

INVESTIGATION OF COLOURING MECHANISM OF REE-PEROVSKITES  
THROUGH COMBINING STRUCTURAL AND  
UV-VIS-NIR SPECTROSCOPY DATA

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The research of red ceramic pigments is a current topic in traditional ceramics since most industrial products give hues far away from the pure red. New red pigments have been developed based on the perovskite  $A^{III}B^{III}O_3$  structure, with  $A=Y$  or REE and  $B=Al_{1-x}Cr_x$ , where  $0.03 < x < 0.12$  (BALDI & DOLEN, 1999). Though extensively characterised from the technological viewpoint, perovskite pigments still present unsolved questions concerning the mechanisms involved in their coloration. This study was carried out through combining high resolution XRPD, performed using synchrotron radiation at the ESRF, with UV-Vis-NIR spectroscopy, performed using diffuse reflectance measurements.

Rietveld refinements of XRPD data confirmed the substitution of Cr for Al in the 6-coordinated B site and a decrease of B-O distance when the A site is filled with bigger REEs; hence an inverse correlation exists between the A-O and B-O distances.

UV-Vis-NIR spectra showed the existence of rare earth multiplets in the red region and the occurrence of peaks due to  $Cr^{3+}$  transitions  ${}^4A_2-{}^2E$ , but the final colour of pigments is due to a broad band absorbing the blue and green visible region never observed in the literature (WEBER & VARITIMOS, 1974). Besides, a shift of the broad band in the visible region was observed and related with the type of REE inside the site A. The origin of this broad absorption band is still unknown, but on the basis of the up to date results it can be hypothesized the following origins:

coalescence of the two  $Cr^{3+}$  peaks due to  ${}^4A_2g({}^4F) \rightarrow {}^4T_2g({}^4F)$  and  ${}^4A_2g({}^4F) \rightarrow {}^4T_1g({}^4F)$  transitions, but the shift of the absorption band does not follow the trend predicted by the crystal field theory;

charge transfer between Cr-O, but from literature data (POOLE & ITZEL, 1963) the absorption band for  $Cr^{4+}$  and  $Cr^{6+}$  is predicted at higher energies than those observed.

In conclusion, the red colour of (Y or REEs)  $(Al_xCr_{1-x})O_3$  perovskites is due to multiple mechanisms, involving crystal field  $d-d$  and  $f-f$  spin allowed and spin forbidden transitions and particularly an absorption band, whose origin is still debated.

#### References

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