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Short communication

The solid state reaction between lanthanum oxide and strontium carbonate

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Abstract

The reaction between lanthanum oxide and strontium carbonate was studied non-isothermally between 350 and 1150 °C at different heating rates, intermediates and the final solid product were characterized by X-ray diffractometry (XRD). The reaction proceeds through formation of lanthanum oxycarbonate $La_2O(CO_3)_2$, lanthanum dioxycarbonate $La_2O_2CO_3$, and non-stoichiometric strontium lanthanum oxide La_2SrO_x ($x = 4 + \delta$). La_4SrO_7 was found to be the final product which begins to form at ∼700 °C. Li^+ doping enhances the formation of the final product as well as commencement of the reactions at lower temperatures.

Keywords: La_2O_3; Li^+-doping; $SrCO_3$; La_4SrO_7; DTA; TG; X-ray

1. Introduction

Recently, lanthanum-based perovskites have attracted much attention due to their electrical, magnetic, structural and catalytic properties [1–6].

Doping metal oxides may strongly influence solid state reactions [7]. Li^+ incorporation increases the point defects in the La_2O_3 lattice [8]. Zaki et al. [7] reported that formation of $SrAl_2O_4$ was enhanced by Li^+ doping and was retarded by Cd^{2+} doping.

The present paper examines phase changes in La_2O_3 and $SrCO_3$ powder mixtures at different stages in the reaction, and the effect of doping with Li^+.

2. Experimental

2.1. Materials

La_2O_3, with hexagonal structure, was a 99.99% pure product of Feinchemie Eisenach Laboratories (Germany). It was calcined at 800 °C for 2 h, prior to use.

Uncalcined lanthanum oxide was doped with Li^+ at 3, 5 and 10 mol% of La. A calculated amount of La_2O_3 was immersed in impregnation solution containing the required amount of LiOH (Naser Company, AR-grade), in doubly distilled water. The slurry was dried over a water bath with constant stirring and calcined subsequently at 600 °C for 2 h. The resulting materials are indicated in the text as (% Li-La_2O_3). $SrCO_3$ was 99.9% pure Merck product (Germany).

Powder Mixtures were prepared in accordance with Hulbert and Smoak [9], amounts of samples of La_2O_3 and $SrCO_3$ in a 1:1 mole ratio, were weighed to the nearest milligram and thoroughly mixed by first tumbling the dry powders together for 48 h and then blending with a mortar and pestle. The resulting mixtures were dried at 110 °C for 24 h and kept over $CaCl_2$ until further use.

Samples of the dried mixture ($SrCO_3 + La_2O_3$) were calcined at 400, 520 and 800 °C for 0.5 h and at 1150 °C for 5 h. Doped samples were calcined at 350, 500 and 700 °C for 0.5 h and at 1000 °C for 5 h in a static atmosphere of air. The desired temperatures were selected in view of the thermal analysis results. The samples were placed in sintered alumina crucibles inserted into a muffle furnace controlled within 1 °C of the set point. The resulting materials were kept over $CaCl_2$.

Thermal analysis was performed with a 7-series Perkin-Elmer Analyzer. Thermogravimetry (TG) and differential

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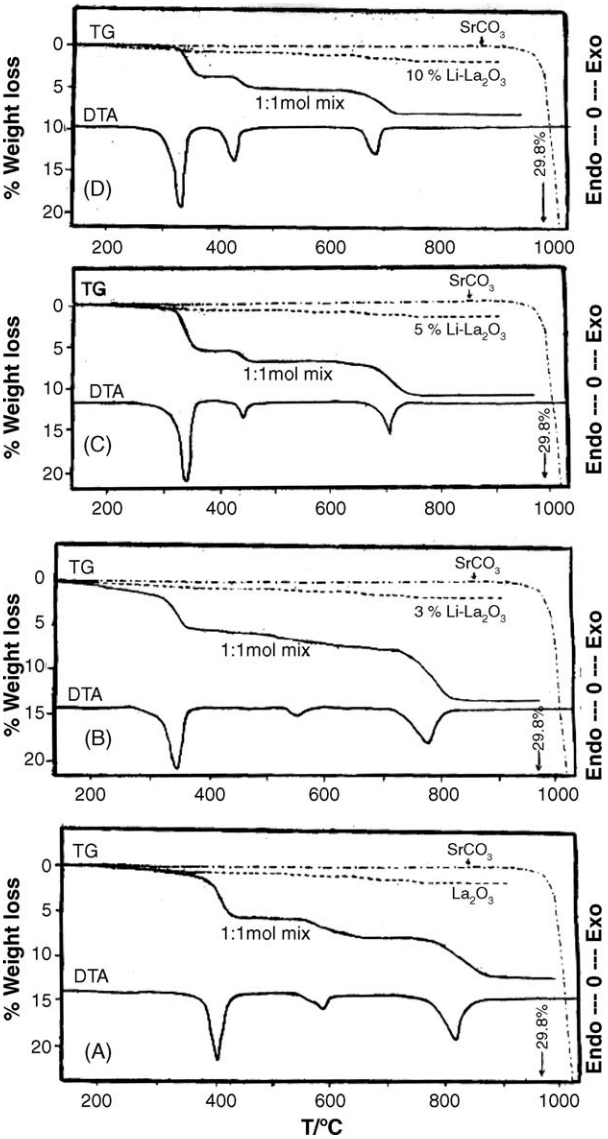

Fig. 1. TG and DTA curves for (A) pure La_2O_3 (- - - -) and $SrCO_3$ (– – –) and a molar mixture of both (–); (B) for 3% Li-La_2O_3 (- - - -) and $SrCO_3$ (– – –) and a molar mixture of both (—); (C) for 5% Li-La_2O_3 (- - - -) and $SrCO_3$ (– – –) and a molar mixture of both (—); (D) for 10% Li-La_2O_3 (- - -) and $SrCO_3$ (– – –) and a molar mixture of both (—) at 10 °C/min, in a dynamic atmosphere of air (20 ml/min.).

thermal analysis (DTA) curves were recorded to 1000 °C at heating rates of 5–20 °C/min. in a dynamic atmosphere of air (20 ml/min). Ten to 15 mg portions of the test sample were used for the TG measurements and highly sintered η-Al_2O_3 was used as the reference material for the DTA measurements. Shifts in the DTA peak temperature ($T_{\max}$) as a function of the heating rate (θ) were used to calculate the activation energy (ΔE, kJ/mol) according to [10]:

$$E = -R/bd \log \theta \, d(1/T_{\max})$$

where R is the gas constant (8.314 kJ/mol) and b is a unitless constant (=0.457).

XRD powder patterns were obtained with a JSX-60P JEOL diffractometer (Japan) with Ni-filter and Cu Kα radiation

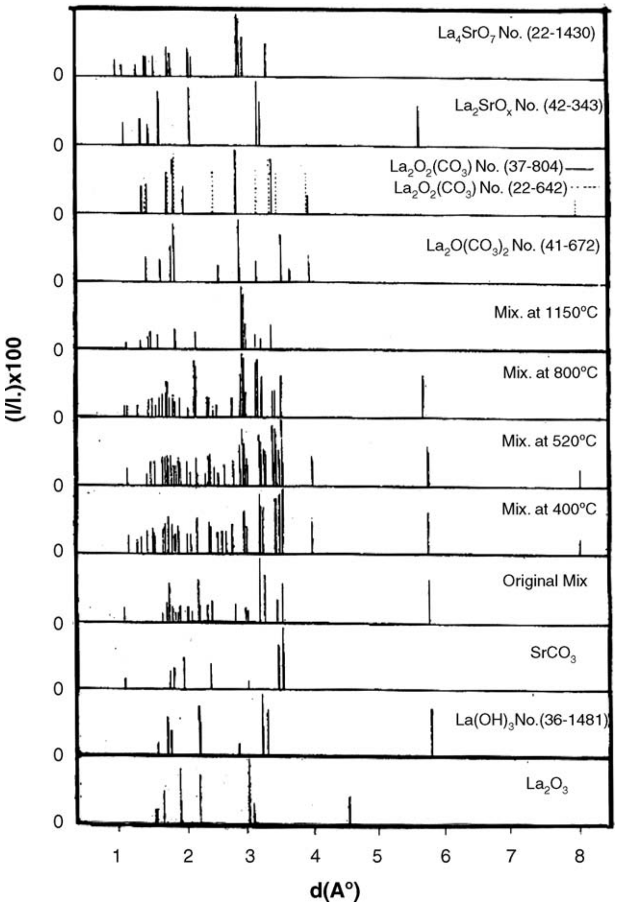

Fig. 2. X-ray diffraction pattern for the reaction of pure La_2O_3, $SrCO_3$ mixtures and calcination products at the temperatures indicated, and standard data for comparison purposes.

(λ = 1.5418 Å). The relative intensities ($I/I°$) and d-spacings (Å) are compared to standard diffraction patterns in the ASTM powder diffraction File [11] and JCPDS standards [12].

3. Results and discussion

The TG curves of pure La_2O_3, $SrCO_3$ and the mixture are shown in (Fig. 1A). $SrCO_3$ does not decompose below 930 °C. The weight loss of La_2O_3 result from the removal of water and carbonate as well as the transformation of $La(OH)_3$ to La_2O_3 [13]. The reaction between La_2O_3 and $SrCO_3$ shows three endothermic weight losses. the first commences near 290 °C, peaks at 400 °C and slows at 470 °C, consistent with the formation of $La_2O(CO_3)_2$ and $La_2O_2CO_3$. The activation energy calculated is (E = 54 kcal/mol).

The XRD patterns for the calcined mixtures are given in (Fig. 2). Fig. 2 also shows data for crystalline phases of La_2O_3, $La(OH)_3$, $La_2O(CO_3)_2$, $La_2O_2CO_3$, La_2SrO_x ($x = 4 + \delta$) [12] and La_4SrO_7 for comparison purposes. For the original mixture, diffraction data should be indexed to hexagonal $La(OH)_3$ (36–1481) [12] as a result of aging the powder mixture for a long time in air (48 h) which is in agreement with the literature [13,14].

Heating at 400 °C for 0.5 h does not result in a significant departure from the initial composition (La_2O_3, $La(OH)_3$ and $SrCO_3$), except for the formation of a new phase identified as $La_2O(CO_3)_2$ (41–672) [11].

Raising the temperature to 520 °C results in the appearance of $La_2O_2CO_3$ as a major compound. The XRD pattern (Fig. 2) shows the characteristic lines of crystalline $La_2O_2CO_3$ (37–804) and (22–642) [12] besides lines characteristic to a new phase identified as La_2SrO_x ($x = 4 + \delta$) (42–343) [12], as a minor component.

The second thermal event, maximized at 589 °C (Fig. 1A), ending at 617 °C, the activation energy calculated ($E = 47$ kcal/mol) is consistent with the decomposition of the oxycarbonate phases.

Above 800 °C, the third process slows down and the weight becomes invariant at ~850 °C (Fig. 1A). $T_{max} = 815$ °C, the activation energy calculated ($E = 78.8$ kcal/mol).

The XRD pattern for the mixture calcined at 800 °C for 0.5 h. (Fig. 2) indicates the presence of La_2SrO_x besides the formation of another new phase La_4SrO_7 (22–1430) [12], the intensity of the characteristic lines indicate that La_2SrO_x begins to decompose and that La_4SrO_7 is the dominant phase.

The final X-ray pattern at 1150 °C for 2 h (Fig. 2) proves the final phase formed in the reaction is only La_4SrO_7 (22–1430) [12].

The X-ray diffraction results (Figs. 3–5) for reaction mixtures calcined at different temperatures (350–1150 °C), showed no

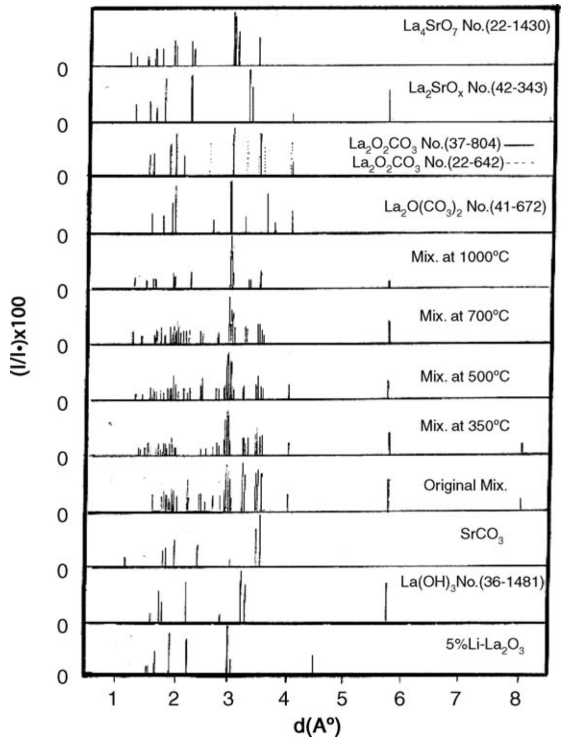

Fig. 4. X-ray diffraction pattern for the reaction of 5% Li-La_2O_3, $SrCO_3$ and calcination products at the temperatures indicated, and standard data for comparison purposes.

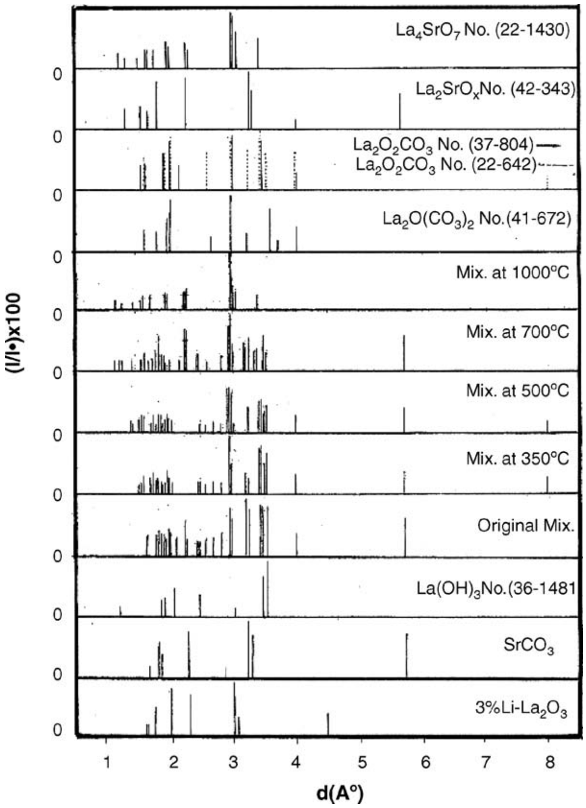

Fig. 3. X-ray diffraction pattern for the reaction of 3% Li-La_2O_3, $SrCO_3$ mixtures and calcination products at the temperatures indicated, and standard data for comparison purposes.

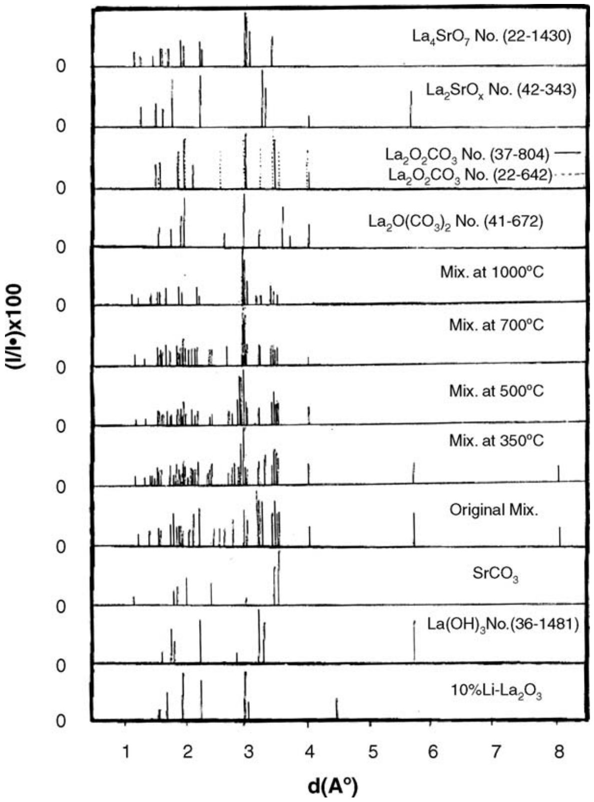

Fig. 5. X-ray diffraction pattern for the reaction of 10% Li-La_2O_3, $SrCO_3$ and calcination products at the temperatures indicated, and standard data for comparison purposes.

diffraction pattern for SrO, thus indicating that gas evolution was not from decomposition of $SrCO_3$ to SrO.

Li^+ doping decreases the solid state reaction temperatures of all three thermal events, results are shown in Fig. 1B–D. Li^+ ion decreases the commencement temperature by ∼50 °C and the final temperature by ∼150 °C.

XRD and IR results (not shown) indicate that doping of La_2O_3 with Li^+ does not alter the products formed, $La_2O(CO_3)_2$ is the initial product and La_4SrO_7 is the final product. Doping enhances the early appearance of the intermediates even in the original mixture after aging for 48 h. The results indicate no separate phases involving Li^+. These results are in line with the thermogravimetry results in (Fig. 1) in proving formation of solid solutions of the dopant in La_2O_3 involving all the added of Li^+.

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