SCIENCES FONDAMENTALES

APPLICATION OF RIETVELD METHOD TO THE STRUCTURAL CHARACTERISTICS OF SUBSTITUTED SPINEL SYSTEM $Cu_yCr_yM_{2-y}X_4$ (M=Sn, Zr; X=S, Se).

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Application de la méthode de Rietveld aux caractèristique stricturales du système spinel substitué $Cu_yCr_yM_{2-y}X_4$ (M=Sn, Zr; X=S, Se

RESUME: Il a été établi que les séries de compositions chimiques $Cu_yCr_yZr_{2-y}Se_4$ $Cu_yCr_ySn_{2-y}S_4$ (y = 1.00, 1.05, 1.15, 1.20, 1.25 et 1.30) préparées possèdent la structure spinelle cubique. En appliquant le full pattern fitting de la méthode de Rietveld par l'utilisation du programme FullProf, les coordonnées exactes des atomes, les dimensions de la maille élémentaire, le taux d'occupation, le facteur de température isotopique, le paramètre de profil de forme ainsi que les distances interatomiques ont été déterminés pour les deux composés spinelles $Cu_yCr_yZr_{2-y}Se_4$ et $C_{uy}C_{ry}S_{n2-y}S_4$

Il a été établi que le paramètre diminue avec l'augmentation du substituant. De même la variation de la distribution des cations a été discutée sur la base des sites préférentiels et des cations substitués.

Mots clés : Affinement de Rietveld, diffraction X sur poudre et structure spinelle.

دراسة و تعيين خصائص السبينال للنظام) $Cu_yCr_yM_{2-y}X_4$ (M=Sn, Zr; X=S, Se

ملخص: لقد تم تبيين أن المركبات الكيميائية المحضرة $Cu_yCr_ySn_{2-y}S_4$ و $Cu_yCr_yZr_{2-y}Se_4$
(y = 1.00, 1.05 1.15, 1.20, 1.25 and 1.30) تملك البنية المكعبة للسبينال.
باستخدام طريقة Rietveld و تطبيق برنامج FullProf مواقع الدرات، أبعاد الخلية الأولية، معامل التعبئة،
معامل الحرارة المتماثل، معامل الشكل و الأبعاد الدرية للمركبين $Cu_yCr_ySn_{2-y}S_4$ و $Cu_yCr_yZr_{2-y}Se_4$تم
إيجادهم من اجل y = 1. و وجد أن ثابت الشبكة يتناقص بتزايد الدرة المنغرسة. كما تم مناقشة تغير توزيع
الكتيونات اعتمادا على المواقع التفضيلية و الكتيونات المنغرسة.

الكلمات المفتاحية : بنَية السبينال ، الانعراج على المساحيق ، طريقة Rietveld

INTRODUCTION

Along the last decade, several new materials have attracted the attention to be potentially suitable for applications in fast magnetoresistive devices. Several chalcogenide spinels with the generic chemical formula AB_2X_4 (A, B = transition metal and X = chalcogen atom) [1, 2, 3, 4] are well known to show a number of interesting physical properties [5]. Among the crystal structures reported for transition-metal chalcogenides of AB_2X_4 stoechiometry, two of the most frequently found are the CrS_4 and the spinel structures.

The occurrence of the cations A and B to occupy octahedrally coordinated sites. The Cr_3S_4 is a defective structure containing layers of edge-sharing MS_6 octahedra of overall stoichiometry MS_2, separated by a cation-deficient layer in which half of the available octahedral sites are occupied in an ordered manner. In ternary phase, there are the two limiting cases of A and B cation arrangements: (a) the normal $(A)[B_2]S_4$ and (b) inverse $(B)[AB]S_4$ structures where parentheses and square brackets represent sites in the vacancy and filled layers, respectively.

As a general rule, transition metal ions from the left side of the 3d series exhibit a marked preference for sites in the dichalcogenide layer, whereas the latter transition-series cations favour sites in the vacancy layer. The second possible structure adopted by these compounds is the spinel, which can be described as a cubic close-packed arrangement of oxygen ions, with A^{2+} and B^{3+} ions at two different crystallographic sites. These sites have tetrahedral and octahedral oxygen coordination (A-and B-sites, respectively), so the resulting local symmetries of both sites are different.

The ionic distribution in this kind of structure may be represented by $[\ A_\delta\ B_{1+\delta}\ ]_{Tet}[A_{1-\delta}B_{1+\delta}]]_{Oct}$, where δ is the inverse and normal cases, respectively. In both cases described above, the situation is often intermediate ($0<\delta<1$) and depends both on the identity of the A and B ions and on the mode of preparation. In turn, different final cation populations will strongly influence the transport and magnetic properties of the resulting materials.

The $CuCr_2Se_4$ is semiconductor with a magnetic spiral structure and metallic ferromagnetic to paramagnetic phase transition at about 420K. On the other hand substitution of Cu with Cr with Zr ions and Cu with Cr with Sn ions gives a structural solid solution of the normal spinel structure $Cu_yCr_yZr_{2-y}Se_4$, and $Cu_yCr_ySnr_{2-y}S_4$.

The aim of the present work is to study the effect of the replacing cations type and content on their distribution, in spinel structure $Cu_yCr_yM_{2-y}X_4$, between its two lattice sites (A and B) using X-ray diffraction and program for full pattern structure refinement of Rietveld method.

EXPERIMENTAL CONDITIONS

The proposed powder samples of the compounds under study were obtained as following:

- ***Preparation of $Cu_yCr_yM^{IV}_{2-y}X_4$***

M^{IV}= Zr and X=Se: The present samples are obtained by heating, according to the stoichiometric ratio, a mixture of high purity powders of the elements, and sealed into evacuated quartz ; this method leads to a better homogeneity than a starting mixture y ($CuCrSe_2$) + (2-y) $ZrSe_2$. A progressive rise by stages until 900°C with an agitation at 500°C of the tubes under vacuum lefted. It is necessary to be followed it at 900°C of a crushing of the obtained powders putting it again in tubes under vacuums carried 5 days at 950°C. Then the furnace is stoped. In the system $Cu_yCr_yZr_{2-y}Se_4$ a spinel phase is observed with an homogeneity domain ranging from y =1.00 to y = 1.30. For 1.00 < y < 1.30, the formula corresponds to a metal excess with respect to the available A-sites [6].

M^{IV}= Sn and X=S: The experimental method is as the previous one but, the final temperature being 850C° as described previously [7]. For the system $Cu_yCr_ySn_{2-y}S_4$ a spinel phase is observed with an homogeneity domain ranging from y =0.20 to y = 1.36. For 1.00<y<1.36, the formula corresponds to a metal excess with respect to the available A-sites [8, 9].

Powder X-ray diffraction data were collected on a Siemens D-5000 diffractometer at room temperature. The scanning range was (2θ), with step size = 0.02° (2). Fig.1 and Fig.2 show respectively the XRD patterns of $Cu_yCr_yZr_{2-y}Se_4$ and $Cu_yCr_ySn_{2-y}S_4$. Identification of the crystalline structure and the determination of the lattice constants for our samples were carried out by the powder X-ray diffraction method using Cu K a radiation at room temperature. XRD peaks are indexed with the help of the software DICVOL04 [10]. The data were processed to realize the conditions of the software program FullProf for the structure refinement [11, 12].

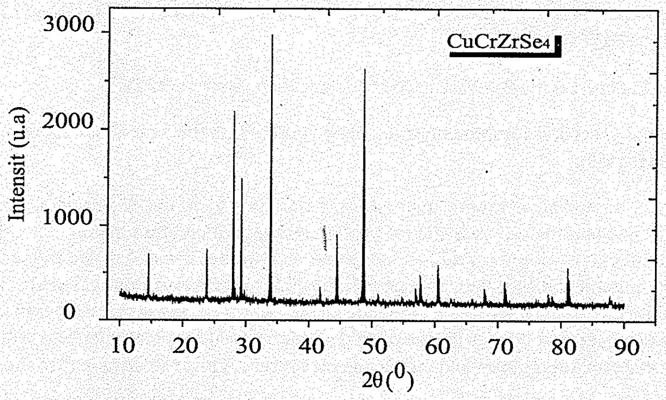

Fig. 1: XRD patterns of $CuCrZrSe_4$ spinel

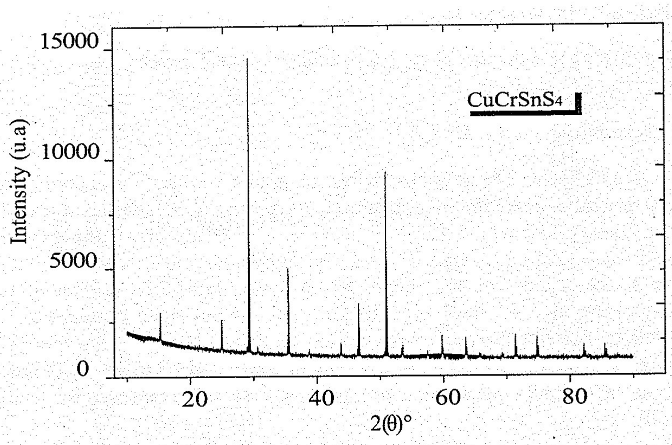

Fig. 2: XRD patterns of $CuCrSnS_4$ spinel.

RESULTS AND DISCUSSION

For all the compositions, a search in the ICDD-PDF database using the software available with the diffractometer, was performed. The program DICVOL04 gave a unique solution in a cubic cell for the stoichiometric compositions ($y = 1$). The materials crystallize in the cubic system with space group Fd3m (N°.227) [13]. A summary of the crystallographic data and structure refinement for the samples is given in Table 1. We use the computer program FullProf in the Rietveld method in total 12 parameters have been refined: scale factor, zero-point shift, resolution parameters, lattice parameter a, sulphur and positional parameters in fractional coordinates (f.c). Using FullProf program, the refinement of the first sample was started in space group Fd3m, origin at -3m, with Se in 32e, tetrahedral site in 8a and octahedral site in 16d. The experimental profile was fitted by a modified TOMPSON COXHASTING PSEUDOVOIGT function.

$H_G = (U\tan^2\theta + V\tan\theta + W + Z/\cos^2\theta)^{1/2}$ and $H_L = X\tan\theta + Y/\cos\theta$

H_G is the Gaussian component of the peak width, H_L is the Lorentzian component of the peak width,

U is the Gaussian isotropic microstrain parameter, Z is the Gaussian isotropic crystallite size parameter, X is the lorentzian isotropic microstrain parameter, and Y is the Lorentzian isotropic crystallite size parameter. In the first step of the refinement the global parameters (2θ-zero, instrumental profile, profile asymmetry, background, and specimen displacement) were refined. In the next step, the structure parameters (atomic coordinates, specimen profile breadth parameter, lattice parameter, temperature factors, preferred orientation and site occupancy) were refined in sequence mode.

Table 1: Summary of refinement results of $CuCrZrSe_4$ and $CuCrSnS_4$ structural determination

Common data:	
Crystalline System	Cubic
Space group	Fd-3m
Motif	Z = 8
÷ (Å)	CuK_{a1} CuK_{a2}
Field angular	10° à 90°
Temperature	300K
Counting	0.02°
Type of profiles function	Pseudo-Voigt
$CuCrZrSe_4$:	
Cell parameter	a =10.6487 (2) (Å)
Calculated volume	V =1207.50(2) (Å^3)
Density calculated	0.8484
Number of refined parameters	12
Numbers atom per asymmetrical unit	8
R_B	0.116
R_P	0.339
R_{wp}	0.232
$CuCrSnS_4$:	
Cell Parameter	a =10.1707(2) (Å)
calculated volume	V = 1052.0891(2) (Å^3)
Density calculated	0.8208
Number of refined parameters	12
Numbers atom per unit asymmetrical	8
R_B	0.115
R_P	0.400
R_{wp}	0.250

The site occupancy in the two positions (octahedral and tetrahedral sites) were constrained in order to keep the sum of the same cations in the two sites always have its stoichiometric value. In the last cycle, when the discrepancy factor R_{WP} has reached its minimum value, we can see that it is higher, because our data are quite good (maximum limit 90° for 2θ). Consequently, the reliability factors are higher. It seems that the preferential orientation or the bad counting time could be the cause. The curve difference shows a good agreement between observed and calculated spectrum. Fig.3 and Fig.4 illustrate observed and calculated X-ray patterns as well as their difference for samples $CuCrSnSe_4$ and $CuCrZrSe_4$ respectively. All the parameters (global and structural) were refined simultaneously giving the goodness of fit, given in Table 3.

Table 4 shows the variation of the lattice parameters for the investigated samples as a function of zirconium concentration, which is represented graphically in Fig.5. It is clearly shown that the lattice parameters decrease with increasing zirconium for all samples, but then increase from y = 1.25 in $Cu_yCr_yZr_{2-y}Se_4$. We note that obviously from the examination of the curve a = f(y) that the cubic cell parameter evaluates in a significant manner. We check the limit of $Cu_yCr_yZr_{2-y}Se_4$ for: 1< y <1.25. The cubic cell parameter evaluates in a significant manner; Parameter a decreases with y, the slope is accentuated from y = 1.04.

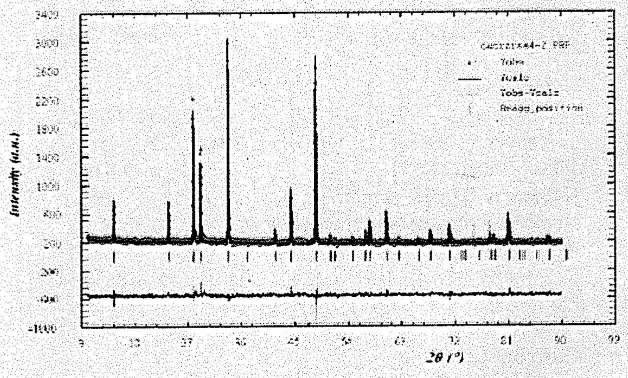

Fig.3: X-ray diffraction diagram observed and calculated of $CuCrZrSe_4$

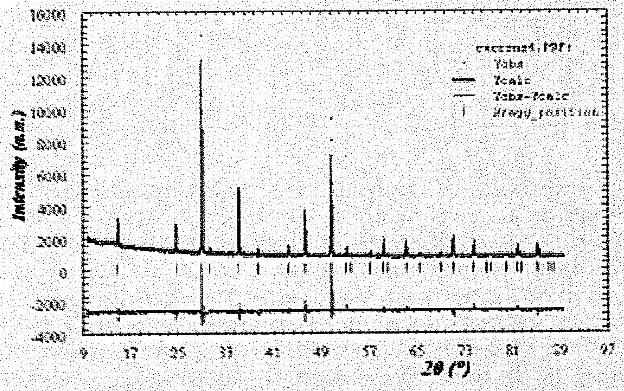

Fig.4: X-ray diffraction diagram observed and calculated of $CuCrSnS_4$

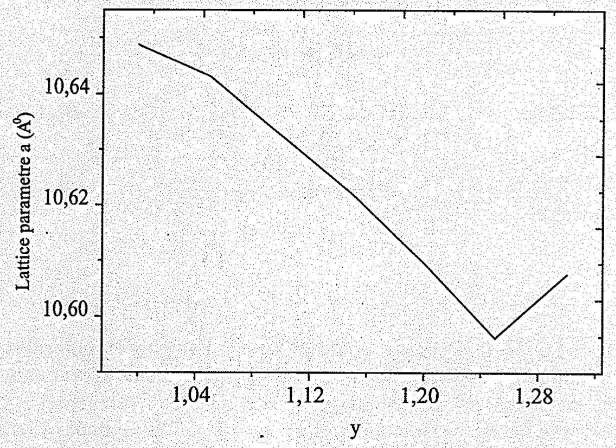

Fig.5: Variation of lattice constant 'a' (Å) with y for $Cu_yCr_yZr_{2-y}Se_4$

Table 2: Lattice constant a of spinel-type $Cu_yCr_yZr_{2-y}Se_4$ phases at room temperature

Compounds	y	a (Å)
	1.00	10.6487 (2)
	1.05	10.6431 (0)
$Cu_yCr_yZr_{2-y}Se_4$	1.15	10.6220 (3)
	1.20	10.6096 (3)
	1.25	10.5962 (3)
	1.30	10.6076 (2)

Table 3: Values of atomic coordinates (x, y, z), temperature factor (B) of $CuCrZrSe_4$ and $CuCrSnS_4$

Atoms	X	Y	Z	Biso($Å^2$)
Cu	0.125	0.125	0.125	0.753
Cr	0.500	0.500	0.500	1.583
Zr	0.500	0.500	0.500	1.583
Se	0.254	0.254	0.254	1.032
Cu	0.125	0.125	0.125	1.486
Sn	0.500	0.500	0.500	1.841
S	0.246	0.246	0.246	1.914

Table 4: Comparison of the interatomic distances of $CuCrZrSe_4$ and $CuCrSnS_4$

Interatomic distances (Å)		
$CuCrZrSe_4$	$(Cu\text{-}Se)_{Td}$	$(Cr, Zr\text{-}Se)_{Oh}$
	2.38	2.65
$CuCrSnS_4$	$(Cu\text{-}S)_{Td}$	$(Cr, Sn\text{-}S)_{Oh}$
	2.14	2.58

For $Cu_yCr_ySn_{2-y}S_4$, it has been reported in the literature that the cubic phase exists, alone, in a limit range of composition, and the two-phase fields appear only far from $CuCrM^{IV}S_4$ the stoichiometric composition. The cubic cell parameters evolve to a significant degree has decrease continuously when y = 1. The continuity of the powder spectra, the surplus of metal introduction into a spinel matrix necessarily leads to short metal-metal distance. Under such conditions, the appearance of connections metal-metal is inevitable, and the metal formation of clusters is possible. The creation of a metal-metal interaction should be accompanied by a contraction of the corresponding distance and consequently of the cell parameter. The extent of the parametric evolution is weak here. As well as the first remarkable structural fact is the absence of deformation of the octahedral and tetrahedral sites (see Figure 6)

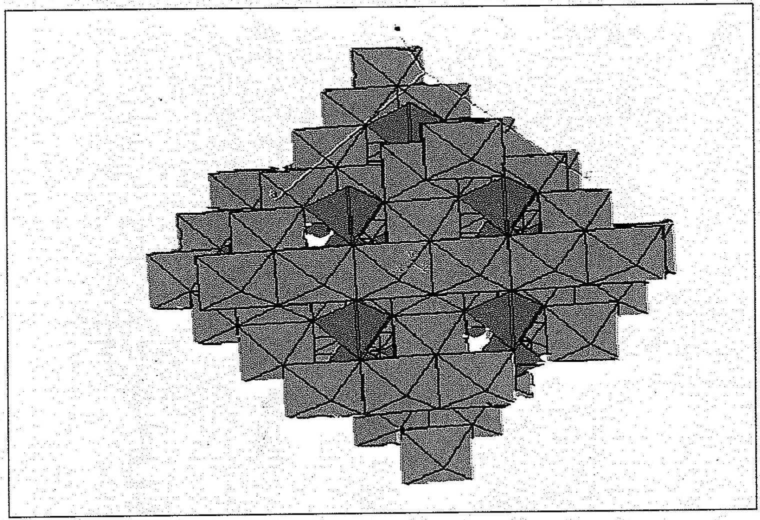

Fig 6: Structure of $CuCrZrSe_4$: CrS_6 octahedral and $CuSe_4$ tetrahedral

In addition the stoichiometric composition is passed through as y increases, drastic changes occur in electrical properties the activation energy drops [9] magnetic interactions the θp Weiss constant increases, which indicates that ferromagnetic extra couplings appear [14], E.P.R. spectra: the linewidth rapidly decreases, which suggests an enhancement of the exchange narrowing. The origin of such features certainly lies in the structure of the extra metal compounds [8]. The refined values of atomic coordinates, occupancy and temperature parameters are given in Table 3. It can bee noticed that the unit cell parameters decreases as the Cr concentration decreases. The previous crystallographic calculations carried out from X-ray powder patterns did not allow the extra metal position to be determined for that a detailed structural analysis of the systems using the Rietveld method by neutron diffraction is in progress. In the spinel structure, it is interesting to determine the distribution of the various metal cations on the various crystallographic sites which are offered to them. The derivatives $CuCrMSe_4$ and $CuCrMS_4$ offer three possibilities: $(Cu)_{Td}$ $[Cr, M]_{oh}$, $(M)_{Td}$ $[Cu, Cr]_{oh}$, $(Cr)_{Td}$ $[M, Cr]_{oh}$. The most probable is certainly the first, since all the concerned metal elements; copper is placed most voluntarily in tetrahedral site. The structure of $CuCrSnS_4$ is extremely of $CuCrZrSe_4$; chromium thus shares the octahedral sites with tetravalent metal. Along the C axis, the structure makes up of an alternate stacking of two layers of copper and chromium atoms (Fig 6). The chromium atoms share the octahedral crystallographic sites with tetravalent metal (Zr): it is interesting to note that the $CuCrZrSe_4$ compound presents the crystallographic characteristic to contain two atoms of Cr and Zr on the same atomic positions. As these two metals are also abundant, an order 1.1 is possible on these sites. This order is obviously more probable between Cr and Sn than Cr and Zr, much closer in the periodic Table [9]. The size of a site must be in agreement with M-S distance characteristic of affected metal to this site. We have to check this fact with the calculation of their interatomic distances (Table 4). We can note that the distances are affected by the substitution of tin to zirconium and sulphur to selenium, distances $(Cu\text{-}Se)_{Td}$;, $(Cr, Zr\text{-}Se)_{Oh}$, $(Cu\text{-}S)_{Td}$ and $(Cr, Sn\text{-}S)_{Oh}$ are in good agreement with the tetrahedral and octahedral sites respectively.

CONCLUSION

$Cu_yCr_yM^{IV}_{2-y}X_4$ spinels have been prepared by heating, according to the stoichiometric ratio, mixture of high purity powders of the elements of the starting mixture $y(CuCrX_2) + (2\text{-}y)MSe_2$. All of the prepared powders were identified as a spinel phase with $Fd\overline{3}m$ space group. From the refined parameters it can be concluded that the $CuCrSnS_4$ structure is extremely the same of $CuCrZrSe_4$; chromium shares the octahedral sites with tetravalent. The spinel structure is preserved for our system $Cu_yCr_yM^{IV}_{2-y}X_4$ (M = Sn, Zr; X = S, Se) for y = 1.00, 1.05, 1.15, 1.20, 1.25 and 1.30. On other hand note that the distances are affected by the substitution of tin to zirconium and sulphur to selenium, distances $(Cu\text{-}Se)_{Td}$, $(Cr, Zr\text{-}Se)_{Oh}$, $(Cu\text{-}S)_{Td}$ and (Cr, Sn-S)Oh are in good agreement with the tetrahedral and octahedral sites respectively.

BIBLIOGRAPHICAL REFERENCES

1 - **G.F. GOYA AND V. SAGREDO**, Solid State Comm.125, 247-251, (2003)

2 - **M.A. SUBRAMANIAN, B.H. TOBY, A.P. RAMIREZ, W.J.MARSHALL, A.W.SELEIGHT, G.H. KWEI**, Science 273, 81, (1996).

3 - **R. XU, A. HUSMANN, T.F. ROSENBAUM, M.-L. SABOUNGI, J.E. ENDERBY, P.B. LITTLEWOOD,** Nature, 390, 57, (1997).

4 - **T. DIELT**, Semicond. Sci. Technol. 17, 377, (2002).

5 - **K.G. NIKIFOROV**, Prog. Cryst. Growth Ch.39, 1, (1999).

6 - **K. BELAKROUM**, Magister thesis, Mentouri University, (2004).

7 - **P. COLOMBET**, Doctorat thesis, Nantes University, (1982)

8 - **M. DANOT, PIERRE COLOMBET, MICHEL TREMBLET**, Mat. Res. Bull. Vol.20.pp.463-468, (1985)

9 - **M. TREMBLET, P. COLEMBET, M. DANOT AND J. ROUXEL**, Rev. Chim. Min.17, 183, (1980).

10 - **D. LOUËR, A. BOULTIF**, Indexing with the successive dichotomy method, DICVOL04, Z. Kristallogr. Suppl. 23, 225-230, (2006).

11 - **H. M. RIETVELD**, J. Appl. Cryst. 2, 65-71, (1969).

12 - **J. RODRIGUEZ-CARVAJAL**, Structural Analysis from Powder Diffraction Data the Rietveld Method Ecole Thématique: Crystallography and Neutrons (1997).

13 - **T. HAHN**, International Tables for Crystallography volume A Space, Group Symmetry, Ed. D. Reidel Publishing Company Holland, Boston: U.S.A (1983).

14 - **P. COLOMBET**, M. Tremblet and M. Danot, Phys. Stat. Solidi (a) 72, 105 (1982).