Conference Proceedings

Solar World Congress 2015
Daegu, Korea, 08 – 12 November 2015

STRUCTURAL AND OPTICAL PROPERTIES OF SEVERAL IRON-MANGANESE OXIDES TO PREPARE THIN FILMS AS SOLAR SELECTIVE ABSORBERS

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Abstract

In this work, the behavior of the mixture to form manganese iron oxides used as pigments for application in solar absorbers is investigated. Polished aluminum as substrate was covered with mixed Fe:Mn oxide by the impregnation method. After drying the thin films, the samples were submitted to different heat treatment temperatures. Chemical structure and optical properties were respectively evaluated using XRD and UV-Vis-IR spectrophotometry technique. The evolution of different structural phases during the addition of manganese ions process is discussed with Rietveld refinement of the X-ray diffraction. The results indicated a phase mixture of the two oxides for concentrations x = 0.87, 0.5 and a solid solution x = 0.93, 0.35, however the best selectivity values were obtained in the sample x = 0.35, indicating the addition of manganese is crucial for the pigment applied to solar applications substrate.The thin film profilometry let us to evaluate thin film thickness and the surface roughness. Finally, the effects of mixed oxides chemical composition on the solar selectivity (α / ε), will be discussed.

Keyword; *Selective coatings, hematite, absorptance*, *emittance, Rietveld method.*

1. Introduction

Domestic water heating systems with solar energy technologies, are still at the date, a subject of study because the conversion of thermal solar energy in these systems depends largely on the materials used as absorbers, specially in their optical properties[Kenenndy 2002]. Selective surfaces of high solar absorptance (α) and low thermal emittance (ε) are used as the solar absorber [Duffie, 199, Zhang 2000]. The selectivity values (α/ε) depend on the precursors, the deposition method and also of the substrate used.
The most significant methods are chemical electrodeposition [Reza et al, 2015], sputtering [Barshilia, 2008], vacuum evaporation, spray pirolysis [Avila et al, 2004], sol gel [Tulchinsky et al, 2014, Vince et al 2003], painting technique [Orel, 2005] and electroplating[Driver 1977] have commercial application for large-scale production. Today, the problem of the available selective surfaces is that they are not only rather expensive but also appropriate for large scale production. The solution lies in the selective properties paints applied with a method easy and inexpensive: painting method.

The types of paint can be categorized as Thickness Insensitive Spectrally Selective (TISS) or Thickness Sensitive Spectrally Selective (TSSS) [Orel, 2005, 2007]. It is possible to obtain a high solar absorptance (> 0.95) but the thermal emittance should be about 0.5 for TISS paints [Orel et al., 2007]. Several studies have shown that using paints based on metal oxides [Geng, 2012] as $FeMnCuO_x$ transition can achieve acceptable selectivity values. The solar selective coating is one of the most important components of the solar collectors. Their optical properties must influence favorable both the efficient absorption of sunlight and low heat energy losses through the solar collector [1]. Some preparation methods for these coatings are spray pyrolysis, [2] and by the impregnation of FeCuMnOx and Fe_3O_4 pigments [3], [4]. In this work, it is

doi:10.18086/swc.2015.10.07 Available at http://proceedings.ises.org

investigated the behavior of the mixture to form manganese iron oxides used as pigments for application in solar absorbers. Polished aluminum as substrate was covered with several mixed ratios Fe:Mn oxide by the impregnation method. After drying the thin films, the samples were submitted to different heat treatment temperatures. Chemical structure and optical properties, using XRD and UV-Vis-IR spectrophotometry technique, were respectively evaluated. The thin film profilometry let us to evaluate thin film thickness and the surface roughness. Finally, the effects of mixed oxides chemical composition on the solar selectivity (α / ε), is discussed.

The hematite (α-Fe_2O_3) [Hosseini, 2008] and α-Mn_2O_3 in bixbite phase were used as red and black pigments since ancient times. Now they are used in various industrial applications for paints, enamels and plastics thanks to its low price, low toxicity and high thermal and chemical stability. In phase α-Mn_2O_3 the Mn 3+ ions are coordinated octhaedrically, while ions O are 4 Mn ions, so close. The $(Fe1\text{-}xMnx)_2O_3$ [Saha, 2002] system is interesting because the extreme phases crystallize in different space groups. The phase with x = 0 (Fe_2O_3) does in the rhombohedra system with space group R-3c (Fig 1a) while the phase with x = 1 (Mn_2O_3) crystallizes in the cubic system (Fig 1b), with space group Ia3. The crystal structure of the pigment has an influence on its optical properties. The objective of this work is to study the optical characterization of selective surfaces containing different amounts of Fe-Mn ions for use as pigments for solar absorbers. The crystal structure of the pigment has been studied by XRD [Rietveld, 1969, Lutterotti, 1992], the optical surface characterization was performed by uV-VIS-infrared spectrometry and the details of the surface morphology were conducted with profilometry.

Theoretically solar absorptance is defined as the fraction between absorbed radiation and solar radiation. It was calculated according to equation 1. where λ is wavelength, R(λ) reflectance and Is (λ) normal irradiance.

$$\alpha_s = \frac{\int_{0.3}^{2.5} I_s(\lambda)\left(1-R(\lambda)\right)d\lambda}{\int_{2.5}^{20} I_s(\lambda)d\lambda} \qquad (eq\ 1)$$

The thermal emittance is a ratio between a radiation emitted by the surface and the radiation that a black body at the same temperature emmit , which is presented as:

$$\varepsilon_s = \frac{\int_{2.5}^{25} E(\lambda,T)\left(1-R(\lambda)\right)d\lambda}{\int_{2.5}^{25} E(\lambda,T)d\lambda} \qquad \text{(eq 2)}$$

Where E (λ, T) is the spectrum of the radiation of a black body at temperature T.
The objective of this work is to obtain the chemical, surface and optical characterization of solar selective thin films containing different quantities of Fe-Mn ions, used as pigments, for solar absorbers applied with a method type painting.

2. Experimental

2.1 Preparation of $(Fe_xMn_{1-x})_2O_3$

Mixed Fe:Mn and single oxide powder by the co-precipitation method were prepared, under the following procedure: Iron (III) chloride hexahydrate ($FeCl_3\ 6H_2O$) and manganese (II) chloride ($MnCl_2\ 4H_2O$) were mixed while maintaining a molar ratio 2: 1. This mixture was added to a 1M solution of NH_4OH, where a chemical precipitate occurred, that after washed with distilled water, let's to obtain our powder to prepare the solar selective thin film on Al substrate. Other compositions of mixed oxides prepared were in the proportions: Fe: Mn (2.2: 0.8, 2.8: 0.2)

2.2 Paint coatings

The Aluminum substrate were immersed in the different suspension containing various Fe:Mn, molar ratios. The thin film were submitted at different thermal treatments: 100, 150, 200 and 300° C, in order to observe the thermal stability of the films.

2.3 Instrumental

The phase identification of the synthesized powders was performed using a Bruker-D8 Advance X-ray diffractometer with Cu Kα radiation (1.5406 A°) in a Bragg Brentano geometry and a one-dimensional position-sensitive silicon strip detector (Bruker, Lynxeye) operating in the 0-D mode. The 2θ step size used in the registered data is equal to 0.02^0. The patterns have been analyzed by the Rietveld method of the Fullprof program [Rodriguez, 2001]. The Rietveld method consists of simulating a diffraction pattern and refining a proposed structural model until a satisfactory match is found between the experimental and simulated patterns, the method is a full-profile approach that was initially introduced for the refinement of crystal- structure parameters but has been expanded for application in quantitative phase-analysis. The simulated XRD pattern is calculated from a large number of parameters, including crystal-structure parameters of each component phase, a scale factor for each constituent phase to adjust the relative intensities of the reflections, parameters describing the peak profile and the background, and other parameters in the simulation.
Reflectance spectral of the spectrally selective paint coatings were measured in the wavelength interval 0.3-20 µm. A Varian UV/ Vis/NIR spectrophotometer equipped with an integrating sphere was used to record reflectance spectra in the wavelength interval 0.3-2.5 mm. The infrared wavelength interval, 2.5-20 mm, was covered with an Infrared spectra are recorded on a Thermo Scientific Nicolet IS50 FTIR equipped with a gold-coated integrating sphere

With the total spectral reflectance, measured into two wavelength range is it easy build a reflectance spectra both in the uV.Vi and NIR in a Medium IR Those measurements can be used to determine the optical properties of the solar selective thin films.
The average thickness and surface morphology of the coatings were measured by means of a profilometer Bruker DektakXT.

3. **Results and discussion**

3.1 XRD patterns and Rietveld Method

Results are shown in Fig. 1 and reflection lines at 2θ = 24.18°, 33.20°, 35.67°, 40.91°, 49.5°, 54.11°, 62.49° and 64.05° indicate pure Fe_2O_3 structure, relative to (0 1 2 1), (1 0 40), (1 1 0), (1 1 3), (0 2 4), (1 1 6), (2 1 4) and (3 0 0) planes,. The diffraction lines at 2θ = 23.27°, 33.14°, 38.45° assigned to (2 1 1), (2 2 2), (4 0 0) planes correspond to the pure oxide Mn_2O_3, indicate the diffraction pattern of a solid solution. The absence of Manganese oxide in the samples x=0.93 in the diffraction pattern indicate that Mn^{3+} cations are introduced in the Fe_2O_3 lattice structure and confirms the formation of a solid solution, as identified by the displacement of the diffraction line. The sample x=0.87 to x=0.5 present phase segregation.
Rietveld Refinement graphs (experimental data and difference theoretical data) of the materials after the heat treatments are presented in Fig. 2. The parameters such as refined cell parameters, atomic positions and percentage of phases present in the mixtures are presented in Table 1.

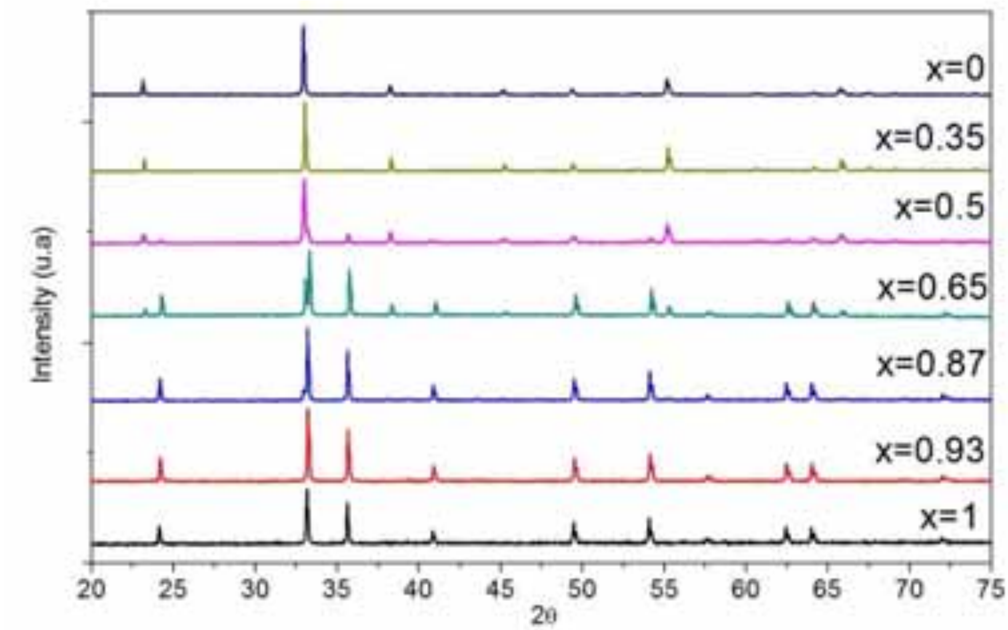

Fig. 1 XRD patterns of oxides prepared at different molar concentration at 800 °C.

The structural parameters of each sample were evaluated by the XRD study. A Corundum and a bixbyite structural phase for Fe_2O_3 and Mn_2O_3 pure compound was obtained respectively. Also both phases in the samples with mixtures of ions, are observed. A Rietveld Refinement graph (experimental data and theoretical data difference) of a representative material after heat treatments is presented in Fig. 2. The parameters such as refined cell parameters, atomic positions and percentage of phases present in the mixtures, are summarized in Table 1.

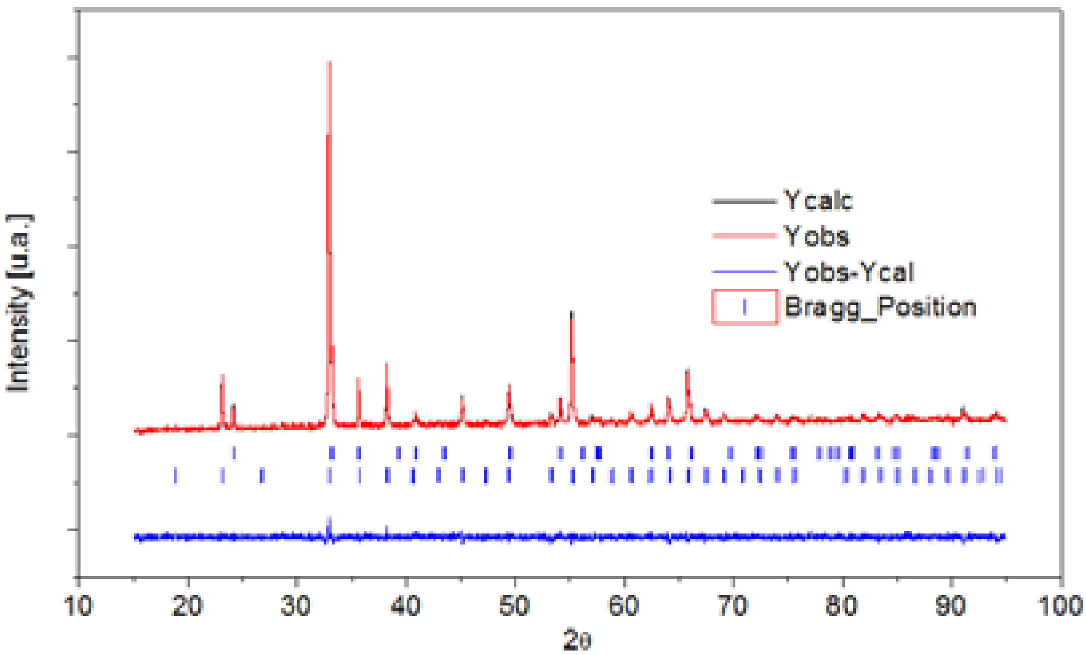

Fig. 2 XRD patterns of oxides prepared at different molar concentration at 800 °C.

Table 1: Result of the Rietveld refinement for the several pigments prepared.

Experimental Composition	%wt Phase	Space group	Lattice parameters (°A)			
			a=b=c	a=b	c	$\chi 2$
0	(100) Mn_2O_3	Ia-3	9.4173	-	-	1.36
0.35	(100) Mn_2O_3	Ia-3	9.4174	-	-	1.39
0.5	(58.9)Mn_2O_3	Ia-3	9.414	-	-	1.38
	(41.1) 2.70	R-3c	-	5.037	13.737	
0.87	(97.30) Fe_2O_3	Ia-3	9.414	-	-	1.39
	(2.70)Mn_2O_3	R-3c		5.036	13.738	
0.93	(100) Fe_2O_3	R-3c	--	5.036	13.738	1.36
1	(100) Fe_2O_3	R-3c	--	5.037	13.734	1.38

Quality refinement setting for the samples studied has a satisfactory value. No traces of hydroxyl groups into the structures are observed. The concentration of the two phases for the Fe: Mn samples, 1: 1, 2.2: 0.8, 2: 1, were obtained. Different concentrations result in a change in the percentages of each phase present in the solution, i.e., a greater amount of Mn in the solution, increased the cubic phase (Mn_2O_3), these results are summarized in Table 1.

3.2 Spectral selectivity

Considering the reflectance spectra of some representative samples, figure 3, using the two equations, 1 and 2, it was easy evaluate the solar absorptance and thermal emittance of the films, respectively, with the procedure described by Duffie and Beckman, in the regions of UV / Vis / NIR wavelength, see table 2. Also in this table it is represented some other properties of the prepared thin films, like the thin film thickness and surface roughness.

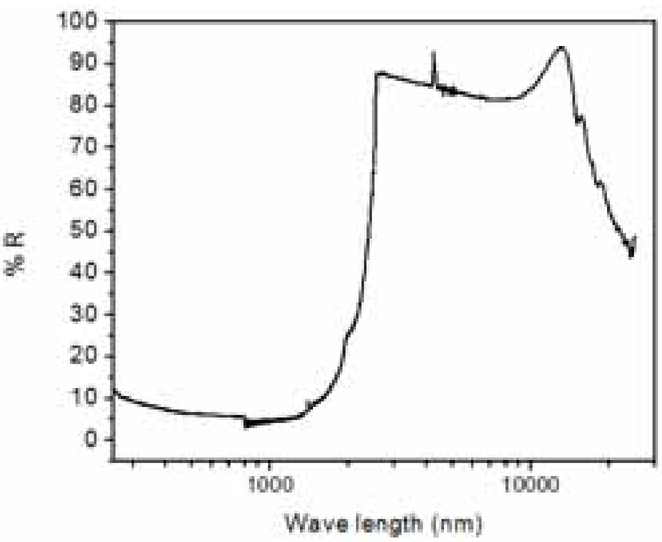

Fig. 3 Direct-hemispherical reflectance of a representative sample $(Fe_xMn_{x-1})_2\ O_3$; x=0.35 at 800°C

3.3 Perfilometry

In addition, 3D roughness parameters based on the value of Ra, were obtained in this work; where Ra is defined as the roughness average. Table 2 includes the results in this parameter and Fig. 4 shows 3D surface images employed to obtain this parameter for the thin films onto Al substrate. The strong increase in roughness with paint technique is clear

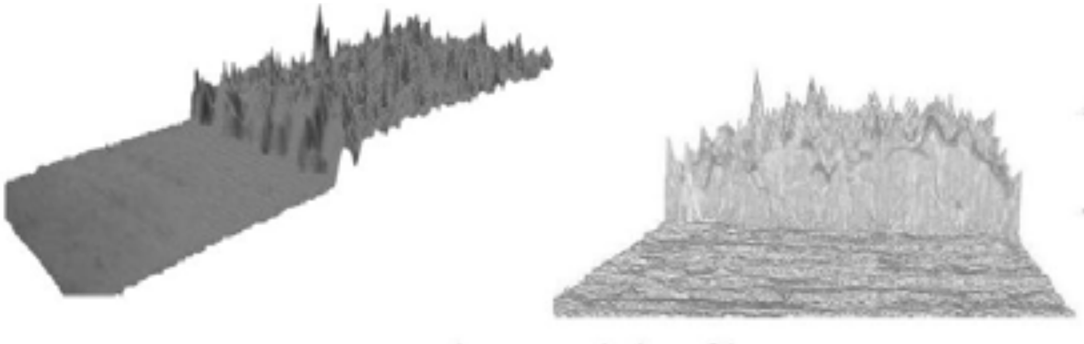

Fig. 3. Surface morphology representation 3D of representative *(*$Fe_xMn_{1-x})_2O_3$ thin films on Al substrate.

Table 2 The optical properties, surface roughness and thin film thickness as a function of the chemical composition of the thin films.

Sample x=	Property			
	Optical		Morphology	
	absortance	emittance	Surface Roughness(μm)	Film thickness(μm)
0	0.918	0.31	0.55	15
0.35	0.931	0.29	0.45	20
0.5	0.899	0.38	0.41	18
0.87	0.894	0.30	0.5	16
0.93	0.897	0.38	0.6	14
1	0.695	0.49	0.75	18

4. **Conclusions**

Solar selective thin films of iron oxides and mixed oxides of Fe:Mn were prepared and characterized by several chemical and spectrophotometric technique like XRD (Rietvelt method), surface profilometry and UV-Vis-NIR. This way, it was possible to evaluate the photothermal optical properties of several thin film coatings. The mixed oxides prepared, show better optical properties for the photothermal conversion of solar energy, having a great thermal stability, that could be used for solar colector working even at mid temperature. At the date we are optimizing the main experimental parameters in order to optimize the optical properties of the solar films.

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6. Acknowledgments

The authors would like to thank CONACyT, México for supporting this research (CB-2011-01-166032; CB-2010-01-154962)