Revista ION
ISSN: 0120-100X
ISSN: 2145-8480
Universidad Industrial de Santander

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Revista ION, vol. 31, no. 1, January-June, 2018, pp. 65-69
Universidad Industrial de Santander

DOI: 10.18273/revion.v31n1-2018011

Available in: http://www.redalyc.org/articulo.oa?id=342060884012

Revista ion | ISSN web: 2145-8480 | DOI: http://dx.doi.org/10.18273/revion.v31n1-2018011

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Influencia del radio ionico en la respuesta estructural y magnética del sistema $Pr_{0.48}TR_{0.02}Ca_{0.5}Co0_{3-\delta}$

Influência do rádio iónico sobre resposta estrutural e magnética do sistema $Pr_{0.48}TR_{0.02}Ca_{0.5}Co0_{3-\delta}$

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Fecha recepción: 15 de agosto de 2017
Fecha aceptación: 12 de mayo de 2018

Abstract
The metal - insulator transition (MIT), of the oxides type perovskite formed by elements of Rare Earths (TR), presents an interesting behavior in the family derived from $Pr_{0.5}Ca_{0.5}Co0_{3-\delta}$ .In this paper it is studied the influence of ionic radius of the rare earth TR in the crystalline structure and in the synthesis of the new family perovskite type $Pr_{0.48}TR_{0.02}Ca_{0.5}Co0_{3-\delta}$ (TR=Eu,Sm,Dy),produced by the technique of the solid state reaction. The structural characterization of the system was realized by X-rays diffraction (XRD) and Rietveld analysis, demonstrating that the samples crystallize in a orthorhombic structure with spatial group *Pnma* (#62), without significant changes in phase structural generated by the variation of the ionic radius. They were measurements of magnetization as a function of temperature with the vibrating sample magnetometer VSM of the Quantum Design, in temperature range from 50 to 310K. The curves of the magnetization as a function of temperature presented a similar behavior for all system.

Keywords: *cobaltite, structure crystalline, paramagnetic.*

Resumen
La transición metal-aislante (MIT), de óxidos tipo perovskita formados por elementos de tierras raras (TR), presenta un comportamiento interesante en la familia derivada del $Pr_{0.5}Ca_{0.5}Co0_{3-\delta}$. En este trabajo se estudia la influencia del radio iónico de la TR en la estructura cristalina y en la síntesis de la nueva familia tipo perovskita $Pr_{0.48}TR_{0.02}Ca_{0.5}Co0_{3-\delta}$ (TR =Eu, Sm, Dy), producida por la técnica de reacción en estado sólido**.** La caracterización estructural del sistema se realizó a través de la técnica de difracción de rayos X (DRX) y análisis de refinamiento Rietveld, con lo cual se demuestra que las muestras cristalizan en una estructura ortorrómbica de grupo espacial Pnma (#62), sin cambios significativos de fase estructural generados por la variación del radio iónico. Se realizaron medidas de magnetización, en función de la temperatura con el magnetómetro de muestra vibrante VSM de la Quantum Design, en un rango de temperatura de 50 a 310 K. Las curvas de magnetización en función de la temperatura presentan un comportamiento similar para todo el sistema.

Palabras clave: *cobaltita, estructura cristalina, paramagnético*

Cita: Saavedra Gaona IM, Supelano GI, Ortiz C, Parra Vargas CA, Barón-González AJ. Influence of the ionic radius on Structural and Magnetic response of the system $Pr_{0.48}TR_{0.02}Ca_{0.5}Co_{03-\delta}$. rev.ion. 2018;31(1):65-69. doi: 10.18273/revion.v31n1-2018011

Resumo
O metal de transição - isolador (MIT), do tipo perovskita de óxidos formado por elementos de Rare Earths (TR), apresenta um comportamento interessante na família derivado de $Pr_{0.5}Ca_{0.5}CoO_{3-\delta}$. Neste artigo, estuda-se a influência de radio-iónico do TR na estrutura cristalina e na síntese do novo tipo familiar $Pr_{0.48}TR_{0.02}Ca_{0.5}CoO_{3-\delta}$ (TR = Eu, Sm, Dy), produzido pela técnica de reação do estado sólido. A caracterização estrutural do sistema foi realizada por difração de raios-X (DRX) e análise de refinamento Rietveld, demonstrando que as amostras cristalizam em uma estrutura ortorrôbbica com o grupo espacial *Pnma* (62), sem alterações significativas na fase estrutural gerada pela variação da radio-iónico. Foram medições da magnetização em função da temperatura com o magnetometro de amostra vibratório VSM do Quantum Design, na faixa de temperatura de 50 a 310K. As curvas da magnetização em função da temperatura apresentaram comportamento semelhante para todo o sistema.

Palavras-chave: *cobaltite, estrutura cristalina, paramagnética*

Introduction

The perovskite like cobaltite $Pr_{0.5}Ca_{0.5}CoO_{3-\delta}$, exhibits an interesting properties such as physical phenomena of spin-state transition, metal-insulator transition and magnetoresistance effect [1-3]. In last years, an important number of researches have been studying the ceramic materials based on this cobaltite using doping for replacement the position of the atoms inside in the crystalline symmetry [4]; in this work, the influence of the ionic-radio will be analyzed for the structural system response of $Pr_{0.48}TR_{0.02}Ca_{0.5}CoO_{3-\delta}$ where TR=Eu, Sm and Dy by means of the X-rays diffraction patterns (XRD) and Rietveld's refinement analysis in GSAS software.

Experimental details

From the precursors Pr_6O_{11}, Co_3O_4, CaO, Sm_2O_3, Eu_2O_3 y Dy_2O_3 of high purity (>99.99%), three polycrystalline samples were prepared $Pr_{0.48}TR_{0.02}Ca_{0.5}CoO_{3-\delta}$ (TR=Eu,Sm,Dy) by the solid state reaction method [5]. Oxides were dried at 200°C for 12h and subsequently weighed in appropriate quantities and macerated for 3h in an agate mortar, then they press tablets at a pressure of 2MPa. They surrendered to thermal calcination treatments to 750°C and sinterization to 830°C. The Structural characterization of the samples was carried out through diffraction (XRD) technique in a Diffractometer panalytical x´pert PRO-MPD, using Cu radiation (λ = 1.54186Å) in intervals of 10° and 90° with steps of 0.02° [6]. The patterns were analyzed by Rietveld refinement. In addition were measurements of magnetization as a function of temperature with the vibrating sample magnetometer VSM from Quantum Design in the temperature range from 50K to 300K using the ZFC-FC (zero-Field Cooled) method. They were measurements of magnetization as a function of the field applied, in a range between – 30kOe to 30kOe to 50K.

Results and discussion

The theorical model of the crystal structure of the system $Pr_{0.48}TR_{0.02}Ca_{0.5}CoO_{3-\delta}$ is exposed in the Fig1 whit (TR=Eu,Sm,Dy). This was built from Crystallographic databases, software SPUDS and models proposed by other authors [1,7].

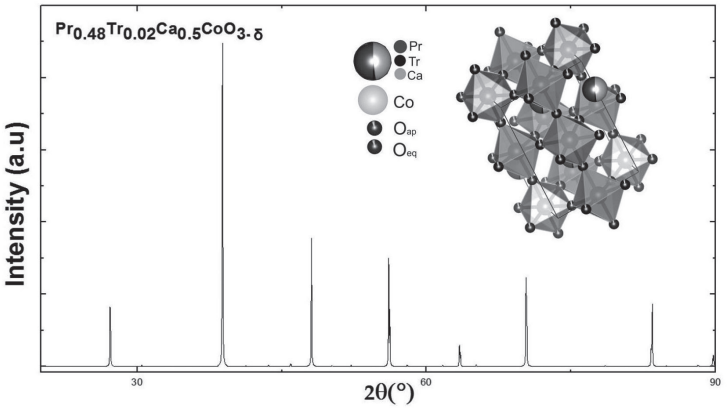

Figure 1. Theoretical pattern of XRD system

The three samples present peaks of secondary phases, with the symbol ♦ the corresponding reflections are represented to Co_3O_4 and with the symbol ♣ the reflections corresponding to CoO are represented. The respective XRD bosses allow to infer that the whole system $Pr_{0.48}TR_{0.02}Ca_{0.5}CoO_{3-\delta}$ it crystallizes in the same spatial group. The results suggest that the size of the ionic radius affects the presence of the second phases. The results by means of analysis for method Rietveld indicate that the samples crystallize in the spatial group orthorhombic Pnma (#62) as the mentioned one in the Fig 1. In the Table 1 the structural parameters are recorded of structure obtained by the Rietveld for every rare earth refining process; these are shown in Fig 3, shown that volume increases in proportion to the ionic radius of rare earth. By comparing the values obtained for these parameters with other authors shows that they are similar [1].

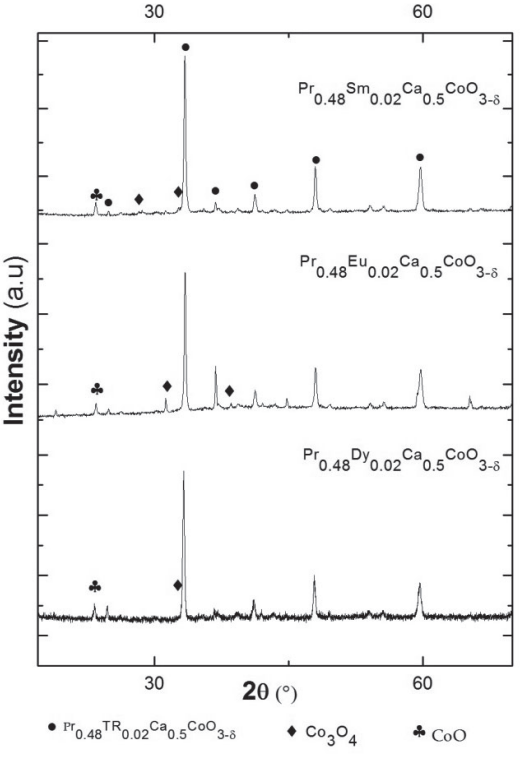

Figure 2. XRD patterns for system

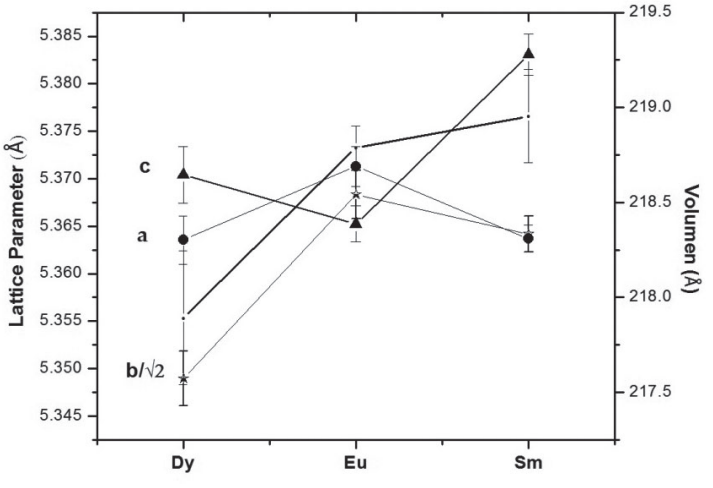

Figure3. Lattice Parameters and volume according to the Ionic Radius for system

Table 1. Lattice parameters for the system $Pr_{0.48}TR_{0.02}Ca_{0.5}Co0_{3-\delta}$ obtained from the Rietveld refinement of the XRD patterns.

System	Lattice Parameters		
	a	b	c
$Pr_{0.48}Sm_{0.02}Ca_{0.5}CoO_{3-\delta}$	5.3642(19)	7.5854(29)	5.3831(21)
$Pr_{0.48}Eu_{0.02}Ca_{0.5}CoO_{3-\delta}$	5.3683(25)	7.5962(41)	5.3652(19)
$Pr_{0.48}Dy_{0.02}Ca_{0.5}CoO_{3-\delta}$	5.3489(29)	7.5852(50)	5.3704(29)

The figure 4 shows the magnetization curve in function the temperature mode ZFC and FC for a field of 1000 Oe in a range from 50K to 300K, is a behavior observed paramagnetic type. Around 180K the value of the magnetization is similar in rare-earth Eu and Sm, while it is higher in Dy, the curves ZFC and FC are separated near the 70K, 60K y 150K, for the Sm, Eu and Dy respectively; indicating a possible order weak ferromagnetic due to the presence of ferromagnetic clusters.

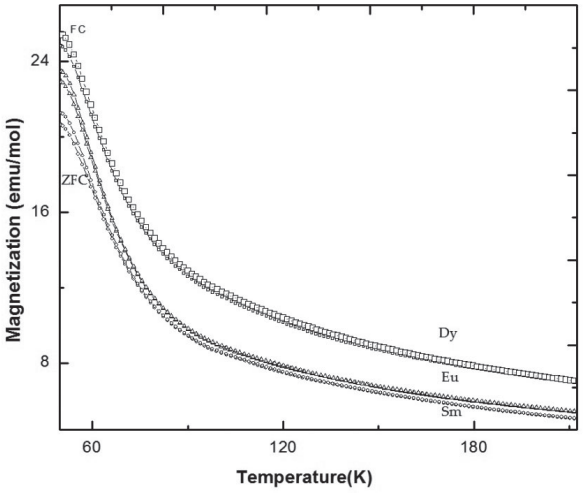

Figure 4. Magnetization as a function of temperature curves for system $Pr_{0.48}TR_{0.02}Ca_{0.5}Co0_{3-\delta}$

The Figure 5 shows the magnetization in function of the field to 50K, is perceived as more radio ionic value of magnetization is greater without reaching a saturation value. In the inset shows a behavior ferromagnetic weak which is in accordance with the temperature of the branch FC and ZFC. In the Table 2 summarizes the fields of coercion (HC) and the magnetization remnant (Mr) of each one of the three systems. [8]

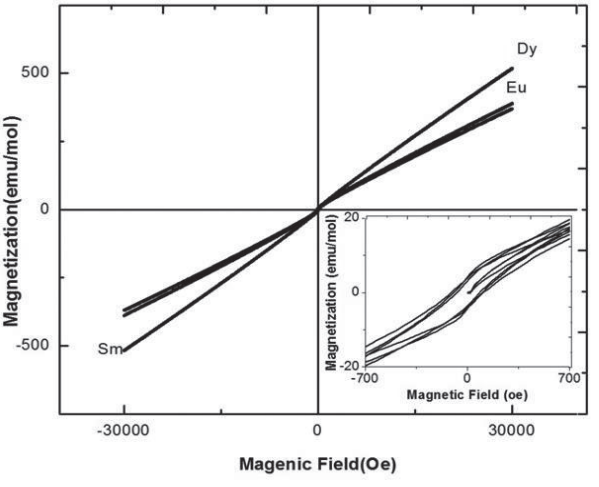

Figure 5. Magnetization as a function of the applied field (Oe) curves for system $Pr_{0.48}TR_{0.02}Ca_{0.5}Co0_{3-\delta}$

Table 2. Coercive field and magnetization remnants of each one of the systems.

Sistema	Mr(emu/mol)	Hc(Oe)
$Pr_{0.48}Sm_{0.02}Ca_{0.5}CoO_{3-\delta}$	3.8817	108.4726
$Pr_{0.48}Eu_{0.02}Ca_{0.5}CoO_{3-\delta}$	4.1628	100.2423
$Pr_{0.48}Dy_{0.02}Ca_{0.5}CoO_{3-\delta}$	3.1227	82.1979

The Figure 6 shows the inverse of the susceptibility χ-1(T) in function of the temperature for the branch ZFC, showing a linear behavior. In the temperature range between 100K to 200K, an adjustment was made type Curie-Weiss (1/X=1/C T-θ/C) from which was calculated the effective magneton (μeff), obtaining values of 3.30 (4) **μB**, 3.48 (6) **μB** and 3.95 (6) **μB** for Sm, Eu and Dy respectively.

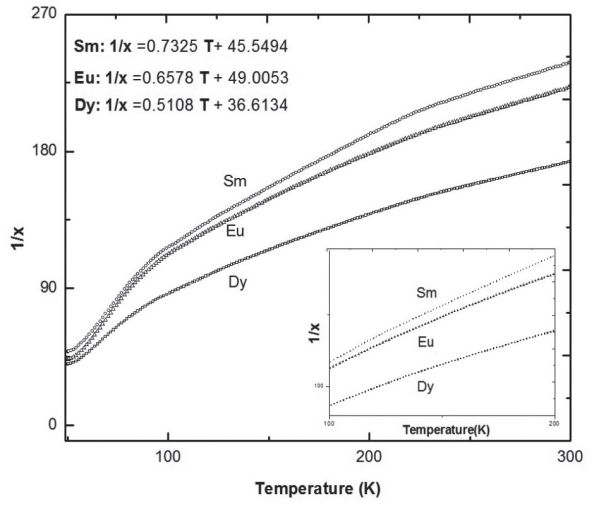

Figure 6. Inverse of temperature-dependent susceptibility χ-1 (T) by the system $Pr_{0.48}TR_{0.02}Ca_{0.5}Co0_{3-\delta}$

Conclusions

The new system $Pr_{0.48}TR_{0.02}Ca_{0.5}Co0_{3-\delta}$ was produced by the solid state reaction method. According to the results of Rietveld structure refinement (XRD), the system crystallizes in an orthorhombic system for *Pnma* space group (#62); the results show that the volume increases with the ionic radius of the Rare Earth doping; however, it preserves the space group. The precedent shows that the employment of CaO as precursor is equally effective in comparison with another samples made with calcium-carbonate precursor ($CaCO_3$) used by other authors [1,4]. By another hand, the magnetization measures have a paramagnetic behavior with a weak ferromagnetic component in low field, and temperatures and the magnetic date interpreted lead to the value between μ = 3.30(4) μB and μ = 3.95(6)μB Bhor magnetons. The Conductivity and magnetization analyses below 50K studies are necessaries, in order to verify the possible existence of metal-insulator transition (MIT) reported on similar systems.

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