rare-earth sesquioxides $RE_2O_3$, have a very large thermal conductivity and low phonon energy values, required for laser operation. Special attention is focused in $Lu_2O_3$ doped with thulium ($Tm^{3+}$). The tunable laser emission of $Tm^{3+}$ $^3F_4 \rightarrow {}^3H_6$ around λ= 1.8-2.1 μm has many interesting applications as Tm-based lasers are being developed as depth-selective surgical scalpels due to the favorable coincidence with the 1.94 μm absorption peak of water [3].

Furthermore, $Tm^{3+}$ in $Lu_2O_3$ shows optical absorption and emission cross sections as well as crystal field splitting superior to those observed for corresponding Y- or Gd-based sesquioxides [4].They can be highly doped with lanthanide ions but the growth of high quality $Tm^{3+}$-$Lu_2O_3$ bulk single crystals is difficult due to its high melting temperature (over 2673 K) [2]. Therefore, synthesis at low temperature of nanocrystalline $Tm^{3+}$-$Lu_2O_3$ with narrow size distribution is a first step for obtaining transparent $Lu_2O_3$ ceramics by sintering.

Here we report the synthesis of $Lu_2O_3$ nanocrystals doped with different concentrations of $Tm^{3+}$ (0.5, 5, 8, 15 at. %) by a modified sol-gel Pechini method. The maximum temperature at which these nanocrystals have been synthesized has been 1073 K. In all cases, the obtained nanoparticles crystallize in the cubic system, with the space group of symmetry $Ia\bar{3}$. The mean particle size in all the cases was found from 10 to 30 nm with a mean particle size of 17 nm. Linear thermal expansion value was determined by refinement of X-ray diffraction patterns at different temperatures with a value of $\alpha = 7.5 \times 10^{-6}$ $K^{-1}$. Time evolution of grain size obtained from Scherrer equation show a crystal growth activation energy of $\Delta E = 76$ kJ/mol in the range of 723-1267 K. A grain growth exponent of n = 2.28 was obtained and associated to a diffusion growth mechanism.

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**Keywords: nanocrystal, thermal, expansion, rare-earth, crystal, growth**

## MS74.P08

*Acta Cryst.* (2011) A**67,** C673

**Structural elucidation of functional MOFs using Powder X-ray diffraction**

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Research on Metal-Organic Frameworks (MOFs), more generally defined as coordination polymers, has strongly relied over the years in the systematic isolation of crystals large enough for full structure elucidation using X-ray diffraction. Due to the intrinsic properties of either the synthetic methods or the building blocks of the networks, many of these compounds can only be isolated as microcrystalline powders and their structure remains, therefore, unexplored. For many direct applications microcrystalline powders possess, however, a great number of advantages over large single-crystals. Most of these structures are not porous and functionality arises at the surface of the individual crystallites. A striking example, concerns their use as heterogeneous catalysts. The higher external specific area of microcrystalline powders can, thus, boost the observed properties. In addition, synthetic methods leading to microcrystalline powders are significantly less time-consuming and the isolated materials are more easily processed into devices for potential industrial applications.

Over the last years our research group has been using highly flexible organic ligands based on chelating phosphonic acid groups: (carboxymethyl)iminodi(methyl-phosphonic acid) [1], [3] and nitril otris(methylenephosphonic acid) [4], [5]. The self-assembly of these molecules with rare-earth cations has led to the preparation of new photoluminescent materials [1], [2], [4], [5], many of which also exhibit interesting heterogeneous catalytic activity [2], [5] or can be employed as potential MRI contrast agents [3]. All these compounds were, however, systematically isolated as microcrystalline powders. This communication summarises our efforts to fully elucidate the fine structural features of these families of structures when combining X-ray diffraction data (high-resolution powder and micro-crystal X-ray data collected at the ESRF – Grenoble, France; laboratory powder data) with information from other techniques, in particular, solid-state NMR, FT-IR and FT-Raman spectroscopies, thermodiffractometry and photoluminescence studies. It will be shown that these techniques can provide crucial information on both the composition of the asymmetric unit and the local symmetry of the metallic centres to help in the unequivocal crystal solution and refinement of the materials.

Thanks are due to *Fundação para a Ciência e a Tecnologia* (Portugal) for their general financial support through the R&D project PTDC/QUI-QUI/098098/2008, and the ESRF (Grenoble, France) for granting access to the ID31, ID13 and BM01a research beamlines.

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**Keywords: metal-organic frameworks, powders, functional**

## MS74.P09

*Acta Cryst.* (2011) A**67,** C673-C674

**Particle statistics in φ- and ω-scan powder diffraction intensity measurements**

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We have recently reported that the effect of particle statistics [1] in powder diffractometry can experimentally be evaluated by statistical analysis of observed diffraction intensity data collected on stepwise in-plane ($\varphi$) rotation of a flat specimen with a laboratory Bragg-Brentano diffractometer [2]. The method can be applied to estimate crystallite size of several μm-order. It has also been suggested that the statistical errors in the observed diffraction intensities caused by finite number of crystallites can be evaluated for a stationary specimen by the same method.

A theory for particle statistics in symmetric reflection measurements of a rotating specimen has been proposed by De Wolff [3]. The validity of the theory may be examined by analysis of incident-angle ($\omega$) scan intensity data, but there still remains theoretical difficulty, because no theory for particle statistics has been established for asymmetric reflection-mode diffraction measurements. The $\omega$-scan measurements inevitably implies deviation of the $\varphi$-axis from the direction of the diffraction vector, which makes the situation further complicated.

In this study, $\varphi$-scan profile and $\omega$-scan profiles for both stationary and rotating specimens, measured at a synchrotron powder diffraction beam-line, KEK-PF BL-4B2, are compared. It is suggested that the

effect of particle statistics can be evaluated from the $\omega$-scan as well as the $\varphi$-scan data in the synchrotron parallel-beam geometry.

It has been proved that the effective number of diffracting crystallites is increased by a factor of about 100, by applying continuous $\varphi$-rotation of a flat specimen during the measurement, as predicted by the theory [3]. Errors caused by particle statistics, which should be incorporated in any analysis of powder diffraction data, will also be discussed.

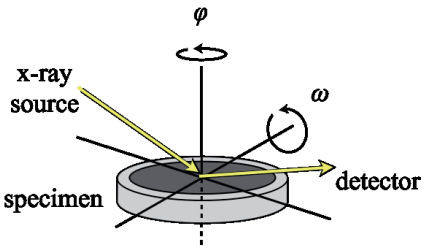


**Fig. 1 Definitions of $\varphi$ & $\omega$**

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**Keywords: powder, particle, statistics**

## MS74.P10

*Acta Cryst.* (2011) A**67,** C674

**A new mechanism of negative thermal expansion in an interpenetrated framework material**

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Negative thermal expansion (NTE) is an unusual property that has only been recorded in a small number of materials. However, we have recently found that metal-organic framework (MOF) materials have a number of structural characteristics that promote NTE.[1]

Conventionally, porous materials tend to support transverse vibrations, as motion into the empty pores is unhindered. Hence, in frameworks in which the previously empty space is occupied either by guest molecules or an interpenetrating framework, NTE is diminished. Here, however, we show that framework interpenetration can increase the magnitude of NTE over a similar framework when the normal thermal expansion of the intermolecular contacts between the two frameworks results in a structural distortion – a phenomenon unreported in other materials.

The studied material is MOF-14, a highly porous copper-carboxylate framework which forms a singly interpenetrated network.[2] We present single-crystal and powder diffraction data demonstrating the structural change of the material over a wide temperature range, clearly showing the nature of this new mechanism for NTE.

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**Keywords: negative thermal expansion, metal-organic framework, interpenetration**

## MS74.P11

*Acta Cryst.* (2011) A**67,** C674

**Advances in guinier-type powder diffraction**

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X-ray powder diffraction may be considered the main 'workhorse' in almost any field regarding solid state and materials sciences. Advances with instrumentation in recent years provided for major improvements with established methods but also induced the development of new and more specialized applications. The application of shorter wavelength (higher energy) X-rays while looking for higher resolution in the diffraction experiment is a principal contradiction calling for combinations of 'smart' solutions.

The Huber G670 Guinier system is very versatile and reliable, but at the same time simple and flexible for modifications towards more dedicated experiments. The imaging plate based detector system is well suited for any kind of typical lab-based X-ray sources ranging from Cr-Kα (5.4116 keV) up to Ag-Kα (22.1054 keV). However, much higher energies or synchrotron radiation may be used without any problems.

We have started to evaluate improvements and dedicated applications of the instrument on a broad basis. Concerning conditioning of the primary X-ray beam several options will be presented including 1-D and 2-D multilayer optics along with Johansson-type crystal monochromators. Such devices become very demanding in many respects when high-energy X-rays are targeted. Spot shaped beams are not commonly used with Guinier-type setups, however, a small but brilliant spot provides an excellent basis for studying small samples in general, but in particular with diamond-anvil cells or for typical samples in the fields of art and cultural heritage. Any setup discussed may be easily adapted to a broad range of X-ray sources. New ideas and developments towards improvement and modifications of the imaging plate itself but also for the entire detector system will be carefully considered.

Finally, improvements of the unit with respect to resolution but also concerning signal-to-noise ratio will be discussed with respect to the camera setup and the detector. Diffraction data of well defined samples will be presented for any particular setup evaluated. In numerous experiments we got increasingly convinced that Yttriumoxide is in many respects superior to most generally used standard materials.

**Keywords: powder, guinier, optics**

## MS74.P12

*Acta Cryst.* (2011) A**67,** C674-C675

**Real-time behaviour of crystallizing cocoa butter. Time-resolved SAXS-WAXS study**

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Almost 80% of cocoa butter (CB) in chocolate is crystalline. This is due to four different mono-unsaturated triacylglyceroles (SOS, POP, POS and SOA) which are structurally closely related and crystallise together. Their crystal structures are determined from XRPD together with the structures of the two most stable polymorphs of CB itself [1], [2]. In chocolate generally the β-V polymorph is present rather than the somewhat more stable form β-VI.

We studied the crystallisation process of pure CB time-resolved