Sr and Ni Effect in Doped LaCoO$_3$ on the Phase Formation of the Perovskite-type Oxides

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Abstract

A series of the solid solution oxides $La_{(1-x)}Sr_xCo_{(1-y)}$-$Ni_yO_{3-\delta}$ (x : 0·2, 0·4, 0·5, 0·6 and y : 0·2, 0·25, 0·3, 0·4, 0·6) was prepared. The effect of Sr and Ni substitution on the formed phases was studied by means of X-ray diffraction starting from room temperature up to 1000°C. Within the same range of temperature thermal expansion measurements were carried out by using a dilatometer.

It was found that Sr substitution up to 60% does not affect the crystal system formed by the compounds, being cubic in all the cases. A remarkable contraction of the unit cell is observed up to 50% Sr content.

For Ni substitution in the range of 0·2 < y < 0·6 two phases, the cubic and the tetragonal, are formed, while for y = 0·6 only the tetragonal phase appears. Thermal expansion is increased by Sr and decreased by Ni substitution. Finally, O^{2-} vacancies creation is observed to start from 500°C.

Eine Reihe fester Lösungen $La_{(1-x)}Sr_xCo_{(1-y)}Ni_yO_{3-\delta}$ (x : 0·2, 0·4, 0·5, 0·6 und y : 0·2, 0·25, 0·3, 0·4, 0·6) wurde hergestellt. Der Effekt von Sr- und Ni-Substitution auf die Bildung der einzelnen Phasen wurde mittels röntgenographischer Analyse von Raumtemperatur bis zu 1000°C untersucht. Im gleichen Temperatur- bereich wurden Messungen der thermischen Aus- dehnung mit Hilfe eines Dilatometers durchgeführt.

Den Untersuchungen zufolge kristallisieren Ver- bindungen mit bis zu 60% Sr im kubischen Kristall- system. Eine beträchtliche Kontraktion der Basiszelle findet bis zu einem Sr-Gehalt von 50% statt.

Für Ni-Substitution im Bereich 0·2 < y < 0·6 werden zwei Phasen, eine kubische und eine tetragonale, gebildet, während für y = 0·6 nur die tetragonale auftritt. Die thermische Ausdehnung wird durch die Sr-Substitution erhöht und die Ni-Substitution ernie- drigt. O^{2-}-Leerstellen werden oberhalb von 500°C gebildet.

Une série de compositions dans le système à solution solide $La_{(1-x)}Sr_xCo_{(1-y)}Ni_yO_{3-\delta}$ (x : 0·2, 0·4, 0·5, 0·6 et y : 0·2, 0·25, 0·3, 0·4, 0·6) a été préparée. L'effet de la substitution du Sr et du Ni sur les phases formées a été étudié par diffraction de rayons-X de la température ambiante jusqu'à 1000°C. Dans le même domaine de température, l'expansion thermique a été déterminée à l'aide d'un dilatomètre.

Les résultats montrent que la substitution avec jusqu'à 60% Sr ne modifie pas le système crystallo- graphique, qui reste toujours cubique. La maille élementaire montre un retrait significatif pour des substitutions avec Sr jusqu'à 50%.

Pour des substitutions avec Ni dans le domaine 0·2 < y < 0·6 deux phases crystallographiques, cubique et quadratique, coexistent, tandis que pour y = 0·6 seulement la phase quadratique est formée. L'expan- sion thermique augmente avec la substitution avec Sr et diminue avec Ni. Enfin, la création de lacunes d'oxygène est observée à partir de 500°C.

1 Introduction

Mixed ionic/electronic conductivity shown by some non-stoichiometric oxides has increasingly attracted technological interest due to their many practical

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applications.[1-3] Among these, perovskite-type oxides (ABO_3) are very interesting materials, where various functional properties can be easily modified by the total or partial substitution of cations of A and/or B sites.

The type of crystal structure adopted by a given ABO_3 composition is determined by the relative sizes of A and B ions with respect to oxide ion.[4-8]

A member of this rich variety of perovskites is the well-known $LaCoO_3$, exhibiting temperature-dependent spin and valence changes of trivalent cobalt.[9,10] A number of compounds have been prepared and studied by partial substitution of lanthanum by a divalent cation, particularly alkaline earth metals, and/or of cobalt by another transition metal.[11-21] However, there is not a consensus on some points, especially those that concern the stability range of the perovskite phase of lanthanum cobaltite solid solutions.

As part of the extensive program to investigate and improve the properties of some ceramics having mixed ionic/electronic conductivity, the authors have examined various aspects of materials with the perovskite-related structures. In the present paper the authors report on the stability range of the phases formed and their thermal properties after substitution of Sr and Ni for La and Co, respectively, in $LaCoO_3$.

2 Experimental

A series of compositions was prepared to give the non-stoichiometric compounds $La_{(1-x)}Sr_xCo_{(1-y)}$-$Ni_yO_{3-\delta}$ (x: 0·2, 0·4, 0·5, 0·6 and y: 0·2, 0·25, 0·3, 0·4,

0·6) by the amorphous citrate technique route.[22] The composition of the samples is presented in Table 1.

The starting materials used were the acetate salts of La, Sr, Co and Ni, respectively, and citric acid, all of analytical grade. Four solutions were prepared by dissolving in distilled water a weighed amount of the relevant salt. The concentration of each solution, with respect to the ion contained, was measured by means of atomic absorption spectroscopy (AAS). Thus, in every batch the required proportions were used by taking the right volume from each solution. Citric acid was added to the formed solution in sufficient quantity in order to react with all the metal ions.

The solution was then heated at about 150°C until polymerization took place. The powders of the desired oxides were obtained by subsequent heating and drying of the polymerized gel at higher temperature (c. 400°C). Calcination of the powders was carried out at 1000°C for 10 h. Finally, the powders were pressed into pellets under a uniaxial compaction pressure of 300 MPa and sintered in air at 1250°C for 12 h. Heating and cooling was performed at a rate of 5°C/min.

In all cases the bulk density of the specimens prepared was measured and found to be higher than 92% of the theoretical density. Also, the specimens were examined by means of SEM-EDAX, with respect to La, Sr, Co and Ni concentrations, in order to confirm the synthesis of the compositions presented in Table 1.

X-Ray diffraction (XRD) study of the samples was carried out by using a computerized Philips PW 1710 diffractometer and CuK_α radiation. The diffractometer was operated at 40 kV and 40 mA, by

Table 1. Composition, lattice parameters and crystal structure of the phases prepared

Code	Composition	Lattice parameter		Crystal structure
		a ($\mathring{A}$)	c ($\mathring{A}$)	
A_0	$La_{0.8}Sr_{0.2}CoO_{2.9}$	3·849 (2)		Cubic
A_{01}	$La_{0.8}Sr_{0.2}Co_{0.8}Ni_{0.2}O_{2.8}$	3·844 (3)		Cubic
A	$La_{0.6}Sr_{0.4}CoO_{2.80}$	3·840 (1)		Cubic
A_1	$La_{0.6}Sr_{0.4}Co_{0.8}Ni_{0.2}O_{2.70}$	3·835 (1)		Cubic
$A_{1.1}{}^a$	$La_{0.6}Sr_{0.4}Co_{0.75}Ni_{0.25}O_{2.675}$	3·837 (1)		Cubic
		3·831 (2)	12·536 (8)	Tetragonal
$A_{1.2}{}^a$	$La_{0.6}Sr_{0.4}Co_{0.7}Ni_{0.3}O_{2.65}$	3·828 (1)		Cubic
		3·815 (2)	12·407 (9)	Tetragonal
$A_2{}^a$	$La_{0.6}Sr_{0.4}Co_{0.6}Ni_{0.4}O_{2.60}$	3·827 (1)		Cubic
		3·805 (2)	12·443 (8)	Tetragonal
A_3	$La_{0.6}Sr_{0.4}Co_{0.4}Ni_{0.6}O_{2.50}$	3·813 (1)	12·503 (2)	Tetragonal
B_1	$La_{0.5}Sr_{0.5}Co_{0.8}Ni_{0.2}O_{2.65}$	3·828 (1)		Cubic
$B_2{}^a$	$La_{0.5}Sr_{0.5}Co_{0.6}Ni_{0.4}O_{2.55}$	3·820 (2)		Cubic
		3·805 (3)	12·422 (9)	Tetragonal
B_3	$La_{0.5}Sr_{0.5}Co_{0.4}Ni_{0.6}O_{2.45}$	3·811 (1)	12·505 (2)	Tetragonal
C_1	$La_{0.4}Sr_{0.6}Co_{0.8}Ni_{0.2}O_{2.60}$	3·827 (1)		Cubic
$C_2{}^a$	$La_{0.4}Sr_{0.6}Co_{0.6}Ni_{0.4}O_{2.50}$	3·839 (2)		Cubic
		3·811 (1)	12·473 (6)	Tetragonal
C_3	$La_{0.4}Sr_{0.6}Co_{0.4}Ni_{0.6}O_{2.40}$	3·811 (1)	12·509 (5)	Tetragonal

^{a} Two phases are observed.

scanning continuously at a rate of $1°2\theta/\text{min}$. Indexing of the XRD patterns and calculation of the unit cell lattice parameters were obtained by using a least-squares refinement program named Pulver. Three representative specimens were studied by means of high-temperature X-ray diffractometry (HTXRD) at various temperatures up to 1000°C. Also, thermal expansion of the samples was measured using the dilatometer technique up to 1000°C.

3 Results and Discussion

In Table 1 the crystal form and the unit cell lattice parameters of the phases prepared are shown. With respect to the A-site, it is clearly observed that the partial substitution of Sr for La does not bring about any significant change in the crystal system, within the region investigated (20–60%). In all cases the phases formed have the pseudocubic distorted perovskite structure. The peaks of the XRD patterns were indexed and they are best fitted to the cubic system.

When the Sr content is increased from 20% to 50%, a remarkable decrease in the dimensions of the unit cell is observed, approaching a limit for substitution of Sr between 50% and 60%, as is shown in Fig. 1. This unit cell decrease is mainly attributed to the transition of Co^{3+}, with an ionic radius (IR) of 0·61 Å to the smaller ion Co^{4+} (IR = 0·53 Å), since it is well known that the partial substitution of Sr^{2+} for La^{3+} brings about the oxidation of Co^{3+} to Co^{4+} and/or formation of O^{2-} vacancies.[14,15,18] The rate of change in the unit cell parameters significantly decreases for Sr additions in the range 50–60% and it is possible that a different compensation mechanism begins to operate in this range.
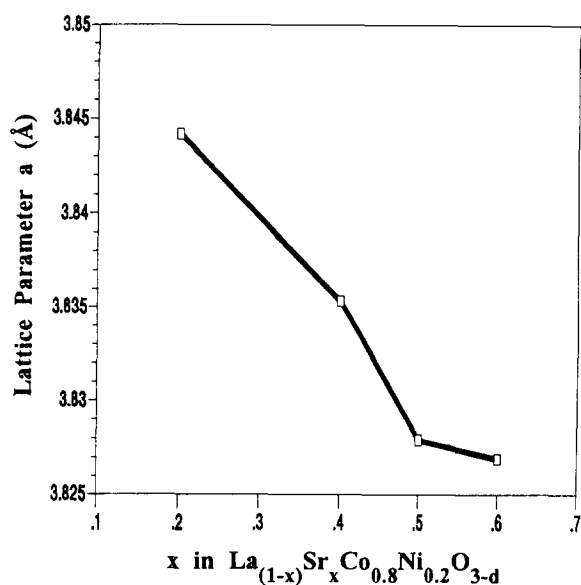
With respect to B-site substitution, it is observed from the results of Table 1 that for Ni concentrations up to 20% the formed phase has the pseudocubic perovskite structure. When $0·2 < y < 0·6$, two phases are formed, having the pseudocubic and tetragonal structure, respectively. Comparing the intensities of the peaks in the XRD patterns, it is estimated that the ratio of the tetragonal/cubic phase is about 1/3. At 60% ($y = 0·6$) substitution of Ni for Co, one phase is formed, which crystallizes in the tetragonal system. Although it has been reported that the tetragonal phase is of the type K_2NiF_4,[8,13,15,18] the results obtained by SEM-EDAX analysis do not correspond to the simple A_2BO_4 stoichiometry.

No major structural transition was observed, as was found by HTXRD analysis of the samples B_1, B_2 and B_3 having the cubic, cubic + tetragonal and tetragonal structure, respectively. Some ordering–disordering phenomena are shown, but in any case the crystal system does not change from room temperature up to 1000°C. Figures 2 and 3 present the variance of the unit cell parameters (a) and (c/a) versus temperature for the cubic phase (B_1 and the cubic phase of B_2) and the tetragonal phase (B_3 and the tetragonal phase of B_2), respectively.

In Figs 4, 5 and 6 the results obtained from the thermal expansion measurements are presented $(\Delta l/l_0 - T)$, matched to the three series of the samples (A_1, B_1, C_1), (A_2, B_2, C_2) and (A_3, B_3, C_3), respectively, that have phases of the same structure. In Fig. 4 the relative increase $(\Delta a/a_0 - T)$ of the unit cell lattice parameter of the cubic phase B_1 is also shown obtained from HTXRD analysis. From these dilatometric results it is observed that the tetragonal phase expands less than the cubic one, particularly above the temperature of 600°C. In the same region of temperature a deviation from the straight line is presented, which is mostly attributed to the high
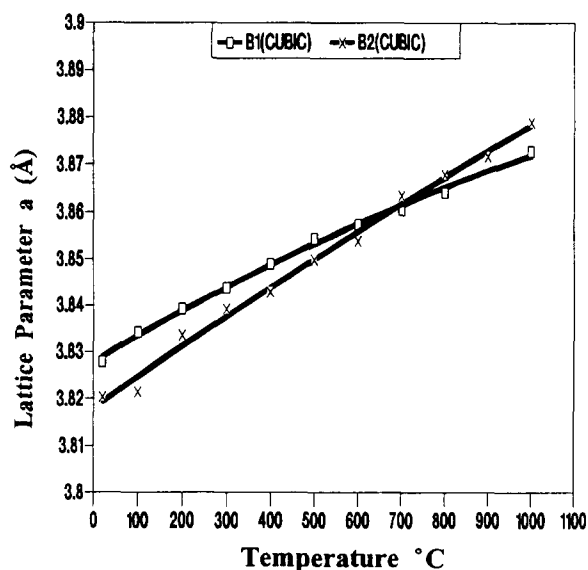

Fig. 1. Lattice parameter (a) of the cubic phase versus Sr content in $La_{(1-x)}Sr_xCo_{(1-y)}Ni_yO_{3-\delta}$.

Fig. 2. Lattice parameter (a) of the cubic phases contained in B_1 and B_2 as a function of temperature.
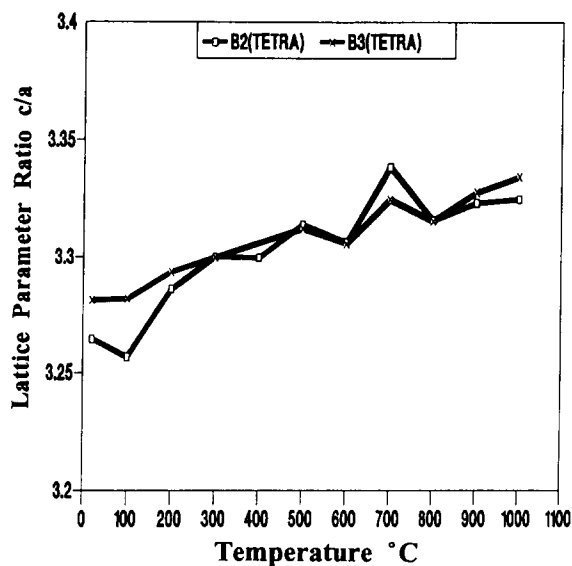
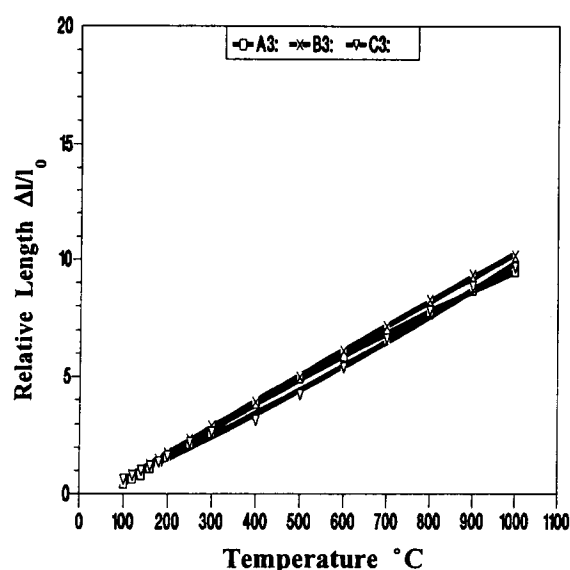**Fig. 3.** Lattice parameter ratio (c/a) of the tetragonal phases contained in B_2 and B_3 versus temperature.
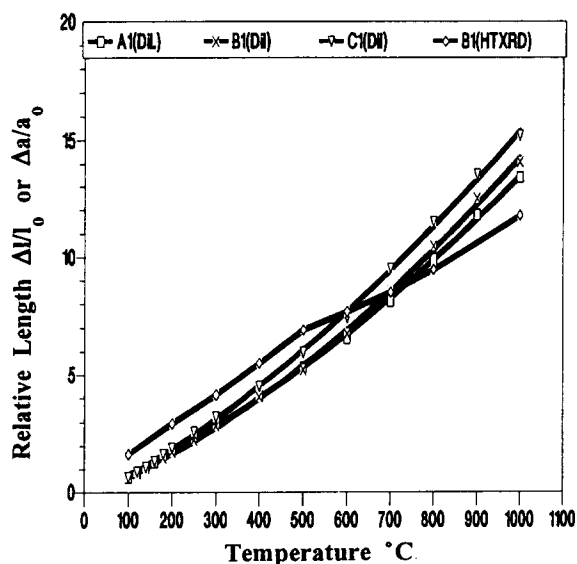

Fig. 4. Relative length expansion ($\Delta l/l_0$) of the phases A_1, B_1, C_1 (dilatometry) and ($\Delta a/a_0$) of the cubic cell parameter (a) of the B_1 (HTXRD) versus temperature.
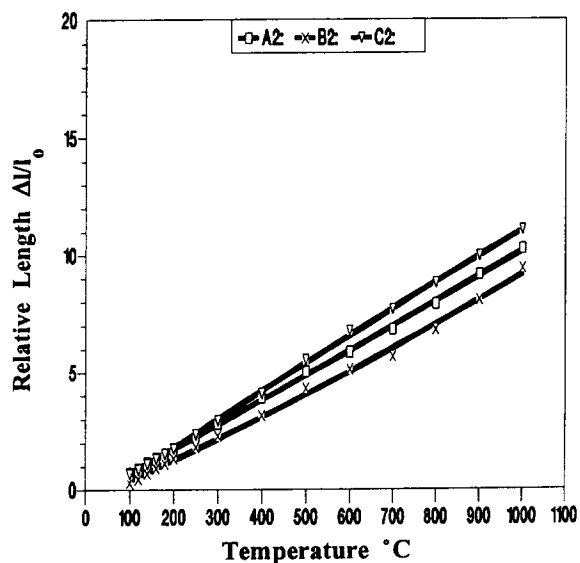

Fig. 5. Relative length expansion ($\Delta l/l_0$) of the phases A_2, B_2 and C_2 (dilatometry) versus temperature.

Fig. 6. Relative length expansion ($\Delta l/l_0$) of the phases A_3, B_3 and C_3 (dilatometry) versus temperature.

concentration of O^{2-} vacancies. This is more evident from Fig. 4, where the relative increase of the lattice parameter is shown. In that case, it is clearly observed that the deviation starts at about 500°C.

Furthermore, the results suggest that substitution of Ni for Co significantly reduces the thermal expansion coefficient. For the pure cobaltites ($La_{(1-x)}Sr_xCoO_{3-\delta}$), however, it has been reported[23-25] that they have higher thermal expansion coefficients than the present oxides.

4 Conclusions

The following conclusions can be drawn from this study concerned with the effect of Sr and Ni substitution in the composition $La_{(1-x)}Sr_xCo_{(1-y)}Ni_yO_{3-\delta}$ on the phase formation of the perovskite-type oxides and their thermal properties.

(a)   Within the range 20–60% of Sr substitution for La the phases formed have the pseudo-cubic distorted perovskite structure.

(b)   Sr content increased up to 50% brings about a remarkable decrease in the unit cell, which takes a limit within the region 50–60%.

(c)   Substitution of Ni for Co up to 20% does not affect crystal system formed, remaining cubic. When $0.2 < y < 0.6$, two phases are formed, having the cubic and tetragonal structure, respectively. For $y = 0.6$ only the tetragonal phase exists.

(d)   In all cases there is no transition of the crystal system formed up to 1000°C.

(e)   Thermal expansion of the cubic phase is higher than the tetragonal one. Also, Ni substitution for Co reduces significantly thermal expansion coefficient, whilst the

greater the Sr content the greater the expansion.

(f) Finally, it is particularly evident in the cubic phase that O^{2-} vacancy creation starts from 500°C.

Acknowledgements

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