


**Experiment title:**

Crystal structure of perovskite-type ceramic pigments

**Experiment number:**

CH-1321

<b>Beamline:</b> SNBL BM01B	<b>Date of experiment:</b> from: 21/09/2002                      to: 24/09/2002	<b>Date of report:</b> 01/03/04
<b>Shifts:</b> 9	<b>Local contact(s):</b> Hermann Emerich	<i>Received at ESRF:</i>

**Names and affiliations of applicants (\* indicates experimentalists):**

\*Cruciani Giuseppe, University of Ferrara, Italy

\*Matteucci Francesco, ISTECCNR – Faenza, Italy

\*Baldi Giovanni, Colorobbia Italia, Sovigliana – Vinci , Italy

\*Barzanti Andrea, Colorobbia Italia, Sovigliana – Vinci , Italy

Dondi Michele, ISTECCNR – Faenza, Italy

**Report:**

A ceramic pigment is a coloured crystalline inorganic material, having high thermal stability and chemical resistance, that colors ceramic bodies through dispersion. The development of new red ceramic pigments is a pressing problem, as the current products (e.g. malayaite  $\text{CaSn}_{1-x}\text{Cr}_x\text{SiO}_5$ , corundum  $\text{Al}_{2-x}\text{Mn}_x\text{O}_3$ , zircon  $\text{ZrSiO}_4\text{-Fe}_2\text{O}_3$ ) give hues far away from the pure red<sup>[1]</sup>. Besides, greenockite-cadmoseelite included in zircon ( $\text{CdSe}_x\text{S}_{1-x}\text{-ZrSiO}_4$ ) – though developing an intense red colour – presents environmental problems due to the toxicity of Cd and Se. A new red pigment, with perovskite structure of type  $\text{A}^{\text{III}}\text{B}^{\text{III}}\text{O}_3$  and composition  $\text{A}_x(\text{Al}_{1-x-y}\text{Cr}^{3+}_y)\text{O}_3$  with  $0.90 < x < 1$  and  $0.03 < y < 0.12$  and  $\text{A} = \text{Y, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb}$  has been developed and characterized from the technological viewpoint<sup>[2]</sup>.

In order to improve our understanding of the relationships between the structural modifications induced by the incorporation of the different REE ions and the coloration mechanisms, an investigation combining Rietveld refinements and UV-Vis-NIR spectroscopy has been undertaken on two series of perovskite pigments prepared through the conventional ceramic route: a)  $\text{A}^{\text{III}}\text{Al}_{0.965}\text{Cr}_{0.035}\text{O}_3$  where  $\text{A}^{\text{III}} = \text{Y, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb}$  ('REE-varying series') and b)  $\text{YAl}_{1-x}\text{Cr}_x\text{O}_3$  where  $x=0.015, 0.055, 0.075$  ('Cr-varying series'). Data collections at the SNBL BM01B beam line were performed in transmission capillary geometry (Debye-Scherrer) using two different set-ups to minimize the absorption effects: a) REEs-varying series: 0.3 mm capillary;  $1^\circ \leq 2\theta \leq 32.5^\circ$ ;  $\lambda = 0.49997 \text{ \AA}$ . b) Cr-varying series: 0.7 mm capillary;  $1^\circ \leq 2\theta \leq 52.5^\circ$ ;  $\lambda = 0.79982$ .

The results of Rietveld refinements of powder diffraction data study can be resumed as follows: i) the introduction of the increasing ionic size REEs into the A site, with a constant Cr doping in the octahedral B site, was accompanied by regular increase of the cell volume (Fig. 1), increase of the  $\langle \text{A-O} \rangle$  distance and decrease of the  $\langle \text{B-O} \rangle$  distance (Fig. 2); a lowering of symmetry occurred from hexagonal ( $R\bar{3}cH$ , Nd-perovskite) to orthorhombic ( $Pnma$ , Sm-Yb perovskites), confirming literature data; ii) the Goldschmidt tolerance factor (*t-factor*) based on refined distances also increased with ionic size of REE remaining between 0.90 and 0.97 as for a stable perovskite

structure; iii) the shortening of the  $a$  cell parameter and lengthening of  $b$  and  $c$  (orthorhombic setting), with increasing ionic size of REE, related to the decrease of the octahedral rotations around [110], [001] and [111], were consistent with the  $a^+b^-b^-$  tilting system; iv) in the A=Y series with increasing Cr content, the substitution of Cr for Al in the B site was confirmed by the regular increase of the  $\langle B-O \rangle$  distance (Fig. 3) and the  $a$  cell parameter; the  $t$ -factor decreased whereas the octahedral bond-length distortion increased. The Rietveld refinements also allowed to quantify some impurity phases produced during the perovskite pigment synthesis from reaction of the raw materials with mineralizers (sodium and calcium fluorides).

The UV-Vis spectra measured on the same powders as used for diffraction experiments revealed the existence of a strong and broad absorption band at  $\sim 17000\text{ cm}^{-1}$ , overlapping the two main crystal field transitions of  $^{[6]}\text{Cr}^{3+}$ , and of some less intense peaks due to REE  $4f$  multiplets. The edge of the absorption band exhibited a shift to higher energy as the average octahedral distance  $\langle B-O \rangle$  increases and  $\langle A-O \rangle$  decreases. This was directly associated to the variation of the hue and colour saturation parameters, in particular for the red colour, among the studied perovskite pigments (Fig.4).

In conclusion, the results achieved from structure refinements were fundamental towards a better understanding of the colour development in perovskite-based ceramic pigments<sup>[3]</sup>. In fact, they showed that the energy shift of the optical band cannot be explained simply by the variation of the  $^{[6]}\text{Cr}^{3+}$ -O distance ( $d$ ) as predicted by the crystal field formalism (i.e.  $\Delta = k d^{-5}$ ). Different phenomena must be invoked to explain the variation in the optical spectra and colour.

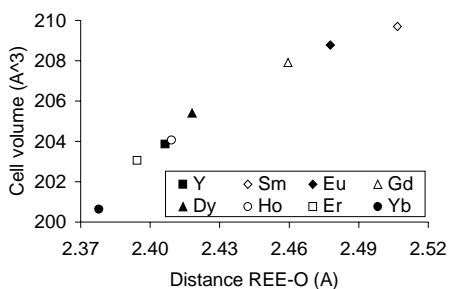


Fig. 1 Correlation between cell volume and the REE-O distance.

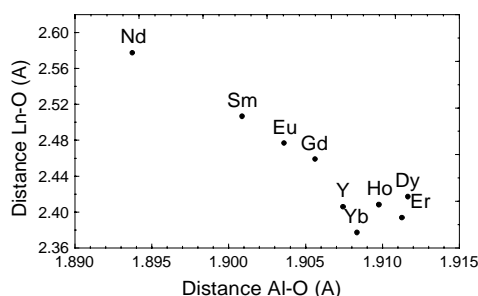


Fig. 2 Correlation between the Al-O and REE-O distances.

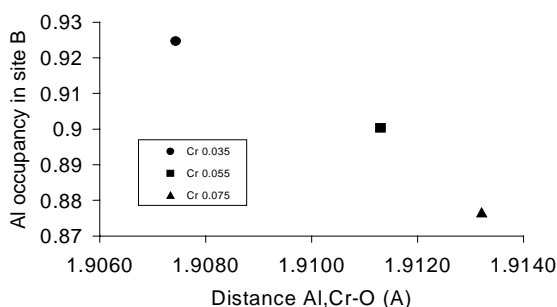


Fig. 3 Correlation between Al-O distance and Al occupancy in site B.

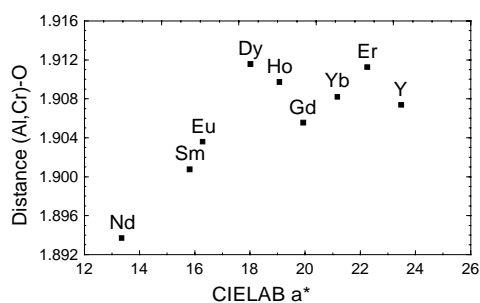


Fig. 4 Correlation between red colour (CIELab  $a^*$ ) and the Al-O distance.

## References

- [1] Costa A.L., Cruciani G., Dondi M., Matteucci F. (2003) *Ind. Ceram.*, 23(1), 1-11
- [2] Baldi G. and Dolen N. (1999) *Mat. Eng.*, 10(2), 151-164
- [3] i) Matteucci F., Cruciani G., Dondi M., Baldi G., Barzanti A. (2003) *ECM-21*, Durban, Aug. 2003; ii) Matteucci F., Dondi M., Cruciani G., Baldi G., Barzanti A. (2004) *Key Eng. Mat.* (in press).