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Multiferroics have engendered increasing interest because of their many potential applications for micro- or nano-electronic devices, magnetic storage elements and interesting fundamental physics. The term "multiferroic" means coexistence of ferroelectric and magnetic ordering in a single phase or multiphase material. However, the two ordering parameters are mutually exclusive because ferroelectricity and magnetism require different filling states of the d-shells of transition metal ions. Empty d- shells mainly exist in ferroelectricity, while partially filled d-shells are required in magnetism. Therefore multiferroics are rare.

It exists several different microscopic mechanisms which may cause multiferroic behaviour . One of the most interesting is when a spontaneous polarization exists in a spiral or cycloidal magnetic structure. Accordingly, one strategy to find new multiferroic materials is to look for magnetic systems with that kind of magnetic structures.

The complex metal oxides  $Mn_3TeO_6$  and  $Co_3TeO_6$  have been prepared both as single crystals by chemical transport reaction and as polycrystalline powders by a solid state reaction route. The crystal structure and magnetic properties have been investigated using a combination of x-ray and neutron powder diffraction, electron microscopy, calorimetric and magnetic measurements. It has been shown that at room temperature  $Mn_3TeO_6$  adopts a trigonal structure, space group R-3 ( $a=8.8679(1)\text{\AA}$ ,  $c=10.6727(2)\text{\AA}$ ) and  $Co_3TeO_6$  the monoclinic spacegroup C 2/c ( $a=14.7830(2)\text{\AA}$ ,  $b=8.8395(1)\text{\AA}$ ,  $c=10.3426(2)\text{\AA}$ ).

A long-range magnetically ordered state has been identified through variable temperature neutron diffraction and magnetic susceptibility measurements. The magnetic structure for the two compounds is very different.  $Mn_3TeO_6$  has an incommensurate helix structure while  $Co_3TeO_6$  shows a complicated but commensurate spin structure.

**Keywords:** neutron, ferroic, magnetism

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### Thermal decomposition of ternary layered hydroxides

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Hydrotalcite are natural clays or synthetic defined as layered double hydroxides (LDH). These compounds exhibit various structural and chemical properties, besides having a high thermal stability, making them of great technological importance in obtaining new catalysts [1], [2].

Hydrotalcites samples containing Co, Mg and Al were subjected to increasing temperature in the range of 250-950 °C and measurements made X-ray diffraction in situ at Brazilian Synchrotron Light Laboratory (LNLS). The major changes occur between 250 and 400 °C, where the reflections of MgO begin to appear in X-ray diffraction (XRD) pattern. The XRD pattern reveals that the Mg-Al-Co hydrotalcite structure at 250 °C is not fully decomposed. It can be seen in relation to peaks in similar positions of the sample at room temperature, although only slightly wider and overlapped peak are observed. At temperatures above 400 °C the sample is completely decomposed and shows the disappearance of reflections at angles less than 30° indicating that the

structure of hydrotalcite collapsed during the calcination. In this stage occurs the formation of corresponding mixed oxides, a spinel mixture ( $MgAl_2O_4$ ,  $Co_2MgO_4$ ,  $Al_2MgO_4$ ), and overlapping peaks of oxides as  $Co_3O_4$ . Between 400 and 600 °C, small variations are observed.

Calcination temperatures above 400 °C, occurs the  $Co^{2+}$  to  $Co^{3+}$  oxidizes forming phases  $Co_3O_4$ ,  $Co_2AlO_4$  and  $CoAl_2O_4$ . All these compounds have cubic symmetry Fd-3m and it is not possible to distinguish one type of spinel phase from each other. At temperatures higher than 950 °C apparently is no longer observed any kind of modification.

A study was conducted to verify the regeneration capacity of the layered structure of hydroxides triple by simple exposure of the calcined material into the atmosphere where there is the presence of carbon dioxide and moisture. This material was characterized by X-ray diffraction. For this study, the calcined products performed at 800 °C and at 950 °C were calcined for one hour at each temperature. The samples were left in an inert atmosphere of nitrogen until the measurement of XRD was performed. Upon completion of the measurement, the samples were exposed to the atmospheric environment for 1 week and again performed the XRD measurements. It could prove the existence of two crystalline phases after calcination, attributed to a magnesium oxide and another characterized as spinel. The second phase is thermodynamically more stable and contributes to the broadening of diffraction peaks of the sample. The product of calcination showed a low-quality crystal, although there was a slight increase in the crystallinity of the material after exposure to the atmospheric. After exposure of the samples the air for one week there was no change in the diffraction pattern, indicating that calcination above 800 °C do not regenerate the layered structure of hydrotalcite therefore did not have the memory effect.

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### The reordering transition in layer disordered solids: Rare earth-transition metal intermetallic.

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Planar faults are very frequently crystal defects. The quantification of this kind of defects has been the focus of attention since decades due to the fact that many alloys and compounds can be described as layer structures. The disruption of the periodicity in the stacking order leads to measurable effects in the profiles of the maxima of the diffraction pattern of a crystal. In this work, planar faulting is quantitatively studied beyond the model of independent faulting events [1], [2], [3] showing the strength of direct methods to extract defects information from the diffraction patterns [4], [5], [6]. The correlation length can be extracted from the diffraction data without need to assume the random faulting model by directly fitting the diffraction data. It is showed that the analysis of the decaying term of the probability correlation function, does not only allow quantifying the loss of memory in the system through the correlation length but also, the strength of interaction between faults. The behavior of the decaying terms turns

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  $\text{RE}_2\text{Co}_{17}$  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 LNL S 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 follow a path where the new phase appears within the disordered phase and grows without homogeneous reordering of the disordered arrangement.

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### 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  $\text{Sr}_5(\text{PO}_4)_3\text{Cu}_{0.1}\text{O}_{0.2}(\text{OH})_{0.8}$  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.

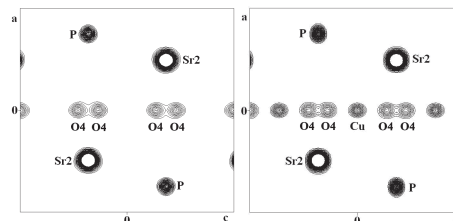


Fig. 1. Two-dimensional electron-density maps at  $y=0$  of pure hydroxyapatite (left) and hydroxyapatite with copper atoms (right).

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### 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