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Thermochimica Acta 390 (2002) 61–66

thermochimica acta

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Dilatometric and high temperature X-ray diffractometric studies of $La_{1-x}M_xCrO_3$ ($M = Sr^{2+}$, Nd^{3+}, $x = 0.0$, 0.05, 0.10, 0.20 and 0.25) compounds

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Received 11 June 2001; received in revised form 5 August 2001; accepted 8 December 2001

Abstract

The phase transition, bulk and lattice thermal expansion behaviour of the strontium and neodymium substituted lanthanum chromites have been studied by dilatometry and high temperature X-ray powder diffractometry from room temperature to 1123 and 1073 K, respectively, in static air. The studies revealed that the temperature of the orthorhombic to rhombohedral phase transition, which occurred at ~550 K in undoped $LaCrO_3$, decreased on substitution of Sr^{2+} ions and increased on substitution of Nd^{3+} ions, systematically. However, the coefficients of average linear and volume thermal expansion (α_l and α_v) of $LaCrO_3$ showed a marginal increase on Sr^{2+} substitution to different extent, whereas a reverse trend was observed with Nd^{3+} substitution. The phase transition temperatures and α_l and α_v of the compounds as determined by dilatometric and high temperature X-ray diffractometric methods are reported.

Keywords: Strontium and neodymium substituted lanthanum chromites; Phase transitions; Thermal expansion

1. Introduction

$LaCrO_3$ and its strontium substituted compounds, $La_{1-x}Sr_xCrO_{3-\delta}$, find wide spread applications due to their high electrical conductivity and refractory properties [1–4]. $LaCrO_3$ is orthorhombic at room temperature, undergoes crystallographic phase transitions first to the rhombohedral (hexagonal) and then to the cubic modification at higher temperatures [5,6]. In case of $La_{1-x}Sr_xCrO_{3-\delta}$ compounds, it is reported that depending up on the experimental conditions of synthesis and their Sr^{2+} content, either the phase transition temperature is lowered or in some cases the rhombohedral phase is stabilized at room temperature [4,5]. While many investigators have reported the synthesis, characterization and some thermophysical properties of these compounds, very little is known on their thermal expansion behaviour. Likewise, no data is available on suitable trivalent metal ion substituted $LaCrO_3$ compounds, and on the effect of such substitution on their phase transition and thermal expansion characteristics. In view of this, studies on $La_{1-x}M_xCrO_3$ ($M = Sr^{2+}$, Nd^{3+}, $x = 0.0$, 0.05, 0.10, 0.20 and 0.25) compounds have been undertaken. For this purpose, the above mentioned compounds were prepared, characterized and their phase transition, bulk and lattice thermal expansion behaviour were studied by means of dilatometry and high temperature X-ray diffractometry in the temperature range from ambient to 1123 K in air.

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0040-6031/02/$ – see front matter
PII: S0040-6031(02)00003-5

2. Experimental

The undoped and Sr^{2+} and Nd^{3+} substituted lanthanum chromites were prepared by a standard solid state reaction starting from well heated La_2O_3, Cr_2O_3, $SrCO_3$ and Nd_2O_3 in their appropriate molar ratios. The mixtures were uniformly mixed and heated at 1423 K in air for 48 h with several intermittent grindings. For the identification of compounds, the XRD patterns were recorded using monochromatic Cu Kα radiation on a Philips X-ray diffractometer Model PW 1729. The bulk thermal expansion was measured up to 1123 K in air, as a function of temperature on an LKB 3185 fused quartz thermo dilatometer. The high temperature X-ray powder diffraction studies were carried out using an MRC Model X-86-N3 high temperature diffractometer attachment. A small amount of finely ground sample was mounted on a Pt–40% Rh stage as heating element. A Pt/Pt–13% Rh thermocouple, spot welded to the bottom of the stage was used for the temperature measurement. The temperature was controlled by an MRC-Model X-8600-5000-2 proportional temperature controller. The XRD patterns were recorded in static air at different temperatures up to 1073 K in the range of $20 < 2\theta < 70^\circ$ with a scan rate of 1°/min. The unit cell parameters of the compounds at different temperatures were determined using a least square refinement program. The unit cell volumes and the coefficients of average volume thermal expansion were also evaluated.

3. Results and discussion

The room temperature XRD data obtained for all the compounds are summarized in Table 1. As can be seen, all the compounds except $La_{0.75}Sr_{0.25}CrO_{3-\delta}$, showed an orthorhombic symmetry at room temperature. The unit cell parameters of $LaCrO_3$, $La_{0.95}Sr_{0.05}CrO_{3-\delta}$, at room temperature, are in good agreement with the literature data [6–8]. However, the formation of $La_{1-x}Sr_xCrO_{3-\delta}$ $(0.10 < x < 0.20)$ compounds with single orthorhombic symmetry at room temperature, as observed in the present investigation, is not in good agreement with some literature data [5,9]. Khattak and Cox [5] observed that, when mixtures pertaining to the mole percent composition of $La_{0.90}Sr_{0.10}CrO_{3-\delta}$ and $La_{0.85}Sr_{0.15}CrO_{3-\delta}$ were heated at 1573 and 1773 K, respectively, in air, the corresponding compounds obtained were not a single phase but a mixture of both orthorhombic and rhombohedral phases. However, Tezuka et al. [9] reported the coexistence of orthorhombic and rhombohedral phases in the mole percent compositions of $La_{0.90}Sr_{0.10}CrO_{3-\delta}$ and $La_{0.85}Sr_{0.15}CrO_{3-\delta}$, respectively, after their final heat treatment at 1723 K in oxygen atmospheres. The existence of single phase orthorhombic $La_{1-x}Sr_xCrO_{3-\delta}$ $(0.10 < x < 0.20)$ compositions at room temperature after their heat treatment at 1423 K in air as found in this study, which also indicate that the method of synthesis has a substantial effect on stabilization of a particular symmetry. The orthorhombic symmetry is stabilized in this series, if they are

Table 1
XRD data for $La_{1-x}M_xCrO_3$ compounds at room temperature

Serial no.	X	Symmetry	Unit cell parameters			
			a (Å)	b (Å)	c (Å)	α^0
For M = Sr^{2+}						
1	0.0	Orthorhombic	5.478(2)	5.504(2)	7.757(2)	
2	0.05	Orthorhombic	5.471(2)	5.501(2)	7.758(2)	
3	0.10	Orthorhombic	5.473(2)	5.501(2)	7.748(2)	
4	0.20	Orthorhombic	5.460(2)	5.506(2)	7.750(2)	
5	0.25	Rhombohedral	5.44(1)			60.8
For M = Nd^{3+}						
6	0.05	Orthorhombic	5.440(2)	5.500(1)	7.750(2)	
7	0.10	Orthorhombic	5.441(2)	5.490(2)	7.750(1)	
8	0.20	Orthorhombic	5.441(2)	5.490(2)	7.740(2)	
9	0.25	Orthorhombic	5.432(2)	5.480(2)	7.738(3)	

formed at lower temperatures. This aspect is further investigated in the present work. It is for the first time the XRD data of $La_{1-x}Nd_xCrO_3$ $(0.05 < x < 0.25)$ compounds are reported herein by substitution of Nd^{3+} in $LaCrO_3$.

The bulk thermal expansion behaviour of all the compounds was investigated in the temperature range 298–1123 K on dense pellets (70–75% of theoretical density) using a thermo-dilatometer. Except $La_{0.75}Sr_{0.25}CrO_{3-\delta}$, the dilatometry studies revealed that the parent $LaCrO_3$ and Sr^{2+} and Nd^{3+} substituted $LaCrO_3$, have almost the same thermal expansion behaviour in the temperature range of 298–1123 K in air. The results showing the variations of percent linear thermal expansion with temperature for $La_{0.75}Sr_{0.25}CrO_{3-\delta}$ and typical results of $LaCrO_3$, $La_{0.90}Sr_{0.10}CrO_{3-\delta}$ for rest of the compounds are shown in Fig. 1. As can be seen, $La_{0.75}Sr_{0.25}CrO_{3-\delta}$ exhibited a linear relation between expansion and temperature in the entire range of investigation. However, $LaCrO_3$, $La_{0.95}Sr_{0.05}CrO_{3-\delta}$, $La_{0.90}Sr_{0.10}CrO_{3-\delta}$,

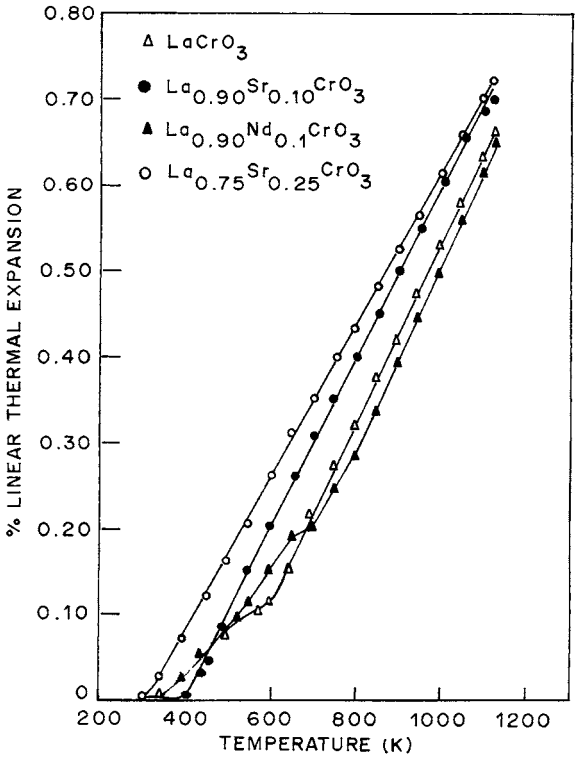

Fig. 1. The variations of percent linear thermal expansion as a function of temperature for $La_{1-x}M_xCrO_3$.

Table 2
Phase transition temperature for $La_{1-x}M_xCrO_3$ compounds determined by dilatometry and HTXRD

Serial no.	Compound	Phase transition temperature (K)
1	$LaCrO_3$	$540 < T < 575$
2	$La_{0.95}Sr_{0.05}CrO_{3-\delta}$	$505 < T < 550$
3	$La_{0.90}Sr_{0.10}CrO_{3-\delta}$	$375 < T < 405$
4	$La_{0.80}Sr_{0.20}CrO_{3-\delta}$	$375 < T < 405$
5	$La_{0.75}Sr_{0.25}CrO_{3-\delta}$	–
6	$La_{0.95}Nd_{0.05}CrO_3$	$623 < T < 673$
7	$La_{0.90}Nd_{0.10}CrO_3$	$675 < T < 720$
8	$La_{0.80}Nd_{0.20}CrO_3$	$825 < T < 870$
9	$La_{0.75}Nd_{0.25}CrO_3$	$975 < T < 1025$

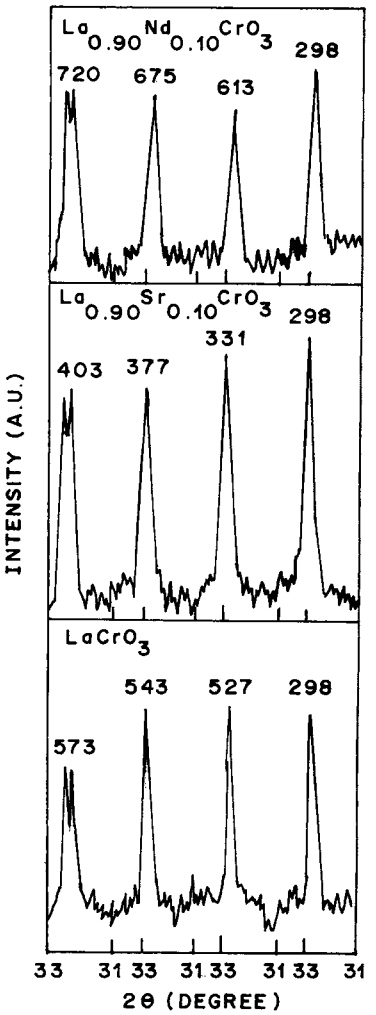

Fig. 2. Scan of peak intensity (1 1 2) of $La_{1-x}M_xCrO_3$ on heating.

$La_{0.80}Sr_{0.20}CrO_{3-\delta}$, $La_{0.95}Nd_{0.05}CrO_3$, $La_{0.90}Nd_{0.10}CrO_3$, $La_{0.80}Nd_{0.20}CrO_3$ and $La_{0.75}Nd_{0.25}CrO_3$ showed a smooth expansion up to maximum temperatures of 550, 505, 375, 375, 623, 674, 825 and 975 K, respectively, and thereafter a gradual expansion but at a decreasing rate for a temperature range of ~50 K. Above this temperature, the rate of expansion increased and remained almost constant up to 1123 K (typical curves in Fig. 1). A distinct small discontinuity at each temperature for these compounds is attributed to the orthorhombic to rhombohedral phase transition. The transition temperature for the compounds, as determined, are given in Table 2. As can be seen from this table, the transition temperature of $La_{1-x}Sr_xCrO_{3-\delta}$ compounds decreased with increasing Sr^{2+} content, up to a certain composition limit ($x = 0.10$) and thereafter the transition temperature remained constant, in spite of increase in Sr^{2+} content, which suggested that there was an optimum composition threshold up to which the temperature could be lowered. It may be noted that for $La_{0.75}Sr_{0.25}CrO_{3-\delta}$, the rhombohedral phase is stabilized, at room temperature. On the contrary, the phase transition temperature of orthorhombic to rhombohedral modification increased systematically by increasing the amount Nd^{3+} substitution.

The phase transition temperature of all the compounds as determined by dilatometry was also confirmed by high temperature X-ray diffractometry. For each sample, the phase transition was located by step scanning of the maximum intensity reflection 112 during heating when the 112 peak of orthorhombic was found to split into two reflections namely 101 and 211 reflections of rhombohedral phase. The phase transition temperatures observed in typical compounds of $LaCrO_3$, $La_{0.90}Sr_{0.10}CrO_{3-\delta}$ and $La_{0.90}Nd_{0.10}CrO_3$ by this method are shown in Fig. 2.

The unit cell parameters of the compounds at different temperatures were determined from the XRD patterns and the unit cell volume per molecule, evaluated from the cell parameters at various temperatures for $La_{1-x}Sr_xCrO_{3-\delta}$ and $La_{1-x}Nd_xCrO_3$ compounds. These are given in Tables 3 and 4, respectively. As can be seen from the tables, the unit cell volume per molecule of all the compounds increased with increase in temperature and the phase transition of the compounds was not accompanied by a considerable change in volume. The average coefficients of volume thermal expansion (α_v) for the compounds in the temperature range of 298–1073 K are given in Table 5. The coefficients of average linear thermal expansion (α_l) as determined by dilatometry are also included in this table. Based on the assumption that α_v is almost equal to three times of α_l of a material, the values of α_v obtained for the compounds are found to be slightly smaller than that are expected. This difference can be attributed to the porosity which decreases the bulk thermal expansion.

It is found that compared to the coefficient of average linear thermal expansion (α_l) and (α_v) of $LaCrO_3$, the α_l and α_v of Sr^{2+} substituted compounds showed a systematic marginal increase with increase in Sr^{2+} content, but the Nd^{3+} substituted compounds

Table 3
Unit cell volume per molecule of $La_{1-x}Sr_xCrO_{3-\delta}$ compounds at various temperatures in the temperature range 298–1073 K in air

Temperature (K)[a]	Volume/molecule (Å^3)[b]				
	$x = 0.0$	$x = 0.05$	$x = 0.10$	$x = 0.20$	$x = 0.25$
298	58.47 (O)	58.37 (O)	58.32 (O)	58.25 (O)	57.95 (R)
375	58.65 (O)	58.52 (O)	58.52 (O)	58.51 (O)	58.20 (R)
425	–	–	58.89 (R)	58.63 (R)	–
481	58.82 (O)	58.63 (O)	–	–	58.52 (R)
550	–	58.71 (R)	59.01 (R)	–	–
579	59.09 (R)		–	58.77 (R)	
677	59.41 (R)	58.84 (R)	59.23 (R)		58.90 (R)
825	–	–	–	59.20 (R)	
879	59.53 (R)	59.37 (R)	59.35 (R)		59.16 (R)
1073	59.80	59.70 (R)	59.67 (R)	59.62 (R)	59.36 (R)

[a] Selected depending on the phase transition.
[b] 'O' denotes orthorhombic and 'R' denotes rhombohedral.

Table 4
Unit cell volume/molecule of $La_{1-x}Nd_xCrO_3$ compounds at various temperatures in the temperature range 298–1073 K in air

Temperature (K)[a]	Volume per molecule (Å^3)[b]				
	$x = 0.0$	$x = 0.05$	$x = 0.10$	$x = 0.20$	$x = 0.25$
298	58.47 (O)	57.97 (O)	57.86 (O)	57.68 (O)	57.58 (O)
375	58.65 (O)	–	–	–	–
481	58.82 (O)	58.15 (O)	58.15 (O)	57.97 (O)	57.86 (O)
579	59.09 (R)	–	–	–	–
623	–	58.54 (O)	–	–	–
675	59.41 (R)	58.77 (R)	58.36 (O)	58.15 (O)	58.04 (O)
723	–	–	–	58.58 (R)	–
825	–	58.84 (R)	–	–	58.44 (O)
877	59.53 (R)	–	–	58.71 (R)	–
926	–	–	58.82 (R)	–	–
973	–	58.95 (R)	–	–	58.62 (O)
1025	–	–	–	–	58.71 (R)
1073	59.80 (R)	59.23 (R)	59.11 (R)	58.92 (R)	58.81 (R)

[a] Selected depending on the phase transition.
[b] 'O' denotes orthorhombic and 'R' denotes rhombohedral.

exhibited a reverse effect. The systematic marginal increase in α_l and α_v of the Sr^{2+} substituted compounds compared to that of $LaCrO_3$ indicates that the inter-atomic bonding in these compounds is weaker than that of the parent compound. The 1ow values of α_l and α_v the Nd^{3+} substituted compounds compared to the rest of the compounds show that with increased substitution of Nd^{3+} ions in place of La^{3+}, the strength of the inter-atomic bonds increases, and higher the bond strength, less the expansion.

The reverse trend in the phase transition temperature with concentration of Sr^{2+} or Nd^{3+} ions can be explained based on the tolerance factor, $t = (R_A + R_O)/\sqrt{2}(R_B + R_O)$. The higher the tolerance factor the higher is the stability of the higher symmetry perovskite. The tolerance factor of $LaCrO_3$ is expected to increase on increasing Sr^{2+} substitution whereas it should decrease on increasing the Nd^{3+} substitution, due to the relative ionic sizes. This is why the phase transition temperature of $LaCrO_3$ has a reverse trend on substituting with Sr^{2+} or Nd^{3+}.

Table 5
Average coefficients of linear thermal expansion (α_l) and volume thermal expansion (α_v) of $La_{1-x}Sr_xCrO_{3-\delta}$ and $La_{1-x}Nd_xCrO_3$ compounds

Serial no.	Compound	α_l ($\times 10^6$ K^{-1}) (± 0.05) (298–1123 K)	α_v ($\times 10^6$ K^{-1}) (± 0.20) (298–1073 K)
1	$LaCrO_3$	8.08	29.38
2	$La_{0.95}Sr_{0.05}CrO_{3-\delta}$	8.32	29.70
3	$La_{0.90}Sr_{0.10}CrO_{3-\delta}$	8.48	29.97
4	$La_{0.80}Sr_{0.20}CrO_{3-\delta}$	8.60	30.62
5	$La_{0.75}Sr_{0.25}CrO_{3-\delta}$	8.70	30.70
6	$La_{0.95}Nd_{0.05}CrO_3$	8.00	28.04
7	$La_{0.90}Nd_{0.10}CrO_3$	7.96	27.87
8	$La_{0.80}Nd_{0.20}CrO_3$	7.70	27.72
9	$La_{0.75}Nd_{0.25}CrO_3$	7.50	27.56

4. Conclusions

From the dilatometric and HT-XRD studies, it was concluded that Sr^{2+} and Nd^{3+} substitution in $LaCrO_3$ have marked effect on their phase transition, bulk and lattice thermal expansion behaviour. The results obtained by dilatometry were in good agreement with those obtained by high temperature XRD. This study also revealed that the phase transition of $LaCrO_3$ and its thermal expansion behaviour can be tuned by suitable substitution. These findings are useful in designing high temperature devices, such as *solid oxide fuel cells*, with $LaCrO_3$ as one of the components.

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