

Single crystal elastic constants (SCEC) for new materials not available as single crystals can not be measured using conventional techniques. In principle, neutron diffraction patterns from a polycrystalline solid under known uni-axial stress contain sufficient information. The direction dependent strains and known applied stress yield the diffraction elastic constants (DEC) which may be used to estimate the SCEC via a tensor transformation and appropriate averaging. However, the external stress is not experienced identically by each crystal orientation and a micromechanical model is needed.

It is a long standing problem that, for a given set of DEC, to determine the micro-mechanical state has required known SCEC and *vice versa*. We report a novel method to solve this problem by adopting a parameter similar to the 'volume fraction' in the non-dilute Eshelby model [1] for overlapping strain fields in a polycrystalline solid. In detail, this parameter indicates how the elastic anisotropy of the crystallite affects its averaged internal stress when it is treated as an inclusion embedded in a matrix material – in this case the averaged effect of all the other crystals. Moreover the strain gradient solution for Eshelby's ellipsoidal inclusion [2] has been applied in this method to verify how the grain size and shape affect the micro-mechanical state and hence the experimental SCEC. In addition, the influence of crystallographic texture on both the micro-mechanical state and the experimental SCEC has been integrated into the new method. Taken together, the method demonstrates how the micro-mechanical state of a polycrystalline material is dependent not only on the macroscopic elastic properties, but also on the grain size and orientation of the crystallites. For given Young's modulus, Poisson's ratio, grain size, texture and a set of carefully determined diffraction elastic compliances, the proposed method is capable of simultaneously optimizing the micro-mechanical model AND the single-crystal elastic constants. This is achieved by an iterative routine that minimises the usual least squares residual constrained to be self consistent through balancing the microscopic and macroscopic strain energies and constrained to give the correct computed Young's modulus and Poisson's ratio compared with those measured independently.

Two MAX phase polycrystalline materials (Ti_3SiC_2 , Ti_3AlC_2) and a ceramic (ZrO_2) have been analysed using DEC from *in situ* neutron diffraction patterns, neutron diffraction texture measurements, the crystallite size, macroscopic Young's modulus and Poisson's ratio. According to these inputs, the optimized micro-mechanical state was then estimated as well as the SCEC for those materials. The SCEC of Ti_3SiC_2 were determined to be $s_{11}=5.094$, $s_{12}=-1.859$, $s_{13}=-1.199$, $s_{14}=4.823$ and $s_{44}=2.243$ and this outcome matches fairly well with our recently published results from an independent method [3].

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Morphotropic phase transition in a lead-free system $(1-x)\text{NaNbO}_3-x\text{CaTiO}_3$

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The phase diagram of solid solutions of PbTiO_3 with several ABO_3 type perovskites contains a morphotropic phase boundary (MPB) separating tetragonal and pseudo-rhombohedral (monoclinic) phase fields. The MPB composition has been found to be of special technological significance for numerous sensor and actuator devices, as the dielectric permittivity, electromechanical coupling coefficients and piezoelectric strain coefficients are maximized around this composition. In the well known commercial MPB systems, like $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT), $(1-x)[\text{Pb}(\text{Mg}_{(1/3)}\text{Nb}_{(2/3)})\text{O}_3]-x\text{PbTiO}_3$ (PMN-xPT) and $(1-x)[\text{Pb}(\text{Zn}_{(1/3)}\text{Nb}_{(2/3)})\text{O}_3]-x\text{PbTiO}_3$ (PZN-xPT), this peak in the composition dependence of dielectric and piezoelectric properties around the MPB has been linked with a change of crystal structure from tetragonal to rhombohedral through a narrow range of stability of monoclinic phases. The toxicity of lead oxide and its high vapour pressure during processing of these MPB ceramics have led to the search for alternative environmentally friendly materials free from lead. We present here the results of powder x-ray diffraction, powder neutron diffraction and electron diffraction studies in conjunction with dielectric measurements on a new lead free system, $(1-x)\text{NaNbO}_3-x\text{CaTiO}_3$ (NN-xCT), which reveal morphotropic phase transition. This morphotropic phase transition is unique as none of the end members are non-centrosymmetric (NaNbO_3 and CaTiO_3 are well known antiferroelectric and paraelectric materials, respectively under ambient conditions). The composition dependence of the room temperature dielectric permittivity of this mixed system exhibits a sharp rise in the composition range $0.12 < x < 0.20$ with a peak at $x \approx 0.16$. This anomalous rise in the dielectric permittivity is linked with a change of crystal structure from an orthorhombic structure in the Pbma space group for $x \leq 0.10$ to another orthorhombic structure but in the Pbnm space group for $x \geq 0.20$. This behavior is reminiscent of a similar rise in the dielectric permittivity near the MPB composition of the technologically important PZT and PMN-xPT ceramics due to a change of crystal structure from tetragonal to rhombohedral/monoclinic. We have also shown that the huge dielectric response in the morphotropic phase transition region $0.12 < x < 0.20$ is due to the presence of an incommensurately modulated structure in the morphotropic phase boundary region as confirmed by transmission electron microscopic studies. The peak in the room temperature value of dielectric permittivity of NN-xCT at $x=0.16$ is linked with a relaxor ferroelectric instability below the room temperature. The low temperature electron diffraction and powder x-ray diffraction studies suggest the possibility of a lock-in phase transition associated with the relaxor ferroelectric behaviour.

Keywords: morphotropic phase transition, incommensurate modulation, relaxor ferroelectric transition

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Structural characterization of $\text{Tm:Lu}_2\text{O}_3$ nanocrystals for laser ceramics

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Highly transparent cubic ceramic materials have received great attention due to the improvement reached in nanocrystalline technology [1] to obtain optimum isotropic precursor. Cubic materials, such as

rare-earth sesquioxides RE₂O₃, have a very large thermal conductivity and low phonon energy values, required for laser operation. Special attention is focused in Lu₂O₃ doped with thulium (Tm³⁺). The tunable laser emission of Tm³⁺ ³F₄→³H₆ 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, Tm³⁺ in Lu₂O₃ 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 Tm³⁺-Lu₂O₃ bulk single crystals is difficult due to its high melting temperature (over 2673 K) [2]. Therefore, synthesis at low temperature of nanocrystalline Tm³⁺-Lu₂O₃ with narrow size distribution is a first step for obtaining transparent Lu₂O₃ ceramics by sintering.

Here we report the synthesis of Lu₂O₃ nanocrystals doped with different concentrations of Tm³⁺ (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 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 (ϕ) 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 (ω) 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 ω -scan measurements inevitably implies deviation of the ϕ -axis from the direction of the diffraction vector, which makes the situation further complicated.

In this study, ϕ -scan profile and ω -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