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Mutual influence of '3d' and '4f' atoms in K_2NiF_4-type structure diluted solid solutions $Y_{1-x}Nd(Ce)_xCaCr_yAl_{1-y}O_4$ ($x \leq 0.1$; $y \leq 0.1$)

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Abstract

Diluted solid solutions of '3d' (chromium) and '4f' (neodymium and cerium) elements in the K_2NiF_4-type 1/1 perovskite rock salt intergrowth structure of mixed aluminates were investigated in order to get evidence of mutual influence phenomena. Crystal chemical data obtained for the solid solution $Y_{1-x}Nd_xCaCr_yAl_{1-y}O_4$ ($x \leq 0.1$; $y \leq 0.1$) point to the existence of an Nd(III)-O-Cr(III) coupling in the bridge bonds which connect the perovskite and rock salt slabs. A non-statistical distribution of Nd(III) is very likely to occur in the rock salt slabs. A magnetochemical characterization brings the proof of a partial reduction of Ce(IV) to Ce(III) in the composition $Y_{0.9}Ce_{0.1}CaAlO_4$, as in $Y_{0.8}Ce_{0.1}Ca_{1.1}AlO_4$ the only (IV) valence state is found. The simultaneous presence of Ce(IV) and Ce(III) is confirmed by the results of structure calculations, in terms of a splitting of the Ce-O distances in the rock salt slabs. © 1997 Elsevier Science S.A.

Keywords: Nd-diluted layered oxides; Ce-diluted layered oxides; Cr-diluted layered oxides; Structure calculations; Magnetic susceptibility

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1. Introduction

The simultaneous presence of several transition elements in oxide diluted solid solutions usually results in rich properties, such as optical, electrical and magnetic ones, depending on the mutual influence of these elements. The dependence on the symmetry of the nearest surrounding electronic states and the interactions between the paramagnetic species is of main importance. In this respect, perovskite-like oxides bring the opportunity to check the existence of such mutual influence. In the layered $AA'BO_4$ oxides with the K_2NiF_4 type 1/1 intergrowth structure, '3d' paramagnetic cations occupy the (BO_6) octahedra in the perovskite (P) layers and lanthanoids, the (AO_9) polyhedra in the rocksalt type (RS) slabs (Fig. 1). The connection of the (P) and (RS) layers occurs in terms of the strongly anisotropic A-O_{ap}-B bridge bond, as coupling an elongated B-O_{ap} distance with a shortened A-O_{ap} one [1–5].

The diluted solid solutions which were considered for the problems of the mutual influence concern mixed yttrium calcium aluminochromites (10% maximum of Cr(III)), where a small amount of yttrium (III) (10% maximum) is substituted for neodymium (III) or cerium (IV). In this study we report the results of a crystallochemical (cell parameters and interatomic distances) and magnetochemical investi-

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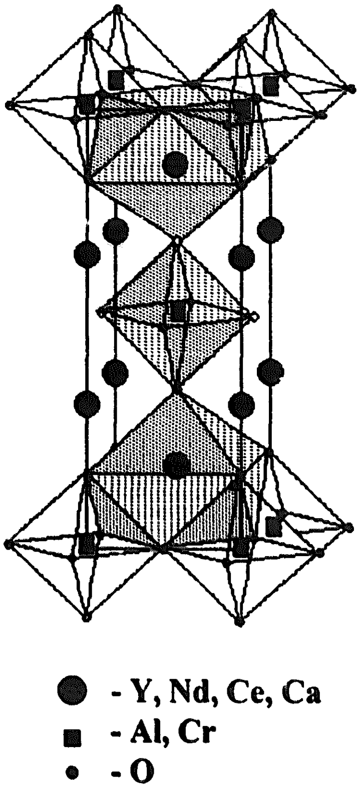

Fig. 1. K_2NiF_4-type 1/1 intergrowth structure.

gation, which was carried out in the following solid solutions: $Y_{1-x}Nd_xCaCr_yAl_{1-y}O_4$, $Y_{0.9}Ce_{0.1}CaCr_yAl_{1-y}O_4$ and $Y_{0.8}Ce_{0.1}Ca_{1.1}Cr_yAl_{1-y}O_4$ ($x, y \leq 0.1$).

2. Experimental

The different compositions of the three solid solutions were synthesized from solid state reactions of oxide mixtures ($CaCO_3$ for calcium) heated in alumina containers in air, first at 1100°C to ensure the decarbonation and then at 1400°C. Several annealings at 1400°C during 30–40 h were performed in order to ensure an equilibrium state of the distribution of the cations, this being of importance in the case of diluted solid solutions.

The crystallographic characterization, including cell parameters and structure calculations (Rietveld analysis), was performed from X-ray diffractograms recorded on a D500 Siemens diffractometer using the Cu Kα radiation.

The magnetic susceptibility was measured from liquid nitrogen temperature to room temperature for cerium-containing solid solutions by the Faraday method using a pendulum type device, the DSM-8 equipment.

A control of the actual amount of the elements in the solid solutions was carried out by X-ray analysis: Tracor equipment on a JEOL 100CX electron microscope.

3. Results and discussion

3.1. The $Y_{1-x}Nd_xCaCr_yAl_{1-y}O_4$ diluted solid solution ($x, y \leq 0.1$)

The cationic substitutions of Nd(III) for Y(III) in the (RS) slabs and Cr(III) for Al(III) in the (P) layers, as made separately in the aluminate $YCaAlO_4$ i.e. the solid solutions $Y_{1-x}Nd_xCaAlO_4$ and $YCaCr_yAl_{1-y}O_4$, exhibit rather monotonic tendencies, namely:

- a simultaneous linear increase of the *a* and *c* parameters of the tetragonal cell, due to the larger size of Nd(III) as compared to Y(III);
- an increase of *a* and a slight decrease of *c*, when Cr(III) is substituted for Al(III).

The progressive substitution of Nd(III) for Y(III) in the aluminochromite solid solution results in a deviation from the linearity of the variation of *a* versus the Nd(III) content, as the variation of *c* which remains linear, exhibits a slight increase of its slope (Fig. 2). Conversely, the effect of the progressive substitution of Cr(III) for Al(III) is not modified when the Nd(III) content increases.

The increasing non-linearity of the variation of *a* versus the Nd(III) content when the Cr(III) content increases, brings early evidence of the mutual influence of Nd(III) and Cr(III) in the solid solution. The results of structure calculations confirm this fact. Two data exemplify the effects of this coupling (Table 1 and Fig. 3): the apical A-O_{ap} distance and the ratio $d_{B\text{-}O_{ap}}/d_{B\text{-}O_{eq}}$ i.e. the anisotropy of the (BO_6) octahedra. In the full extent of the solid solution, from $YCaAlO_4$ to $NdCaAlO_4$, the A-O_{ap} distance slightly increases due to the 'pure' influence of Nd(III) and the anisotropy of the octahedra is unchanged (≈ 1.094). In the diluted aluminochromite $Y_{1-x}Nd_xCaCr_{0.1}Al_{0.9}O_4$, there is a complex variation of these data: the A-O_{ap} distance first increases and then decreases, as the anisotropy of the octahedra increases from the content of neodymium $x = 0.07$ (1.102 to 1.104).

From these results, one can assume that the disordered distribution of Nd(III) in the (RS) slabs which occurs in the aluminate, gives way to a segregated one in the aluminochromite. This segregation is likely to originate in a preferential formation of Nd(III)-O-Cr(III) bridge bonds, in connection with a paramagnetic coupling of Nd(III) and Cr(III).

3.2. The $Y_{0.9}Ce_{0.1}CaCr_yAl_{1-y}O_4$ and $Y_{0.8}Ce_{0.1}Ca_{1.1}Cr_yAl_{1-y}O_4$ diluted solid solutions ($y \leq 0.1$)

The introduction of cerium in the (RS) slabs of the

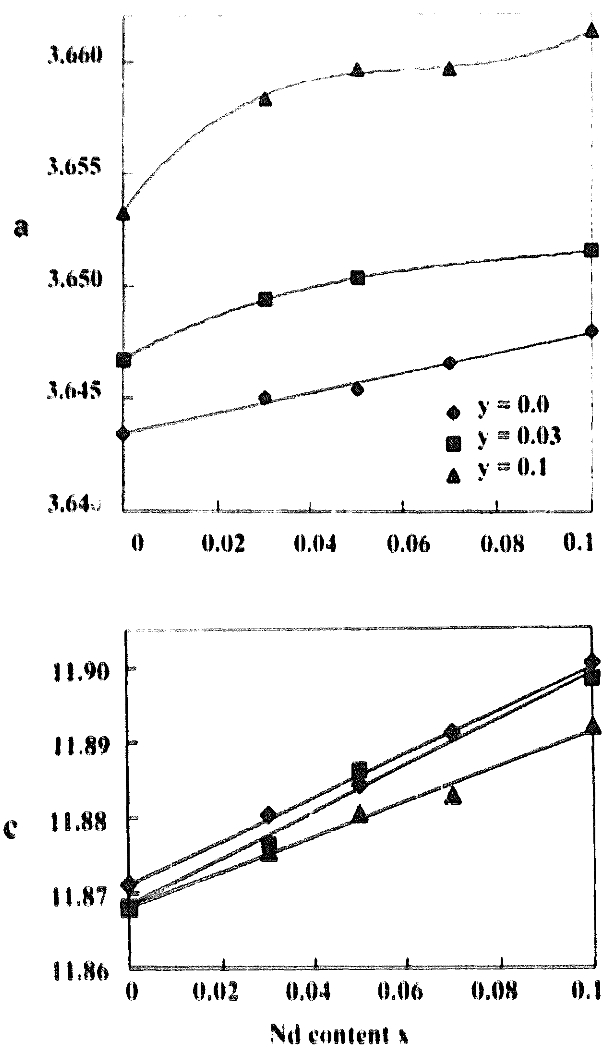

Fig. 2. Variation of the cell parameters (Å) in the diluted solid solution $Y_{1-x}Nd_xCaCr_yAl_{1-y}O_4$.

aluminochromite solid solution $YCaCr_yAl_{1-y}O_4$ was decided in order to check the possible occurrence of a partial reduction of Ce(IV) to Ce(III), this one being further able to interact with Cr(III) in the (P) layers. In this respect, two different substitutions were operated:

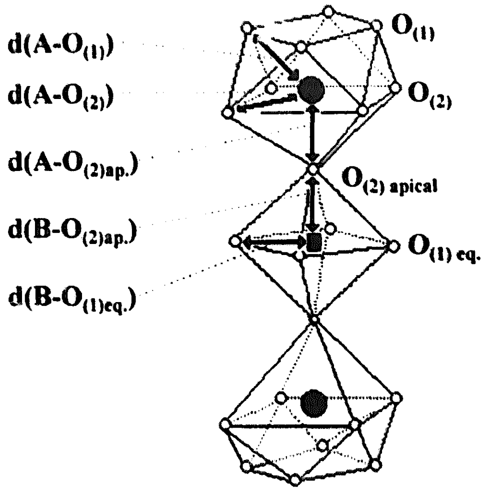

Fig. 3. Metal-oxygen distances in the (BO_6) octahedron and the (AO_9) polyhedron.

- the simple one Y → Ce, which in the case of Ce(IV) results in an excess positive charge, this being favourable to a partial reduction in Ce(III);
- the double one 2Y → Ce + Ca, which gives an exact charge compensation if the valence state of Ce remains equal to (IV).

On Fig. 4 is drawn the variation of the cell parameters of the two Ce-containing solid solutions $Y_{0.9}Ce_{0.1}CaCr_yAl_{1-y}O_4$ and $Y_{0.8}Ce_{0.1}Ca_{1.1}Cr_yAl_{1-y}O_4$, together with that of $YCaCr_yAl_{1-y}O_4$. The typical anisotropic behaviour evidenced for $YCaCr_yAl_{1-y}O_4$ [3] i.e. *a* increases when *c* decreases as an effect of the Cr(III) enrichment, is saved. Both the values of *c* and, to a smaller extent that of *a*, are larger when Ce is present, except for the composition $Y_{0.9}Ce_{0.1}CaCr_{0.1}Al_{0.9}O_4$ which exhibits a somewhat smaller value of *c* as compared with that of $YCaCr_{0.1}Al_{0.9}O_4$. Such an increase can be explained for the solid solution $Y_{0.8}Ce_{0.1}Ca_{1.1}Cr_yAl_{1-y}O_4$ on the basis of a larger amount of the bigger Ca^{2+} cation: in nine-fold coordination $R(Ca^{2+})$

Table 1

Metal-oxygen distances (Å) in the $Y_{1-x}Nd_xCaCr_yAl_{1-y}O_4$ diluted solid solution

Distance	$Y_{1-x}Nd_xCaAlO_4$			$Y_{1-x}Nd_xCaCr_{0.1}Al_{0.9}O_4$			
M-O	$YCaAlO_4$	x = 0.10	$NdCaAlO_4$ [5]	x = 0.00	x = 0.05	x = 0.07	x = 0.10
$B-O_6$							
$B-O_{(1)eq} \times 4$	1.822	1.824	1.842	1.827	1.830	1.830	1.830
$B-O_{(2)ap} \times 2$	1.993	1.996	2.018	2.002	1.997	2.021	2.016
d_{B-Oap}/d_{B-Oeq}	1.094	1.094	1.095	1.096	1.091	1.104	1.102
$A-O_9$							
$A-O_{(1)} \times 4$	2.484	2.488	2.518	2.484	2.486	2.490	2.493
$A-O_{(2)} \times 4$	2.595	2.597	2.623	2.603	2.607	2.609	2.609
$A-O_{(2)ap} \times 1$	2.256	2.261	2.326	2.249	2.260	2.232	2.242
$d_{average}$	2.508	2.511	2.544	2.511	2.515	2.514	2.517

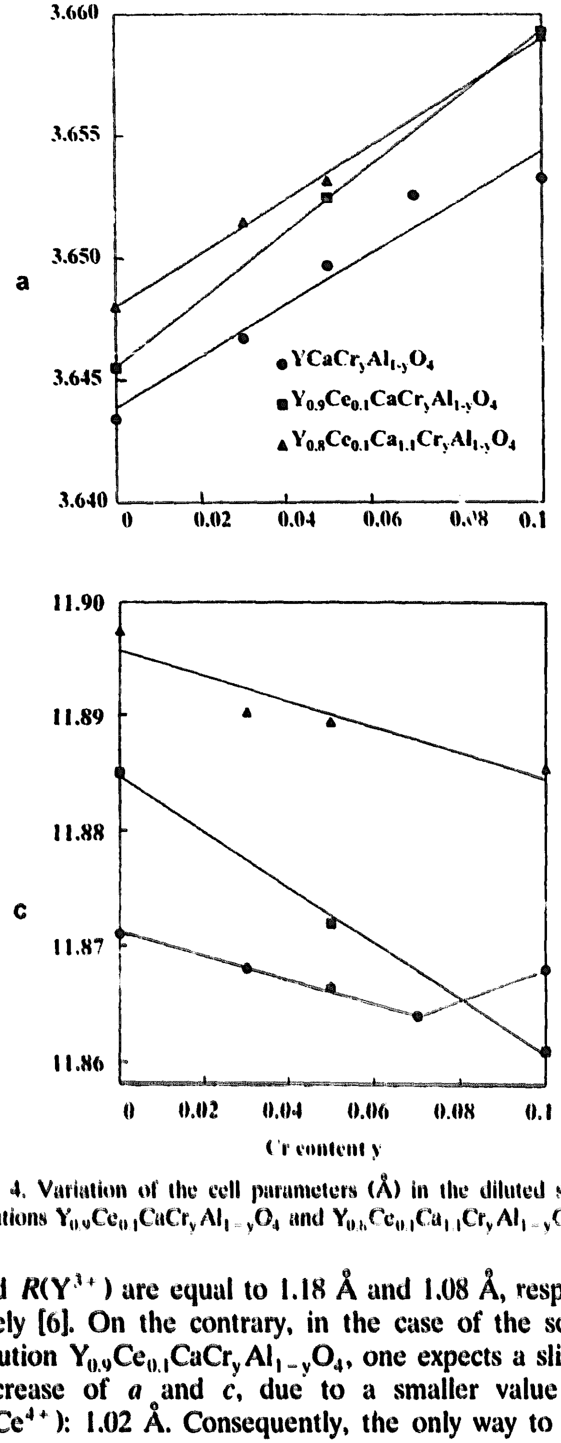

Fig. 4. Variation of the cell parameters (Å) in the diluted solid solutions $Y_{0.9}Ce_{0.1}CaCr_yAl_{1-y}O_4$ and $Y_{0.8}Ce_{0.1}Ca_{1.1}Cr_yAl_{1-y}O_4$.

and $R(Y^{3+})$ are equal to 1.18 Å and 1.08 Å, respectively [6]. On the contrary, in the case of the solid solution $Y_{0.9}Ce_{0.1}CaCr_yAl_{1-y}O_4$, one expects a slight decrease of a and c, due to a smaller value of $R(Ce^{4+})$: 1.02 Å. Consequently, the only way to account for the increase of the cell parameters is the formation of Ce(III): $R(Ce^{3+})$ is close to 1.20 Å.

An unambiguous signature of the presence of Ce(III) is found in the results of the investigation of the magnetic susceptibility, which was carried out for the two aluminates $Y_{0.9}Ce_{0.1}CaAlO_4$ and $Y_{0.8}Ce_{0.1}Ca_{1.1}AlO_4$. As deduced from the data reported in Fig. 5, paramagnetism is observed for '$Y_{0.9}$' composition and diamagnetism for the '$Y_{0.8}$' one. This result settles at least the partial presence of Ce(III) in '$Y_{0.9}$' and that of Ce(IV) only, in '$Y_{0.8}$'. Because of this, in the aluminochromite solid solution $Y_{0.8}Ce_{0.1}Ca_{1.1}Cr_yAl_{1-y}O_4$, the paramagnetic susceptibility is determined only by the electronic state of Cr(III); as to the solid solution $Y_{0.9}Ce_{0.1}CaCr_yAl_{1-y}O_4$, the magnetic data can be assumed to take into account the simultaneous presence of Cr(III) in the (P) layers and Ce(III) in the (RS) slabs.

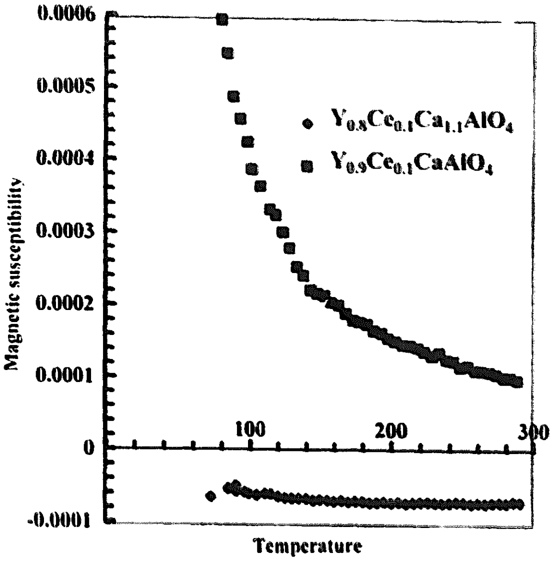

Fig. 5. Temperature dependence of the magnetic susceptibility (cm^3/mole) in $Y_{0.9}Ce_{0.1}CaAlO_4$ and $Y_{0.8}Ce_{0.1}Ca_{1.1}AlO_4$.

Structure calculations were performed in the case of '$Y_{0.9}$'. The metal-oxygen distances are reported in Table 2 together with that of $YCaAlO_4$. As a result of the refinement procedure, the thermal agitation of the apical oxygen i.e. the oxygen which connects a (P) layer to an (RS) slab, was found to be rather large ($B \approx 4$ Å^2). As previously observed for the nickelate La_2NiO_4 [7], such agitation is well understood in terms of a splitting of the position of the apical oxygen in a (001) plane, due to some crystal chemical constraints, for example supplementary oxygen in the (RS) slab or too small La-O distances [7,8]. Checking the occurrence of such splitting of O_{ap} in '$Y_{0.9}$' allowed us to get evidence of two types of in-plane A-O_{ap} distances (Table 2), a short one 2.485 Å and a long one 2.710 Å. A likely explanation of this phenomenon can be found in the presence of two Ce-O_{ap} distances: as the difference between these values (0.225 Å) is close to the difference of the ionic radii between the oxidized and reduced Ce (0.18 Å), the short distance is ascribed to Ce(IV) and the long one to Ce(III).

On the basis of these different results which concern crystal chemistry and magnetochemistry of cerium-containing aluminates, evidence of the occurrence of some reduction of Ce(IV) to Ce(III) is obtained. It is worthy of note that the extent of such reduction depends on working a precise crystal chemical constraint, namely an increase of the cationic charge in

Table 2

Metal-oxygen distances (Å) in $Y_{0.9}Ce_{0.1}CaAlO_4$ and $YCaAlO_4$

Distance M-O	$YCaAlO_4$	$Y_{0.9}Ce_{0.1}CaAlO_4$	
$B\text{-}O_6$			
$B\text{-}O_{(1)eq.} \times 4$	1.822	1.823	
$B\text{-}O_{(2)ap.} \times 2$	1.993	1.995	
$d_{B\text{-}Oap.}/d_{B\text{-}Oeq.}$	1.094	1.094	
$A\text{-}O_9$			
$A\text{-}O_{(1)} \times 4$	2.484	2.487	
$A\text{-}O_{(2)} \times 4$	2.595	2.710	2.485
$A\text{-}O_{(2)ap.} \times 1$	2.256	2.261	
$d_{average}$	2.508	2.511	

the (RS) slabs. As a result of the charge compensation mechanism, the valence state of Ce is lowered from (IV) to (III). Quantitative information can be obtained from the magnetic data: approximately half of the Ce is reduced. Such behaviour of cerium was previously emphasized in the superconducting neodymium-cerium cuprate $Nd_{2-x}Ce_xCuO_4$ ($x = 0.18$) where a similar tendency to get an increase of the c parameter was observed and ascribed to the presence of the bigger Ce^{3+} cation [9].

4. Conclusion

The investigation of oxide-diluted solid solutions with the K_2NiF_4-type structure, brings the opportunity to get evidence of 'exotic' phenomena concerning the distribution and the valence state of '3d' and '4f' transition elements. As an example, a non-statistical distribution of Nd(III) in the rock-salt part of the intergrowth structure is triggered when there is a mutual influence of Cr(III) in the perovskite layer. Concerning cerium in the (RS) slabs, the ability to lower its valence state from (IV) to (III) due to a charge compensation mechanism, is proved. In any case, the role of the bridge bond which connects the (P) and (RS) parts of the intergrowth is crucial: the mutual influence of the transition elements finds that their preferential location and the overall anisotropy of the intergrowth originates in this place.

Acknowledgements

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