STRUCTURAL MODIFICATION OF COBALT CHROMITE BY DOPING WITH Mg^{2+} AND Zn^{2+} IONS AND THEIR EFFECT ON COLOUR IN GLASSY MATRICES

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1. INTRODUCTION

Cobalt chromite is known as a green ceramic pigment with assigned number DCMA 13-30-3 [1]. From a structural point of view, cobalt chromite is a normal spinel with Co^{2+} occupying tetrahedral lattice positions and Cr^{3+} occupying octahedral positions [2]. The green spinel colour can in reality be affected by the presence of non-chromophore ions in the lattice such as alkaline earth or post-transition elements. This is evident in structures such as Co_2SiO_4 olivine or the $CoAl_2O_4$ spinel, which are widely used as highly stable base colours, and are therefore employed in porcelain tile body staining techniques. The present work was undertaken to study how the introduction of this type of ion in a tetrahedral position affected structure and the development of colour. The result could allow minimising the quantity of cobalt in synthesising stable green and turquoise colours and thus reduce costs.

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1. DCMA *Classification and Chemical Description of de Mixed Metal Oxide Inorganic Coloured Pigments,* 2n ed. Metal oxides and ceramic colours subcommitee, Dry Color Manufacturer's Assn., Washington D.C., 1982
2. MONRÓS G., CARDA J., TENA M.A., ESCRIBANO P., BADENES J., CORDONCILLO, E., *Spinels from Gelatine Protected Gels,* J. Mat. Chem. 5[53] 85-90 (1995).

2. EXPERIMENTAL

Compositions $Co_{0,5}Mg_{0,5}Cr_2O_4$ and $Co_{0,5}Zn_{0,5}Cr_2O_4$ were prepared. Both compositions were obtained by the traditional ceramic process from oxides (CE) and by the technique involving joint hydroxide co-precipitation from dissolved chlorides in water (CO). The samples were heat treated in an aluminosilicate crucible at 800°C/3h and then at 1100°C/3h. The samples were characterised by the following techniques: (1) Planchromatic microscopy: viewing the unfired powders of the materials indicated the formation of microparticle agglomerates in the case of the co-precipitates; in the ceramic powders the ceramic particles of the different precursor oxides could be distinguished. (2) X-ray diffraction: Figure 1 depicts the evolution of the diffractograms of the co-precipitated sample $Co_{0,5}Mg_{0,5}Cr_2O_4$ as an example of the evolution. In the gels, NH_4Cl was detected in the unfired gels, at 800°C the spinel crystallised that developed peaks at 1000°C. The evolution was quite similar in the ceramic powders: at 1000°C there were no appreciable differences between the four samples that were prepared, which all exhibited spinel peaks. The method of internal addition was used in each case to refine the resulting chromite cell. The data are presented in Table 1. Lattice contraction can be observed in the case of the spinel with zinc. (3) UV-V spectroscopy by diffuse reflectance and measurement of the CIE-L*a*b* colorimetric parameters: Figure 2 presents the UV-V spectra of four glazed samples in a porous single-fire glassy matrix at 4% colour. Table 1 gives the CIEL*a*b* data corresponding to these glazed samples. The band appearing in the spectrum at 440 nm is associated with the transition $^4A_2(F)\rightarrow{}^4T_1(F)$ of Cr^{3+} in O_h symmetry and the multiple band between 500-750 nm with $^4A_2(F)\rightarrow{}^4T_1(F)$ of Co^{2+} in a tetrahedral environment.

Considering only the relative size of the ions involved in the substitution (Pauling ionic radii in an octahedral environment Co^{2+}=0,74 Å, Mg^{2+}=0,65, Zn^{2+}=0,74 Å), the unit cell should not significantly modify its size with zinc doping and should decrease slightly with magnesium. However, the experimental data run counter to this hypothesis (Table 1). In reality, the zinc tendency to covalence involves lattice contraction, increasing the field in the sphere of Cr^{3+} octahedral antagonist coordination as well as in that of Co^{2+} by shortening the Zn(Co)-O distance, so that a shift can be expected of the chromophore absorption bands towards higher wavelengths, producing colours tending towards yellow (green-yellow colour observed as reflection minimum at 550 nm). However, Mg does not produce this modification of the spinel lattice, as the experimental lattice parameter measurements show. The entry of this cation in the tetrahedral gap therefore exhibits a reflection maximum at 490 nm producing turquoise colours.

3. CONCLUSIONS

The entry of Zn^{2+} and Mg^{2+} ions replacing Co^{2+} in the cobalt chromite spinel lattice allows reducing pigment costs and modulating the shade of colour from green and yellow with magnesium to turquoise colours with zinc. The zinc tendency to covalence explains the lattice shrinkage found with this cation and the consequent rise in wavelength of the Cr^{3+} and Co^{2+} absorption bands, owing to the increase in the crystalline field of its coordination sphere. The use of alternative methods by co-precipitation did not modify the position of the bands, and exhibited very similar reactivity and colour strength.

Sample	L*	a*	b*	a(Å) *ASTM 22-1084* *8.330*
Mg(CE)	44.7	-11.9	-6.6	8.327(8)
Mg(CO)	44.4	-9.8	-2.7	-
Zn(CE)	36.4	-7.7	1.3	-
Zn(CO)	40.8	-10.8	2.0	8.314(9)

Table 1. *Lattice parameter of the powders at 1000°C and CIEL*a*b* coordinates of the glazed samples.*

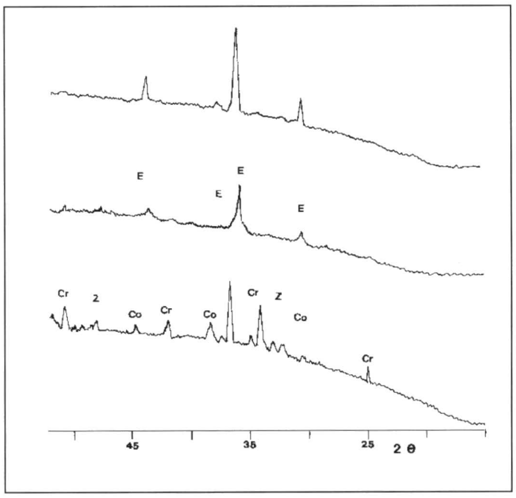

Figure 1. *Thermal evolution of the diffractograms in sample Zn(CE):* $Cr(Cr_2O_3)Co(Co(OH)_2)Z(ZnO)E(ZnCr_2O_4)$.

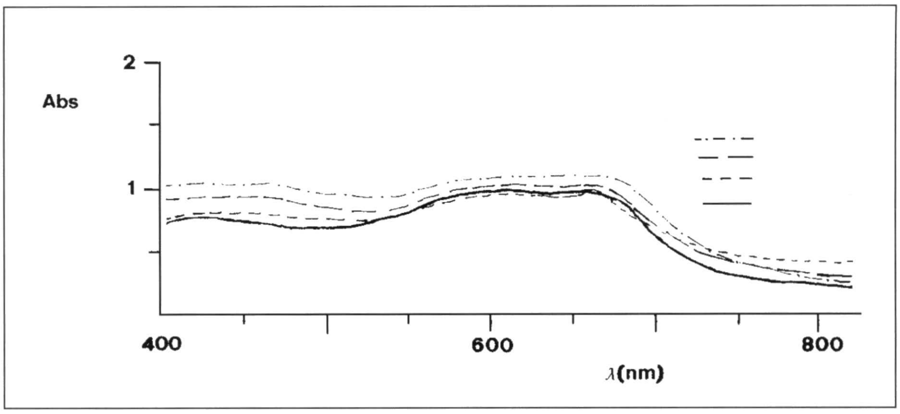

Figure 2. *UV-V spectra of the powders at 1000°C: (-)Mg(CE), (—)Mg(CO), (- -)Zn(CO), (-.-.)Zn(CE)*

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