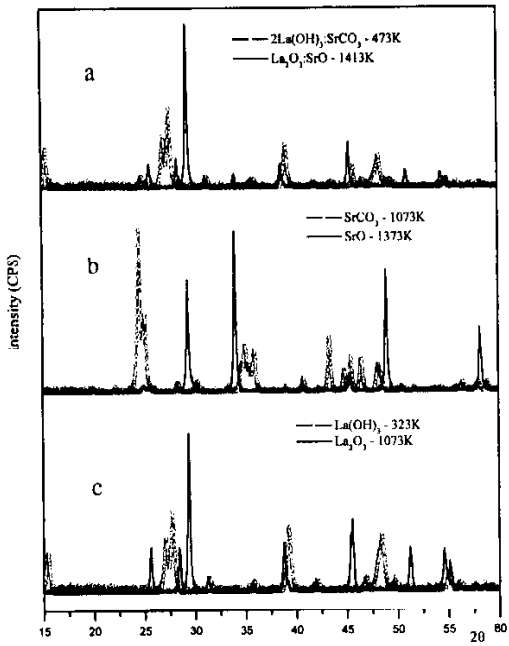

Fig. 2 XRD patterns at different temperature of a – $2La(OH)_3$–$SrCO_3$, b – $SrCO_3$ and c – $La(OH)_3$ going to La_2O_3–SrO, La_2O_3 and SrO, respectively

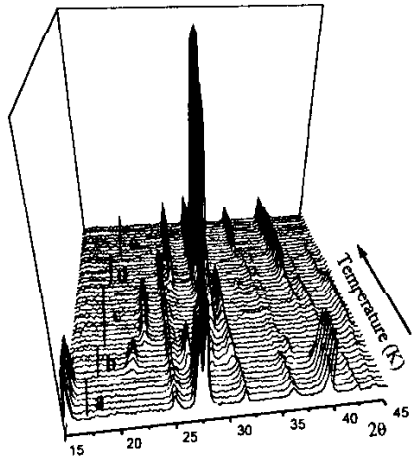

Fig. 3 XRD patterns evolution of the mixture $2La(OH)_3$–$SrCO_3$ from 493 to 1433 K showing the phases transitions (ΔT=20 K)

The thermal decomposition of the mixture was checked out with X-ray diffraction from 493 to 1433 K (Fig. 3). There are $2La(OH)_3$ (PDF n° 36-1481) and $SrCO_3$ (PDF n° 5-0418) in the region a of Fig. 3a which corresponds to the temperature range from 493 to 613 K. The peaks assigned to phases LaOOH (PDF n° 19-0656) and $SrCO_3$ in the range from 613 to 733 K are in region bof Fig. 3. The region c (733 to 993 K) in Fig. 3 show $La_2O_2CO_3$ (PDF n° 22-1127) and $SrCO_3$ structural phases. La_2O_3 (PDF n° 5-0602) and $SrCO_3$ phases are present in the region d (993 to 1153 K). Figure 3e corresponds to the temperature range from 1153 to 1413 K showing SrO (PDF n° 6-0520) and La_2O_3. The mass losses verified in the thermal analysis were found in same temperatures by X-ray diffraction analysis through the structural patterns evolution. Although, it was already observed by X-ray diffraction, the $La_2O_2CO_3$ formation from the LaOOH decomposition does not show a mass loss. Such an absence of mass loss may be caused by a sharing of the CO_3^{2-} group between strontium carbonate and lanthanum oxide.

Table 3 Discrepancy factors and phases fractions obtained by Rietveld refinement

Phase name	$La(OH)_3$	$SrCO_3$
Fraction (%)	70	30
R_{Bragg}	2.33	4.53
R_f	1.45	2.03

Structural refinement by Rietveld method was carried out to determine the phases quantities in the mixture. $La(OH)_3$ was refined in the space group P63/m and atomic parameters based on reference [12]. Strontium carbonate was refined in the space group Pmcn and atomic parameters based on reference [13]. Refinement results show 70% of $La(OH)_3$ and 30% of $SrCO_3$ to exposed mixture with good structural refinement discrepancy factors (Table 3). These results suggest that the JCPDS-ICDD n° 42-0343 was mistakenly attributed to the La_2SrO_x compound, because the X-ray diffraction patterns are due to the mixture $2La(OH)_3$–$SrCO_3$.

Conclusions

La_2O_3 and SrO when exposed in the laboratory atmosphere absorbed water and carbon dioxide to form $La(OH)_3$ and $SrCO_3$. The absorption process may be used as a CO_2 reversible sensor because it causes a remarkable bulk expansion. $La_2O_2CO_2$ formation accomplished by XRD was not detected by thermoanalysis. This result suggest that are a sharing of the CO_3^{2-} group between strontium carbonate and La_2O_3.

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