Crystallographic Study by X-ray Rietveld Analysis of New Synthetic Pyroclorhose 

\[ \text{[Eu}_{2-x}\text{M}_x]\text{[Sn}_{2-x}\text{M}_x]O_{7-3x/2} \quad (M = \text{Mg or Zn}) \]

/Raquel Trujillano (1,*), Mohamed Douma (1), El Hoassain Chtoun (2), Vicente Rives (1)

INTRODUCTION.

Pyroclorhose are mixed metal oxides which general formula is \( \text{A}_2\text{B}_2\text{O}_7 \) and the exact formula is \( \text{A}_2\text{B}_2\text{O}_6\text{O'} \) 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 octahedron), \( \text{A}_3^+\text{B}_2^+\text{O}_4^+ \text{ pyroclorhose, in which A sites are generally occupied by rare earth ions, are more common than which A sites are generally occupied by oxygen sites are possible to a certain extent. The possibilities of selecting A and B cationic sites as well as oxygen sites is possible. Vacancies in the crystal lattice at A and B cationic sites and one-eighth of the anion sites are possible to a certain extent. The possibilities of selecting A and B cationic sites 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 LnSnO\(_3\) (Ln = Y, La–Lu) have been recently shown to be potential phosphor materials (Sharma, 2006) and resistant materials to radiation damage (Sickafus, 2000). 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 pyroclorhose structure (space group \( Fd-3m \), no. 227, \( Z = 8 \)), with general formula \( \text{A}_2\text{B}_2\text{O}_6\text{O'} \), is often considered as a fluorite structure with ordered defects, except that in the isomeric pyroclorhose structure two cationic 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 \((48f_o)\) 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 \( \text{Eu}_2\text{Sn}_2\text{O}_7\text{MO}_x \) (\( \text{M} = \text{Mg, Zn} \)). The structural study for the host pyroclorhose \( \text{Eu}_2\text{Sn}_2\text{O}_7\) has also been performed.

MATERIALS AND METHODS.

In order to obtain solids with the formula \( \text{[Eu}_{2-x}\text{M}_x]\text{[Sn}_{2-x}\text{M}_x]O_{7-3x/2} \) where 0\( x \leq 0.40 \), we have chosen to perform phosphor materials analysis by the Rietveld method with Fullprof software using the atomic position set and the space group of the pyroclorhose structure \( Fd-3m \), \( Z = 8 \). The PXRD patterns were recorded from 12 to 85 \( \theta \) \( \text{Cu} K\alpha \) radiation \( (\lambda = 1.5405 \text{ Å}) \) in a Siemens D-500 diffractometer with a DACO-MP microprocessor.

RESULTS AND DISCUSSION.

Structural refinements of the two solid solutions \( \text{[Eu}_{2-x}\text{M}_x]\text{[Sn}_{2-x}\text{M}_x]O_{7-3x/2} \) (\( \text{M} = \text{Mg, Zn} \)) have been achieved for \( x = 0.22 \). The same analysis has been also performed for the \( \text{Eu}_2\text{Sn}_2\text{O}_7 \) pyroclorhose in order to obtain data not available in 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 \( 0 \) oxygen atoms are located in \( 48f \) special Wyckoff positions, the \( O \) oxygen atoms in the \( \text{8(b)} \) positions, the \( \text{Sn} \) atoms in the \( 16(c) \) positions and the \( \text{Eu} \) atoms in the \( 16(d) \) positions. The quantities \( x \) of the Refinement has been obtained from 0.22 to 0.397 over the series of stannate pyroclorhose: we have started with the value 0.33. The anionic vacancies have been placed in the \( 48f \) 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 \( 48f \) positions. The occupancy factors for \( \text{M} = \text{Mg, Zn} \), \( \text{Eu} \) atoms, \( \text{Sn} \) atoms and anionic vacancies have been correlated and refined.

The conventional Rietveld agreement indices and the refined structural parameters for \( \text{Eu}_2\text{Sn}_2\text{O}_7 \), \( \text{[Eu}_{2-x}\text{M}_x]\text{[Sn}_{2-x}\text{M}_x]O_{7-3x/2} \) and \( \text{[Eu}_{2-x}\text{Zn}_x]\text{[Sn}_{2-x}\text{Zn}_x]O_{7-3x/2} \) (\( x = 0.22 \)) 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

\[ \text{Rwp} = 100 \left( \frac{\sum |I_i - I_{ci}|}{\sum I_i} \right) \]
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 $[Eu_2-M_x][Sn_2-M_x]O_{7-3x/2}$ ($0< x < 0.45$ for $M = Mg$ and $0< x < 0.45$ 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 48f positions (Chtoun, 1997).

In the pyrochlore A$_2$B$_2$O$_7$ 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 4B sites, O' occupied 4A sites, three kinds of tetrahedral sites: not ordered A and B cations leads to a shift of the average effective ionic radii of the $A^3+$ and $B^4+$ ions; as a consequence, an increase of the $t$ shift and a decrease of $x$ positional parameter takes place (Table 1).

**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 $x \leq 40\%$ ($MgO$) and $x \leq 45\%$ ($ZnO$). Lattice parameter $a$ of these solid solutions $[Eu_2-M_x][Sn_2-M_x]O_{7-3x/2}$ ($M = Mg, Zn$) 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 $[Eu_2-M_x][Sn_2-M_x]O_{7-3x/2}$ is carried on with simultaneous creation of vacancies in the anionic sublattice.

**ACKNOWLEDGEMENTS**

Authors acknowledge financial support from AECI for the PCI (España-Mediterráneo) project. M. Douma acknowledges the MAEC-AECID grant.

**REFERENCES**


