Crystallographic Study by X-ray Rietveld Analysis of New Synthetic Pyrochlores $[Eu_{2-x}M_x][Sn_{2-x}M_x]O_{7-3x/2}$ (M = Mg or Zn)

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INTRODUCTION.

Pyrochlores are mixed metal oxides which general formula is $A_2B_2O_7$ and the exact formula is $A_2B_2O_6O'$ because the oxide ions occupy two crystallographically nonequivalent sites. The larger A cation, which anionic radius is 0.9–1.2 Å, has an eight-fold coordination (distorted cube), while the smaller B cation, ionic radius 0.5–0.75 Å, is in a six-fold coordination (distorted octahedron). $A_2^{3+}B_2^{4+}O_7$ pyrochlores, in which A sites are generally occupied by rare earth ions, are more common than those of formula $A_2^{2+}B_2^{5+}O_7$. Partial substitution at A and B cationic sites as well as oxygen sites is possible. Vacancies in the crystal lattice at A and oxygen sites are possible to a certain extent. The possibilities of selecting A and B cations or introducing lattice defects in these solids gives rise to a wide variety of chemical and physical properties (Subramanian, 1983, Zhu, 2007).

The rare earth stannates with formula $Ln_2Sn_2O_7$ (Ln = Y, La–Lu) have been recently shown to be potential phosphor materials. These mixed oxides have been tested as ionic/electric conductors, catalysts (Li, 2006), lithium ion batteries (Sharma, 2006) and resistant materials to radiation damage (Sickafus, 2000). The cubic pyrochlore structure (space group *Fd-3m*, no. 227, Z = 8), with general formula $A_2B_2O_6O'$, is often considered as a fluorite structure with ordered defects, except that in the isometric pyrochlore structure two cation sites and one-eighth of the anion sites are empty. The cations and oxygen vacancies are ordered. The loss of one-eighth of the anions reduces the coordination of the B-site cation from 8 to 6. The Ln and Sn metal cations occupy the 16d (1/2, 1/2, 1/2) and 16c (0, 0, 0) sites, respectively, and the O and O' oxygens are in the 48f (*x*,1/8,1/8) and 8b (3/8, 3/8, 3/8) positions, respectively .

The anion sublattice can be completed by adding the missing oxygen in the 8a site to recover the fluorite structure.

The aim of this work is to determine by X-Ray Rietveld analysis the structure of new solid solutions $Eu_2Sn_2O_7$-MO (M=Mg, Zn). The structural study for the host pyrochlore structure $Eu_2Sn_2O_7$ has been also performed.

MATERIALS AND METHDODS.

In order to obtain solids with the formula $[Eu_{2-x}M_x][Sn_{2-x}M_x]O_{7-3x/2}$ where $0 \le x \le 0.40$ for M= Mg and $0 \le x \le 0.45$ for M=Zn, stoichiometric amounts of the oxides (Eu_2O_3, SnO_2, MgO and ZnO) were ground so as to obtain homogenized mixtures. The mixtures were submitted to consecutives calcinations under static air atmosphere: a first calcination at 1000ºC for 48h, and a second one after grinding at 1400ºC for 96h. The heating rate was 2 º/min.

The PXRD patterns were recorded from 12 to 85º 2θ using 0.01º step-intervals counting steps of 6 s and Cu Kα radiation (λ = 1.5405 Å) in a Siemens D-500 diffractometer with a DACO-MP microprocessor. The patterns were analyzed by the Rietveld method with Fullprof software using the atomic position set and the space group of the pyrochlore structure *Fd-3m*, nº. 227 (Origin at center -3m). A pseudo-Voigt function was chosen to generate the line shape of the diffraction peaks. The background was estimated by linear interpolation between points corresponding to regions without reflections. A Rietveld refinement was performed to minimize the function: $Sy = \sum_i wi\,(y_i - y_{ci})^2$ where *yi* and *yci* are the observed and calculated intensities at the i^{th} step and *wi is* the weighting factor ($wi = 1/yi$). The *R* factors calculated were: the profile factor, $Rp = 100 \sum_i [|yi - yci|/\sum_i |yi|]$, the weighted profile factor, $Rwp = 100[\sum_i wi|yi - yci|^2/\sum_i wi|yi|^2]^{1/2}$ and the Bragg factor, $R_{Bragg} = 100[\sum_i |Ii - Ici|/\sum_i |Ii|]$, where *Ii* and *Ici* are the observed and calculated integrated intensities, respectively.

RESULTS AND DISCUSSION.

Structural refinements of the two solid solutions $[Eu_{2-x}M_x][Sn_{2-x}M_x]O_{7-3x/2}$ (M= Mg, Zn) have been achieved for x = 0.22. The same analysis has been also performed for the $Eu_2Sn_2O_7$ pyrochlore in order to obtain data not available in the literature. The refinements using both anionic and cationic vacancies do not agree with experimental data so we only present results concerning the anionic vacancies.

The O oxygen atoms are located in 48(f) special Wyckoff positions, the O' oxygen atoms in the 8(b) positions, the Sn atoms in the 16(c) positions and the Eu atoms in the 16(d) positions. The magnesium atoms are placed in the 16(d) and 16(c) positions. The unique atomic coordinate is the *x*(48f) oxygen atoms. This one varies from 0.3294 to 0.3397 over the series of stannate pyrochlores; we have started with the value 0.33. Rietveld analysis of similar solid solutions show that the anionic vacancies have been placed in the 48(f) positions and for the 8(b) sites no stable solutions or good agreement factors were obtained. So we have placed the anionic vacancies in the 48(f) positions. The occupancy factors for M (Mg, Zn), (Eu) atoms, (Sn) atoms and anionic vacancies have been correlated and refined.

The conventional Rietveld agreement indices and the refined structural parameters for $Eu_2Sn_2O_7$, $[Eu_{2-x}Mg_x][Sn_{2-x}Mg_x]O_{7-3x/2}$ and $[Eu_{2-x}Zn_x][Sn_{2-x}Zn_x]O_{7-3x/2}$ (x=0.22) are given in Table 1. The observed profile for the solid solutions and the difference between the observed and calculated profiles are plotted in Fig.1. The agreement between the observed and calculated profile is

palabras clave: Estructura Cristalina, Análisis Rietveld de Rayos-X, Pirocloro

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excellent and the final R factors are good, particularly for R_B factors which depend on both the atomic coordinates and the chemical composition.

When a M^{2+} ion replaces simultaneously a Eu^{3+} ion at the A site and a Sn^{4+} ion at the B site in $Eu_2Sn_2O_7$, this will lead to a positive charge deficiency in the compound. Hence, anionic vacancies must be created to balance the positive charge deficiency of the compound. The ratio of the average effective ionic radii of the Eu^{3+} and M^{2+} ions to those of Sn^{4+} and M^{2+} (M = Mg, Zn) ions for the two solid solutions $[Eu_{2-x}M_x][Sn_{2-x}M_x]O_{7-3x/2}$ ($0 \le x \le 0.4$ for M= Mg and $0 \le x \le 0.45$ for M=Zn) are in the 1.467-1.540 range, where the formation of the pyrochlore is favored.

We have observed that when the value of x increases, the rA^{3+}/rB^{4+} ratio decreases reaching values close to the limit 0.46, so the degree of disorder increases in the host $Eu_2Sn_2O_7$ pyrochlore structure.

The formation of the solid solutions corresponds to the substitution of M^{2+} (Mg^{2+} or Zn^{2+}) for Eu^{3+} and Sn^{4+} ions with simultaneous developing of anionic vacancies in the 48(f) positions (*Chtoun, 1997*).

In the pyrochlore $A_2B_2O_7$ structure, the order of the A and B cations leads to three kinds of tetrahedral sites: not occupied 4B sites, O' occupied 4A sites, and O occupied (2A+2B) sites. So O located in (2A+2B) tetrahedral sites shifts toward the middle of the edge joining the two ions of higher electric charges (B^{4+}). The *t* shift is correlated to the *x* coordinate of 48f oxygen atoms by the relationship: $x = 6/16 - t$ *(Srivastava, 2009)*. For the solid solution $[Eu_{2-x}M_x][Sn_{2-x}M_x]O_{7-3x/2}$ (M= Mg, Zn) the less charged cations M^{2+} substitutes the Eu^{3+} and Sn^{4+} cations; as a consequence, an increase of the *t* shift and a decrease of the *x* positional parameter takes place (Table 1).

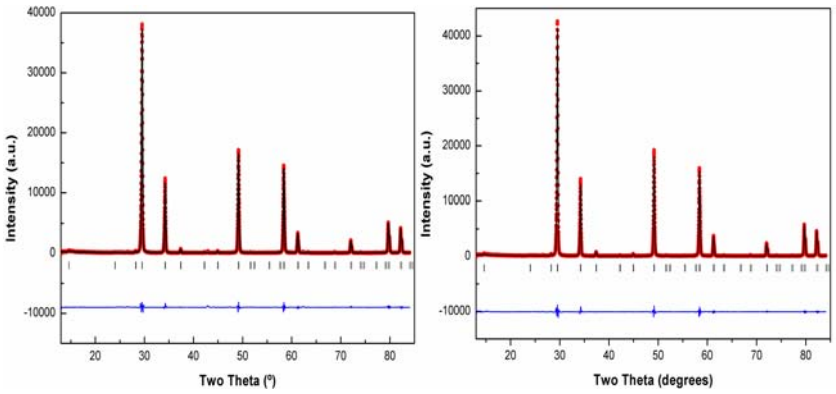

Fig. 1. *Observed (dots) calculated (solid line) and difference X-ray diffraction profiles for* $[Eu_{2-x}Mg_x][Sn_{2-x}Mg_x]O_{7-3x/2}$ (left) and $[Eu_{2-x}Zn_x][Sn_{2-x}Zn_x]O_{7-3x/2}$ (right). Vertical marks correspond to the allowed reflections for the space group Fd-3m.

CONCLUSIONS

The study of the binary systems $Eu_2Sn_2O_7$-MgO and $Eu_2Sn_2O_7$-ZnO shows that both correspond to new pyrochlore solid solutions in large composition domain $x \le 40\%$ (MgO) and $x \le 45\%$ (ZnO). Lattice parameter *a* of these solid solutions $[Eu_{2-x}M_x][Sn_{2-x}M_x]O_{7-3x/2}$ (M= Mg, Zn) decreases when x increases, but the pyrochlore structure is maintained. Refinement results confirm a cubic structure with *Fd-3m* space group. Crystal structure analysis revealed that the substitution of M^{2+} (Mg^{2+} or Zn^{2+}) on to the Eu^{3+} and Sn^{4+} sites in the pyrochlore oxide $[Eu_{2-x}M_x][Sn_{2-x}M_x]O_{7-3x/2}$ is carried on with simultaneous creation of vacancies in the anionic sublattice.

	$Eu_2Sn_2O_7$	$[Eu_{2-x}Mg_x][Sn_{2-x}Mg_x]O_{7-3x/2}$	$[Eu_{2-x}Zn_x][Sn_{2-x}Zn_x]O_{7-3x/2}$
Space group	Fd-3m	Fd-3m	Fd-3m
a(Å)	*10.4822*	*10.4817*	*10.4804*
Z	*8*	*8*	*8*
V(Å³)	*1151.74*	*1151.596*	*1151.169*
x(O_{48f})	*0.333(4)*	*0.3328(5)*	*0.3325(4)*
Isotropic thermals			
Eu (Å²)	*0.853(3)*	*0.631(3)*	*0.703(3)*
Mg_1 or Zn_1(Å²)		*0.631(3)*	*0.703(3)*
Sn (Å²)	*0.144(2)*	*0.442(4)*	*0.176(3)*
Mg_2 or Zn_2(Å²)		*0.442(2)*	*0.176(3)*
O (Å²)	*0.996(9)*	*1.903(1)*	*1.195(1)*
O' (Å²)	*0.252(3)*	*0.940(4)*	*0.265(4)*
Selected contacts			
Sn-O (Å)	*2.049(3)*	*2.046(2)*	*2.045(3)*
Eu-O (Å)	*2.546(2)*	*2.550(3)*	*2.552(2)*
Eu-O' (Å)	*2.269(4)*	*2.269(3)*	*2.269(1)*
Sn-O-Sn /	*129.43(7)*	*129.80(9)*	*129.96(7)*
Eu-O-Eu /	*93.43(9)*	*93.19(11)*	*93.09(9)*
R_p (%)	*4.06*	*5.15*	*5.29*
R_{wp} (%)	*6.48*	*8.57*	*7.63*
R_{exp} (%)	*3.90*	*3.98*	*3.84*
R_{Bragg} (%)	*0.74*	*1.39*	*1.16*
χ^2 (%)	*3.40*	*5.19*	*4.59*

Table 1: Refinement parameters for the samples (x=0.22).

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