of P are invariable, the extinction-affected P_m values suffer systematic percentage errors that vary between over 6% for the highest level of interaction and less than 1% for the lowest one. The main advantage of this approach is the gain in accuracy and, hence, physical reality of the data. Another advantage is that it allows for the capability of internal experimental checks without reference to any theoretical estimates. Indeed, the degree of approximation of the $R_{i,i*}$ value to the absolute value of the $i/i*$ ratio qualifies the capability of the XRD apparatus to acquire precise and accurate data.

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MS74.P03

Microstructural characterization of polycrystalline materials using a X-ray single-crystal diffractometer equipped with an area detector

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Two-dimensional (2D) diffraction patterns collected with an X-ray area detector (i.e., CDD, Image plate), available in modern X-ray single-crystal diffractometer (i.e., SMART APEX, Bruker, Germany), contain much more information than conventional linear scans (i.e., θ-2θ scan), collected using standard X-ray powder diffractometers equipped with a point detector [1]. For instance, depending on sample microstructural characteristics (grain size, crystallinity, preferential orientation, stress, etc.), Debye-Scherrer rings displayed in the 2D pattern might be continuous, spotty or display specific variation in the intensities along them. These features facilitate to differentiate among mineral phases that might be present in a sample and posibilite to extract useful information regarding their microstructural characteristics (grain size, preferred orientation of mineral grains). To facilitate the analysis of these patterns, we have developed a software tool (XRD2Dscan).

This software allows users to take full advantage of diffractometers equiped with an area detector but that can not readily process the information of diffraction patterns from polycrystalline materials. It has many capabilities for generating different types of scans (2Theta scan, Chi scan, d-spacing versus Chi angle, pole figures) which allows users to extract the maximum information from 2D patterns and use their single-crystal diffractometer as an advanced materials research equipment [2]. It also has a database with main crystalline phases for fast mineral identication. The benefits of using area detectors as applied to polycrystalline sample characterization will be illustrated through several examples. Specifically, we will show how crystal sizes can be calculated from the intensity profile of spotty diffraction rings produced by a polycrystalline sample (i.e., quartz, SiC and α-Al$_2$O$_3$).

This technique is complementary to X-ray line-broadening analyses (e.g. Scherrer method) and size range that can be determined is from 3 to 100 microns. On the other hand, we will show how to determine pole figures describing the 3D orientation of crystals in a textured polycrystalline material. In particular, we apply this methodology to study the crystallographic properties (epitaxy, twinning) of different biomaterials such as mollusk shells which are constituted by superimposed layers of calcium carbonate (calcite or aragonite) crystals arranged in highly organized and complex shell microstructures.

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MS74.P04

To Deuterate or not? That is the question

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Accepted wisdom when performing diffraction experiments with neutrons is, wherever possible, to deuterate the sample as collecting data from the hydrogenous analogue is complicated by the large incoherent scattering background contribution from hydrogen. Recent work has shown that high-flux, medium-resolution continuous wavelength (CW) instruments can overcome this background problem. [1-5] Here, I present the case for not deuterating small-molecule inorganics and organics as, with proper optimisation procedures for the instrument set-up, data collection strategy and correction techniques, it is possible to investigate a wide range of systems.

Specific focus will be given to the ongoing project to re-determine σ_H incoherent as a function of incident neutron wavelength. The lack of an in-depth study to accurately quantify its variation with wavelength is surprising as it is the largest contributing factor to the absorption coefficient that is used in both single-crystal and powder neutron diffraction experiments to calculate the optimal absorption correction and sample size for hydrogen containing compounds.

The practical effect is that the attenuation of the neutron beam (both incident and scattered) by the sample changes as a function of neutron wavelength and path length through the sample, with striking implications for quantitative analysis of time-of-flight (t-o-f) neutron data. The aim is to collect the necessary information to implement an empirical correction routine for CW and t-o-f data as a function of wavelength in the thermal neutron range. This correction would allow a significant number of users to perform routine data collections on hydrogenous materials without the need for deuteration (and the often observed changes in properties upon deuteration) impacting directly research in technologically important fields such as proton conductors, fuel cells and pharmaceuticals.

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MS74.P05

Determining single-crystal elastic constants from neutron powder diffraction

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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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Keywords: single-crystal elastic constants, micro-mechanical state, ellipsoidal inclusion

MS74.P06

Morphotropic phase transition in a lead-free system (1-x)NaNbO$_3$-xCaTiO$_3$

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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 $Pb(Zr_xTi_{(1-x)})O_3$(PZT), $(1-x)[Pb(Mg_{(1/3)}Nb_{(2/3)})O_3]$-$xPbTiO_3$(PMN-xPT) and $(1-x)$ $[Pb(Zn_{(1/3)}Nb_{(2/3)})O_3]$-$xPbTiO_3$(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, $(1-x)NaNbO_3$-$xCaTiO_3$ (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 $x\approx0.16$. 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 $x\leq0.10$ to another orthorhombic structure but in the Pbnm space group for $x\geq0.20$. 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

MS74.P07

Structural characterization of Tm:Lu$_2$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