



**B SITE CATIONIC PARTIAL SUBSTITUTION BY La³⁺ DOPING IN THE Sr₂CoWO₆
DOUBLE PEROVSKITE: A XRPD STRUCTURAL STUDY**

Carlos A. López*, Maria del C. Viola and José C. Pedregosa

Área de Química General e Inorgánica "Dr. Gabino F. Puellas", Departamento de Química, Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis, Chacabuco y Pedernera, 5700 San Luis, Argentina .

***E-mail:** calopez@unsl.edu.ar **FAX:** 02652-430224

Received September 26, 2008. In final form February 10, 2009.

Abstract

La-doped Sr₂CoWO₆ double perovskites have been prepared in air in polycrystalline form by solid state reaction at 1300 °C. The structure of these materials with Sr_{2-x}La_xCoW_{1-x/4}Co_{x/4}O₆ stoichiometry where x = 0.4, 0.8, 1.2 and 1.6, has been studied by X-ray diffraction (XRPD) applying Rietveld method. The replacement of Sr²⁺ by La³⁺ induces a change of the tetragonal structure, space group I4/m of the undoped Sr₂CoWO₆ into the distorted monoclinic crystal structure, space group P2₁/n, Z = 2. The structure of La-doped phases contains alternating CoO₆ and (Co/W)O₆ octahedra, almost fully ordered.

Keywords: Sr₂CoWO₆, double perovskite, La-doped, structure, Rietveld method.

Resumen

Se prepararon perovskitas dobles Sr₂CoWO₆ dopadas con lantano en aire como fases policristalinas por reacción al estado sólido a 1300°C. La estructura de estos materiales con estequiometría Sr_{2-x}La_xCoW_{1-x/4}Co_{x/4}O₆ donde x = 0,4; 0,8; 1,2 y 1,6 fueron estudiadas aplicando el método Rietveld a partir de datos de difracción de Rayos X de polvos. La sustitución de Sr²⁺ por

La³⁺ produce un cambio desde la estructura tetragonal I4/m de la fase sin dopar Sr₂CoWO₆ a una estructura monoclinica distorsionada P2₁/n, Z = 2, a temperatura ambiente. La estructura de las fases dopadas contienen octaedros CoO₆ y (Co/W)O₆ alternados, completamente ordenados.

Palabras clave: Sr₂CoWO₆, perovskita doble, dopadas con La, estructura, método Rietveld.

Introduction

Since the discovery of colossal magnetoresistance (CMR) in manganites there was an increasing interest of solid-state chemists and physicists to prepare new compounds that could have this property due to this effect is of technological interest for the detection of magnetic fields in magnetic memory devices. A few years ago, a study on Sr₂FeMoO₆ [1] demonstrated that only minority spins are present at the Fermi level in its electronic structure and that it exhibited intrinsic tunneling-type magnetoresistance (TMR) at room temperature (RT). This fact motivated the study of this material [2-3] and triggered the interest to prepare new double perovskites which potentially could present half-metallic properties.

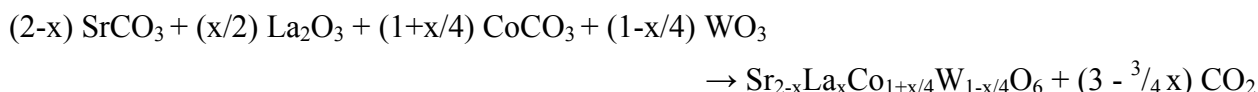
We recently reported the induction of CMR in Sr₂CoMoO₆ [4] upon chemical reduction, via topotactical removal of oxygen atoms. We also prepared Sr₂CoWO₆ [5]. At room temperature, the crystal structure was tetragonal, space group I4/m, with $a = 5.58277(1)$ Å and $c = 7.97740(1)$ Å. The structure contains alternating CoO₆ and WO₆ octahedral units, tilted in anti-phase by 7.24° in the basal *ab* plane along the [001] direction of the pseudo cubic cell. This corresponds to the $a^0a^0c^-$ Glazer's notation as derived by Woodward for 1:1 ordering of double perovskites [6], consistent with space group I4/m. Magnetic and neutron diffraction measurements indicate an antiferromagnetic ordering below $T_N = 24$ K. Magnetic and electrical properties and bond valence sums are consistent with the electronic configuration Co²⁺(3d⁷)-W⁶⁺(5d⁰). Based on our findings with Sr₂CoWO₆ we tried to induce semiconductivity and magnetotransport by chemical reduction in this compound but we were unsuccessful, probably due to the difficulty in reducing W⁶⁺. Another possibility is to induce semiconductivity by electron doping replacing Sr²⁺ in the A site by a trivalent cation [7-9]. It has been previously reported that the replacement of A²⁺ by Ln³⁺ in A₂FeB''O₆ (where B'' = Mo) induces magnetic and structural changes [10]. When doping with La, an important fraction of the injected electrons is localized at Mo sites which is harmful concerning the potential applicability, since it promotes the occurrence of anti-site disordering between Fe and Mo cations [11-13]. In a previous study, the attempts to induce the injection of electrons using the low La-doping were unsuccessful. However, an interesting cationic re-ordering in monoclinic system was observed since in order to maintain electroneutrality, as La³⁺ is incorporated into the 4*e* Wyckoff site, a fraction of W⁶⁺ is replaced by Co²⁺ ions into the 2*d* Wyckoff sites with segregation of SrWO₄ (scheelite type) [14].

In the present work we describe the synthesis of higher La(III)-doped Sr₂CoWO₆ double perovskites prepared by a solid-state reaction in order to confirm this cationic partial substitution by La³⁺ in the B site of the Sr₂CoWO₆ double perovskite. The results of Rietveld refinement of X-ray powder diffraction (XRPD) data on well-crystallized samples are analyzed. Crystal structures for these compounds as a function of La doping are discussed and the highest grade of substitution is established.

Experimental

Sr_{2-x}La_xCo_{1+x/4}W_{1-x/4}O₆ double perovskites with nominal $x = 0.4$ (SL04), 0.8 (SL08), 1.2 (SL12) and 1.6 (SL16) were prepared as dark brown polycrystalline powders by a solid-state reaction. Stoichiometric amounts of analytical grade SrCO₃, La₂O₃, CoCO₃ and WO₃ were mixed, ground, placed in a platinum crucible and treated at 600 °C in air for 12 h. The resulting powder was reground and calcined at 1000 °C for 12 h. Finally the product was fired at 1300 °C in three

periods totaling 24 h with intermediate milling of the reaction mixture. The rate of heating was of 5 °C min⁻¹. The general proposed reaction is:



where nominal $x = 0.4; 0.8; 1.2$ and 1.6 .

The initial structural identification and characterization of the samples was carried out by XRPD (Cu K α , $\lambda = 1.5418$ Å). The XRPD patterns are characteristic of a perovskite structure, showing the splitting of certain reflections, typical of a monoclinic distortion, for instance, the (004) reflection of the prototype cubic (Fm $\bar{3}$ m space group).

XRPD patterns were refined with the Rietveld method [15] using the FULLPROF program [16]. In the refinements, the shape of the peaks was simulated by a pseudo-Voigt function and the background was fitted by a fifth-degree Chebyshev polynomial. In the final runs, the following parameters were refined: scale factors, background coefficients, zero-point error, unit-cell parameters, pseudo-Voigt correction for asymmetric parameters, positional coordinates, isotropic atomic displacement parameters, and relative Sr/La and Co/W occupancy factors.

Results and Discussion

Unlike the Sr₂CoWO₆ which presents tetragonal I4/m symmetry [5] in these doped compounds the Bragg reflections were indexed with a monoclinic unit cell and the structure was refined in the space group P2₁/n (monoclinic, N^o14, non-standard setting) (Unique axis b, cell choice 2 [17]). Sr and La atoms were located at $4e$ (x,y,z) positions, Co at $2c$ ($\frac{1}{2},0,\frac{1}{2}$) and Co/W at $2d$ ($\frac{1}{2},0,0$) sites, and oxygen atoms at $4e$ (x,y,z). La₂O₃ was included in the refinement as a second phase only for the sample SL16, defined in the hexagonal space group P6₃/mmc [18]. From the scale factor of the main and secondary phases we estimated the following impurity level as weight %: 1.0(1)% of La₂O₃.

The structural refinement of SL04, SL08, SL12 and SL16 doped double perovskites was performed from XRPD data at RT. An excellent fit was obtained for this model (Figure 1). The differences with the same other models are very subtle since they involve mainly small shifts of the in-plane oxygen atoms. However, the splitting at $2\theta \cong 46^\circ$ can be correctly accounted by considering a monoclinic symmetry P2₁/n, N^o 14, non-standard setting (unique axis b, cell choice 2). In fact, these symmetry and space group are adopted by other related and well known double perovskites, [19] with small tolerance factors, such as Ca₂FeMoO₆ [20].

Table 1 includes the final atomic coordinates and discrepancy factors after the refinement for La-doping phases at 298 K. Table 2 lists the main interatomic distances and angles. As can be seen there is a gradual decrease in cell parameters and in the mean distance <A-O> as doping with La³⁺ increases, consistent with the lower ionic radius of La³⁺ (ir: 1.36 Å) compared to Sr²⁺ (ir: 1.44 Å). This smaller size of La³⁺ is the responsible for the larger monoclinic distortion as doping increases (see Figure 2).

We found La occupancies in the A site ($4e$ Wyckoff position) were 14; 34; 54.5 and 83.5% for SL04, SL08, SL12 and SL16 respectively. The possibility of Co/W antisite disordering, assuming that some Co from the $2c$ positions could randomly replace some W at $2d$ positions was also checked. The $2c$ site was always fully occupied by Co. On the other hand in the $2d$ site, Co occupancy increases as La doping increases, being 7, 17, 27 and 42% for SL04, SL08, SL12 and SL16 respectively. On the other hand, the re-ordering of the Co ions in different B-sites is confirmed by the variation of the (Co)_{2c}-O and (W/Co)_{2d}-O bond distances. This bond distance remains constant in the Co²⁺ fully occupied $2c$ site whereas it increases with higher La-doping in the $2d$ site where Co²⁺ (ir: 0.745 Å) and W⁶⁺ (ir: 0.6 Å) are present (see Table 2).

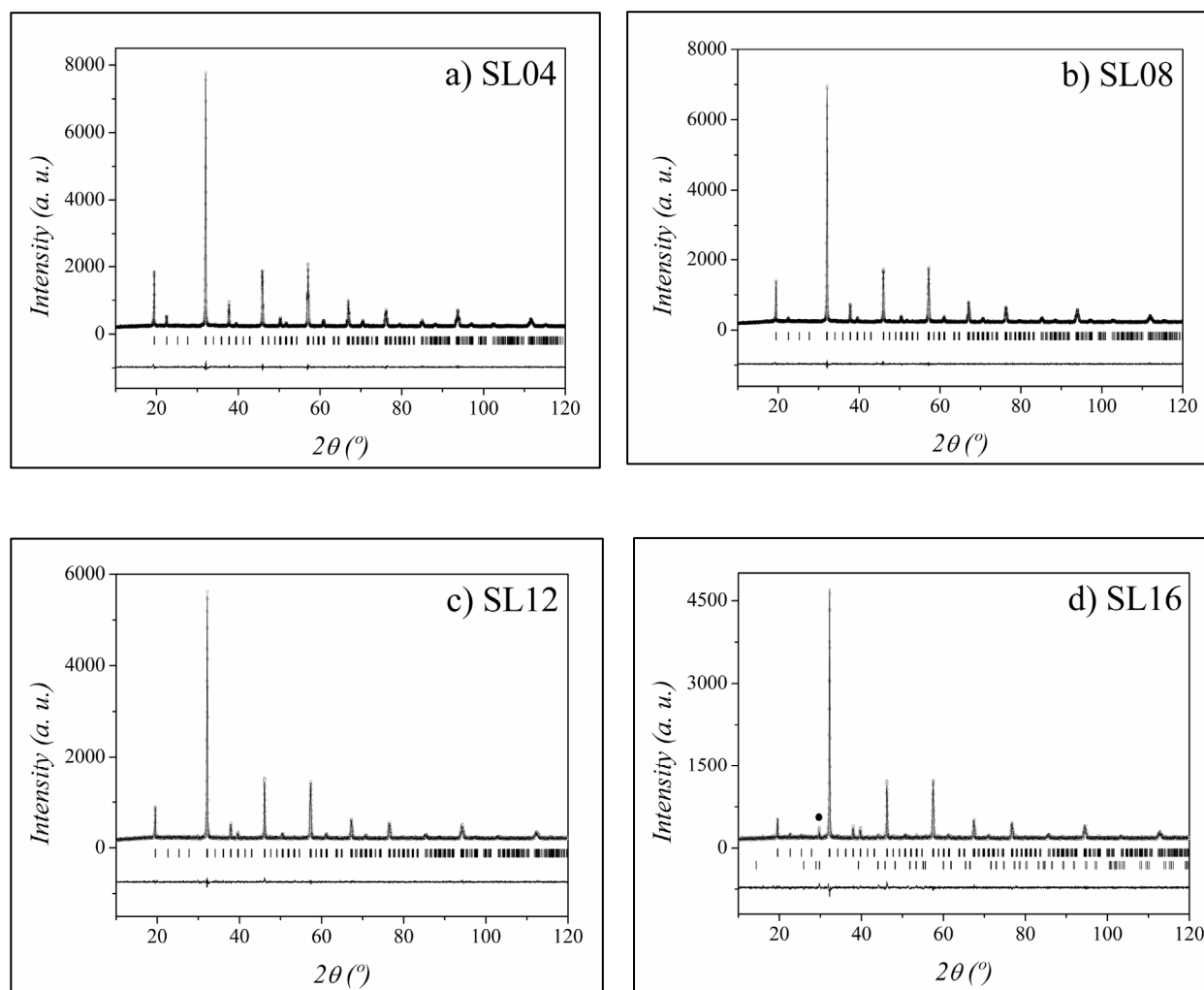
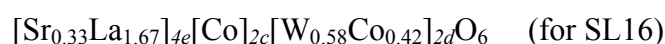
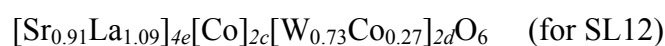
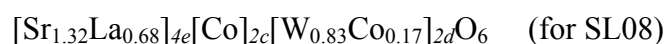
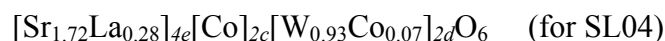


Figure 1.- XRPD patterns for La-doped double perovskites at RT a) SL04; b) SL08; c) SL12 and d) SL16. The circle indicates the main reflection of the La_2O_3 impurity phase in d) SL16.

The monoclinic double perovskite is formed as pure compound up to a maximum value of $x = 1.6$; for higher x values ($x = 2$) this phase appears mixed with La_2O_3 and the new phase $\text{La}_2\text{W}_2\text{O}_9$.

As a consequence, real stoichiometries can be written as:



A drawing of the structure is shown in Figure 3; it contains alternating CoO_6 and $(\text{Co},\text{W})\text{O}_6$ octahedra, tilted in phase along the (100) direction of the pseudo cubic cell and in anti-phase along the (010) and (001) directions, which corresponds to the $a^-a^+b^+$ Glazer's notation as derived by Woodward [6] for 1:1 ordering of double perovskites, consistent with space group $P2_1/n$. The average tilting angles can be estimated as $\varphi = (180 - \theta)/2$ where $\theta = \langle \text{Co-O-B} \rangle$; we obtain $\varphi = 8.7^\circ$; $\varphi = 8.0^\circ$, $\varphi = 9.5^\circ$ and $\varphi = 13.4^\circ$ for SL04, SL08, SL12 and SL16 respectively, clearly there is an increase in the tilting angle as La doping increases.

Table 1. Positional, isotropic atomic displacement and cell parameters for La-doped double perovskites [Sr_{2-x}La_x]_{4e}[Co]_{2c}[W_{1-x/4}Co_{x/4}]_{2d}O₆ in the monoclinic *P2₁/n* Space Group, *Z* = 2, from XRPD data at 298 K. Reliability factors after the Rietveld refinement are also given.

Sample	SL04	SL08	SL12	SL16
<i>a</i> (Å)	5.5831(2)	5.5717(3)	5.5569(3)	5.5434(3)
<i>b</i> (Å)	5.6102(2)	5.5946(3)	2.5795(3)	5.5629(4)
<i>c</i> (Å)	7.8911(2)	7.8789(3)	7.8627(4)	7.8437(4)
β	90.01(1)°	90.05(2)°	89.99(2)°	90.01(3)°
<i>V</i> (Å ³)	247.17(1)	245.60(2)	243.78(2)	241.88(3)
Sr/La	4e (x,y,z)			
x	1.007(2)	1.007(3)	1.008(4)	1.001(5)
y	1.003(1)	1.003(1)	1.006(1)	1.006(1)
z	0.2485(6)	0.247(1)	0.246(1)	0.245(1)
Biso	1.13(7)	1.47(9)	1.8(1)	2.0(2)
Co	2c(½,0,½)			
Biso	0.6(1)	0.3(2)	0.2(2)	0.2(4)
Co/W	2d(½,0,0)			
Biso	0.50(5)	0.54(8)	0.28(9)	0.2(2)
O1	4e (x,y,z)			
x	0.97(1)	0.98(2)	0.98(3)	1.01(3)
y	0.544(4)	0.561(5)	0.552(7)	0.576(7)
z	0.262(3)	0.262(5)	0.272(8)	0.28(1)
Biso*	1.00	1.00	1.00	1.00
O2	4e (x,y,z)			
x	0.740(7)	0.745(9)	0.76(1)	0.74(1)
y	0.22(1)	0.21(1)	0.21(1)	0.24(2)
z	1.033(7)	1.01(1)	1.001(9)	1.01(1)
Biso*	1.00	1.00	1.00	1.00
O3	4e (x,y,z)			
x	0.219(7)	0.208(8)	0.21(1)	0.175(9)
y	0.216(9)	0.24(1)	0.251(9)	0.24(1)
z	0.981(9)	0.971(9)	0.944(6)	0.917(6)
Biso*	1.00	1.00	1.00	1.00
R _p (%)	21.8	23.8	28.9	39.7
R _w (%)	13.7	14.3	16.3	21.4
R _{exp} (%)	17.9	19.4	22.3	26.1
χ^2	0.58	0.59	0.59	0.67

* Parameters fixed at 1.00

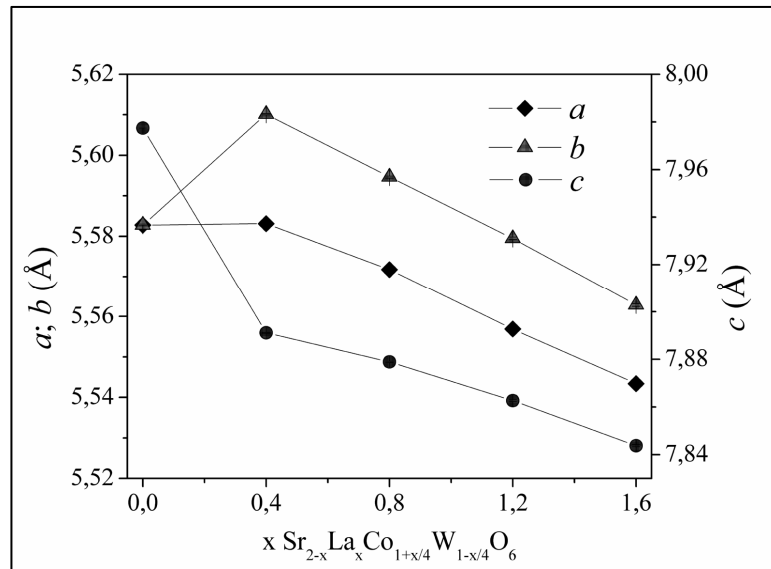


Figure 2. Cell parameters evolution with La-doping. a) SL04; b) SL08; c) SL12 and d) SL16.

Table 2. Main bond distances (Å) and selected angles (°) for monoclinic La-doped double perovskites $[\text{Sr}_{2-x}\text{La}_x]_{4e}[\text{Co}]_{2c}[\text{W}_{1-x/4}\text{Co}_{x/4}]_{2d}\text{O}_6$ from XRPD data at 298 K.

	SL04	SL08	SL16	SL16
CoO ₆ octahedra				
Co–O1 (x2)	2.09(2)	2.10(4)	2.16(6)	2.20(8)
Co–O2 (x2)	2.14(5)	2.16(6)	2.07(6)	2.06(8)
Co–O3 (x2)	2.01(5)	1.88(5)	1.86(5)	1.86(5)
<Co–O>	2.08(2)	2.04(2)	2.03(2)	2.04(3)
B''O ₆ octahedra				
B''–O1(x2)	1.90(2)	1.91(4)	1.82(6)	1.82(8)
B''–O2(x2)	1.85(5)	1.80(6)	1.89(6)	1.87(8)
B''–O3(x2)	1.99(4)	2.11(5)	2.19(5)	2.33(5)
<B''–O>	1.91(2)	1.94(2)	1.97(2)	2.01(3)
Co–O1–B''(x2)	163(1)°	159(2)°	162(3)°	155(3)°
Co–O2–B''(x2)	164(2)°	171(2)°	168(3)°	172(3)°
Co–O3–B''(x2)	163(2)°	162(2)°	153(2)°	139(2)°
<Co–O– B''>	162.7°	164.0°	161.0°	155.3°
AO ₁₂ polyhedra				
<A–O>	2.81	2.80	2.76	2.65

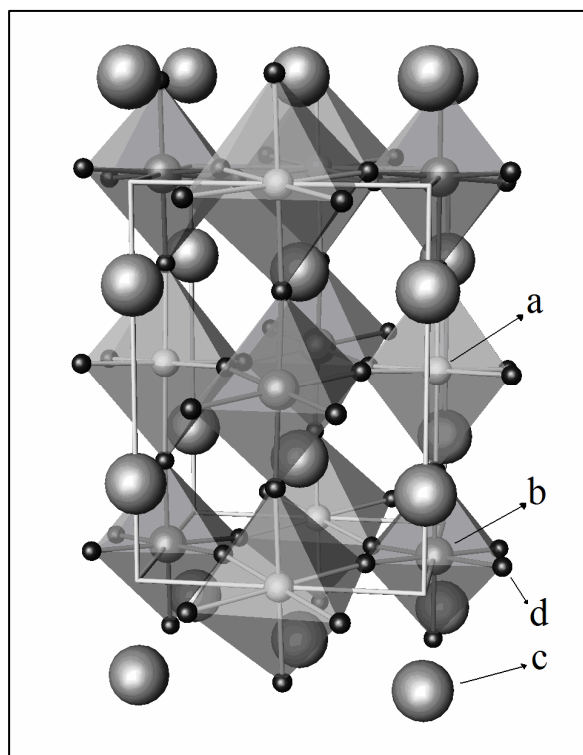


Figure 3. A view of the crystal structure of the La-doped double perovskites for a tilting of 13.4° (SL16). a) Co atoms with octahedral coordination b) Co or W with octahedral coordination c) Sr or La atoms with cubooctahedral coordination d) oxygen atoms.

Conclusions

We have prepared a series of mixed Co-W double perovskites of the type $\text{Sr}_{2-x}\text{La}_x\text{CoW}_{1-x/4}\text{Co}_{x/4}\text{O}_6$ where A is Sr^{2+} doped with La^{3+} as well-crystallized samples. In particular, we have settled how the structure responds to changes in the effective size and charge of the A-type site, using a XRPD method. The results of Rietveld analysis indicate the occurrence of a structural phase transition from a tetragonal ($I4/m$) lattice in Sr_2CoWO_6 to a monoclinic ($P2_1/n$) one from higher grade of substitution (maximum value $x = 1.6$). The doping in the A site for a higher charged cation did not lead to an injection of electrons as it effectively occurs in systems with $B' = \text{Fe}$. However, an interesting structural change due to the re-ordering of the Co ions in different B-sites has been observed. This modification is unprecedented since it has never been observed before in similar systems.

Acknowledgements. C.A.L. thanks to CONICET fellowship. J. C. P. thanks CONICET (PIP N° 6246), ANPCyT (Project PICT 25459) and SECyT-UNSL (Project 7707), for financial support. J. C. P. is member of CONICET.

References

- [1] K. I. Kobayashi, T. Kimura, H. Sawada, K. Terakura, Y. Tokura, *Nature*. **1998**, 395, 677.
- [2] D. Niebieskikwiat, R.D. Sánchez, A. Caneiro, L. Morales, M. Vásquez-Mansilla, F. Rivadulla, L. Hueso. *Phys. Rev. B*. **2000**, 62, 3340.

- [3] D. Niebieskikwiat, A. Caneiro, R.D. Sánchez, J. Fontcuberta, *Phys. Rev. B.* **2001**, *64*, 180406.
- [4] M.C. Viola, M.J. Martínez Lope, J.A. Alonso, P. Velazco, J.L. Martínez, J.C. Pedregosa, R.E. Carbonio, M.T. Fernández-Díaz, *Chem. Mater.* **2002**, *14*, 812.
- [5] M.C. Viola, M.J. Martínez-Lope, J.A. Alonso, J.L. Martínez, J.M. De Paoli, S. Pagola, J.C. Pedregosa, M.T. Fernández-Díaz, R.E. Carbonio, *Chem. Mater.* **2003**, *15*, 1655.
- [6] P.M. Woodward, *Acta Crystallogr. B.* **1997**, *53*, 32.
- [7] D. Sánchez, J.A. Alonso, M. García-Hernández, M.J. Martínez-Lope, M.T. Casais, J.L. Martínez, *J. Mater. Chem.* **2003**, *13*, 1771.
- [8] J. Lindén, T. Shimada, T. Motohashi, H. Yamauchi, M. Karppinen, *Solid State Commun.* **2004**, *129*, 129.
- [9] Q. Lin, M. Greenblatt, M. Croft, *J. Solid State Chem.* **2005**, *178*, 1356.
- [10] J. Navarro, J. Nogués, J.S. Muñoz, J. Fontcuberta, *Phys. Rev. B.* **2003**, *67*, 174416.
- [11] C. Frontera, D. Rubí, J. Navarro, J.L. García-Muñoz, C. Ritter, J. Fontcuberta, *Phys. B.* **2004**, *350*, E285.
- [12] D. Rubí, C. Frontera, G. Herranz, J.L. García-Muñoz, J. Fontcuberta, C. Ritter, *J. Appl. Phys.* **2004**, *95*, 7082.
- [13] C. Frontera, D. Rubi, J. Navarro, J.L. García-Muñoz, J. Fontcuberta, C. Ritter, *Phys. Rev. B.* **2003**, *68*, 012412.
- [14] C. A. López, M. del C. Viola, R. D. Sánchez, R. E. Carbonio, M. T. Díaz, J. C. Pedregosa, *J. Solid State Chem.*, In Press, Accepted Manuscript, **2008**, doi:10.1016/j.jssc.2008.08.007, Available online 15 August.
- [15] H.M. Rietveld, *J. Appl. Crystallogr.* **1969**, *2*, 65.
- [16] J. Rodríguez-Carvajal, *Phys. B.* **1993**, *192*, 55.
- [17] International Tables for Crystallography, Vol. A, "Space-group Symmetry" Edited by Theo Hahn, Published for International Union of Crystallography (IUCr) by D. Reidel Publishing Company, Dordrecht: Holland/Boston: U.S.A., page 177, 1983.
- [18] P. Aldebert, J.P. Traverse, *Mater. Res. Bull.* **1979**, *14*, 303.
- [19] M.W. Lufaso, P. W. Barnes, P. M. Woodward, *Acta Cryst. B.* **2006**, *62*, 397.
- [20] J. A. Alonso, M. T. Casais, M. J. Martínez-Lope, P. Velasco, A. Muñoz, M. T. Fernández-Díaz, *Chem.Mater.* **2000**, *12*, 161.