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STRUCTURAL ANALYSIS OF THE CHALCOGENIDE SPINEL SYSTEM $CoIn_{(2-2X)}Cr_{(2X)}S_4$

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The chalcogenide system $CoIn_{(2-2X)}Cr_{(2X)}S_4$ (x = 0.75, 0.85, 1.0) was characterized using X-ray powder diffraction data. All compounds crystallize in the space group $Fd\bar{3}m$ (Nº227) and belongs to a normal spinel structure which can be expressed by the formula $[Co^{2+}]^{tetr}[In^{3+},Cr^{3+}]_2^{oct}S_4$, where the Co(II) atoms occupying the tetrahedral sites while the In(III) and Cr(III) atoms share the octahedral sites.

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1. Introduction

Ternary chalcogenide sulfides of the type II-Cr_2S_4 (II= Mn, Fe, Co, Ni), belonging to the family of semiconductor compounds II-III_2-VI_4, have been extensively studied recently owing to the combination of semiconducting behavior and strong ferrimagnetism [1,2]. The colossal magnetoresistance (CMR) observed in $FeCr_2S_4$ [3] has led to renewed interest in the some thiospinels compounds such as $MnCr_2S_4$, $FeCr_2S_4$ and $CoCr_2S_4$ [4]. Thus, $CoCr_2S_4$ has been described as a ferrimagnetic semiconductor with a critical temperature of 223 K [5], which is the highest Curie temperature among the mentioned ternary chromium sulfides compounds [6,7]. For the other hand, the $CoIn_{(2-2X)}Cr_{(2X)}S_4$ semiconducting system is attractive from the crystallographic viewpoint, because the phase with x= 1 ($CoCr_2S_4$) crystallizes with a normal spinel structure [1] while the phase with x= 0 ($CoIn_2S_4$) crystallizes with a inverse spinel structure [8,9]. From the magnetic point of view should be interesting to study the influence of the In^{3+} admixtures on the cation distribution and magnetic ordering in this spinel. Recent studies has shown interesting magnetic properties related with the exchange interaction between the Cr^{3+} ions [10,11]. In this work we present the structural analysis of the spinel system $CoIn_{(2-2X)}Cr_{(2X)}S_4$.

2. Experimental

Single crystals of each phase were grown by the chemical transport method from ternary polycrystalline material prepared by solid state reaction. Starting material for the crystal growth was a polycrystalline compound prepared by firing suitable mixtures of high purity elements in evacuated silica ampoule. The single crystals were grown in a two zone furnace. The optimal growing condition was 950°C for the source zone and 900°C for the crystallization region over a period of nine days. The transporting agent was chromium chloride. The samples were finely ground in an agate mortar and then sieved to 106 μm to get a homogeneous grain size. The resulting powders were loaded on a zero-background holder covered with a thin layer of grease. X-ray powder pattern were collected, at room temperature, in a Siemens D5005 diffractometer using

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Bragg-Brentano geometry in θ/θ reflection mode. CuKα radiation (λ= 1.5418 Å) was used at 30kV and 15mA. This instrument is equipped with a diffracted beam graphite monochromator and a scintillation detector. The diffraction patterns were collected by steps of 0.02° (2θ) over the angular range 10-120°, with a counting time of 35 s per step. Quartz was used as an external standard.

3. Results and discussion

X-ray powder diffracton patterns of $CoIn_{(2-2)}Cr_{(2X)}S_4$, x = 0.75, 0.85, 1.0, are show in Figure 1. A search in the ICDD-PDF database [12], using the software available with the diffractometer, indicated that the powder patterns , for x = 0.75 and x= 0.85, contained small amounts of $CoIn_2S_4$ (PDF N° 76-1973). The peak positions of the interest phase were indexed using the program Dicvol04 [13], and cubic cells were founds. The Rietveld refinement [14] were performed using the Fullprof [15] program and the atomic coordinates of previously reported for $CoCr_2S_4$ from neutron powder diffraction [1]. In each case, Indium and Chromium cations share the 16d Wickoff position. Atomic positions of $CoIn_2S_4$ [9] were included as a second phase in the refinement. Rietveld refinement results are summarized in Table. Figure 2 shows the observed, calculated and difference profile for the final cycle of refinements. This Figure show the unit cell diagram for the three phases.

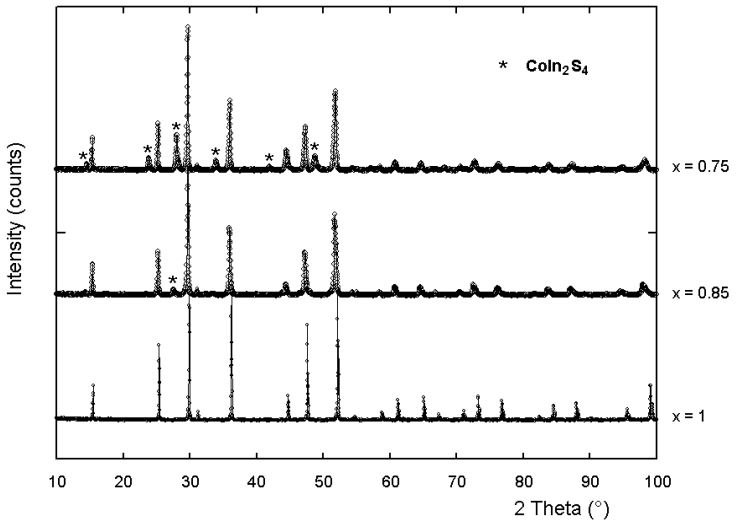

*Fig. (1) Powder X-ray diffraction patterns for the diluted magnetic semiconductor system $CoIn_{(2-2X)}Cr_{(2X)}S_4$. The * indicate the $CoIn_2S_4$ phase present in each pattern*

The crystallographic analysis confirms that the alloys with x = 0.75, 0.85 and 1.0 belongs to a normal spinel structure which can be expressed by the formula $[Co^{2+}]^{tetr}[In^{3+},Cr^{3+}]_2^{oct}S_4$, where the Co(II) atoms occupying the tetrahedral sites while the In^{3+} and Cr^{3+} cationes share the octahedral sites. This arrangement is shown in Figure 2, and is based on a cubic close-packed of large anions with smaller cations occupying tetrahedral and octahedral sites.

Table (1) Rietveld refinement results for $CoIn_{(2-2X)}Cr_{(2X)}S_4$.

Composition (x)		0.75	0.85	1
crystal system		cubic	cubic	cubic
space group (N°227)		$Fd\bar{3}m$	$Fd\bar{3}m$	$Fd\bar{3}m$
a (Å)		10.0700(6)	10.0096(5)	9.9247(1)
V (Å^3)		1021.2(1)	1002.88(9)	977.58(2)
mol. w. (g/mol)				291.2
d_{calc} (g/cm^3)				3.96
% $CoIn_2S_4$		10.1	2.1	0
	Site	occupancy factors for cations		
Co 8(a)	⅛, ⅛, ⅛	1	1	1
Cr 16(d)	½, ½, ½	0.74(1)	0.86(1)	1
In		0.26(1)	0.14(1)	1
	Site	atomic coordinate for anion *x*		
S 32(e)	*x*, *x*, *x*	0.2571(2)	0.2579(2)	0.2583(1)
		bond distances		
Co-S (tetr.)		2.271(2)	2.304(2)	2.291(1)
Cr(In)-S (oct.)		2.413(2)	2.426(2)	2.402(1)
Cr-Cr (shorter)		3.510(2)	3.539(2)	3.509(1)
Rietveld factors				
R_{exp} (%)		4.9	5.0	4.6
R_p (%)		6.0	6.2	4.4
R_{wp} (%)		6.7	7.0	5.7
χ^2		1.9	2.0	1.6

The Co-S and Cr(In)-S bond distances in the three alloys (Table 1) are in good agreement with those observed in other chalcogenide structure compounds such as $CoFeS_2$ [19], $CoGa_2S_4$ [20], $FeCr_2S_4$ [21] and $NiCr_2S_4$ [22].

Figure 3 shows the evolution of the unit cell volume for the $CoIn_{(2-2)}Cr_{(2X)}S_4$ system as function of Cr content (x), which decreases linearly with increasing Cr^{3+} content and follows, within the limits of experimental error, Vegard's law. This curve suggests for this system, a solid solution formation in all range of compositions.

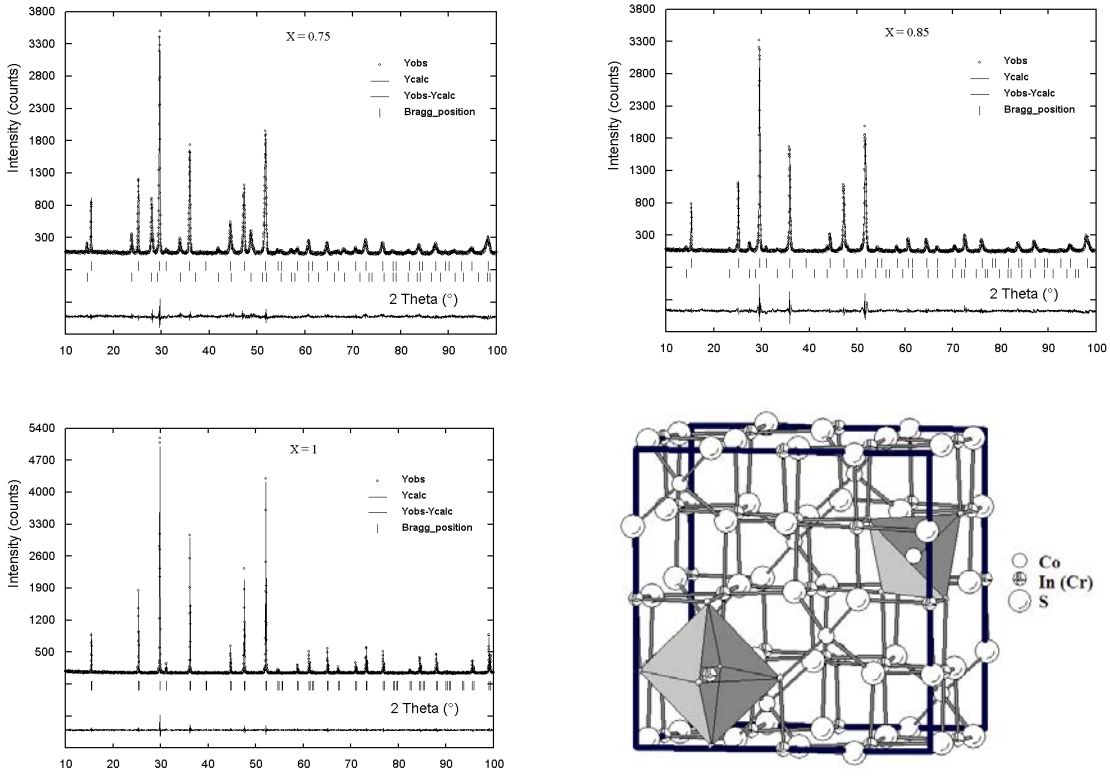

Fig. (2) Rietveld refinement plots and unit cell diagram for $CoIn_{(2-X)}Cr_{(2X)}S_4$

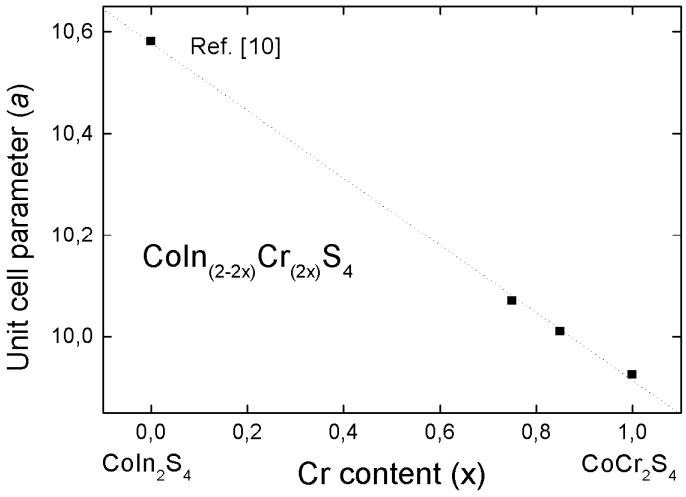

Fig. (3) Unit cell volume as function of the Cr content (x) in $CoIn_{(2-2X)}Cr_{(2X)}S_4$. The dot lines represent linear regression. $CoIn_2S_4$ (x = 0) value was taken from Ref. [10]

4. Conclusions

The chalcogenide system $CoIn_{(2-2X)}Cr_{(2X)}S_4$ (x = 0.75, 0.85, 1.0) was studied by the X-ray powder diffraction technique which confirms that these alloys crystallizes with a normal spinel structure.

Acknowledgements

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References

[1] P. Vaqueiro, S. Sommer, A.V. Powell. J. Mater. Chem. **10**, 2381 (2000).
[2] C.S. Kim, M.Ha, H.M. Ko, Y.J. Oh, H.S. Lee, S.Y. Lee, J.C. Sur, J.Y. Park. J. Appl. Phys. **75**, 6078 (1994).
[3] A.P. Ramirez, R.J. Cava, J. Krajewski. Nature **386**, 156 (1997).
[4] V. Tsurkan, J. Hemberger, M. Klemm, S. Klimm, A. Loidl, S. Horn, R. Tidecks. J. Appl. Phys. **90**, 4639 (2001).
[5] V. Sagredo, M.C. Morón, G.E. Delgado, Phys. B **384**, 82 (2006).
[6] B. Hoekstra, R.P. van Stapele. Phys. Stat. Sol. (b) **55**, 607 (1973).
[7] P. Gibart, J. Dormann, Y. Pellerin. Phys. Stat. Sol. **36**, 187 (1969).
[8] D. Fiorani, L. Gastaldi, S. Viticolli. Sol. Stat. Com. 48, 869 (1983).
[9] H.D. Lutz, M. Jung. Z. Anorg. Allg. Chem. **579**, 57 (1989).
[10] P. Silva, C. Zamora, V. Sagredo. Rev. Mex. Fís. 52, 150 (2006).
[11] G.E. Delgado, V. Sagredo, F. Bolzoni. Cryst. Res. Technol. **43**, 141 (2008).
[12] PDF-ICDD-Powder Diffraction File (Set 1-57), International Centre for Diffraction Data, 12 Campus Boulevard, Newtown Square, PA, USA (2007).
[13] A. Boultif, D. Louër. J. Appl. Cryst. **24**, 987 (1991).
[14] H. M. Rietveld. J. Appl. Cryst. **2**, 65 (1969).
[15] J. Rodriguez-Carvajal, Fullprof: (version 3.90), LLB (CEA-CNRS), France (2007).
[16] X. Zhang, R. Yu, J. Tejada, G. Sun, Y. Xinand, K. Wong. Appl. Phys. Lett. **68**, 22 (1996).
[17] S. Pouget, M. Alba, J. Nogues. J. Appl. Phys. **75**, 5826 (1994).
[18] G. Srinivasan, M.S. Seehra. Phys. Rev. B **28**, 1 (1983).
[19] E. Barthelemy, C. Carcaly. J. Solid State Chem. **66**, 191 (1987).
[20] E. Agostelli, S. Gastaldi, S. Viticoli. J. Solid State Chem. **46**, 1345 (1985).
[21] S.-J. Kim, W.C. Kim, C.S Kim. J. Applied Phys. **91**, 7935 (2002).
[22] A.V. Powell, D.C. Colgan, C. Ritter. J. Solid State Chem. **134**, 110 (1997).