

orientation of the grains in the marginal and central zones of the walls or the lack of the preferential orientations, associated with some obvious directional changes in the very limited spaces. emphasizing in such way different techniques of moulding-fashioning of the ceramic paste. No engobe has been identified.

Though, they have been found in the same area and they are considered contemporary, the mineralogical aspects emphasize (i) different historical periods, (ii) the same period, but some changes in the processing of ceramic material could taken place, or (iii) different geographical areas, for their origin.

Keywords: ceramics, mineralogy, properties

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Cobalt Incorporation in Mullite

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Mullite (nominally $3Al_2O_3 \cdot 2SiO_2$) is technologically important material for advanced ceramics applications. Depending on the synthesis procedure, mullite is able to incorporate considerable amounts of transition metal cations [1]. While Cr^{3+} , Fe^{3+} and V^{3+} have the strongest tendency of incorporation in mullite, only low or very low amounts of Fe^{2+} , Co^{2+} , Mn^{2+} and Zr^{4+} ions can enter the mullite structure. A major goal of this work is to determine upper limit of Co^{2+} incorporation in mullite. The samples of pure mullite and of Cr-doped mullite were derived from diphasic precursors and sintered at 1600 °C for two hours. Four samples were prepared containing 0, 1, 2 and 3 at% Co. They were examined by XRD at room temperature. Samples contained mullite phase and small amounts of $\alpha-Al_2O_3$ and $CoAl_2O_4$. Unit-cell parameters of the mullite phase were refined by the whole-powder-pattern fitting method [2]. They increased just slightly with increase of cobalt content in the samples. Quantitative phase analysis showed that the samples with 1, 2, and 3 at% Co contained 0.8, 2.5 and 5.1 wt% $CoAl_2O_4$, respectively. These means that ~0.6 at% Co was incorporated in mullite. Same value of upper limit of Co^{2+} incorporation in mullite was obtained on the basis of intensity ratio $I_{(311, CoAl_2O_4)} / I_{(111, mullite\ phase)}$, which was linearly dependent on the Co content in the examined samples.

[1] Schneider H., *Ceramics Transactions*, 1990, 6,135. [2] Toraya H., *J. Appl. Cryst.*, 1986, 19, 440.

Keywords: co-doped mullite, X-ray diffraction, fitting methods

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Rietveld Refinement of Solid Solutions of La_2TiO_5 and $La_4Ga_2O_9$

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Orthorhombic (Pnam) La_2TiO_5 and monoclinic (P2₁/c) $La_4Ga_2O_9$ were found to form solid solutions in the whole concentration range. Samples of $La_2Ti_{(1-x)}Ga_xO_{(5-x/2)}$ with $x = 0.00, 0.20, 0.50, 0.70, 0.90, 0.95$ and 1.00 were prepared by solid state reaction of oxides at 1300 °C in air (fired and remixed several times for 60 h, until no change).

Structure of La_2TiO_5 has already been known, while $La_4Ga_2O_9$ was found in this study to be isostructural with $Y_4Al_2O_9$, $Eu_4Al_2O_9$ and $Pr_4Ga_2O_9$, and was successfully refined from the $Y_4Al_2O_9$ model.

Laboratory data in the range of 10-120 °2 θ were used for an unrestrained Rietveld refinement (TOPAS). Results were consistent and showed random replacement of Ti^{4+} by Ga^{3+} ions in the solid solutions, coupled with oxygen vacancies, most probably preferably occurring at one site. Vacancies at this site are not ordered till $x = 0.90$ and the structures up to this composition are orthorhombic, obeying Vegard's law. Increase of a and c and decrease of b was explained considering ionic radii and shifts of ions towards the vacant site.

Ordering of the oxygen vacancies on one oxygen site at $x = 0.95$ and 1.00 causes doubling of the unit cell and lowering of the

symmetry to monoclinic. In pure $La_4Ga_2O_9$ ($x = 1.00$) the total population at this site reaches 0.5 and the ordering (1 full : 1 empty) produces the superstructure. The structural relationship between the end members (orthorhombic and the other monoclinic) was also clarified by finding the transformation matrix between the two.

Keywords: solid solution, Rietveld refinement, ceramics

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Comparative Study between Synthesized $Zn_{2-x}Co_xSiO_4$ and Cobalt-base Pigments

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Except V-ZrSiO₄, all commercial ceramic pigments are cobalt-base. Most compounds used are Co₂SiO₄, Co₂SnO₄, and CoAl₂O₄ type. Although these pigments show an intense blue color, they present two major disadvantages: the high cost of cobalt and its toxicity. We can reduce these problems by introducing a small quantity of cobalt into chemically and thermally stable crystalline matrix of Zn₂SiO₄.

In this work, we have synthesized blue Zn_{2-x}Co_xSiO₄ pigments with low cobalt content. The powder obtained was characterized by several techniques: X-rays diffraction powder, IR and UV-Visible spectroscopy, LAB color measurement, and Scanning Electron Microscopy. Comparative study was made between our synthesized pigments and the most used commercial pigments produced by different companies.

Keywords: ceramics, pigments, cobalt

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Rietveld Analysis in Biological Apatite Composite Tissues

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A Rietveld analysis has been carried out for two types of hard tissues: bone and dentin. As it is well known, both bone and dentin are composite materials having the presence of an organic matrix (type I collagen) and nanometric crystals of biological apatite. In Rietveld Refinement, the description of the Bragg intensity peaks can be carried out without serious difficulties. In any case, the microstructural contribution must be settled carefully, by introducing an instrumental resolution function. In the correction for absorption we have taken into account the contribution for air scattering, according to Ottani et al. [1]. As part of the background, we have considered the incoherent scattering using the analytical expression published by Smith et al. [2] and the thermal diffuse scattering [1]. The amorphous contribution has been described using the scattering of a pure amorphous collagen, and the Debye equation. This possibility is available in program FULLPROF [3] in which we have used six terms to fit the collagen contribution to the background. The possibility of perform a quantitative analysis in this kind of composite materials is analyzed. A structural study of several biological apatites from bones of humans and animals is presented.

[1] Ottani S., Riello P., Polizzi S., *Powder Diffraction*, 1993, 8, 149-154. [2] Smith V. H., Thakkar A. J., Chapman D. C., *Acta Cryst.*, 1975, A31, 391-392. [3] Rodríguez-Carvajal J., Roisnel T., FullProf.98: New Windows 95/NT Applications for Diffraction, *Newsletter N°20*, 1998.

Keywords: Rietveld analysis, biological apatites, amorphous compounds

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Structural Characterization of CdCO₃-CdS by X-ray

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