not to be of universal character when scaled against the correlation length and instead depends on the interaction of faulting. Furthermore, even in the case where is clear the presence of large density of defects, and therefore independent faulting does not hold, direct methods still applies.

The developed procedure was used to analyse the layer disorder in RE_2Co_{17} alloys (RE: rare earth) which undergo a reordering transition from rhombohedral to hexagonal arrangement when going from the light rare earth elements to the heavy rare earth. In all cases the structures show different degree of planar disorder. The X-ray diffraction experiments were conducted on the beam line XPD at the LNLS synchrotron facility in Campinas, Brazil.

The increasing ordered character of the hexagonal phase was quantified as well as the evolution of the rhombohedral stacking through the value of the correlation length. A k parameter has been introduced in the decaying term of the probability correlation length, allowing to follow quantitatively the interaction of the faulting as well as the distance of the actual faulting to the random non-interacting model. The reconstructive phase transition in this system seems to fallow a path where the new phase appears within the disordered phase and grows without homogeneous reordering of the disordered arrangement.

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Keywords: defect, stacking, alloy

MS74.P21

MEM analysis of electron-density distribution in apatites

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Recently, the possibility was demonstrated that 3d-metals (M = Cu, Ni, Zn) can be incorporated into strontium hydroxyapatite powders, where they partially occupy the channels and form linear O-M-O groups separated by hydroxide anions [1], [2]. The positions and isotropic displacement parameters of the atoms (isotropic ADPs) were refined by the Rietveld method. As unavoidable in Rietveld refinement, the strong correlations between the different crystallographic parameters do not allow the refinement of anisotropic ADPs in the neighborhood of Sr. In order to obtain information about the anisotropic ADPs of the in-channel atoms, the maximum entropy method (MEM) has been used as a complementary tool. In this work, the MEM was used to derive the most probable distribution of the electron density and to determine the ionic charge of atoms of hydroxyapatites with different content of metal atoms from powder diffraction data.

An almost completely *ab-initio* electron-density distribution can be obtained by the MEM using a combination of structure-factor amplitudes from a Le Bail fit of the diffraction data (disregarding any structural model) with phases from Rietveld refinement of the initial structural model [3]. The Le Bail fit provides amplitudes of structure factors as they would have been directly measured by single-crystal diffraction, except that for each group of overlapping reflections only

the sum of the intensities can be used. As an initial model for the determination of the phases of structure factors, the published atomic coordinates of the investigated compounds were used [1], [2] without metal and oxygen atoms in the channels of the apatite. Therefore, no prior structural information about locations of these atoms was used for the determination of the electron-density distribution. For the reconstruction of the electron density in the unit cell the computer program BayMEM [4] was used.

As examples, the two-dimensional maps of the electron-density distribution of the atoms of pure hydroxyapatite and hydroxyapatite with copper atoms in the channels $Sr_5(PO_4)_3Cu_{0.1}O_{0.2}(OH)_{0.8}$ are shown in Fig.1. The electron-density distribution of the Cu atoms is isotropic, suggesting the absence of positional and thermal displacement of the Cu atoms.
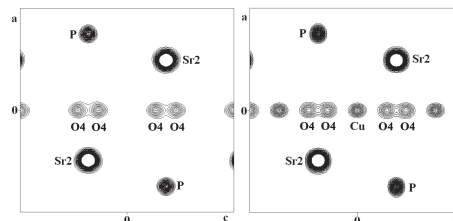

Fig. 1. Two-dimensional electron-density maps at $y=0$ of pure hydroxyapatite (left) and hydroxyapatite with copper atoms (right).

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Keywords: MEM, apatite, powders.

MS74.P22

Detour into two dimensions: a new method for powder structure solution

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A single-crystal charge-flipping algorithm [1] has been applied to 2-dimensional projections derived from X-ray powder diffraction data to retrieve structure factor phases. These phases proved to be as reliable as those obtained from high-resolution transmission electron microscopy (HRTEM) images or from precession electron diffraction (PED) data [2]. In particular, the stronger reflections tend to be correctly phased. The 2-dimensional electron density "images" obtained in this way show the same features as the corresponding HRTEM images, but with higher resolution. Application of the powder charge-flipping algorithm [3] to the full 3-dimensional powder diffraction data in conjunction with phases derived from several such (arbitrarily selected) projections was found to have a significant and beneficial effect on the structure solution.

The approach was first developed and tested using data collected on the complex zeolite TNU-9 [4], IM-5 [5] and SSZ-74 [6]. All three of these structures were originally solved by combining X-ray powder diffraction and electron microscopy data, because X-ray diffraction data alone were not sufficient. In all three cases, the phase information derived from 2-dimensional subsets of the X-ray powder diffraction data resulted in a significant improvement in the electron density maps generated by the powder charge-flipping algorithm. The inclusion of this phase information allowed all three structures to be determined

from the X-ray powder diffraction data alone. An *ab initio* powder structure determination of the novel zeolite SSZ-82 was then performed. While it was very difficult, if not impossible, to derive the structure directly by powder charge flipping, the structure solution procedure became straightforward when the 2D-XPD approach was applied. The positions of all the framework Si atoms and most of the O atoms could be located directly from the 2D-XPD electron density maps.

This approach appears to offer a remarkably simple and powerful method for solving the structures of complex polycrystalline materials.

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Keywords: powder diffraction, structure solution, charge flipping

MS74.P23

Textural evolution of zinc alloys deformed by NECAE method

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One of the main methods for increasing mechanical strength is grain refinement. Ultrafine grains can be obtained by means of several methods of Severe Plastic Deformation (SPD) [1], being the most common Accumulative Roll Bonding (ARB), Torsion Straining (TS), Equal-Channel Angular Pressing (ECAP) y Milling Mechanical (MM) [2], [3]. On the current work we study another method of deformation, NECAP [4] (Non Equal-Channel Angular Pressing), by processing sheets of Zn alloys pre-rolled until 0.65 mm thickness and cut into the directions of 0º, 45˚ and 90˚ with respect to the original Rolling Direction. 21 plates of 14 mm width and 45 mm length were stacked in the channel matrix, with the plane perpendicular to the transversal direction, and deformed with a load of 5000 kg in a single pass of deformation. The matrix was configured with external and internal angles of $\Psi = 81˚$ and $\Phi = 150˚$, respectively. We selected four samples for each rolling direction corresponding to different transverse distances of the channel matrix. The samples were characterized by optical microscopy (OM), x-ray diffraction (DRX) and Electron Back Scattering Diffraction (EBSD) analysis. The purpose of the work was to study the deformation texture, microstructural parameters, such as grain size and crystal orientations and local misorientations. The main purpose of the study is a preliminary assessment of shearing deformations that will be applied to another SPD technique: asymmetric rolling of different metals and alloys.

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Keywords: non equal-channel angular pressing, texture, X-ray diffraction

MS74.P24

Structural characterisation of fluorites and pyrochlores

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Compounds with general formula $A_2B_2O_7$ may adopt the fluorite or pyrochlore structure. This requires 12.5 % anion sites to be vacant (relative to the ideal fluorite, MO_2), due to the different valency of the A and B cations. The formation of the pyrochlore structure over the fluorite structure has been widely reported to be governed by the cation radius ratio, r_A/r_B, with pyrochlore forming in the range 1.46-1.78 [1]. In the fluorite structure, cations and anions are disordered across their respective crystallographic sites, whereas in pyrochlore they are ordered.

$A_2B_2O_7$ compounds with r_A/r_B values close to the fluorite-pyrochlore boundary of 1.46 may crystallise independently in both pyrochlore and fluorite structures. The formation of pyrochlore or fluorite is influenced by the synthetic method (*i.e.* precursor or conventional solid state) and also the thermal treatment of the sample [2,3]. However, due to the closely related structure of fluorite and pyrochlore, it is often difficult to distinguish between polymorphs using average characterisation techniques, such as diffraction, alone. This is especially problematic when precursor routes have been adopted and diffraction patterns show broad peaks, indicating a small crystallite size. This may result in weak pyrochlore superstructure peaks being difficult to detect by laboratory XRD. Therefore, it is important to utilise local structure characterisation techniques for a complete knowledge of the structure adopted.

We report our recent structural characterisation of an $A_2B_2O_7$ compound, using a range of average and local probes, such as powder X-ray Diffraction and neutron diffraction, neutron total scattering, electron diffraction, Raman and NMR spectroscopy.

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Keywords: fluorite, pyrochlore, diffraction

MS74.P25

Expanded austenites studied by PXRD and EXAFS

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Low temperature nitriding (< 450°C) or carburising (<520°C) of stainless steel brings about a transformation of the surface into so-called *expanded austenite* by incorporation of nitrogen and/or carbon in the FCC octahedral interstices. The result is greatly improved wear and fatigue properties without compromising the corrosion resistance. Obviously, this favourable combination of wear, fatigue and corrosion performance is technologically highly relevant as it opens up for new applications of stainless steels, but also scientifically the colossal solubility of interstitials (up to 60 % occupancy) at low temperatures is indeed intriguing. We have recently characterized a series of nitrided and carburized steels by combining powder diffraction (for phase