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 mulllite, 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 ºC 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 α-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 $I_{(311,\ CoAl2O4)}$ / $I_{(111,\ mullite\ phase)}$, 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 ($P2_1/c$) $La_4Ga_2O_9$ 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 ^oC 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 $^o2\theta$ 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 $Zn_{2\text{-}x}Co_xSiO_4$ and Cobalt-base Pigments

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Except V-$ZrSiO_4$, all commercial ceramic pigments are cobalt-base. Most compounds used are Co_2SiO_4, Co_2SnO_4, and $CoAl_2O_4$ type. Although theses pigments show an intense blue color, they present two major disadvantages: the high cost of cobalt and its toxicity. We can reduce theses problems by introducing a small quantity of cobalt into chemically and thermally stable crystalline matrix of Zn_2SiO_4.

In this work, we have synthesized bleu $Zn_{2\text{-}x}$ Co_x SiO_4 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

P.11.06.6

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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, *Newletter N°20*, 1998.

Keywords: Rietveld analysis, biological apatites, amorphous compounds

P.11.06.7

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Structural Characterization of $CdCO_3$-CdS by X-ray

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Thin films of cadmium sulfide (CdS) and cadmium carbonate ($CdCO_3$) were grown onto glass substrates by means of the chemical bath (CB) method. The temperature of grown was selected between 23-80 °C. At low temperatures, $CdCO_3$ is the compound predominant in the layers, whereas at high temperatures CdS is the compound deposited on the substrate. The gradual transition from an insulator $CdCO_3$ to a semiconductor CdS growth occurs when values a mixture increases. Physical properties of films they are studied by means of X-ray diffraction, and optical absorption.

Keywords: semiconductors, diffraction, cadmium carbonate

P.11.08.1

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Scanning X-ray Scattering Study on Structural Changes at Crack Tips in PVDF

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Scanning small angle X-ray scattering approaches have been demonstrated to provide structural information at the supra-molecular level with positional resolution in the micron range. We use this technology on a lab-system with a beam size of 0,1mm to study deformation mechanisms around crack tips in poly(vinylidene fluoride) (PVDF), a semi-crystalline polymer which is known to show deformation-induced phase transitions. Fracture in semi-crystalline polymers is accompanied by the formation of a plastic zone, consisting either of shear bands, micro cavities or crazes. The supra-molecular deformation processes around the crack tip are essential for the progression of the crack and, hence, in defining the toughness of the material. Due to the enormous stress gradients around the crack tip they are difficult to assess and –in most polymers– only poorly understood. The use of position resolved scatting methods for investigations of the crack tip area provides detailed information of the structural changes during crack propagation. Our study shows a localized transformation of α-PVDF into the β-modification near the crack tip. The β-modification is forming fibers bridging crazes and cracks and, hence, considerably contributing to the toughness of the material.

Keywords: polymers, fracture, scanning-SAXS WAXS

P.11.08.2

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An Investigation into the Effects of Temperature and Crystallization Conditions on the Lattice Parameters of Ultra Long n-alkane Crystals

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Ultra-long, strictly monodisperse n-alkanes, with a chain length between 100 and 400 carbons, crystallize into extremely regular lamellae with a thickness that is an integer fraction of the extended chain length. They have been investigated as model systems for polymer crystallisation, crystal annealing and melting.

High resolution time resolved wide angle X-ray scattering has been performed on beamline ID11 at the ESRF, in Grenoble. Changes in the lattice parameters of a range of ultra long n-alkanes have been determined as a function temperature. Emphasis has been placed on observing the transitions of chain unfolding and melting. The principal component of unit cell expansion is directed along the *a* axis, with little change parallel to the *b* and *c* axes, in agreement with previous studies. Subtle differences in the lattice parameters depending on the crystal thickness and the number of folds in the chain have been observed. At room temperature the number of folds has a controlling influence over the lattice parameters, with the more folded crystals having a more expanded lattice. Crystal thickness starts to play a role as the melting temperature is approached. The effect of pressure on the temperature dependance of lattice parameters in these model systems was also investigated, in the range 0-6 kbar.

Keywords: polymer, alkane, crystal refinement

P.11.08.3

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Deformation Process of Polymer Spherulite Observed with Microbeam-SAXS and -WAXS

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In the field of polymer processing, the understanding of polymer deformation under force is very important for the design of polymer with higher performance. Especially, the deformation of polymer spherulite by drawing is the most interested phenomenon in film processes, and clarifying the deformation mechanism of spherulite will give the better direction of polymer design for films.

To observe the inhomogeneous deformation process within a spherulite, we applied the scanning microbeam-SAXS and -WAXS technique to a deformed large isotactic polypropylene(iPP) spherulite (averaged radius is around 200-300μm) by uni-axial hot drawing. By scanning various spherulites, the deformation degree of which is different, with microbeam, we found that the order of crystalline orientation in the up- and down-side area of a spherulite drawn in the horizontal direction came to lower and lamella stacking structure was broken in the initial stage of deformation and that the order of crystalline orientation and lamella structure recovered in the latter stage of deformation. On the other hand, the order of crystalline orientation and lamella stacking in the left- and right-side of a spherulite were kept in the initial stage and they were drastically changed in the latter stage of drawing.

Keywords: microbeam, SAXS WAXS, SAXS polymer

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Crystal Structure and Texture Refinement of Polymers from Diffraction Images

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The crystal structure of not perfectly crystallized polymers has always been difficult to refine or determine with accuracy especially when a single crystal is not available. Most of them crystallize sufficiently only when strained in fibers. Clearly in this form they are not a single crystal but not even a random powder to permit a reliable crystal structure refinement.

In the present work, we present a methodology to analyze diffraction images of polymers to obtain crystal structure, texture and microstructural information. A laboratory image plate system has been used to collect diffraction images in transmission and reflection diffraction of aligned and strained fibers of different polymers.

The images have been processed in Maud [1] and a structure refinement approach including a Rietveld Texture Analysis [2] was performed for each polymer. An energy approach has been incorporated to help the refinement strategy as well as the use of fragments. From the texture point of view the standard function method for quantitative texture analysis has been developed and successfully applied to these systems. It permits to determine with high accuracy and precision the spread of the single polymers chains