

## Optimization design of $\text{CuCr}_x\text{Mn}_{2-x}\text{O}_4$ -based paint coatings used for solar selective applications

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### ARTICLE INFO

#### Article history:

Received 17 December 2011

Received in revised form

25 May 2012

Accepted 19 June 2012

Available online 15 July 2012

#### Keywords:

$\text{CuCr}_x\text{Mn}_{2-x}\text{O}_4$

Sol–gel self-combustion

TSSS paint coatings

Optimization design

Spectral selectivity

Durability

### ABSTRACT

$\text{CuCr}_x\text{Mn}_{2-x}\text{O}_4$  ( $x=0.5, 1$ ) spinels, novel pigments for spectrally selective paints, have been prepared through a sol–gel combustion synthesis process. Thickness Sensitive Spectrally Selective (TSSS) paint coatings, using  $\text{CuCr}_x\text{Mn}_{2-x}\text{O}_4$  ( $x=0.5, 1$ ) obtained at varied calcined temperatures (500–1100 °C) as pigment, were deposited on top of aluminum substrates by a cost-effective spray coating method and characterized by reflectance measurements over the spectral range of 0.3–20  $\mu\text{m}$ . Influence of pigment species and coating thickness on optical properties of paint coatings was investigated. Results suggest that  $\text{CuCr}_{0.5}\text{Mn}_{1.5}\text{O}_4$ -based coatings are more favorable than  $\text{CuCrMnO}_4$ -based ones and coatings using 700 °C calcined  $\text{CuCr}_{0.5}\text{Mn}_{1.5}\text{O}_4$  as pigment exhibit the optimum spectral selectivity ( $\alpha_s=0.92\sim 0.93$ ,  $\varepsilon_T=0.22\sim 0.31$ ). Difference in powder thermal emittances reveals that suitable pigments can be pre-chosen before fabricating paint coatings to obtain optimum spectral selectivity. Long-term stability tests of the TSSS paint coatings were performed according to the methodology worked out within IEA-SHC Task X and the results confirmed that coatings in this study could be safely used during collector's lifetime without degradation in performance.

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### 1. Introduction

The efficiency in solar-thermal energy conversion system strongly depends on the materials used as absorber coatings, especially on their optical properties and thermal stability. In previous papers, we reported on the preparation and characterization of TSSS paint coatings based on transition metal oxides,  $\text{CoCuMnO}_x$  [1] and  $\text{CuCr}_2\text{O}_4$  [2], with spinel structure. Results obtained revealed that paint coatings using spinel  $\text{CoCuMnO}_x$  powder as pigment showed better spectral selectivity than ones based on  $\text{CuCr}_2\text{O}_4$  pigment. However, mass production of TSSS paint coatings based on  $\text{CoCuMnO}_x$  is not cost-effective enough due to the relatively high price of the cobalt nitrate precursor. To overcome this problem we substitute Co with Cr expecting to decrease the production cost of the paint coatings and do not sacrifice their optical properties at the same time. Among the Cu–Cr–Mn oxides,  $\text{CuCrMnO}_4$  and  $\text{CuCr}_{0.5}\text{Mn}_{1.5}\text{O}_4$  have spinel structure, so formula  $\text{CuCr}_x\text{Mn}_{2-x}\text{O}_4$  ( $x=0.5, 1$ ) is introduced to denote both of them in context.

As a conventional method to prepare  $\text{CuCr}_x\text{Mn}_{2-x}\text{O}_4$  spinel pigment, solid-state reaction based on oxides of metal components

has been used, with thermal treatment at 750 °C for a long period of time (about 300 h) [3]. The disadvantages of this process lie in the appearance of unwanted phases, high energy consumption, and also the poor reproducibility. The second industrially used method for spinel pigment preparation is coprecipitation from aqueous solution of raw materials [4,5]. The main advantage is that the size and shape of pigments can be controlled easily by the reaction conditions. However, it is difficult to control all the metal cations to precipitate from the solution at the same time, which results in composition segregation, low yield, and environmental contamination. There are a variety of possibilities of laboratory spinel pigment preparation proposed in literature including Pechini method (polymer precursor method) [6,7], sol–gel process and others [8,9]. Among these synthetic strategies, sol–gel self-combustion stands out as it represents an environmental friendly route with advantages like:

- cost-effective (inexpensive precursors and low power consumption);
- minimization of synthesis steps (one or two step procedure);
- reactions with little non toxic byproducts (gas like nitrogen, oxygen, and water);
- high yield (the conversion of metal atoms to product reaches nearly 100%);
- efficiency of scale-up (it does not require specialized equipment).

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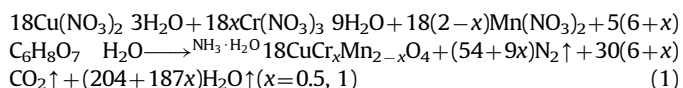
In the present work, we report the synthesis of  $\text{CuCr}_x\text{Mn}_{2-x}\text{O}_4$  ( $x=0.5, 1$ ) spinel by a nitrate–citrate sol–gel self-combustion process. Literature data showed that many ceramic pigments were obtained directly by the sol–gel self-combustion route [10,11]. However, a calcining step, following the sol–gel self-combustion process, was indispensable for some other ceramic pigments [12,13]. Thus, in this contribution the as-burnt powders are calcined at a wide range of elevated temperatures and subsequently the XRD patterns and optical properties of the obtained powders are analyzed.

TSSS paint coatings based on  $\text{CuCr}_x\text{Mn}_{2-x}\text{O}_4$  ( $x=0.5, 1$ ) pigments are prepared by a simple spray coating technique.  $\text{CuCr}_x\text{Mn}_{2-x}\text{O}_4$  ( $x=0.5, 1$ ) powders present different optical properties when calcined at varied elevated temperatures and the effect of the difference on the spectral selectivity of paint coatings are discussed in detail. Thus, the composition and calcining temperature of the pigment are optimized to obtain coatings with the highest spectral selectivity. Apart from low price and good optical property, the other sales argument for solar absorber coatings concerns their long term stability during the serve time. Durability tests established by the IEA-SHC Task X for low temperature absorbers are therefore carried out to see whether paint coatings fabricated here have excellent stability during collectors' lifetime.

## 2. Experimental

### 2.1. Preparation of $\text{CuCr}_x\text{Mn}_{2-x}\text{O}_4$

$\text{CuCrMnO}_4$  and  $\text{CuCr}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders were synthesized by sol–gel self-combustion technique. The analytical grade  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_2$  (50%), polyethylene glycol 200 (PEG 200),  $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ , and ammonia (25%) were used as raw materials. The ideal reaction between citric acid and metal nitrates for  $\text{CuCr}_x\text{Mn}_{2-x}\text{O}_4$  synthesis is presented as the following equation:



Metal nitrates were firstly dissolved in a minimum amount of deionized water with the Cu/Cr/Mn molar ratio of 1:1:1 and 1:0.5:1.5 for  $\text{CuCrMnO}_4$  and  $\text{CuCr}_{0.5}\text{Mn}_{1.5}\text{O}_4$ , respectively. An appropriate amount of citric acid was then added into the prepared aqueous solutions to chelate  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Mn}^{2+}$ . The pH of the mixed solution was neutralized to 7.0 by adding liquor ammonia, obtaining a transparent solution. Then the solution was heated at 70 °C with continuous stirring for dehydration till the solution turned into high-viscous gel. The gel was then kept at 135 °C for a sufficient period of time to ensure the formation of Cu–Cr–Mn–citric xerogel. The xerogel was subsequently ignited in air using a few drops of absolute ethanol as initiating agent and burnt in a self-propagating combustion manner until it was completely burnt out to form a loose product. Finally, the as-burnt powders were calcined at 500–1100 °C for 2 h with a heating rate of 5 °C min<sup>-1</sup> to obtain spinel  $\text{CuCr}_x\text{Mn}_{2-x}\text{O}_4$  ( $x=0.5, 1$ ).

### 2.2. Fabrication of the paint coatings

The aluminum sheets with a purity of 99.5% and dimensions of 60 mm × 60 mm × 0.5 mm were decontaminated by ultrasonic treatment in acetone during 30 min and exhibited a mean solar reflectance ( $r_s$ ) of 0.821 and a thermal emittance ( $\varepsilon_T$ ) of 0.039.

TSSS paints were prepared using a standard procedure [14,15]. Pigment dispersions were prepared by mixing the  $\text{CuCr}_x\text{Mn}_{2-x}\text{O}_4$  powders with the commercially available polyurethane modified by epoxy resin and solvent in specific proportions and then grinding in a ball mill. The concentration (i.e. partial pigment-to-volume concentration ratio, PVC) of the pigment in dispersion was kept the same as that reported previously [1]. Suitable amount of curing agent was then added to the mixture to form paint. Ten minutes later, the paint was sprayed onto the prepared aluminum sheets by means of a K-3 spray gun with an operating pressure of 0.3 MPa. The thickness of coatings varies with the spraying time. All the coatings were cured at room temperature as the binder used is ambient curable.

### 2.3. Instrumental

The phase identification of the as-synthesized powders was performed using Rigaku D/max 2400/PC X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda=1.5406$  Å). TG-DTA was carried out in a NETSCH STA 449 C simultaneous thermal analyzer at a heating rate of 10 °C min<sup>-1</sup>. Air at 20 ml min<sup>-1</sup> was used as purge gas. Infrared spectra are recorded on a Bruker TENSOR 27 FT-IR spectrometer with a resolution of 4 cm<sup>-1</sup> and 32 scans for each sample. For measuring the IR spectra the powder was finely triturated with KBr and pressed into pellets. The morphological characterization was performed by JSM 6701F field emission scanning electron microscope (FE-SEM).

The average thickness of the coatings was measured by QuaNix 4500 coating thickness gauge. For the condensation test a Q8UV3 accelerated weathering chamber was used. In order to evaluate the quality of the paint coatings as spectrally selective absorbers the optical properties were studied. Reflectance spectra of the spectrally selective paint coatings were measured in the wavelength interval 0.3–20  $\mu\text{m}$ . A Perkin-Elmer Lambda 950 UV/Vis/NIR spectrophotometer equipped with an integrating sphere of diameter 150 mm was used to record reflectance spectra in the wavelength interval 0.3–2.5  $\mu\text{m}$ . The infrared wavelength interval, 2.5–20  $\mu\text{m}$ , was covered with a Bruker TENSOR 27 FT-IR spectrometer equipped with a gold-coated integrating sphere (A562-G/Q). The measurements were combined to create one spectrum and the solar absorptance ( $\alpha_s$ ) and thermal emittance values ( $\varepsilon_T$ ) were determined from the reflectance spectra using a standard procedure [16], as reported previously [1,2]. Thermal emittance values of samples in this study were obtained at 373 K.

## 3. Results and discussion

### 3.1. Characterizations of pigments

#### 3.1.1. TG-DTA measurements of the xerogels

The experiment showed that the nitrate–citrate xerogel precursors for  $\text{CuCr}_x\text{Mn}_{2-x}\text{O}_4$  ( $x=0.5, 1$ ) exhibited a self-propagating combustion behavior. Fig.1 gives the TG-DTA curves of the xerogels leading to  $\text{CuCrMnO}_4$  (Fig. 1a) and  $\text{CuCr}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (Fig. 1b), respectively. It can be found that for both powders, there are similar weight loss and exothermic behaviors. The DTA plots present one exothermic peak at about 225 °C, which could be due to the reaction of nitrates and citric acid. During this reaction, large amounts of gases such as  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{N}_2$  are liberated, resulting in a noticeable weight loss in TG plot. After the combustion process, there is still a small weight loss in TG curves which can be attributed to the decomposition of residual PEG 200. It can be seen that when the powders are heated at 400 °C or above, there is no further weight loss, suggesting that the organic groups are burnt off and purely inorganic materials forms.

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