

rare-earth sesquioxides  $\text{RE}_2\text{O}_3$ , have a very large thermal conductivity and low phonon energy values, required for laser operation. Special attention is focused in  $\text{Lu}_2\text{O}_3$  doped with thulium ( $\text{Tm}^{3+}$ ). The tunable laser emission of  $\text{Tm}^{3+} {}^3\text{F}_4 \rightarrow {}^3\text{H}_6$  around  $\lambda = 1.8\text{--}2.1 \mu\text{m}$  has many interesting applications as Tm-based lasers are being developed as depth-selective surgical scalpels due to the favorable coincidence with the  $1.94 \mu\text{m}$  absorption peak of water [3].

Furthermore,  $\text{Tm}^{3+}$  in  $\text{Lu}_2\text{O}_3$  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  $\text{Tm}^{3+}\text{-Lu}_2\text{O}_3$  bulk single crystals is difficult due to its high melting temperature (over 2673 K) [2]. Therefore, synthesis at low temperature of nanocrystalline  $\text{Tm}^{3+}\text{-Lu}_2\text{O}_3$  with narrow size distribution is a first step for obtaining transparent  $\text{Lu}_2\text{O}_3$  ceramics by sintering.

Here we report the synthesis of  $\text{Lu}_2\text{O}_3$  nanocrystals doped with different concentrations of  $\text{Tm}^{3+}$  (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  $\alpha = 7.5 \times 10^{-6} \text{ K}^{-1}$ . Time evolution of grain size obtained from Scherrer equation show a crystal growth activation energy of  $\Delta E = 76 \text{ kJ/mol}$  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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### 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 nitrilotris(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, thermogravimetry 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.

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### Particle statistics in $\phi$ - and $\omega$ -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 ( $\phi$ ) rotation of a flat specimen with a laboratory Bragg-Brentano diffractometer [2]. The method can be applied to estimate crystallite size of several  $\mu\text{m}$ -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  $\phi$ -axis from the direction of the diffraction vector, which makes the situation further complicated.

In this study,  $\phi$ -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