



Research Paper

Synthesis of CoCuMnO_x Pigments for Solar Collectors Absorbent Enamels

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ABSTRACT

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This aim of this research is to produce Co, Cu and Mn mixed oxides by means of one-step solution novel combustion methods using aspartic acid, lysine or ethylenediaminetetraacetic acid as fuels. The pigments were characterized using x-ray diffraction, scanning and transmission electron microscopy, infrared spectroscopy with Fourier transform, Brunauer–Emmett–Teller techniques and the crystal structures refined by the Rietveld method. Finally, an enamel of alkyd- resin base was prepared with the pigment obtained and applied on an aluminum substrate (coating). In this coating, the solar spectral absorbance was determined. The obtained powders showed a CoCuMnO_4 composition with spinel structure. An extraordinary value of absorption on the coatings between 95 and 97% was noted. The temperature achieved by coating to the sun was higher than that obtained for commercial black coating. These results suggest the possibility of utilizing these oxides in absorbent solar enamels.

Key words: Oxides, optical materials, chemical synthesis, X-ray diffraction, electron microscopy, optical properties.

INTRODUCTION

Electricity generation from renewable sources approximately tripled between 2010 and 2035 attaining 31% of the entire energy production. The use of renewable sources is expected to reduce CO_2 emissions by over 4.1 Gt in 2035 contributing to the diversification of energy sources, diminishing oil and gas import bills, and certainly decreasing air pollution (Jebli and Youssef, 2015). In particular, solar energy can be used in industrial, commercial and domestic areas. In domestic applications, households consume energy in air conditioning, heating, water heating, lighting and other applications (Al-Khaffaj and Mossad, 2013).

Solar thermal systems proved to be a valid way of utilizing the huge potential of the available solar energy. Solar thermal collectors convert incident radiation through photo thermal conversion into useful energy, that is, heat. This is transferred to a working fluid and used in a variety of ways such as space heating and electricity production (Trease et al., 2013).

The efficiency of a solar thermal collector depends on the materials used as absorber coatings, especially on their optical properties. As regards the absorption of the solar spectrum, the oxides of transition metals (Co, Mn, Fe and Cr) present a high absorbance owing to the existence of numerous, allowed, electronic transitions between their partially full “d” orbitals (Vince et al., 2003). These oxides are used as absorbents films in solar selective surfaces. For example, CuFeMnO_x highly spectrally selective black films for solar absorbers can be made using sol-gel syntheses combined with dip coating or slip casting deposition techniques (Kaluža et al., 2001); also, titanium-doped and undoped CuCoMnO_x spinel films deposited on Al substrates from sols with their solar absorbance (α_s) ranging between 85 and 91% that presents an infrared emittance of 3.6% (Vince et al., 2003) and finally, selective absorber coatings with composition $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$ can be successfully deposited on aluminum and stainless steel substrates by sol-gel dip-coating method (Pal et al., 2013).

Ternary spinel oxides powders are used as absorber pigments in solar selective surfaces obtained by sol-gel combustion method followed by air calcination at 500°C for 1 h. A novel low-cost spectrally selective coating using CoCuMnO_x powders as solar-absorbing pigment is prepared by means of a spray-coating technique. By optimizing the paint coating thickness, optical parameter values of absorbance reached 92.8% and infrared emittance showed a value of 19.8% (Geng et al., 2011).

By sol-gel techniques, it is possible to obtain thermally stable nano-structured pigments based on mixed metal oxides as CoCuMnO_x (Fawzia et al., 2013: 231 - 236) that could be used as absorber materials for heating collectors due to their high absorption and moderate low reflectance in the solar wavelength range. Similarly, cobalt and nickel oxide nano-pigments were obtained with the same technique (Fawzia et al., 2015: 347 - 357).

Additionally, $\text{CuCr}_{0.5}\text{Mn}_{1.5}\text{O}_4$ pigments were obtained through sol-gel self-combustion methods and then calcined at 700°C. These powders were subsequently used as pigment to prepare selective surfaces, achieving absorbance (α_s) values that ranged between 92 and 93% and emittance (ϵ_t) values ranging between 22 and 23% (Geng et al., 2012: 293- 301). Besides, CuCr_2O_4 spinel powder with high quality black hue was synthesized by sol-gel combustion process using citric acid as fuel and metal nitrates as oxidizers (Geng et al., 2012: 281-288).

Similarly, throughout solution combustion syntheses, it is possible to obtain Co_3O_4 absorbent pigment with the recently proposed novel fuels like aspartic acid (Asp), tris(hydroxymethyl) aminomethane (Gardey et al., 2015: 230 - 238) lysine (Lys) and ethylene diamine tetra-acetic (EDTA) acid among others (Gardey et al., 2015). These syntheses imply a low environmental impact because they are one-step processes; all use low quantities of reactive ashes obtained were always calcined at a relative low temperature of about 500°C. These processes are consistent with the following principles of Green Chemistry (Anastas and Warner, 1998): N°3 Design synthetic methods to use and generate substances that minimize toxicity to human health and the environment, N°5 minimized the use of auxiliary substances wherever possible and make them innocuous when used", N°6 minimize the energy requirements of chemical processes and conduct synthetic methods at ambient temperature and pressure if possible and N° 8 minimize or avoid unnecessary derivatization if possible, which requires additional reagents and generate waste.

By solution combustion syntheses, it is possible to obtain nanoparticles with homogenous crystalline structure by a one step, simple route. The parameters influencing combustion reactions include type of fuel, fuel to oxidizer ratio, use of an excess of oxidizer, ignition temperature and water content of the precursor mixture (Toniolo et al., 2012). The effect of fuel to oxidizer ratio in microstructure was studied in the synthesis of Co_3O_4 using urea as fuel (Venkateswara and Sunandana, 2008); the influence of

glycine and urea as fuels was studied to obtain Co_3O_4 through stoichiometric combustion syntheses and in studies for optimized combustion reaction to obtain Al_2O_3 with eight different fuels as lysine, glutamine and arginine etc (Toniolo et al., 2010).

This work is aimed at the production of Co, Cu and Mn mixed oxides by means of an original one-step stoichiometric combustion methods from $\text{Mn}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and aspartic acid (Asp), lysine (Lys) or ethylene diamine tetra-acetic acid (EDTA) as fuels. Once obtained by combustion processes, the ashes were calcined at 500°C in order to get the pigments with the desired crystalline structure. The powders were characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), infrared spectroscopy with Fourier transform (FT-IR) and Brunauer-Emmett-Teller (BET) techniques and the crystal structures refined by the Rietveld method. Then, alkyd-based enamel was prepared with the pigment obtained through Asp-based process; the so-prepared enamel was then applied on an aluminium substrate. The spectral absorbance plots of those substrates were determined for the solar spectrum range of radiation. Finally, prepared and commercial paint coatings were exposed to the sun and the temperatures measured to contrast with solar absorbance values.

MATERIALS AND METHODS

Synthesis of pigments

CoCuMnO_x powders were obtained by combustion syntheses using three different fuels; Asp, whose molecular formula is $\text{C}_4\text{H}_7\text{NO}_4$; Lys, $\text{C}_6\text{H}_{14}\text{N}_2\text{O}_2$ and EDTA, $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$.

Synthesis with aspartic acid

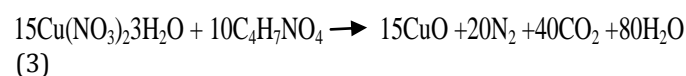
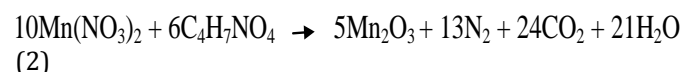
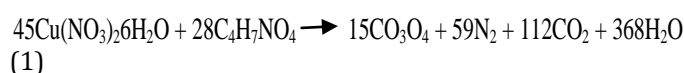
In order to obtain a precursor, three different solutions were prepared dissolving the following components in distilled water: First, 5 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich) and 1.43 g Asp ($\text{C}_4\text{H}_7\text{NO}_4$, Aldrich) getting a pH=3. Second, 5 g $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Aldrich) and 1.83 g Asp getting a pH=2. Third, 5 g of $\text{Mn}(\text{NO}_3)_2$ (10 ml) and 2.23 g of Asp, pH=3. Afterwards, all the solutions were mixed achieving the precursor needed which did not show any precipitation. The result was concentrated on a hot plate (HP) at 250°C. When the remaining liquid was reduced enough, the combustion ignited with sparks and flame. The resulting ashes were placed at 200°C in a furnace for one hour to complete the reaction. Then, the black ashes were exposed to a two-hour-calcination at 500°C in air resulting in a sample labelled as CoCuMnO_x -Asp.

The selection of quantities was carried out on the grounds of the following reactions for obtaining Co_3O_4 , Mn_2O_3 and

Table 1. Formulation of paint.

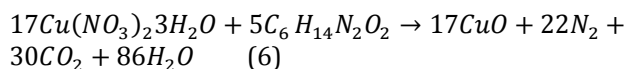
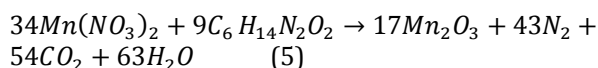
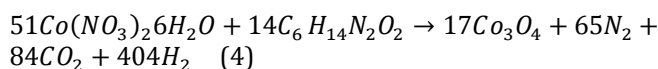
Ingredient	Percentage by weight (%)
CoCuMnO _x -Asp pigment	1
Alkyd resin	50
Ultrathin quartz	7
Aluminum powder	1
Solvent, xylene	22,5
Solvent, water	
Black ferrite	
Thickening agent	9,5
Dispersing agent	
Wetting agent	

CuO shown in reactions 1, 2 and 3 respectively.



Synthesis with lysine

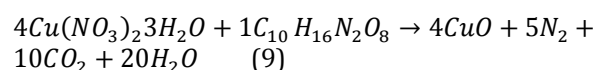
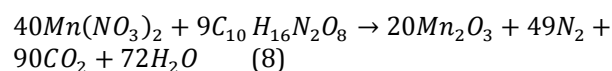
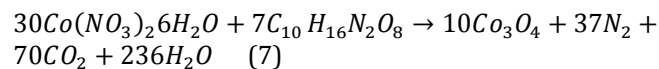
This synthesis was carried out with a similar process as in the aspartic acid, dissolving the elements in distilled water. The first solution contained 5 g of Co(NO₃)₂·6H₂O and 0.85 g of Lys getting a pH=5; for the second one, 5 g of Cu(NO₃)₂·3H₂O and 1.11 g of Lys where pH=3; for the third, 5 g de Mn(NO₃)₂ (10 ml) and 1.34 g of Lys with pH=3. Finally, the three solutions were mixed achieving a precursor which did not show any precipitation. After HP heating, when the remaining liquid was reduced enough, combustion ignited without sparks or flame. Afterwards, the process followed the same procedure as earlier described. The resulting powders after calcination was labelled CoCuMnO_x-Lys. The selection of quantities was carried out based on the reaction for obtaining Co₃O₄, Mn₂O₃ and CuO shown in reactions 4, 5 and 6 respectively.



Synthesis with EDTA

This synthesis was carried out with a similar process as in

the aspartic acid, dissolving the elements in distilled water. The first solution contained 5 g of Co(NO₃)₂·6H₂O and 1.17 g of EDTA (C₁₀H₁₆N₂O₈, Tetrahedron) ; for the second one, 5 g of Cu(NO₃)₂·3H₂O and 1.51 g of EDTA; for the third, 5 g de Mn(NO₃)₂ (10 ml) and 1.84 g of EDTA. Finally, the three solutions were mixed achieving a precursor which did not show any precipitation, getting a pH=3. After HP heating, when the remaining liquid was reduced enough, combustion ignited with sparks and flame. Afterwards, the process followed the same procedure as earlier described. The resulting powders after calcination was labelled CoCuMnO_x-EDTA. The selection of quantities was carried out based on the reaction for obtaining Co₃O₄, Mn₂O₃ and CuO shown in reactions 7, 8 and 9 respectively.



Paint coating production

Paint coatings were obtained from alkyd paints applied over aluminium alloy substrate. First, a wash-primer chromate based (Norm: SSPC-PT 3-64) was applied over the substrate to eliminate surface natural aluminium oxide. After 48 h, absorbent paint was applied with a brush. The absorbent paint was produced following the formulation listed in Table 1 for 100 g. Solid ingredients were mixed in a mortar and then solvents were added. This coating is named "absorbent paint coating".

Pigments characterization

The phases contained in the resulting powders were identified by XRD using a Pan Analytical X'PertPRO with a copper anode. Additionally, it was determined at the

Table 2. Mean temperatures calculated for each period in both coatings.

Pe	Period	Temperature (°C)					
		January		March		April	
Coating type	Hour	Commercial	Absorbent	Commercial	Absorbent	Commercial	Absorbent
	9	24.53	24.61	20.40	20.25	15.61	15.63
	10	34.15	33.85	25.04	23.59	19.84	19.13
	11	47.41	49.90	35.97	36.04	31.10	31.31
	12	58.18	60.59	43.26	44.02	39.33	39.81
	13	64.73	67.06	48.98	49.94	46.34	46.89
	14	64.53	66.96	50.85	51.88	48.80	49.63
	15	59.96	62.23	52.87	53.77	48.35	49.39
	16	57.48	59.65	50.99	51.85	46.67	47.80
	17	56.39	58.44	47.08	48.03	40.77	42.05
	18	50.52	52.32	40.43	42.09	33.54	35.19
	19	41.91	43.31	31.44	32.57	25.45	26.64
	20	33.92	34.71	27.69	28.38	21.86	22.45

average crystallite size from the width of Bragg peaks using Scherrer equation in the peak at 2θ 36° . The morphology of the powders was observed through a JEOL model 6610 LV microscope. The shape and size of the particles were observed by TEM with a JEOL 100 CX II (JAPAN, 1983) microscope using a voltage of 100 kV. FT-IR plots were obtained by a Bruker IFS 66 and textural properties by BET technique with a Micromeritics Accusorb 2100.

Paint coating characterization

The hemispherical reflectance spectra of paint coatings in the wavelength ranged between 0.32 to 2.5 μm were recorded with a UV/Vis/NIR Perkin-Elmer LAMBDA 900 double beam spectrophotometer equipped with a standard Lab sphere 150 mm integrating sphere.

Temperature measurements

A T-type thermocouple was placed underneath the absorbent paint coatings and exposed to the sun. The thermocouple was connected to a data logger HO-BO to save the information. The measurements were carried out taking data every 1 min during periods of 22 days, resulting in 32500 values approximately for each period. The periods considered were three: January, 13th to February, 5th (Period of January), March, 3rd to 27th (Period of March) and April, 1st to 24th (Period of April). Measurements were carried out in Mendoza, Argentina. With the objective to compare temperature measurements, a second coating was obtained from high-temperature aerosol black paint (Special purpose Krylon High Heat and Radiator) applied over the similar alloys substrate used in absorbent paint coating. This second

coating is named commercial coating. For each twenty-two-day period, an hourly average was calculated to obtain 24 mean hourly values. Table 2 shows these values between 9 and 20 h. Additionally, differences of temperatures between prepared and commercial coatings are shown in Table 2 for the three periods. Finally, Figure 7 shows the mean temperature evolution for a day in January.

RESULTS AND DISCUSSION

The diffraction diagrams of the obtained powders correspond to the CoCuMnO_x phase with a cubic spinel structure (Figure 1), according to the PDF card No. 47-0324. As previously reported in scientific literature, from sol-gel combustion synthesis of CoCuMnO_x using citric acid as fuel, the desired phase only appears at above 500°C mixed with other phases (Geng et al., 2011). Another segregated phase such as Mn_2O_3 appears together with CoCuMnO_x phase- in the powders obtained by sol-gel synthesis after calcination at 500°C (Kaluža et al., 2001). Additionally, by solution combustion synthesis it is possible to stabilize the homogenous crystalline phase at 500°C , whereas by sol-gel route it is stabilized at 800°C (Fawzia et al., 2013: 231 - 236). The advantage of the solution combustion synthesis presented here is, therefore, the production of mixed oxides with a pure and homogenous crystalline phase obtained at low-temperature by means of a sustainable and simple method as compared with other methods (Kaluža et al., 2001; Geng et al., 2011; Fawzia et al., 2013: 231 - 236). The Rietveld analysis allowed the refinement of the spinel structure with a model assuming that Cu occupies the tetrahedral A positions and Co and Mn are located at random at the octahedral B sites of the AB_2O_4 structure, that is, $\text{Cu}(\text{CoMn})\text{O}_4$ as shown in Figure 2, with unit-cell

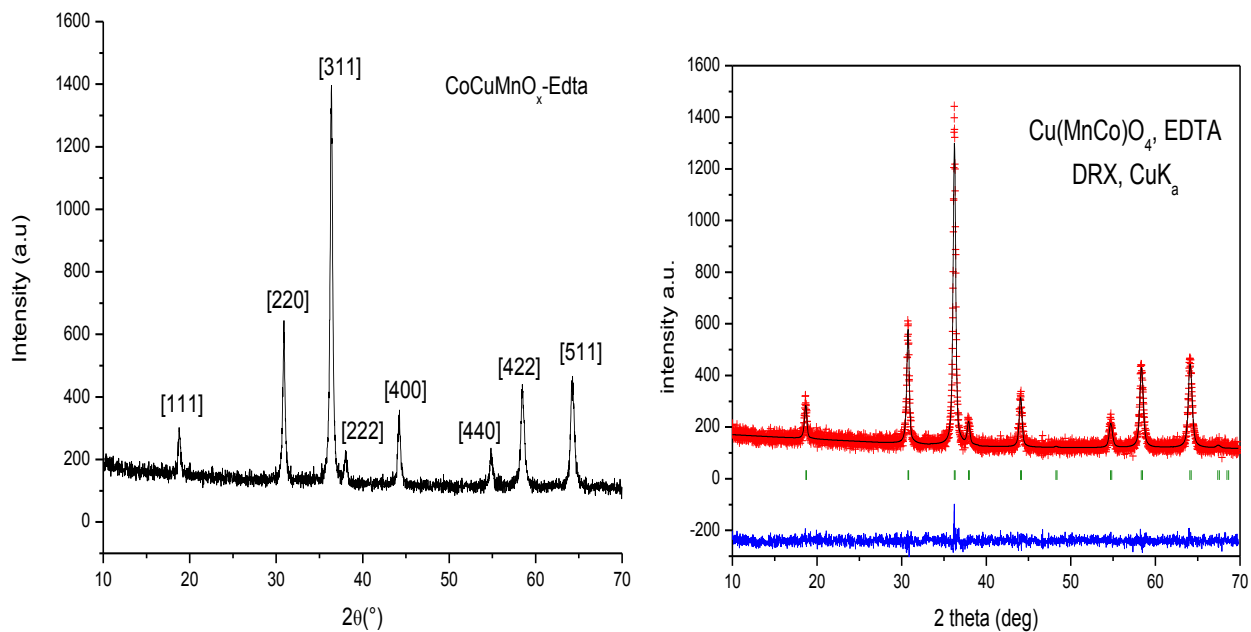


Figure 1. Diffraction diagrams and Rietveld analysis of CoCuMnO_x-EDTA sample.

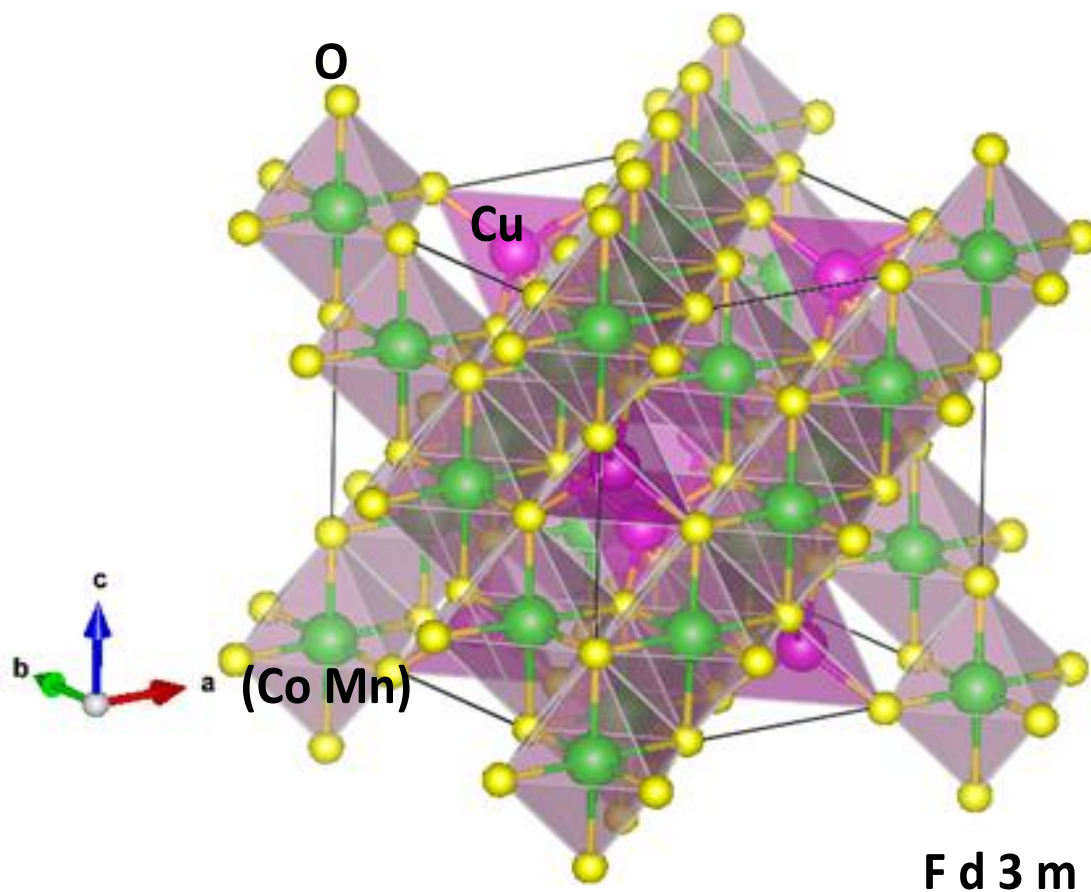


Figure 2. Cubic crystal structure observed for all obtained powders. Cu occupies the tetrahedral A positions and Co and Mn are located at random at the octahedral B sites of the AB₂O₄ spinel structure, with crystallographic formula Cu(CoMn)O₄.

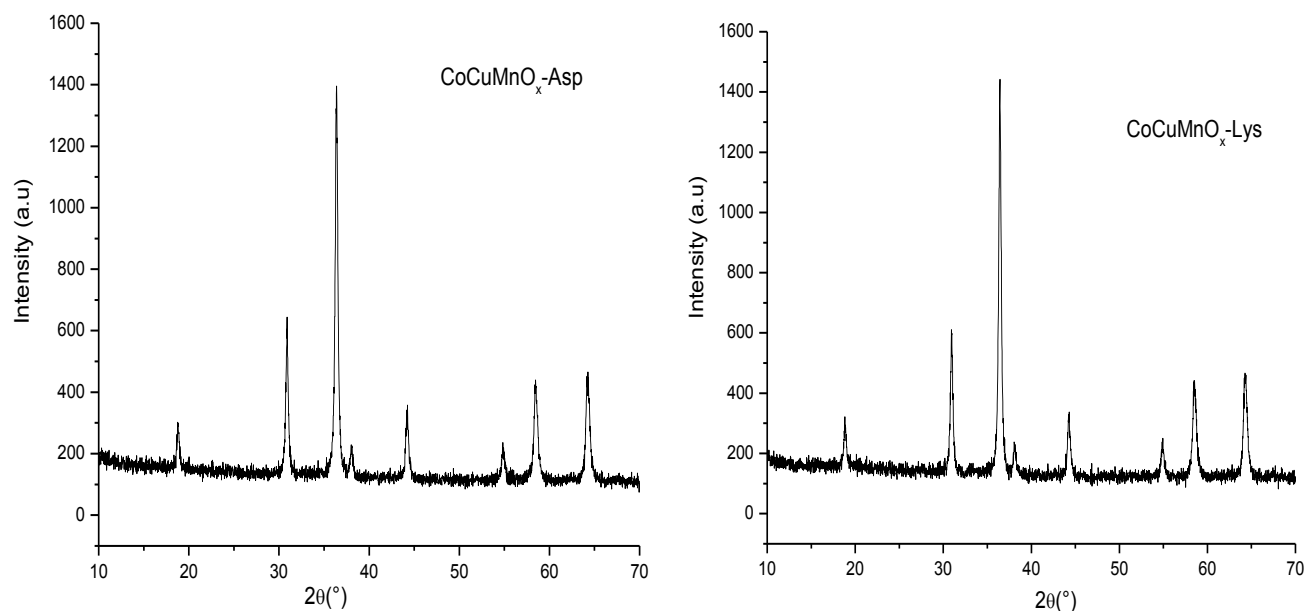


Figure 3. Diffraction diagrams of CoCuMnO_x-Asp and CoCuMnO_x-Lys samples.

Table 3. Average crystallite size and the specific surface area for all obtained powders

Ingredient	Crystalline phase	Crystallite size (nm)	Surface specific area (m ² /g)
CoCuMnO _x - Lys	Cu(CoMnO ₄)	23 ± 2	11 ± 1
CoCuMnO _x - Asp		23 ± 2	7 ± 1
CoCuMnO _x - EDTA		26 ± 3	3 ± 1

parameters in the range 8.18 to 8.21 Å, as described in literature for this composition. In Figure 1, the diffraction diagram and the Rietveld plot for CoCuMnO_x-EDTA powders showed the left and right panels, respectively, while Figure 3 showed other diffraction diagrams for Asp and Lys samples.

In Table 3, the average crystallite size and the specific surface area for all obtained powders are listed. The average crystallite size calculated by the Scherrer equation ranged between 23 and 26 nm while the specific surface areas values ranged between 3 and 11 m²/g. For these powders, the influence of fuel type on the average crystallite size and surface specific area resulted to be low. For powders obtained by sol-gel synthesis, the average crystallite sizes were smaller than or equal to 14 nm (Geng et al., 2011).

By SEM, it can be observed that all the samples exhibit a high degree of agglomeration, as displayed in the left panels of Figure 4a, c and e. In particular, in CoCuMnO_x-Lys Figure 3a, polyhedral particles can be clearly distinguished. Additionally, a high agglomeration of small nanoparticles is evidenced by comparison with the other samples, probably caused by the different characteristics of the combustion process produced in this particular,

flameless and non-sparking synthesis. Similar polyhedral shapes were observed in nanoparticles of CuCrMnO₄ powders synthesized by sol-gel routes (Geng et al., 2012: 293 - 301).

As estimated through TEM, the particle size ranges from 20 to 100 nm, (scale line = 20 nm), as shown in the right panels of Figure 4 (b, d y f), where TEM micrographs of all the obtained powders are displayed. The polyhedral shape of particles is also evidenced. In gel combustion synthesis of CuCr₂O₄ powders calcined at 500°C reported a similar average particle size of 80 nm (Geng et al., 2012: 281-288). Additionally, these authors studied the influence of calcination temperature on optical properties of the pigments (Geng et al., 2012: 293 - 301).

Figure 5 shows FT-IR spectra for the three selected powders. According to the literature, the bands of the spinel oxide type in FT-IR plots was found in a region comprised between 400 and 700 cm⁻¹ corresponding to the vibration produced by metals and oxygen bonds. The bands around 500 cm⁻¹ were assigned to the vibration of the metallic atom in the tetrahedral environment of oxygen atoms (A-O) and the band around 600 cm⁻¹ corresponds to a vibration of B atom in the octahedral sites (Oh) of the spinel structure (Hosseini et al., 2013). In

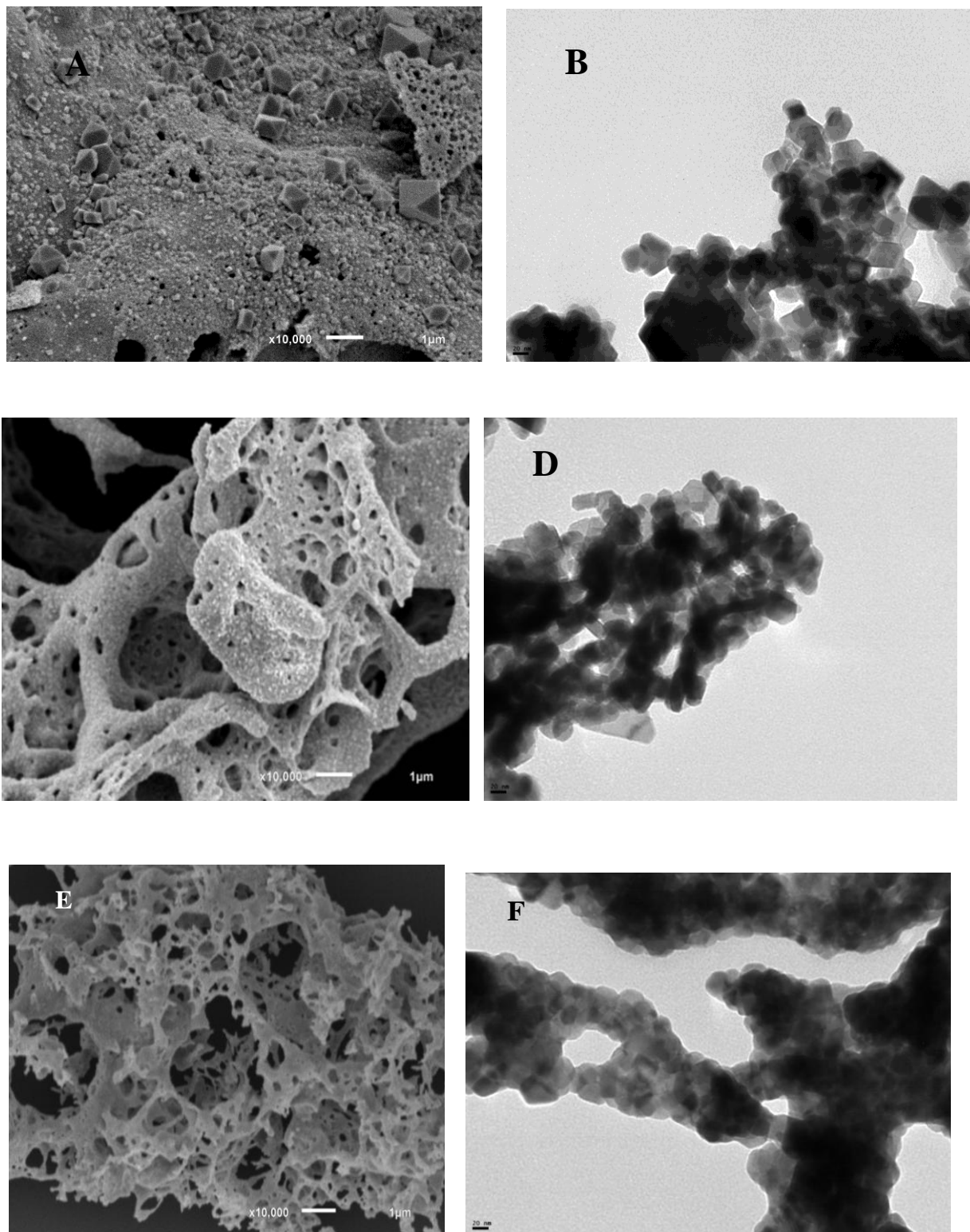


Figure 4. SEM and TEM micrographs of: a) and b) CoCuMnO_x- Lys; c) and d) CoCuMnO_x- EDTA; e) and f) CoCuMnO_x- Asp.

Figure 5, a first band at 568 cm⁻¹ and a second one between 630 and 660 cm⁻¹ were evidenced in all cases. The first band is associated to Cu cations located at the tetrahedral positions according to the Rietveld analysis,

whilst the second one corresponds to the octahedral cations Co and Mn. In particular for Asp powders, the second band presents a lower intensity. Similar bands around 502 and 601 cm⁻¹ are observed for calcined

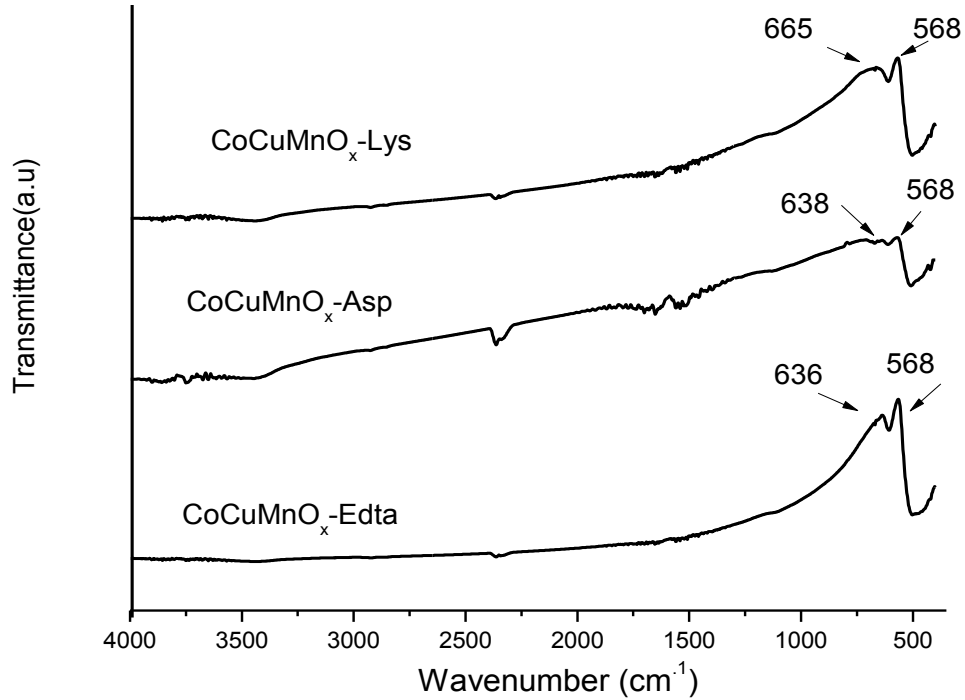


Figure 5. FT-IR spectra a) CoCuMnO_x- Lys b) CoCuMnO_x- Asp c) CoCuMnO_x- EDTA.

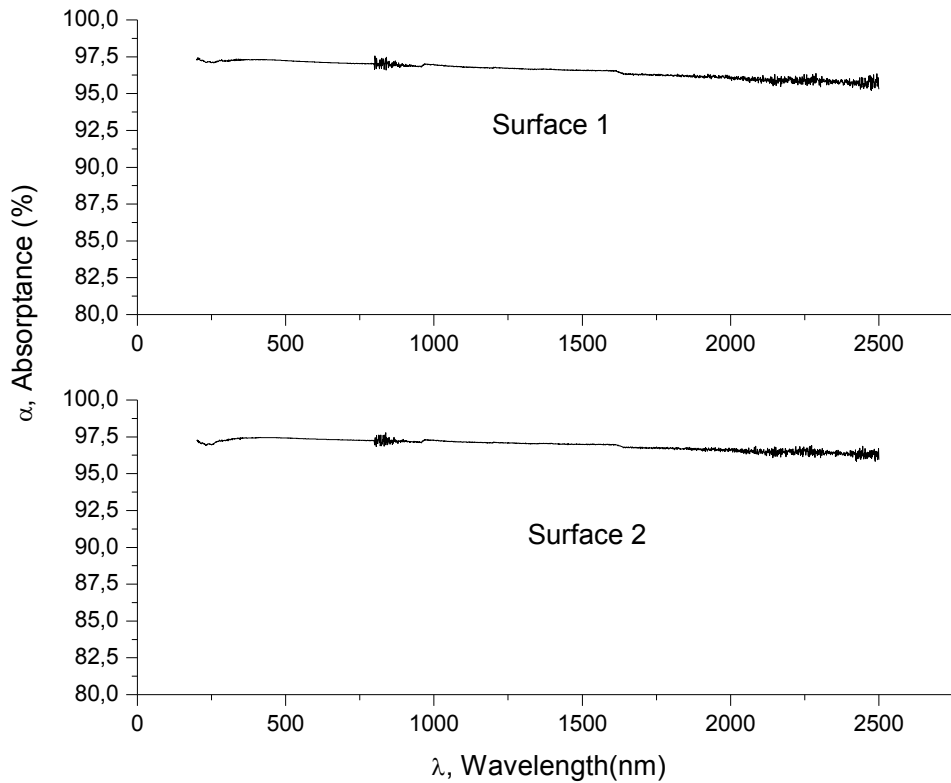


Figure 6. Solar Absorbance- Average value 97%.

powders at 500, 700 and 900°C of CuCrMnO₄ obtained by sol-gel combustion where Mn and Cr are found in octahedral positions (Geng et al., 2012: 293 - 301).

Figure 6 shows the spectral absorbance for painted surfaces. Solar absorption values are above 95% and the average value is 97%. This absorption value is higher than

Table 4. Temperature difference between prepared and commercial coatings for each studied period.

Hour	ΔT ($^{\circ}\text{C}$)		
	January	March	April
9	0.08	-0.15	0.02
10	-0.30	-1.45	-0.71
11	2.49	0.08	0.21
12	2.41	0.76	0.48
13	2.33	0.97	0.54
14	2.43	1.03	0.83
15	2.28	0.90	1.03
16	2.17	0.86	1.13
17	2.06	0.96	1.28
18	1.81	1.67	1.65
19	1.40	1.12	1.19
20	0.79	0.68	0.59

the one observed in other selective surfaces, for example, selective surfaces with CuCuMnO_x or $\text{CuCr}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as pigment only achieved 93% of the solar absorption (Geng et al., 2011; Geng et al., 2012: 293 -301). These absorption ranges suggest the possibility of utilizing the so-prepared combustion synthesized oxides as active pigments in absorbent solar enamels. Geng et al. (2011, (2012: 293 -301) focused on achieving a material with a solar absorption near to the 100% while keeping a low infrared emittance, that is, with a higher optical selectivity. This work is aimed to improve only solar absorption, for which high values have been achieved. Further researches will be intended to reduce infrared emittance.

As a further test of the performance of the pigments in real working conditions, we aimed to corroborate the high solar absorbance values. Table 2 illustrates the results obtained in temperature measurements in coated aluminum solar radiation collectors. Our pigments are compared with a commercial coating. As the same substrates are utilized in this test, the differences observed are directly related to the solar absorbance of the different coatings.

Table 4 shows a higher temperature value for the prepared coating than for the commercial one in a time span of 11 to 20 h. The major difference between the two coatings was 2.43°C at 14 h in January, while for March and April were 1.67 and 1.65°C respectively. Regarding the maximum temperature reached by the collector, the highest value of 67°C was observed in January for our absorbent paint coating, while for commercial coating it is 54°C and 50°C in March and April. The significant temperature increase observed for our coatings must be attributed to the presence of spinel-type CoCuMnO_4 mixed oxide, a pigment used in absorbent paint coating which presents a higher level of solar absorption than commercial coatings. Another cause for the observed improvement could be the width of the painted coating, which is thicker than the commercial one.

In solar collector, it can be observed at a variation of 5°C in two different situations: a) coated with a paint

containing Al and Ni metallic alloys and b) coated with the same paint without any addition (Al-Shamaileh, 2010).

Figure 7 displays a graphic of the mean temperatures in January for both coatings. The graphic makes evident that the temperature of our prepared coatings is significantly higher than the commercial one in a time span of 11 to 20 h. The results showed the possibility of using these pigments as solar absorbent paints.

Conclusions

The synthesis of nanoparticles of CuCoMnO_4 was performed by means of a one-step solution combustion method, using novel fuels such as Asp, EDTA or Lys. No segregated phases were observed. Previously, the nanoparticles were calcined at 500°C. These CuCoMnO_4 nanoparticles were incorporated as pigments in alkyd-resin enamels, utilized to coat aluminum solar radiation collectors. A noticeable coating absorption value ranging around 95 and 97% was evidenced. Additionally, comparative tests with commercial coatings resulted in significantly higher temperature values; these measurements were carried out both coatings exposed at the sun in three different periods. These results suggest the possibility of advantageously utilizing these nanostructured oxides as active pigments in absorbent solar enamels.

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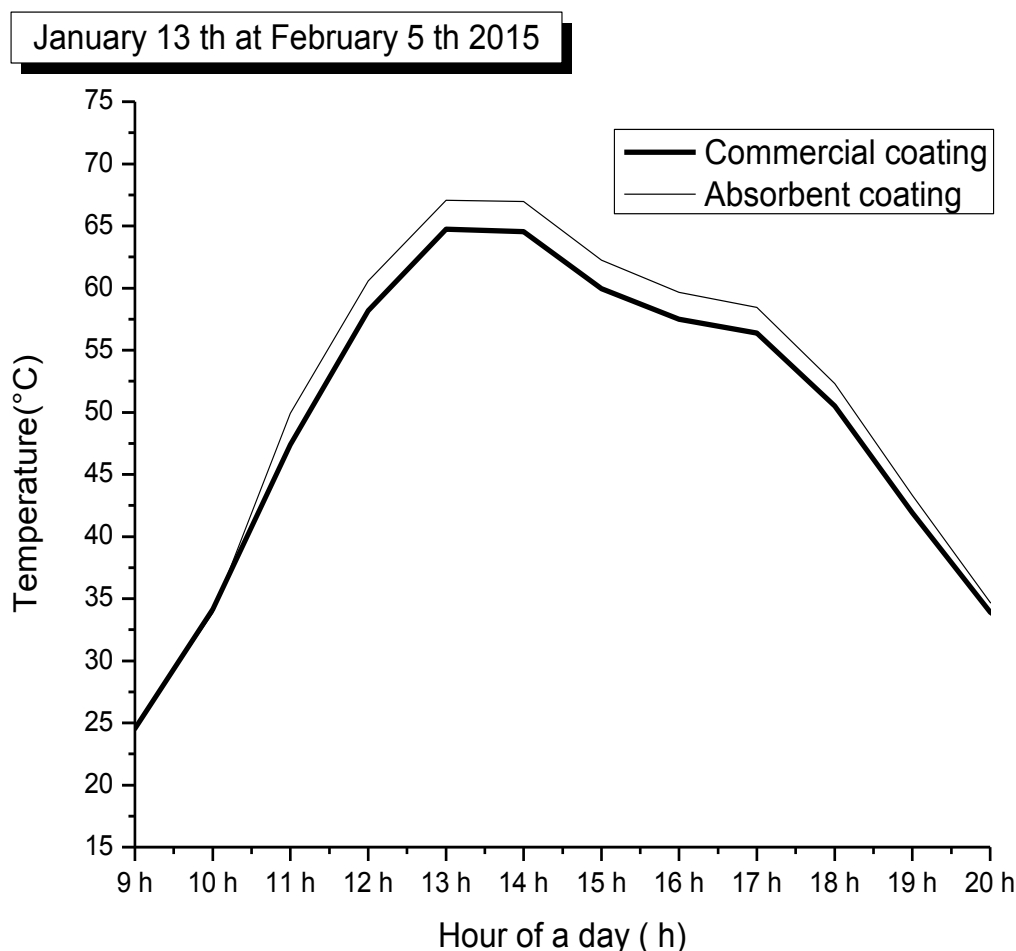


Figure 7. Temperature evolution of the solar collectors during the January period.

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REFERENCES

- Al-Khaffaj M, Mossad R (2013). Optimization of the heat exchanger in a flat plate indirect heating integrated collector storage solar water heating system. *Renew. Energy*. 57: 413-421.
- Al-Shamaileh E (2010). Testing of a new solar coating for solar water heating applications. *Solar Energy*. 84: 1637-1643.
- Anastas PT, Warner JC (1998). *Green Chemistry: theory and practice*, Ed. S. Publications. Oxford University Press, New York, U.S.A.
- Fawzia F, Abdel-Mohsen H, Salah AE (2013). Thermally stable pigments based on mixed metal oxides. *Pigm. Resin Technol.* 42(4): 231-236.
- Fawzia F, Abdel-Mohsen H, Salah AE (2015). Spectrally selective nano-absorber pigments. *Pigm. Resin Technol.* 44(6): 347-357.
- Gardey MC, Fernández de Rapp ME, Pinto M, Etchechoury ME, Lassa MS, Martínez JM, Lascalea GE, Vázquez PG (2015). Combustion synthesis of ultrafine powders of Co_3O_4 for selective surfaces of solar collectors. *Proc. Mater. Sci.* 9: 230-238.
- Gardey MC, Tornello NLD, Montoya WM, Urrutia AJN, Fernandez de Rapp M, Lascalea GE, Vázquez PG (2015). Combustion Syntheses of Co_3O_4 Powders Using Different Fuels. *Proc. Mater. Sci.* 8: 526-534.
- Geng Q, Zhao X, Gao XH, Liu G (2011). Sol-Gel Combustion-Derived CoCuMnO_x Spinels as Pigment for Spectrally Selective Paints. *J. Am. Ceram. Soc.* 94(3): 827-832.
- Geng Q, Zhao X, Gao X, Yang S, Gang L (2012). Low-temperature combustion synthesis of CuCr_2O_4 spinel powder for spectrally selective paints. *J. Sol-Gel Sci. Technol.* 61 (11): 281-288.
- Geng Q, Zhao X, Gao X, Yu H, Yang S, Liu G (2012). Optimization design of $\text{CuCr}_x\text{Mn}_{2-x}\text{O}_4$ based paint coatings used for solar selective applications. *Solar Energy Mater. Solar Cell.* 105: 293-301.
- Hosseini SA, Alvarez-Galvan MC, Fierro JLG, Niaei A, Salari D (2013). MCr_2O_4 (M = Co, Cu, and Zn) nanospinels for 2-propanol combustion: Correlation of structural properties with catalytic performance and stability. *Ceram. Int.* 39: 9253.
- Jebli MB, Youssef SB (2015). Output, renewable and non-renewable energy consumption and international trade: Evidence from a panel of 69 countries. *Renew. Energy*. 83: 799-808.
- Kaluža L, Orel B, Dražič G, Kohl M (2001). Sol-gel derived CuCoMnO_x spinel coatings for solar absorbers: Structural and optical properties. *Solar Energy Mater. Solar Cell.* 70: 187-201.
- Norouzbeigi R, Edrissi M (2011). Modification and optimization of nano-crystalline Al_2O_3 combustion synthesis using Taguchi L16 array. *Mater. Res. Bull.* 46: 1615-1624.
- Pal S, D. Diso, S. Franza, A. Licciulli, L. Rizzo (2013). Spectrally selective absorber coating from transition metal complex for efficient photothermal conversion. *J. Mater. Sci.* 48: 8268-8276.
- Toniolo J, Lima MD, Takimi AS, Bergmann CP (2012). Synthesis of alumina powders by the glycine-nitrate combustion process. *Mater. Res. Bull.* 40: 561-571.
- Toniolo J, Takimi A, Bergmann C (2010). Nanostructured cobalt oxides

- (Co_3O_4 and CoO) and metallic Co powders synthesized by the solution combustion method. *Mater. Res. Bull.* 45: 672–676.
- Trease CH, Hadavinia H, Barrington PE (2013). Solar Selective Coatings: Industrial State-of-the-Art. *Recent Patents on Materials Sci.* 6: 1-19.
- Venkateswara RK, Sunandana C (2008). Co_3O_4 nanoparticles by chemical combustion: Effect of fuel to oxidizer ratio on structure, microstructure and EPR. *Solid State Commun.* 148: 32–37.
- Vince J, ŠurcaVuk A, OparaKrašovec U, Orel B, Köhl M, Heck M (2003). Absorber coatings based on CoCuMnO_x spinels prepared via the sol-gel process: structural and optical properties, *Solar Energy Mater. Solar Cell.* 79: 313-330.

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