IMMOBILIZATION OF HEAVY METALS ON $Sr_4Mn_2CuO_9$ LATTICE: REUSING AS COOL BLACK CERAMIC PIGMENTS

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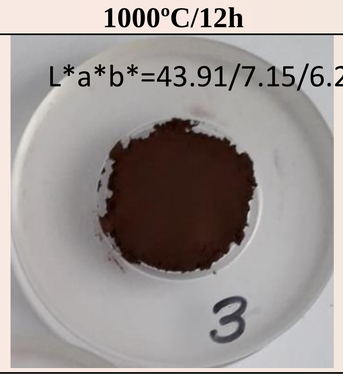
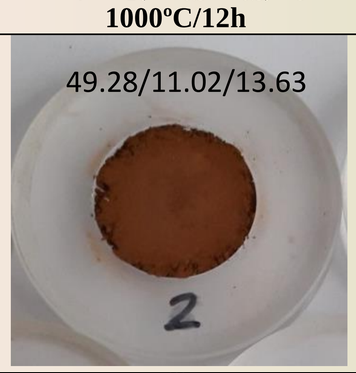
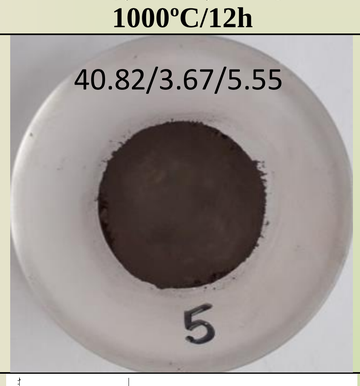
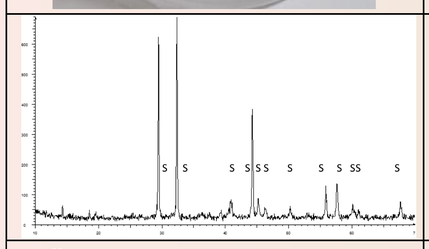
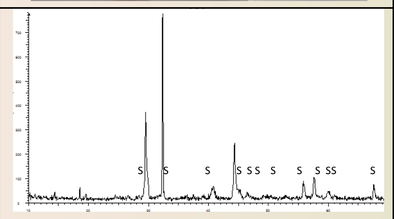
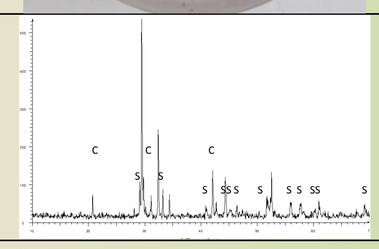
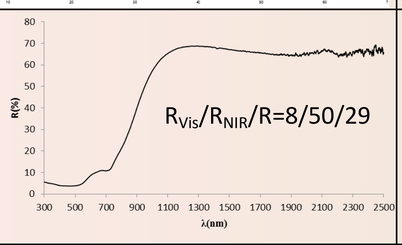
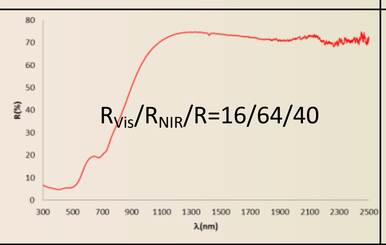
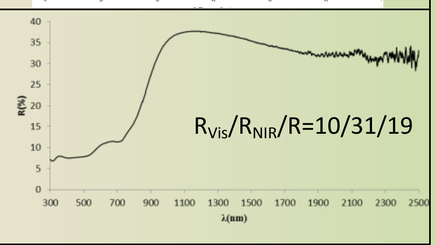
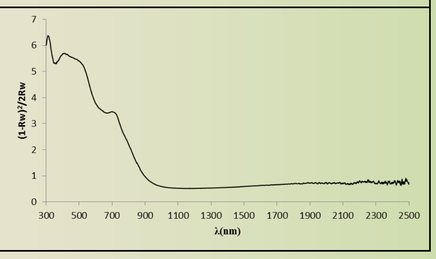
INTRODUCTION

The structure and the electric and magnetic properties of disordered hexagonal perovskite-type oxides A_xMO_3 (A=Sr, M=Co,Ni) have received much attention [1-3]. The structures of these oxides can be viewed in terms of infinite (MO_3) and A chains, where the (MO_3) chains are made up of face-sharing MO_6 octahedra and trigonal prisms. In the (MO_3) chains, single MO_6 trigonal prisms may alternate with single MO_6 octahedra or with M_nO_{3n+3} octahedral oligomers made up of n face-sharing MO_6 octahedra. Crystals of $Sr_4Mn_2CuO_9$ belong to the family of $A_{1+x}(A'_xB_{1-x})O_3$ ($0 \le x \le ½$), which is closely related to the hexagonal perovskite 2H structure having a *P321* space group. The Mn^{4+} ions occupy the octahedral site and Cu^{2+} ions randomly fill the center of the square faces of the trigonal prisms. The hexagonal perovskite-type $Sr_4Mn_2(Cu_xZn_{1-x})O_9$ has been studied as orange cool pigments [4]. Heavy metals are naturally occurring elements that have a high atomic weight and a density at least 5 g/l, and their toxicity depends on several factors including the dose, route of exposure, and chemical species. There has been an increasing ecological and global public health concern associated with environmental contamination by these metals. For an effective immobilization of wastes by sintering (ceramization), ceramic oxide materials such as perovskites have studied for the immobilization of radioactive wastes [5]. The stacking of the metal-oxygen polyhedra in their structure results in the formation of cavities and vacant interlayers, being capable of accommodating a large number of radioactive cations. Its disorder induces a low symmetry and increases the kinetic barrier of nucleation in order to act as pigments in glazes.

AIMS

In this communication the immobilization of Zn and Ce replacing Cu and Mn ions respectively in $Sr_4Mn_2CuO_9$ by sintering up to 1000 ºC of $SrCO_3$, Mn_2O_3 and CuO, and its performance as cool black ceramic pigments are studied.

$Sr_4Mn_2CuO_9$ 1000ºC/12h	$Sr_4Mn_2(Cu_{0.5}Zn_{0.5})O_9$ 1000ºC/12h	$Sr_4(MnCe)CuO_9$ 1000ºC/12h
		
		
		
		

RESULTS

X-ray powder diffraction (XRD) using Cu-Kα radiation (40 kV and 30 mA): at 1000ºC/12h the Zn^{2+} is completely solved in $Sr_4Mn_2CuO_9$ (S) lattice but part of Ce^{4+} remain unreacted and $SrCeO_3$(C) is detected.

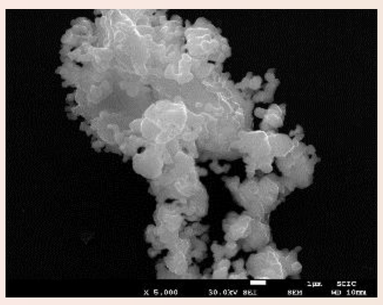
UV-Vis-NIR diffuse reflectance spectroscopy: overlapping absorption bands described for Mn^{4+} (d^3) in octahedral coordination and Cu^{2+} ions in square-plane coordination can explain the positions of the bands in reflectance spectra. However it is not able to justify its anomalously high optical density, therefore spin-exchange interactions of Mn^{4+} ions with adjacent Mn^{4+} ions and also with adjacent Cu^{2+} located at the TP centers should be considered for explain the high intensity of absorption in the visible region by a Paired Spin exchange Transitions (PET)

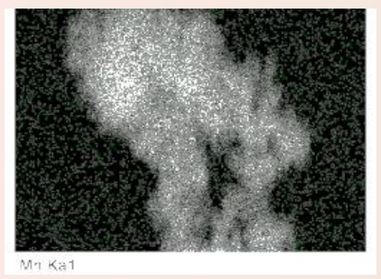
CIEL*a*b* color characterization: $Sr_4CuMn_2O_9$ presents a black-brown color that darken with Ce entrance replacing Mn, in contrast the entrance of Zn replacing Cu produce ligther brown shades.

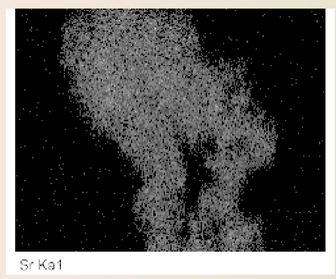
Solar reflectance: the solar reflectance (R) of the product was obtained as the integral of the measured spectral reflectance and the solar irradiance divided by the integral of the solar irradiance in the range of 300-2500 nm, as in the formula:

$$R = \frac{3\int_{502}^{500}(\lambda)i(\lambda)d\lambda}{3\int_{502}^{500}(\lambda)d\lambda} \qquad \text{(eq. 6)}$$

Where, r(λ) is measured spectral reflectance (W/m^2) spectrum and i(λ) is standard solar irradiation ($W/m^2.nm$) according to (ASTM) Standard G173-03. The $Sr_4Mn_2(Cu_{0.5}Zn_{0.5})O_9$ solid solution shows higher NIR reflectance (R_{NIR}=64%) than undoped lattice (50%) and cerium modified sample shows the lower value (31%).







Particle size and morphology by SEM microscopy: samples show a homogeneous distribution of ions in the aggregates, undoped sample shows particles of 0.5-1 µm forming aggregates of 1-7 µm

CONCLUSIONS

Immobilization of Zn and Ce replacing Cu and Mn ions respectively in $Sr_4Mn_2CuO_9$ by sintering up to 1000 ºC of $SrCO_3$, Mn_2O_3 and CuO, and its performance as cool black ceramic pigments are studied. At 1000ºC/12h the Zn^{2+} is completely solved in $Sr_4Mn_2CuO_9$ (S) lattice but part of Ce^{4+} remain unreacted and $SrCeO_3$(C) is detected. $Sr_4CuMn_2O_9$ presents a black-brown color that darken with Ce entrance replacing Mn, in contrast the entrance of Zn replacing Cu produce ligther brown shades. All samples show high NIR solar reflectance but the brown Zn- $Sr_4Mn_2CuO_9$ shows the best performance with R_{NIR}=64%.

Acknowledgement

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