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Sol–gel and sonochemically derived transition metal (Co, Ni, Cu, and Zn) chromites as pigments: A comparative study

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ABSTRACT

Cobalt chromite based pigments $Co_{1-x}M_xCr_2O_4$ (M=Ni, Cu, and Zn) with different transition metal concentrations ($0 \le x \le 1$ with a step of 0.25) have been synthesized applying two aqueous synthesis approaches: sol–gel and sonochemical synthesis routes. The heat treatment of precursor powders was performed between 600 and 800 °C. XRD analysis of the obtained powders revealed that all samples fabricated by sol–gel method have crystallised in a spinel structure, whereas sonochemical synthesis of Ni chromite at lower calcination temperatures showed the formation of mixtures of oxides. In addition, the degree of crystallinity and shaping of sonochemically obtained compounds is lower than sol–gel derived products. The chromites with a higher nickel concentration displayed green colour, while Cu-substituted pigments were nearly black. The spinels with a higher Zn amount were yellowish green.

1. Introduction

Different metal oxides and mixed-metal oxides are employed as ceramic pigments. For various applications pigments have specific requirements such as chemical and thermal stability, particle size, hiding and tinting power, etc. Mixed-metal oxides, displaying general spinel formula AB_2O_4, are characteristic for their high mechanical resistance, high thermal and chemical stability [1,2]. There are two types of spinel structure: the first one known as normal spinel is characterised by cations A^{2+} occupying tetrahedral positions and cations B^{3+} occupying octahedral sites. The second possible structure is inverse spinel, in which cations A^{2+} fill one half of the octahedral sites and cations B^{3+} take up the other half of the octahedral positions and all tetrahedral coordination sites [3]. The formation of inverse spinel can be influenced by synthesis temperature and pressure [4]. Owing to easy incorporation of various metal ions into the spinel lattice, the properties of spinel type materials are remarkable, which lead to wide applications as magnetic compounds [5–7], catalysts and sensors for toxic gases [8–15], refractories, materials for information storage [6,16,17], pigments [1,2,18–24], and many others.

As it was mentioned before, spinel structure is very attractive in pigmentary field. The nature of tetrahedral or octahedral cations and potential of different types of doping give diversity in colours and properties. For example, thermal and chemical stability is necessary for ceramic pigments to obtain high quality glazes [24], $CuCr_2O_4$ is effective for solar-absorbing paints [21] and, conversely, cobalt chromite doped by zinc and aluminium is impressive due to high solar reflectance and could be used for cool coatings of the buildings [23]. Spinels as pigments can be produced by conventional solid-state reactions [18,25], combustion or sol–gel combustion method [6,10,13,16,19–21,26], coprecipitation [7,12,27,28], hydrothermal synthesis [9,15,17,22,29,30], thermolysis of organic precursors [31,32], air plasma spray-drying technique [33], microemulsion [14], polymer precursor method [1,34], sonochemical synthesis [35–37] and sol–gel [11,23,38–40] method.

The latter two procedures are effective for preparing materials of high purity in nanoscale size and good control of stoichiometry and chemical homogeneity. In addition, by controlling sonication output power, time, temperature, and other parameters in sonochemical synthesis one can easily achieve different shapes of the product [36]. On the other hand, sol–gel method requires much lower temperatures and shorter calcination times to obtain the desired product, comparing to conventional solid-state method [40,41]. In the present work, the comparison between these two synthesis methods was accomplished by producing cobalt chromite based pigments $Co_{1-x}M_xCr_2O_4$ (M=Ni, Cu, and Zn) with different transition metal concentrations, where $0 \le x \le 1$ with a step of 0.25. The phase composition, crystallite size, morphological features, and colour parameters of new spinel compositions were investigated in this study.

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2. Experimental section

2.1. Chemicals and instruments

All reagents were of analytical purity and used as received from commercial sources without further purification. Two types of syntheses were used to prepare $Co_{1-x}M_xCr_2O_4$ compounds (M=Ni, Cu, and Zn; x=0; 0.25; 0.5; 0.75; and 1). Aqueous sol–gel synthesis [38] was carried out using $Cr(NO_3)_3 \cdot 9H_2O$ (Sigma-Aldrich), $Co(NO_3)_2 \cdot 6H_2O$ (Alfa Aesar), $Cu(CH_3COO)_2 \cdot H_2O$ (Sigma-Aldrich), $Ni(CH_3COO)_2 \cdot 4H_2O$ (Sigma-Aldrich), $Zn(CH_3COO)_2 \cdot 2H_2O$ (Roth) and 1,2-ethanediol $C_2H_6O_2$ (Sigma-Aldrich) as precursors for gels. For aqueous sonochemical synthesis [35] $Cr(NO_3)_3 \cdot 9H_2O$ (Pliva-Lachema), $Co(NO_3)_2 \cdot 6H_2O$ (Lach-Ner), $Cu(CH_3COO)_2 \cdot H_2O$ (Riedel-de Haen AG), $Ni(NO_3)_2 \cdot 6H_2O$ (Pliva-Lachema), $Zn(CH_3COO)_2 \cdot 2H_2O$ (Pliva-Lachema), ammonia solution (26%, Mikrochem), and acetone C_3H_6O (Mikrochem) were used.

Powder X-ray diffraction (XRD) was used to characterize the phase purity of the obtained samples. The measurements were performed using a Rigaku MiniFlex II diffractometer, operated at 30 kV and 10 mA with a scanning speed of 10°/min, in a scanning range of 2θ=10–80°, using Cu Kα radiation (λ=1.540562 Å). The tentative crystallite sizes were determined by the Scherrer equation:

$$\tau = \frac{0.9\lambda}{B\cos\theta}$$

where τ is the mean crystallite size, λ is the X-ray wavelength, B is the line broadening at half maximum intensity (FWHM) (in radians) and θ is the Bragg angle. UV–vis diffuse reflectance spectra were determined on an Agilent Technologies Cary 5000 spectrophotometer from 200 to 800 nm, using a $BaCO_3$ pellet as white reference. The colour of the pigments was evaluated by the CIELab colourimetric method, which is recommended by the Commission Internationale de l'Eclairage. The L^*, a^*, and b^* parameters were measured on a Perkin Elmer Lambda 950 spectrophotometer in the 780–380 nm range, employing an illuminant D65, which is similar to daylight, and a 10° standard observer. In the CIELab system, the coordinate L^* represents the colour lightness (L^*=0 is for black and L^*=100 is for white), the coordinate a^* corresponds to green/red hue, where negative values are for green and positive for red. The negative/positive values of parameter b^* represent blue/yellow hue, respectively. The morphological features of obtained samples were investigated using a scanning electron microscope Hitachi SU70. Sonication was performed using a Sonics and Materials VCX130 reactor with a titanium 13 mm diameter horn operating at 20 kHz at a power of 20 W/cm^2.

2.2. Aqueous sol–gel synthesis method

For the synthesis of Co–Cr–O precursor gel, stoichiometric amounts of $Co(NO_3)_2 \cdot 6H_2O$ (4.405 mmol, 1.282 g) and $Cr(NO_3)_3 \cdot 9H_2O$ (8.814 mmol, 3.527 g) were dissolved in deionized water and mixed together. The mixed-metal mixtures were prepared analogously but with the respective amount of the appropriate metal salts. After stirring the solutions at 40–50 °C for 20 min, 1,2-ethanediol (2 mL) was added with continuous stirring at the same temperature for 1 h. The solutions were concentrated by continuous stirring and evaporation at 60–70 °C. Prepared gels were dried in a furnace at 105 °C in air. Dried gels were ground in an agate mortar and calcined at 600, 700, and 800 °C in air for 3 h with a heating rate of 10 °C/min.

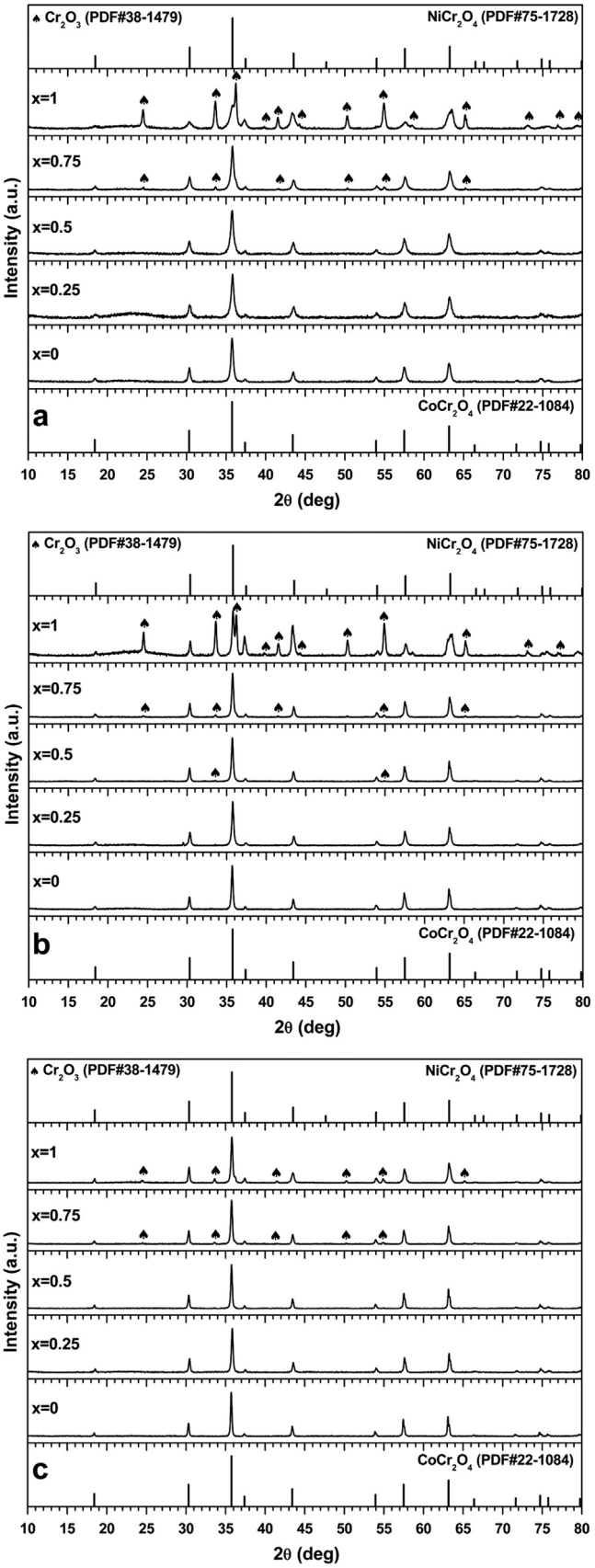

Fig. 1. Powder XRD patterns of sol–gel derived $Co_{1-x}Ni_xCr_2O_4$ (x=0; 0.25; 0.5; 0.75 and 1) samples heated at 600 °C (a), 700 °C (b), and 800 °C (c).