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Influence of A- and B-site doping on the properties of the system $La_2CoO_{4\pm\delta}$

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Abstract

In the present paper the compounds $LaSrCo_{0.5}M_{0.5}O_{4\pm\delta}$ (M = Co, Fe, Mn, Ni) and $La_{1.4}Sr_{0.6}Co_{0.5}M_{0.5}O_{4\pm\delta}$ (M = Co, Ni) were prepared and characterised in order to elucidate the influence of strontium doping on A-site as well as doping with transition metals on B-site of the mixed conductor $La_2CoO_{4\pm\delta}$. All the prepared oxides of this paper possessed the K_2NiF_4 structure, exhibited high electrical conductivity (>100 S/cm) and adequately low linear thermal expansion coefficient. Therefore, they are very promising materials for high temperature electrochemical applications.

Keywords: K_2NiF_4; Electrical properties; Thermal properties

1. Introduction

Oxides possessing the K_2NiF_4 structure are the two-dimensional equivalent of the perovskites. Their lattice consists of alternating layers of perovskites (ABO_3) and rock salts (AO).[1] A large number of cations may be used as A-site dopants allowing therefore controlling of lattice defects, just as in the case of perovskites.[2] These compounds are being studied thanks to their applications as catalysts for the partial oxidation of hydrocarbons, electrodes for solid oxide fuel cells, oxygen pumps, ceramic membranes for oxygen separation but also as dielectric, ferroelectric and piezoelectric materials.[3,4] Due to the presence of perovskite layers, the above mentioned oxides exhibit variable oxygen stoichiometry; introducing therefore strontium to A-site will be compensated from a change in the oxygen vacancy concentration and partial oxidation or even reduction of the B-site transition metal. All the above phenomena define the interaction between the composition, oxygen stoichiometry and the concentration of electronic and ionic carriers of these materials.[5]

In the present paper the compounds $LaSrCo_{0.5}M_{0.5}O_{4\pm\delta}$ ($LSC_{0.5}M_{0.5}$, M = Co, Fe, Mn, Ni) were prepared as well as $La_{1.4}Sr_{0.6}Co_{0.5}M_{0.5}O_{4\pm\delta}$ ($L_{1.4}S_{0.6}Co_{0.5}M_{0.5}$, M = Co, Ni). Their crystal structure was characterised with X-ray diffraction at room temperature, their electrical conductivity with the four-point dc method for temperatures between 20 and 1000 °C and their thermal expansion for the same temperature range.

2. Experimental

The oxides were synthesised using the citrate synthesis and pyrolysis method.[6,7] The compounds used as starting materials were the following: La_2O_3, $Sr(NO_3)_2$, $(CH_3COO)_2Co{\cdot}4H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $(CH_3COO)_2Ni{\cdot}4H_2O$, $(CH_3COO)_2Mn{\cdot}4H_2O$ and citric acid, all of analytical grade pure reagents. The powder was calcined at 1000 °C for 15 h, milled in acetone for 24 h, pressed uniaxially in rectangular rods at 90 MPa and finally sintered at 1250 °C for 15 h.

X-ray diffraction (XRD) was performed at ambient temperature using a D5000 Siemens diffractometer and the crystal lattice constants were calculated with the program LSUCR. Thermal expansion measurements were conducted in air between 20 and 1000 °C using a Netzsch DIL 402E dilatometer (heating/cooling rate: 1 °C/min). Electrical conductivity was measured with the four-point dc method for the same temperature range (heating rate: 5 °C/min).

3. Results and discussion

After examining the XRD spectra (Figs. 1 and 2) it was concluded that all oxides possessed the K_2NiF_4 structure and were crystallized in the tetragonal system. The lattice constants *a*, *c* and the volume of the unit cell are presented in Table 1. Changes

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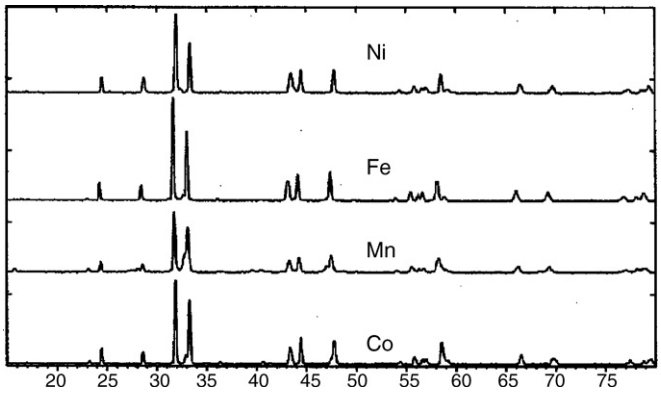

Fig. 1. X-ray diffraction spectrum of the compounds $LSC_{0.5}M_{0.5}$.

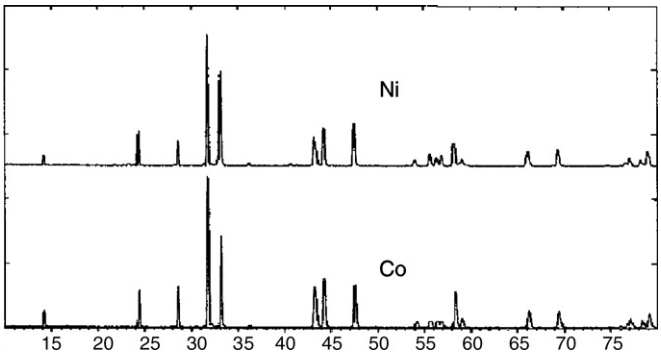

Fig. 2. X-ray diffraction spectrum of the compounds $L_{1.4}S_{0.6}C_{0.5}M_{0.5}$.

of lattice constants are related to the degree of lanthanum substituting on A-site but also to the concentration of B-site metals in their normal or oxidized state, because the size of B-cation affects the length of the B–O bond. Furthermore these compounds usually contain excess oxygen, a fact that also affects the cell dimensions.

Increasing strontium content resulted in reduced unit cell volume and B-site doping reduced the volume in the following order: Ni < Co < Mn < Fe. The length of ionic radius of the transition metals is being reduced in the order Co < Mn < Fe < Ni. Only the compound containing nickel exhibited a different behaviour, a fact that is probably attributed to the excess of Ni^{3+} cations, which have significantly smaller ionic radius than Ni^{2+}.

From thermal expansion measurements (Fig. 3) the corresponding linear expansion coefficients were calculated and their values at 700 °C are presented in Table 1. Compounds

Table 1
Lattice constants and volume of unit cell, linear thermal expansion coefficient (TEC) at 700 °C of the $LSC_{0.5}M_{0.5}$ and $L_{1.4}S_{0.6}C_{0.5}M_{0.5}$ oxides

Compound	a (nm)	c (nm)	V (nm^3)	$TEC_{700} \times 10^6$ (°C^{-1})
$La_{0.5}Sr_{0.5}CoO_{4\pm\delta}$	0.538	1.248	6.717	15.5
$La_{0.5}Sr_{0.5}Co_{0.5}Mn_{0.5}O_{4\pm\delta}$	0.541	1.254	6.781	13.9
$La_{0.5}Sr_{0.5}Co_{0.5}Fe_{0.5}O_{4\pm\delta}$	0.542	1.259	6.823	13.5
$La_{0.5}Sr_{0.5}Co_{0.5}Ni_{0.5}O_{4\pm\delta}$	0.537	1.243	6.681	12.6
$La_{1.4}Sr_{0.6}CoO_{4\pm\delta}$	0.541	1.249	6.756	10.1
$La_{1.4}Sr_{0.6}Co_{0.5}Ni_{0.5}O_{4\pm\delta}$	0.539	1.249	6.739	11.1

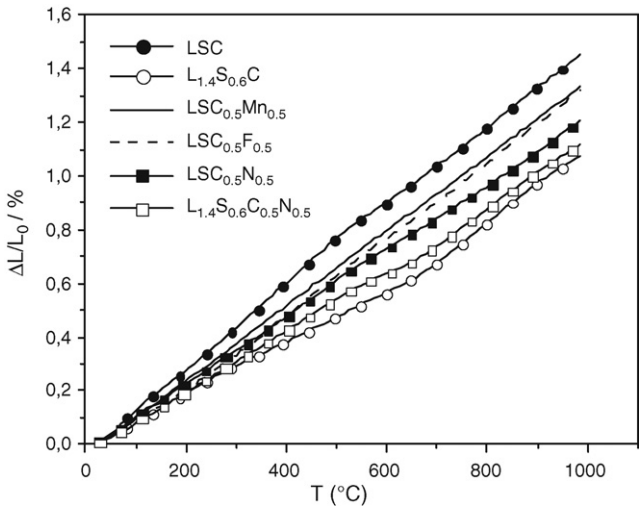

Fig. 3. Linear thermal expansion in air vs. temperature.

containing smaller amounts of strontium exhibited smaller coefficients and also a small deviation from linearity at temperatures higher than 650 °C a behaviour that is attributed to the loss of lattice oxygen. As far as the $LSC_{0.5}M_{0.5}$ compounds are concerned, the oxide containing Ni presented the minimum value.

Electrical conductivity measurements in atmospheric air (Fig. 4) showed, that undoped compounds exhibited linear behaviour, which is described by the small polaron hopping model, and all the rest beyond a certain temperature presented metallic conductivity. This transition temperature lied within the range of 800 °C (M = Mn) to 500 °C (M = Ni). This phenomenon is common among equivalent perovskites and is attributed to the loss of lattice oxygen, which results in reduction of the number of conductivity carriers which are the B-site oxidized ions. Increase of strontium content on A-site reduced electrical conductivity; on the contrary B-site doping enhanced it in the semiconductive area (Mn < Fe < Ni). Absolute conductivity values for the B-site doped oxides were all very satisfactory.

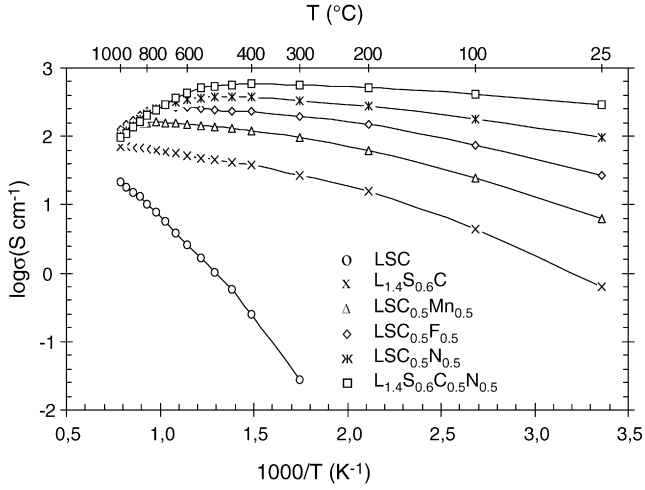

Fig. 4. Electrical conductivity (log σ) vs. reciprocal temperature.

4. Conclusions

Doping of B-site improved greatly the electrical conductivity of the mixed conductor $La_2CoO_{4\pm\delta}$ and slightly increased the linear thermal expansion coefficient. Generally the doped oxides of the $La_2CoO_{4\pm\delta}$ system exhibited better properties than the equivalent perovskites, with the exception of $LaSrCoO_{4\pm\delta}$. Therefore, they are very good candidate materials for catalytic applications, energy production as solid oxide fuel cell electrodes and numerous other electrochemical applications.

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