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Synthesis and characterization of Mn-doped copper chromite black pigments

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Abstract. Mn-doped black pigments $CuMn_xCr_{2-x}O_4$(x=0, 0.05, 0.10, 0.15, 0.20 and 0.25) were synthesized by precursor coprecipitation method, and characterized by TG-DTA, XRD, FTIR and colorimetric analysis. The TG-DTA curves showed the crystal transition temperature was at about 800°C and mass loss ended at about 450°C. The infrared spectra displayed vibrations of spinel phase. XRD patterns displayed the characteristic peaks of the tetragonal phase spinel structure and proved that Mn substituted Cr in the spinel crystal lattice. $L^*a^*b^*$ analysis showed that all samples are black pigments with blue intensity, and Mn-doping could strengthen the black intensity and weaken the blue intensity of such black pigments.

Introduction

Spinel-type composite metal oxides have excellent properties and are used in numerous areas, including magnetic materials, ceramics, catalysis, batteries and pigments[1-3].In the last decade, copper chromite spinel oxides have been studied on its catalytic properties and applications in chemical reactions, such as hydrogenation, dehydrogenation, oxidation, alkylation, propellant combustion, decomposition of organic compounds, etc.[4-10] Copper chromite is also a kind of black pigment, but there are less studies shown on this filed. In practice, copper chromite is a kind of composite inorganic black pigment with very excellent properties such as chemical resistance, outdoor durability, light fastness, heat stability and spectrally absorbing selectivity [11],etc. It has been used in many areas including RPVC, polyolefins, engineering resins, paints and coating. It is also recommended for use in high temperature coatings based on silicone. Its CI (Color Index) number is PBK28.

In the spinel structure, there are 64 tetrahedral sites and 32 octahedral sites featuring the general formula AB_2O_4, in which only 8 tetrahedral sites and 16 octahedral sites are occupied by cations A^{2+} and B^{3+} respectively. Generally, there are 3 kinds of spinels: normal spinel, inverse spinel and partially inverted spinel[12].While copper chromite is a normal spinel with Cu^{2+} occupying the tetrahedral sites and Cr^{3+} occupying the octahedral sites.

Recently, ion-doped copper chromite spinel, such as Al-, Ba-, Mn-, Co-, Ni-, Ag- or Au-doped spinels have been synthesized to improve their catalytic activities and magnetic properties[13-17].In these studies, the catalytic activities are improved remarkably with the ions doped in the copper chromite. However, less study has been reported on copper chromite as a kind of black pigment. Additionally, as a ceramic pigment, ion doping can give a wide variety of coloration. When the colored cation substitutes the cation in spinel crystal lattice, the color often changes .

As we all know, Mn is a kind of multivalent element. Literature[18] showed that during the thermal treatments of Mn-doped $MgAl_2O_4$, the transition metal ion Mn^{2+} was easily oxidized to Mn^{3+} ,when the annealing temperature was higher than 800°C. In this paper, Mn^{2+} was chosen as doping ion and its influences on color property and crystal structure of the pigments were investigated. The Mn-doped copper chromite spinel samples were prepared by precursor coprecipitation and calcination method .

Experimental section

Reagents and materials. Copper (II) nitrate trihydrate [$Cu(NO_3)_2$•$3H_2O$], chromium Cr (III) nitrate nonahydrate [$Cr(NO_3)_3$•$9H_2O$], manganese (II) chloride tetrahydrate [$MnCl_2$•$4H_2O$], sodium hydroxide and ethylalcohol were all analytical grade,used as raw materials.

Preparation. The precursors of Mn-doped copper chromite black pigments $CuMn_xCr_{2-x}O_4$ were prepared by coprecipitation method, the amount of doped Mn in $CuMn_xCr_{2-x}O_4$ samples was listed in Table 1, the amount of Cu(II) used in all six samples was the same. 0.05mol $Cu(NO_3)_2$•$3H_2O$ and stoichiometric ratios of $Cr(NO_3)_3$•$9H_2O$ and $MnCl_2$•$4H_2O$ were mixed and dissolved in 100 mL water, 0.1mol/L excessive sodium hydroxide solution was dropped into the mixed metal ions solution, under continuous stirring at room temperature. After the precipitate precursor was formed, stop stirring and placed for 1h precipitation, then the precipitated precursor was filtrated, washed with water until the filtrate was neutral. The precursor samples washed with ethylalcohol, were dried and calcinated at 800°C for 2h in muffle furnace, cooled to room temperature, nano-sized Mn-doped copper chromite black pigments can be obtained.

The reaction mechanism was investigated as the following reaction equations:

$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2\downarrow$$

$$Cr^{3+} + 3OH^- \rightarrow Cr(OH)_3\downarrow$$

$$Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2\downarrow$$

$$Cu(OH)_2 + (2\text{-}x)\ Cr(OH)_3 + xMn(OH)_2 + x/4O_2 \rightarrow CuMn_xCr_{2-x}O_4 + (4\text{-}x/2)H_2O$$

Table 1 X values of Mn-doped copper chromite black pigment ($CuMn_xCr_{2-x}O_4$) samples

Sample	S1	S2	S3	S4	S5	S6
X	0	0.05	0.10	0.15	0.20	0.25

Characterization. The crystal lattice phase analysis of the samples was performed by X-ray powder diffraction using CuKa radiation(D8 Advance, Bruker). Thermal analysis of the samples was performed by DTA-TG-50 (Shimadzu Company), from 50 to 1000°C with a heating rate of 20°C/min. Infrared spectra of the samples was measured by FTIR spectrometer (MB154S, Bomen). Color of the sample pigments was measured using a LUCI 100 colorimeter(Dr. Lange), *L*a*b** parameters were used to evaluate the color properties of the pigments, according to the Comission Internationale de l'Eclairage (CIE) .

Results and Discussion

Thermal investigation of precursor. Sample S6 was chosen to study the precursor thermal property. Fig. 1 exhibits the thermal property of the precursor of $CuMn_{0.25}Cr_{1.75}O_4$ composite oxide. In Fig.1, the TG-DTA curves showed that there was a weight loss of 27.35% from 50°C to about 450°C, which probably due to the desorption of water and decomposition of precursor, after that there was no any further weight change in TG curve.

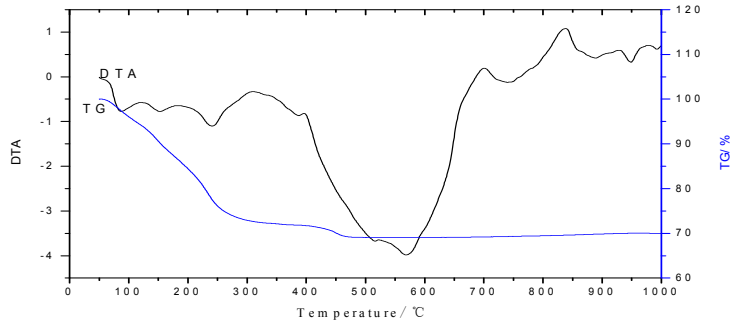

Fig. 1 Thermal curves (TG and DTA) of the precipitated precursor of $CuMn_{0.25}Cr_{1.75}O_4$

In the DTA curve, the endothermic peak under 100°C was attributed to the volatilization of water in the precursor, endothermic peaks between 100°C and 300°C were due to the decomposition of precursor, and the large and broad endothermic peak between 400°C and 650°C was corresponding to

the spinel formation.The exothermic peak at 698°C was due to the oxidation of Mn^{2+} to Mn^{3+} ,the exothermic peak between 800°C and 900°C maybe account for the oxidization of Mn from trivalence to quadrivalence or even higher quantivalency. Thus during the calcination process , 800 °C was chosen as the right annealing temperature, in order to avoid the oxidization of Mn from Mn^{3+} to Mn^{4+}or even higher quantivalency.

X-ray diffractions of Mn-doped spinel pigments. Fig.2 shows the XRD patterns of $CuMn_xCr_{2-x}O_4$ (x=0, 0.05, 0.10, 0.15, 0.20 and 0.25) spinel samples. The XRD diagrams of Mn-doped and undoped copper chromite are basically the same, no other phase was identified except spinel phase, showing that Mn-doping have little effect on spinel structure of the pigments. In Fig.2, diagrams of all samples showed very stable tetragonal phase spinel, it implied that Mn^{3+} ions were doped into the spinel crystal lattice, no structural variation occurred after Mn-doping. Though the source of Mn was from Mn (II) ions, but during the calcination at high temperature, Mn^{2+} was easily oxidized to Mn^{3+}[19]. Previous report showed that Mn^{2+} was not thermodynamically stable under this experimental condition[20]. Mn(III) was to substitute for some Cr (III) in the octahedral sites of copper chromite spinel Lattice.

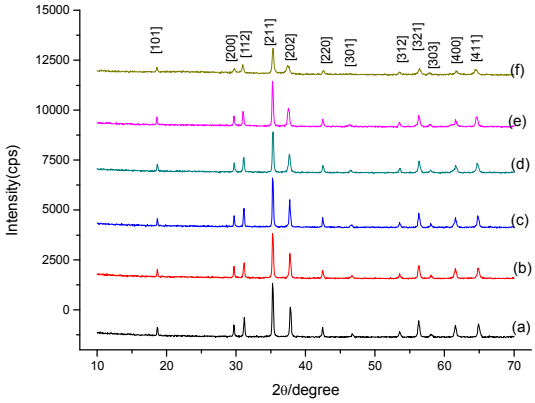

Fig. 2 XRD patterns of $CuMn_xCr_{2-x}O_4$ spinel oxides [x=0(a), 0.05(b), 0.10(c), 0.15(d), 0.20(e) and 0.25(f)]

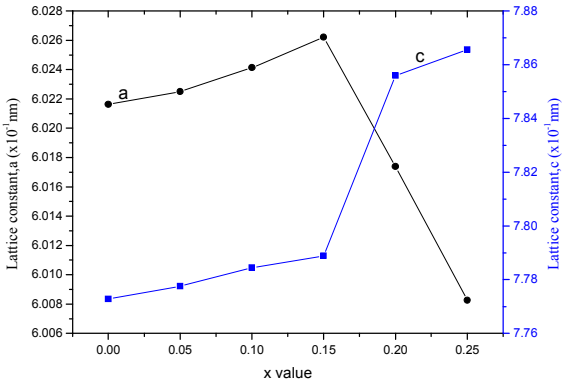

Fig. 3 Lattice constants (a and c, Å) change with Mn contents x in $CuMn_xCr_{2-x}O_4$

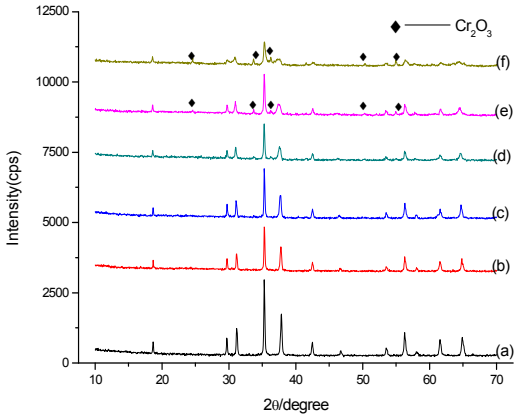

Fig. 4 XRD patterns of $Cu_{1-x}Mn_xCr_2O_4$[x=0(a), 0.05(b), 0.10(c), 0.15(d), 0.20(e) and 0.25(f)]

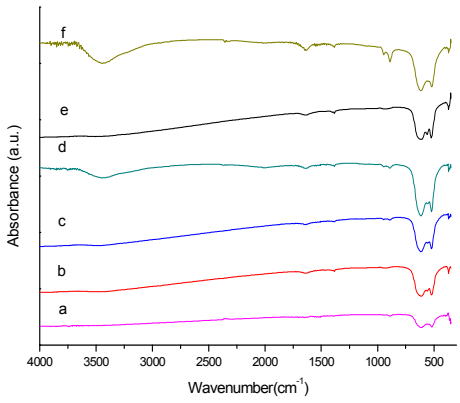

Fig. 5 Infrared spectra of $CuMn_xCr_{2-x}O_4$ [(a) x=0, (b) x=0.05, (c) x=0.10, (d) x=0.15, (e) x=0.20, (f) x=0.25]

Copper chromite is a kind of tetragonal phase spinel which is different from other cubic phase spinel such as $MgAl_2O_4$, $MnFe_2O_4$, $CoAl_2O_4$, etc[21-23]. Lattice constants changed slightly as the dopant concentration increased. In Fig.3, with the increasing content of substituted Mn(III) for Cr(III), the lattice constants both a and c were changed. Lattice constant c increased from 7.7728 Å to 7.8657 Å, but lattice constant a increased slightly and then decreased suddenly, when x=0.15, it reached the maximum value. The reason is not very clear, a possible explanation is that when Mn(III) substituted for Cr(III) in the spinel, lattice distortion happened.

In order to study whether Cu or Cr ion was substituted by Mn ion, samples formulated as $Cu_{1-x}Mn_xCr_2O_4$(x=0, 0.05, 0.10, 0.15, 0.20 and 0.25), in which Cu was substituted by Mn ion in stoichiometric proportion, were prepared with the same method as that of $CuMn_xCr_{2-x}O_4$. Fig. 4 is the XRD patterns of these samples. In Fig. 4, as x value increased, diffraction peak intensity of XRD patterns weakened. Besides, the specific diffraction peaks of Cr_2O_3 appeared, the main diffraction peaks were in accordance with Cr_2O_3 ,which JCPDS number is 38-1479. The result proved that in the spinel lattice Mn ion substituted Cr^{3+} rather than Cu^{2+}. Furthermore, with the increasing of x value, crystallinity of the pigments decreased.

FT-IR spectra of Mn-doped spinel pigments. Fig. 5 is the infrared spectra of $CuMn_xCr_{2-x}O_4$(x=0, 0.05, 0.10, 0.15, 0.20 and 0.25) spinel pigments. Usually, in the range of 400-1000 cm^{-1}, the IR bands of the spinel compounds are assigned to the vibration of metallic ions in the crystal lattice, and the vibration frequency depends on the quality and ionic radius of metallic ions. In the normal spinel structure, two main vibrations of metal-oxygen bands are observed in the IR spectra. Absorption bands in the range of 600-550 cm^{-1}, correspond to the intrinsic stretching vibration of M_{tetra}-O band at the tetrahedral site, whereas bands observed in the range of 450-385 cm^{-1}, are assigned to the octahedral metal ion stretching, M_{octa}-O[24]. In Fig. 5, it can be seen that IR absorption bands of all samples are at 606 and 512 cm^{-1}, which was due to the coupled vibrations of metal-oxygen bands in both tetrahedral and octahedral sites. The absorption bands at 940 and 880 cm^{-1} refer to the vibration of Mn-O. As the content of Mn increased, the characteristic absorption bands became clearer.

Colorimetric analysis of the pigments. The CIE L*a*b* colorimetric coordinates stand for the quantitative and qualitative characterizations of the pigments color. In this color measurement system, L^* is the color lightness(L^*=0 for black and L^*=100 for white), a^* is the green(-)/red(+) axis, and b^* is the blue(-)/yellow(+) axis[25] ,the numerical range of a^* and b^* is -100 to 100. Table 2 shows the colorimetric analysis of the $CuMn_xCr_{2-x}O_4$(x=0, 0.05, 0.10, 0.15, 0.20 and 0.25) black pigments. In Table 2, it can be seen that L^* decreased slightly with the increasing of Mn contents, the blackness of the pigments increased with Mn content. The coordinate a^* indicated irregular trends in red intensity, while b^* indicated irregular trends in blue intensity, with the increasing of Mn contents. In practice, copper chromite is a kind of black pigment with slight blue intensity. This study reveals that Mn-doping can increase the blackness and weaken the blue intensity of this pigment.

Table 2 Colorimetric analysis of $CuMn_xCr_{2-x}O_4$ (x=0, 0.05, 0.10, 0.15, 0.20, 0.25) spinel pigments

Sample	x	L^*	a^*	b^*
S1	0	22.04	0.30	-1.03
S2	0.05	21.27	0.36	-1.05
S3	0.10	19.53	0.34	-0.52
S4	0.15	19.09	0.30	-0.63
S5	0.20	19.00	0.22	-0.50
S6	0.25	16.90	0.17	-0.86

Conclusions

The new kind of black spinel pigments $CuMn_xCr_{2-x}O_4$ (x=0, 0.05, 0.10, 0.15, 0.20 and 0.25), in which the Mn^{3+} ions substituted some of the Cr^{3+} ions in the spinel lattice, were prepared by precursor coprecipitation and calcination method. The calcination temperature for all precursors was 800°C. The spinel pigments structure was determined by XRD patterns and FT-IR spectra, the results proved that all the pigment samples have tetragonal phase spinel structure. CIEL*a*b* analysis showed the colorimetric properties of these black pigments. Higher Mn-doped contents lead to blacker pigments with blue intensity, but no obvious regular changes of coordinates a^* and b^*. Mn-doped pigments can obtain diverse hues, which could offer wide applications in modern industry.

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