

## Electrical and crystallographic properties of the spinel type $\text{ZnCr}_{2-2x}\text{In}_{2x}\text{S}_4$

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In this work, we report the electrical conductivity and lattice constants measurements of the system  $\text{ZnCr}_{2-2x}\text{In}_{2x}\text{S}_4$  as a function of temperature and Indium molar substitution, at concentrations from  $x = 0.0$  to  $x = 0.30$ , and temperatures between 73 and 300 °K. The samples were prepared by heating a mixture of the elements Zn, Cr, In and S in an evacuated silica tube as describe by Vargas-Hernández.<sup>[1]</sup> Depending on the In concentration the room temperature conductivity varied in the ranges from  $10^{-7}$  to  $10^{-11} (\Omega\text{-cm})^{-1}$ . The activation energy increases when we replace Cr ( $\text{Cr}^{+3} = 0.64\text{Å}$ ) by In ( $\text{In}^{+3} = 0.81\text{Å}$ ) because the size of octahedral sites increases, but at the same time the size of tetrahedral sites decreases. The electrical conductivity also decreases, which indicates that there are not direct overlaps of the 3d orbital of the  $\text{Cr}^{+3}$  ions.

### 1. Introduction.

The Chromites  $\text{ACr}_2\text{X}_4$  with spinel structure have been studied with a great interest since the 30's[2],[3]. Both the Oxy-spinels  $\text{MCr}_2\text{O}_4$  and the sulphochromites  $\text{MCr}_2\text{S}_4$  where M is a metallic element as Zn, Cd, Cu, Fe, Hg, Sn, Mg, Ge and Co. Even today it is discussed the distribution of its atomic components in the unitary cell and its relation with the electrical properties. It is discussed also the variation of its properties in function of the substitution of some paramagnetic and diamagnetic elements in special sites compatible with the crystallographic structure. [4],[5],[6]

The sulphochromites  $\text{ZnCr}_{2-2x}\text{In}_{2x}\text{S}_4$  are compounds of FCC structure with special group Oh[7] (Fd3m). It is a normal type of spinel for  $x = 0$  and it has tetrahedral sites, which are occupied by the zinc atoms, and octahedral sites that are occupied by the atoms of chromium. When this happens the spinel is normal type, when the cationic distribution is inverted an inverse spinel configuration is obtained.

On a few  $\text{MCr}_2\text{S}_4$  type spinels have been studied their electrical properties. Those are pure sulphochromites, [8],[9],[10] spinels that do not show substitution by equivalent ions in their tetrahedral and octahedral sites. These types of spinels are attractive particularly because everyone are of the normal type. There are studies of the electric behavior as a function of the size of A ions. Reports show that when the size of the ions is reduced the unitary cell does too and the  $\text{Cr}^{+3}$  ions compacts itself. This reduces the possibility of the electric conductivity by direct overlapping of the wave function of the  $\text{Cr}^{+3}$  ions below of a critical separation  $R_c$ . [8]

The sulphochromite of zinc  $\text{ZnCr}_2\text{S}_4$  is a semiconductor with a conductivity between  $10^{-10}$ - $10^{-11} (\Omega\text{-cm})^{-1}$  at room temperature, and it changes with temperature according to the exponential: [8]

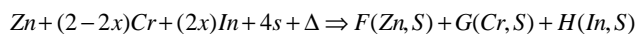
$$s = s_0 \exp\left(\frac{E}{kT}\right)$$

Where  $s_0$  and k are constants and E is the activation energy in the conduction process. A change of the slope in a  $\log(s)$  Vs  $1/T$  Graphic is an indicator of the presence of dispersion mechanism with different activation energy.

In this work we present the results obtained on the electric conductivity behavior and the lattice constant in function of temperature and molar substitution of indium in  $\text{ZnCr}_{2-2x}\text{In}_{2x}\text{S}_4$  with x between 0.0 to 0.30. Temperature ranges from 73 to 300 K. In the spinels preparation element Zn, Cr, In, S, are used. By sintering binary phases are obtained:  $\beta\text{-ZnS}$ ,  $\text{Cr}_2\text{S}_3$  y  $\beta\text{-In}_2\text{S}_3$ . Those will be part of the  $\text{ZnCr}_{2-2x}\text{In}_{2x}\text{S}_4$  system. The conductivity at room temperature of  $\text{ZnCr}_{2-2x}\text{In}_{2x}\text{S}_4$  has a variation between  $10^{-6}$  a  $10^{-11} (\Omega\text{-cm})^{-1}$  and its lattice constant changes from 9.978 to 10.024 Å, when the substitution of indium is between 0.0 and 0.30.

### 2. Experimental procedure

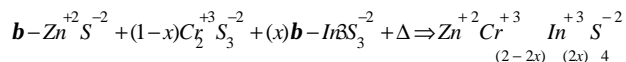
In the spinels preparation  $\text{ZnCr}_{(2-2x)}\text{In}_{(2x)}\text{S}_4$ , we start whit 99.99% pure elements (zinc, chromium sulfur and indium). Then the next solid reaction of addition is obtained:



Where F, G, H are binary compounds whose crystalline structure depends on the thermal treatment that the elements are exposed to. The component  $F(\text{Zn}, \text{S})$  crystallizes in two phases[11], the zinc blend  $b\text{-ZnS}$  with cubic structure, and wurtzite in the hexagonal system. This is the corresponding modification of  $b\text{-ZnS}$  its transition point presents at 1200 °C. For the compound  $G(\text{Cr}, \text{S})$ , having as a reference Cr and S in an inert atmosphere monosulfide  $\text{CrS}$  is obtained at 600 °C. Chromium (iii) Sulfide  $\text{Cr}_2\text{S}_3$  that crystallizes in the hexagonal system, is obtained at 700 °C. This is very stable until 1350 °C.

In the compound  $H(\text{In}, \text{S})$  we have  $b\text{-In}_2\text{S}_4$  that crystallize in the cubic system, and  $a\text{-In}_2\text{S}_4$  that crystallize in the hexagonal system. The system changes the  $b$  system

irreversibly to 360 °C.[12]. From the conditions for the binarian formation of F, G and H we get the compounds  $\beta$ -ZnS, Cr<sub>2</sub>S<sub>3</sub>,  $\beta$ -In<sub>2</sub>S<sub>3</sub>, that will form the structure ZnCr<sub>(2-2x)</sub>In<sub>(2x)</sub>S<sub>4</sub> diluted with indium of the normal spinel type. This is pictured in the next solid addition reaction:



To avoid zinc, chromium an indium oxidation the elements are weighed in well established relations inside of a chamber in nitrogen atmosphere. Subsequently, the samples are placed inside quartz tubes and then evacuated around 10<sup>-5</sup> torr to begin the sinterization process. The favorable conditions[13] to get the zinc sulphochromite are shown in Table 1:

In the sinterization process three thermal treatments were applied with temperatures around 800 °C by 48 hours. In the first treatment we obtained the samples in powder form. Then this powder is subjected to a pressure of 12 tons to make pills of 16 mm of diameter. The samples as a pill form are subjected to the second and third treatment. At each one of the thermal treatments the samples are characterized by x-rays through a Philips multipurpose diffractometer PW1710.

The electrical conductivity measurements were made using a sample holder made of Teflon as shown in fig. 1. In figure 2 the diagram of measurement system is presented. The sample is placed on the sample holder and this is placed inside a liquid nitrogen cryostat, where temperature is regulated by an exterior control at 2 K intervals. The voltage applied to the sample is 9 V. this voltage generates a current in the sample, which is detected by an electrometer. Additionally the signal from the temperature controller is processed by the computer through a data acquisition card to obtain a plot of the conductivity in function of temperature.

**3. Results and discussion**

The diffractogram of x-rays from the sulphochromite ZnCr<sub>2</sub>S<sub>4</sub> is pictured on figure 3. This was obtained after the third thermal treatment. The samples diluted with indium showed a displacement of lines toward minor angles, showing an increment in the lattice constant as the chromium is substituted by the indium.

Table 1. Sinterization of the samples ZnCr<sub>(2-2x)</sub>In<sub>(2x)</sub>S<sub>4</sub>

Thermal treatment N°	T (°C)	t (Hours)	P (Ton.)	Φ (mm)	Vacuum (torr)
1	850	48	powder	----	4x10 <sup>-5</sup>
2	800	24	12	16	4x10 <sup>-5</sup>
3	800	48	12	16	4x10 <sup>-5</sup>

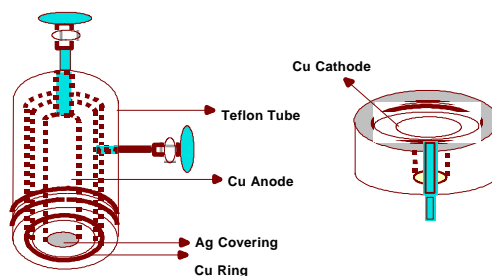


Fig.1. Sample holder used in measurement of electrical conductivity.

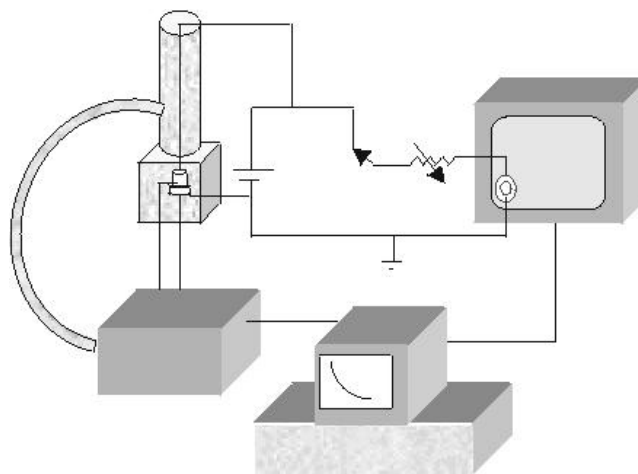


Fig. 2. Circuit configuration of conductivity measurement of the conductivity Vs temperature.

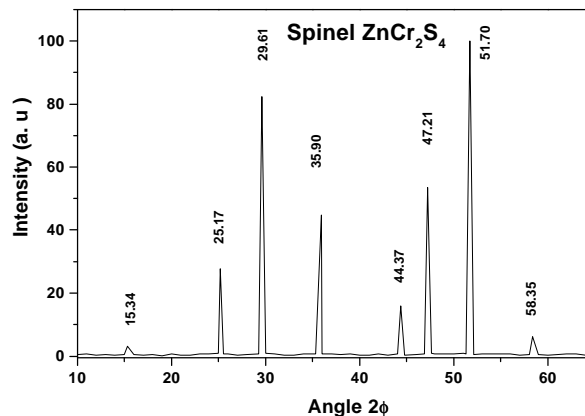


Fig. 3. X-rays diffractogram of the sulphochromite ZnCr<sub>2</sub>S<sub>4</sub>.

In figure 4, we illustrated the behavior of the lattice constant as a function of chromium’s molar substitution by indium in a range of concentrations between x= 0.0 and x= 0.5. We observe an increment of the lattice size from 9.978 to 10.04 Å as we substitute Cr by In. Chromium substitutes zinc preferentially in the octahedral sites when the molar concentration is about of x= 0.30. When the concentration increases up to x= 0.50 its observed that the lattice constant does not change notably and keeps about 10.024 Å. This suggest that a competition is produced inside the unitary cell between the In (In<sup>+3</sup> = 0.81Å) and the Cr (Cr<sup>+3</sup> = 0.64Å) to take place on the octahedral sites

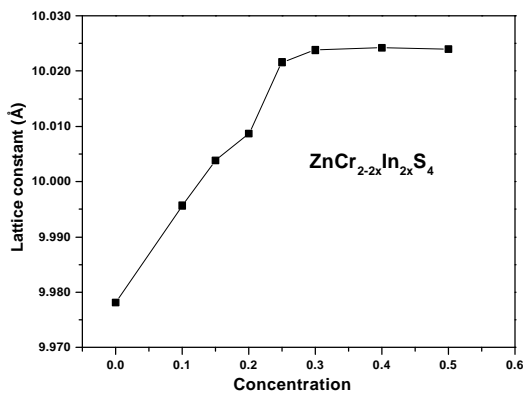


Fig. 4 variation of the lattice constant as a function of the molar substitution of the indium by chromium in a range between  $x=0.0$  and  $x=0.50$

formed by the ions of S ( $s^{-2} = 1.84\text{Å}$ ). At molar concentrations of indium bigger than  $x=0.30$  this competition for the sites is remarked and produces that some atoms of chromium occupy tetrahedral positions of the zinc ( $Zn^{+2} = 0.74\text{Å}$ ), getting a configuration of spinel partially inverse where the size of the cell does not change notably until concentration of indium  $x=0.50$ . This results are according with the ones observed by ESR,[13] where the typical chromium signal is observed in octahedral sites in a center field of 3427 gauss corresponding to the chromium's configuration in tetrahedral sites for bigger of  $x=0.30$ .

In fig. 5 we see the variation of the lattice constant as a function of the temperature for the spinel  $ZnCr_2S_4$ . Here we see a lineal increment of the lattice constant on temperatures about 213 K. and for bigger temperatures up to 450 K. it has a behavior more stable. This suggest that on a minor temperature of 213 K the spinel  $ZnCr_2S_4$  is likely of the normal type and for higher temperatures it shows a normal behavior with a component of the inverse type. The obtained results match the ones obtained by ESR, where is noted that for higher temperatures than 213 K. an intense line is obtained centered in 3308 gauss and a less

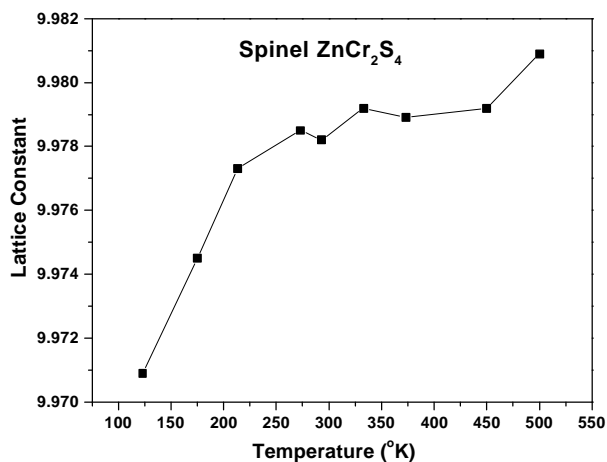


Fig. 5 variation of the lattice constant as a temperature function for the spinel  $ZnCr_2S_4$ .

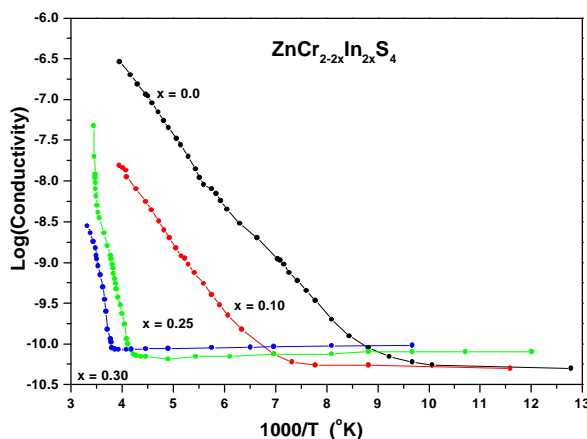


Fig. 6. Electric conductivity in function of the temperature for  $ZnCr_{2-2x}In_{2x}S_4$  with  $x=0.0, 0.10, 0.25, 0.30$ .

intense line centered in 3427 gauss. These correspond to the characteristic spectrum for chromium in octahedral sites and tetrahedral sites respectively. In the figure 6 we show the behavior of the logarithm of the conductivity in function of the inverse of the temperature of the sulphochromites type  $ZnCr_{2-2x}In_{2x}S_4$ , with  $x$  equal to 0.0, 0.10, 0.25 and 0.30 in a temperature range between 73 and 300 °K. The change of the slope in the graphic of  $\log(S)$  Vs  $1/T$  is an evidence of the presence of dispersion mechanisms of the charge carriers due to the substitution of the ions of chromium by In.

We see a change on the activation energy as we substitute chromium by indium. A bigger concentration of indium gives bigger activation energy. This behavior has an influence from the ions of indium that modifies the ionic environment of S, and the distance between ions of Cr. The size of the tetrahedral sites is reduced, but those from the octahedral sites increases and the unitary cell gets bigger. This reduces the possibility of electrical conductivity due to direct overlapping of the wave of the  $Cr^{+3}$  ions function of below a critical separation  $R_c$ . [8]

As we can see on the curves of fig.6, there is a similar behavior and there are two regions or changes of the slope. In terms of energy, this means a change in the activation energy that shows a modification in the conduction mechanisms.

In Table 2 we see the behavior of the activation energy in function of the molar substitution of indium from the samples  $ZnCr_{2-2x}In_{2x}S_4$ .

Table 2. Sinterization of the samples  $ZnCr_{(2-2X)}In_{(2X)}S_4$

x	$\Delta E$ (eV)	Distance Cr-Cr (Å)
0.0	0.065	3.528
0.10	0.073	3.534
0.25	0.262	3.543
0.30	0.325	3.544

#### 4. Conclusions.

Chromium substitutes zinc mainly in octahedral sites when the molar concentration is about  $x=0.30$  and its lattice constant varies from 9.978 to 10.024 Å. When the concentration increases up to  $x=0.50$  it is noted that the lattice constant does not vary and remains around 10.024 Å. This suggests that competitions are produced inside the unitary cell between In and Cr to get the octahedral sites made for the ions of S and bigger molar concentrations of indium  $x=0.30$ . This competition for the sites is emphasized and produces that some atoms of chromium take tetrahedral positions of the zinc obtaining a configuration of the spinel partially inverse.

The conductivity at room temperature of the compound  $ZnCr_{2-2x}In_{2x}S_4$  varies from  $10^{-6}$  a  $10^{-11}$  ( $\Omega\text{-cm}$ )<sup>-1</sup>, when the substitution of the indium is between 0.0 and 0.30. The size of the tetrahedral sites is reduced but the one form octahedral sites increases and the unitary cell gets bigger. This produces that the distance between the chromium increases reducing the possibility of electric conductivity by direct overlapping of the wave function of the Cr<sup>+3</sup> ions.

#### Acknowledgments

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