

## **PHASE FORMATION STUDY OF ALKALINE EARTH-DOPED LANTHANUM CHROMITES**

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### **Abstract**

In this paper the influence of alkaline-earth admixtures on the synthesis of lanthanum chromites of  $\text{La}_{1-x}\text{M}_x\text{CrO}_3$  ( $x=0; 0.3$ ;  $M=\text{Ca, Sr, Ca+Sr}$ ) type was studied.

The formation mechanism as well as the phase composition evolution, under non-isothermal and isothermal conditions, were investigated by thermal analysis and X-ray diffraction.

The structure of the compounds and of the solid solutions formed depends on the solute type by means of the structural distortion induced. The crystallinity of the chromites obtained is obviously influenced by both the temperature and the thermal treatment plateau.

**Keywords:** lanthanum chromite, perovskite, solid solution, thermal analysis

### **Introduction**

Lanthanum chromites-based solid solutions have high potential as electrodes for magnetohydrodynamic generators (MHD) or interconnects for solid oxide fuel cells (SOFC) [1–3].

It has been found that the partial substitution of alkaline-earth metal for lanthanum ions is profitable to increase the chemical stability and electric conductivity of pure lanthanum chromite [4–7]. This compound exhibits a distorted perovskite structure due to  $\text{Cr}^{3+}$  ions which determine the Jahn–Teller effect.  $\text{LaCrO}_3$  is orthorhombic at room temperature and undergoes a phase transition from orthorhombic (Pbnm) to hexagonal (rhombohedral  $R3m$ ) structure at about 240 to 280°C [1, 8, 9]. The alkaline-earth metal incorporation on  $\text{La}^{3+}$  sites determines the disturbing of cooperative ordering of Jahn–Teller distorted  $\text{Cr}^{3+}\text{O}_6$  octahedra of orthorhombic form. As a result, a shift towards lower temperatures of the orthorhombic  $\rightarrow$  hexagonal phase transition occurs. Thus, the transformation temperature of doped  $\text{LaCrO}_3$  is influenced by the solute type and its concentration [10–12].

## Experimental

Pure  $\text{LaCrO}_3$  as well as solid solutions of  $\text{La}_{1-x}\text{M}_x\text{CrO}_3$  ( $x=0.3$ ;  $M=\text{Ca, Sr, Ca+Sr}$  in equimolecular mixture) type were prepared by the classical ceramic method from p.a. grade oxides and carbonates:  $\text{La}_2\text{O}_3$  (Merck),  $\text{Cr}_2\text{O}_3$  (Loba),  $\text{CaCO}_3$  (Merck) and  $\text{SrCO}_3$  (Fluka).

The initial oxide compositions (mass%) of the samples investigated are listed in Table 1.

**Table 1** Starting oxide composition of the samples investigated

Symbol	Formula	Oxide composition/mass%			
		$\text{La}_2\text{O}_3$	$\text{Cr}_2\text{O}_3$	CaO	SrO
LC	$\text{LaCrO}_3$	68.19	31.81	–	–
LCC	$\text{La}_{0.7}\text{Ca}_{0.3}\text{CrO}_3$	57.46	38.30	4.24	–
LSC	$\text{La}_{0.7}\text{Sr}_{0.3}\text{CrO}_3$	55.47	36.97	–	7.56
LCSC	$\text{La}_{0.7}\text{Ca}_{0.15}\text{Sr}_{0.15}\text{CrO}_3$	56.45	37.62	2.08	3.85

The raw materials were proportioned, homogenized by wet procedure in a planetary ball mill using absolute ethanol as dispersing medium and then dried.

In order to evidence the changes occurring during thermal treatments, DTA and TG investigations of raw materials as well as of the mixtures mentioned were performed. The powders were heated in static air atmosphere from ambient temperature to  $1000^\circ\text{C}$  with  $5^\circ\text{C min}^{-1}$ .

In order to characterize the phase composition of the samples, X-ray diffraction analyses, using  $\text{CuK}_\alpha$  radiation, were carried out both on samples resulting from non-isothermal treatments up to different temperatures and on samples resulting from isothermal treatments. The same method was used for the structural characterization of chromites.

The mixtures were shaped by uniaxially pressing at 100 MPa into pellets of  $\phi=20$  mm and  $h=2-3$  mm and thermally treated at temperatures in the  $1000-1400^\circ\text{C}$  temperature range with 3 h plateau.

## Results and discussions

### *Non-isothermal treatments*

Thermal analysis data for the raw materials used are presented in Table 2.

Thermal effects recorded are in agreement with the literature data for the mentioned raw materials. In case of  $\text{La}_2\text{O}_3$  source, the well known tendency of this compound to take up moisture and  $\text{CO}_2$  from atmosphere is obvious.

Thermal analysis of the mixtures studied (Fig. 1) shows, as a general feature, the presence on the DTA curves of the effects specific to  $\text{La}_2\text{O}_3$  ( $380$  and  $540^\circ\text{C}$ ) as well as the existence of an endothermic effect as a result of the complex processes:

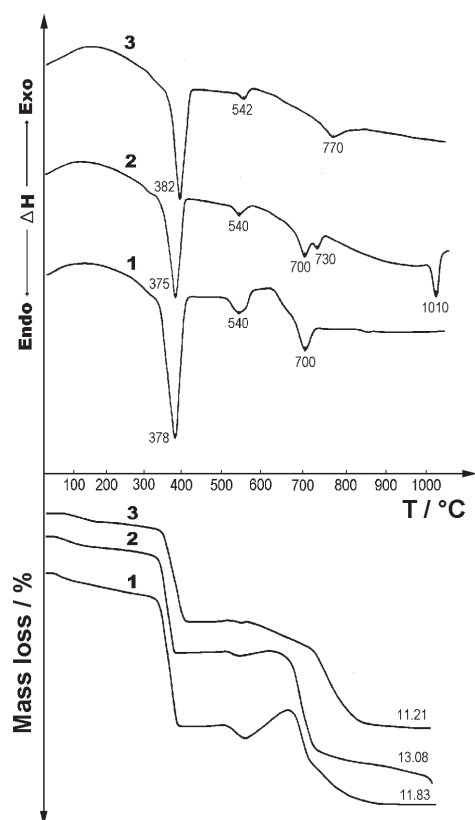


Fig. 1 DTA and TG curves of the mixtures: 1 – LC; 2 – LCC; 3 – LSC

$\text{Cr}^{3+} \rightarrow \text{Cr}^{6+}$  oxidation with  $\text{La}_2\text{CrO}_6$  formation, which subsequently decomposes into  $\text{LaCrO}_3$ . If in case of the pure chromite (LC) and calcium-doped chromite (LCC) the last effect appears at  $700^\circ\text{C}$ , in case of the mixtures with strontium (LSC and LCSC) it is recorded at  $770$  and  $735^\circ\text{C}$ , respectively.

**Table 2** Thermal behavior of the raw materials used

Raw material	Thermal effect endo/ $^\circ\text{C}$	Assignment
$\text{La}_2\text{O}_3$	380	$\text{La}(\text{OH})_3$ dehydration
	530	$\text{La}_2\text{O}_2 \cdot \text{CO}_3$ decomposition
	700	$\text{La}_2\text{O}_2 \cdot \text{CO}_3$ decomposition
$\text{Cr}_2\text{O}_3$	370	$\text{Cr}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ dehydration
$\text{CaCO}_3$	758	$\text{CaCO}_3$ decomposition
$\text{SrCO}_3$	878	rhombohedral $\rightarrow$ hexagonal $\text{SrCO}_3$ phase transition
	1052	$\text{SrCO}_3$ decomposition

In case of mixtures with dopants, TG curves (and even DTA curve for the mixture with calcium) show the effects due to alkaline-earth carbonates decomposition. These processes occur simultaneously with the formation of some compounds:  $\text{CaCrO}_4$  (faster) and  $\text{SrCrO}_4$  (slower). The endothermic effect at  $1010^\circ\text{C}$  on the DTA curve of the LCC mixture is probably due to  $\text{CaCrO}_4$  incorporation into  $\text{LaCrO}_3$  structure with  $\text{O}_2$  release, according to equation:



In order to clarify the solid solutions formation mechanism and to establish the composition of the intermediate compounds, the initial mixtures were submitted to some non-isothermal treatments until various temperatures (560, 630, 660, 740, 880,  $1040^\circ\text{C}$ ). The quenched powders were analyzed by X-ray diffraction.

X-ray diffraction results for the mixtures thermally treated under non-isothermal conditions are presented in Table 3.

**Table 3** Phase composition of the mixtures thermally treated under non-isothermal conditions until various temperatures

Symbol	Temperature/ $^\circ\text{C}$	Phase composition
LC	560	$\text{La}_2\text{CrO}_6$ (+++), $\text{La}_2\text{O}_3$ (++) , $\text{Cr}_2\text{O}_3$ (++)
	660	$\text{La}_2\text{CrO}_6$ (++++), $\text{La}_2\text{O}_3$ (+) , $\text{Cr}_2\text{O}_3$ (+)
	740	$\text{LaCrO}_3$ (+++), $\text{La}_2\text{CrO}_6$ (++)
	1050	$\text{LaCrO}_3$ (++++)
	630	$\text{La}_2\text{CrO}_6$ (++++), $\text{La}_2\text{O}_3$ (++) , $\text{Cr}_2\text{O}_3$ (+++), $\text{CaCO}_3$ (+++)
LCC	740	$\text{LaCrO}_3$ (+++), $\text{CaCrO}_4$ (++++), $\text{La}_2\text{CrO}_6$ (+)
	1040	$\text{LaCrO}_3$ (++++), $\text{CaCrO}_4$ (++)
LSC	790	$\text{LaCrO}_3$ (+++), $\text{La}_2\text{CrO}_6$ (+++), $\text{SrCrO}_4$ (+++), $\text{La}_2\text{O}_3$ (++) , $\text{Cr}_2\text{O}_3$ (++)
	1040	$\text{LaCrO}_3$ (++++), $\text{SrCrO}_4$ (++) , $\text{La}_2\text{CrO}_6$ (t)

++++ – very intense; +++ – intense; ++ – medium; + – weak; t – traces

One may notice that in the presence of the admixtures the formation of the single phase with  $\text{LaCrO}_3$  structure is hindered.

#### *Isothermal treatments*

The solid solution formation was studied for mixtures thermally treated at 1000, 1200 and  $1400^\circ\text{C}$  with 3 h plateau.

XRD data for the mixtures thermally treated under isothermal conditions are listed in Table 4.

**Table 4** Phase composition of the mixtures thermally treated under isothermal conditions

Symbol	Phase composition and Temperature/°C		
	1000	1200	1400
LC	LaCrO <sub>3</sub> (++++) La <sub>2</sub> CrO <sub>6</sub> (t)	LaCrO <sub>3</sub> (++++)	LaCrO <sub>3</sub> (++++)
LCC	(La,Ca)CrO <sub>3</sub> (++++) La <sub>2</sub> O <sub>3</sub> (t)	(La,Ca)CrO <sub>3</sub> (++++)	(La,Ca)CrO <sub>3</sub> (++++)
LSC	(La,Sr)CrO <sub>3</sub> (++++) SrCrO <sub>4</sub> (++) La <sub>2</sub> CrO <sub>6</sub> (+)	(La,Sr)CrO <sub>3</sub> (++++) SrCrO <sub>4</sub> (+)	(La,Sr)CrO <sub>3</sub> (++++)
LCSC	(La,Ca,Sr)CrO <sub>3</sub> (++++) SrCrO <sub>4</sub> (+) La <sub>2</sub> CrO <sub>6</sub> (t)	(La,Ca,Sr)CrO <sub>3</sub> (++++)	(La,Ca,Sr)CrO <sub>3</sub> (++++)

++++ – very intense; +++ – intense; ++ – medium + – weak; t – traces

In case of LC mixture, XRD data evidence at 1000°C as major phase the orthorhombic compound LaCrO<sub>3</sub> (identified by all its main peaks). A small amount of La<sub>2</sub>CrO<sub>6</sub> was detected. The temperature increase leads to complete reactions so at 1200°C a single-phase ceramic material (LaCrO<sub>3</sub> perovskite oxide) was obtained. The higher the temperatures used (1400°C), the higher the crystallinity of compounds obtained.

The phase composition of the mixture LCC at 1000°C consists of (La,Ca)CrO<sub>3</sub> perovskite phase and La<sub>2</sub>O<sub>3</sub> traces which disappear with temperature increase. As a difference from the LC mixture, in this case the main diffraction peaks are not splitted, showing that calcium admixture favours the transition from an orthorhombic structure (Pbnm) to a hexagonal one (rhombohedral R3m). This effect, of alkaline-earth admixture, was pointed out in literature [2], too.

For the mixture with strontium, LSC, XRD data show at 1000°C a multiphase composition consisting of (La,Sr)CrO<sub>3</sub> solid solution as major phase and SrCrO<sub>4</sub> and La<sub>2</sub>CrO<sub>6</sub> as secondary phases enough important quantitatively. This could be explained in terms of the much lower solubility limit of SrCrO<sub>4</sub> in LaCrO<sub>3</sub> perovskite ( $x=0.1$  at 950°C) in comparison to that one of CaCrO<sub>4</sub> ( $x=0.3$  at the same temperature) [10, 11]. The above results agree with thermal analysis data which evidenced the slower incorporation of Sr at lower temperatures. At 1200°C, due to the reactions promotion, the secondary phases are quantitatively reduced (SrCrO<sub>4</sub>) or vanished (La<sub>2</sub>CrO<sub>6</sub>). Just at 1400°C the mixture is single-phase as a consequence of the total incorporation of SrCrO<sub>4</sub> in LaCrO<sub>3</sub>. From the structural point of view the same trend of perovskite phase transition towards the hexagonal (rhombohedral) symmetry was noticed.

In case of the mixture LCSC (Ca and Sr in equimolecular mixture) strontium incorporation occurs easier due to its smaller concentration ( $x=0.15$ ). Consequently, at 1200°C, SrCrO<sub>4</sub> is already completely incorporated in LaCrO<sub>3</sub> structure, yielding a single-phase (La,Ca,Sr)CrO<sub>3</sub> solid solution.

The great number of species contained by the solid solution determines a crystalline disorder, which makes difficult from structural view point to identify its crys-

tallographic symmetry. Anyway, a slight splitting of the diffraction peaks seems to appear again, which let us assume the existence of a mixture of orthorhombic and hexagonal phases.

### Structural data

This study used samples thermally treated in 2 stages: a presintering at 1000°C/10 h and a sintering at 1300°C/4 h. Structural data and phase composition evolution for these samples are presented in Table 5 and Fig. 2.

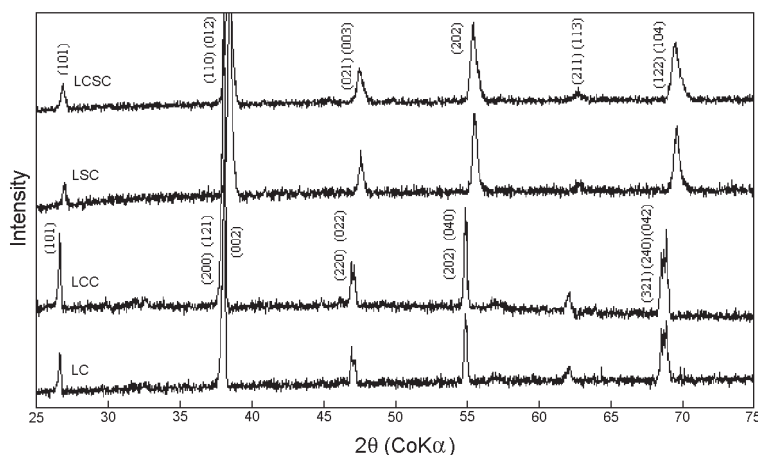
The unit cell parameters, the unit cell volume and the crystallographic density were determined. One can notice that the orthorhombic → hexagonal phase transition induced by the dopants is accompanied by a significant increase both of the unit cell volume (due to the *c* parameter doubling) and of *Z* (the number of chemical formula units/unit cell).

As was expected, the crystallographic density decreases for the samples with admixtures, especially for those ones with calcium.

**Table 5** Structural data of the chromites sintered at 1300°C

Sample	<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å	<i>V</i> /Å <sup>3</sup>	<i>Z</i>	$\rho_{\text{theoretical}}/\text{g cm}^{-3}$	Structure
LC	5.5117	7.7568	5.4760	234.1160	4	6.766	orthorhombic
LCC	5.4317	–	13.2856	339.4560	6	6.069	hexagonal
LSC	5.4789	–	13.3804	347.8440	6	6.331	hexagonal
LCSC	5.4682	7.6950	5.4373	228.7896	4	6.210	orthorhombic+ hexagonal

Figure 2 shows single-phase compositions for all the mixtures thermally treated in the conditions mentioned above.



**Fig. 2** XRD patterns of the compositions studied

## Conclusions

- Concerning the formation mechanism of the chromites, one can observe the trend of  $\text{Cr}^{3+}$  to oxidize to the maximum valence state  $\text{Cr}^{6+}$  below  $1000^\circ\text{C}$ , with the formation of  $\text{La}_2\text{CrO}_6$ , followed in case of substituted chromites, by the  $\text{CaCrO}_4$  and  $\text{SrCrO}_4$  formation.
- In case of the strontium-doped chromites, the reaction is slower than in case of the calcium-doped chromites. This behavior was proved by the lower temperature incorporation of  $\text{CaCrO}_4$  than that one of  $\text{SrCrO}_4$  in the  $\text{LaCrO}_3$  perovskite structure.
- Structural data show, for the substituted chromites, a clear trend of distortion which involves an orthorhombic  $\rightarrow$  hexagonal (rhombohedral) phase transition. This transformation is accompanied by a significant increase of the unit cell volume.

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