

Radiation effects in nano powders. CeO₂ and aliovalent substitutions in CeO₂ as simulants of PuO₂

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Context

- Fluorite-related materials are encountered in nuclear applications
 - Advanced fuels
 - Matrix for minor actinides.
- Several of these compounds display great resistance to radiation-induced amorphisation, but there seem to be differences in the detailed mechanism and even broader structural varieties.

Radiation effects in nanocrystals

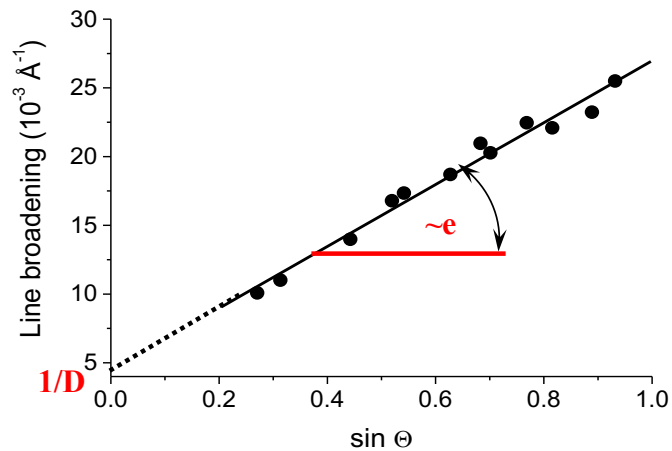
- Our understanding of radiation damage processes in ceramics remains limited, especially in regimes characterized by pronounced dynamic annealing, a process that refers to the migration and interaction of point defects (during irradiation) after the thermalization of ballistically generated collision cascades over time scales of about 1 ps
- Nanocrystalline systems behave distinctly from their coarse-grained counterparts. It is clear from simulation and characterization experiments that crystallinity extends to the interface and that an interface can grow or shrink during plastic deformation. Atomic diffusion processes in nanocrystalline materials differ fundamentally from the processes of their coarse-grained or single-crystal counterparts.

- Nanostructured materials provide us with a way to study the intrinsic influence of these interfaces with the potential to predict irradiation resistance at the nanoscale.
- As an example, the transition to smaller grain sizes, and thus higher grain boundary density, introduces unique mechanical deformation mechanisms that are responsible for various atomic-scale interactions, such as the accumulation of dislocations, which no longer occur below a critical crystal size.
- Our focus is on damage accumulation in nanocrystals when the size of the system is commensurate with the dimension of the subcascade or the ion track

Crystallite size and microstrain

Scherrer's formula

Line broadening only due to the crystallite size. Microstrain is neglected.



$$\frac{B(2\theta)\cos(\theta)}{\lambda} = \frac{1}{D} + \frac{4\varepsilon\sin\theta}{\lambda}$$

Crystallite size

Microstrain

Warren-Averbach or Krivoglaz methods

Fourier analysis of diffraction profiles taken in symmetrical geometry

But problems with low intensity of diffraction lines in thin films and with preferred orientation of crystallites.

Non-Uniform Lattice Distortions

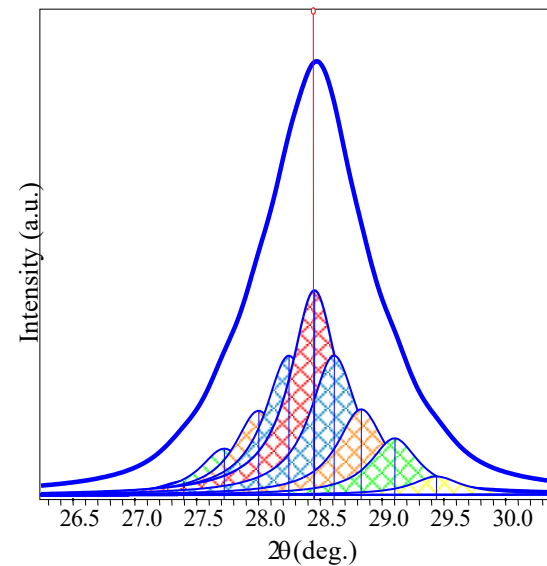
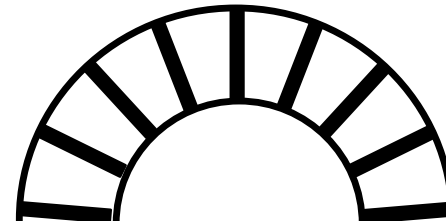
Rather than a single d-spacing, the crystallographic plane has a distribution of d-spaces

This produces a broader observed diffraction peak

Such distortions can be introduced by:

- Anisotropic surface tension
- Morphology of crystal shape
- Interstitials, impurities

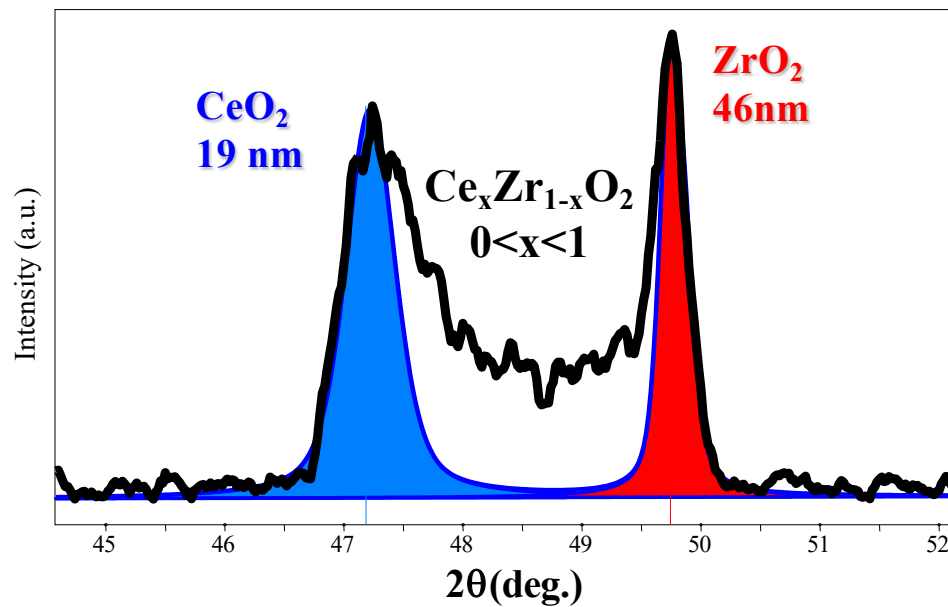
Easily measurable in a XRD experiment



Solid Solution Inhomogeneity

Variation in the composition of a solid solution can create a distribution of **d-spacing** for a crystallographic plane

Similar to the d-spacing distribution created from microstrain due to non-uniform lattice distortions



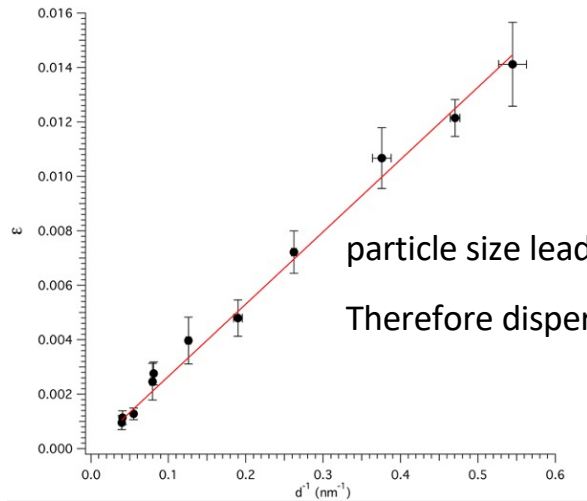
Confinement, strain & defects

In bulk, defect-free crystalline materials, only $q = 0$ phonons can be Raman active and observed

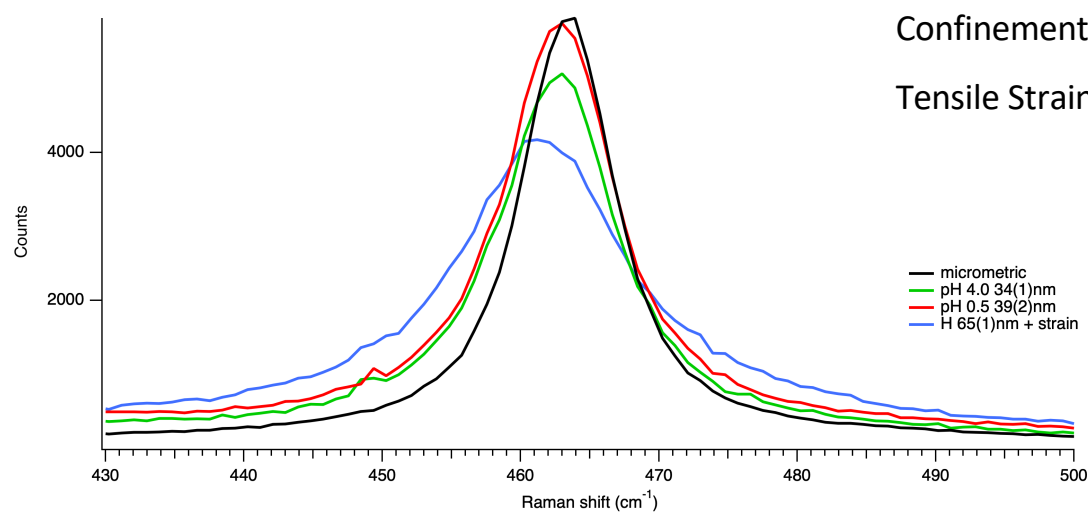
As the crystallite size of a material is reduced, an increasing volume of the reciprocal space is sampled in Raman scattering

$$I(\omega, x) \propto \sum \int \frac{\exp\left(\frac{-q^2 x^2}{8\beta}\right)}{\{\omega - [\omega_i(q) + \Delta\omega_i(q, x)]\}^2 + (\Gamma/2)^2} d^3q$$

Controls phonon spatial confinement



Raman scattering: CeO₂ (monodisperse nanopowders)

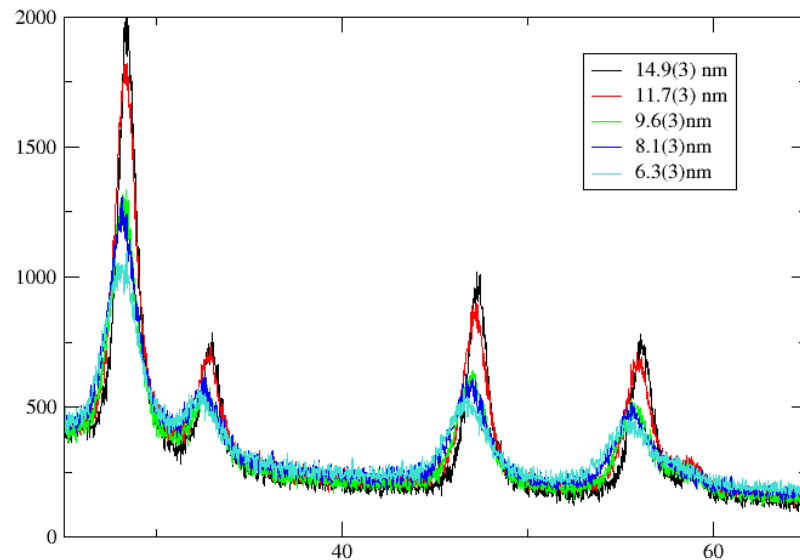


Confinement (size)-> gaussian broadening

Tensile Strain (hydrostatic)-> lattice changes -> softening and broadening

Pure nanocrystals might be sensitive to O partial pressure during irradiation
Our previous experiments show system reduction and O vacancies ordering

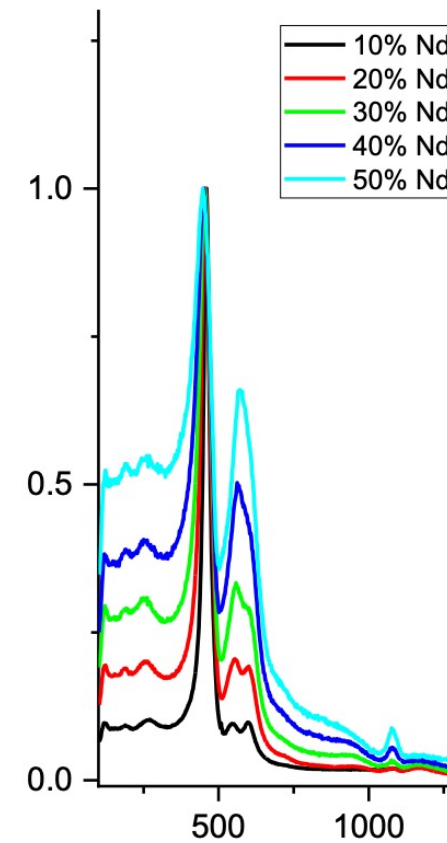
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Confinement (size)-> seems a small effect in Nd substituted samples

presence of oxygen vacancies -> T_{2g} hardening, extra modes

But micro-strain increases with Nd substitution (entropy): asymmetric broadening on T_{2g}



Radiation effects in nanocrystals: open questions we want to address

- Can we effectively use Raman scattering to probe supersaturated defects produced by radiation?
- Do these defects concentration are homogeneous in a nanocrystal?
- What happens when track sizes approach particle sizes?
- Do surfaces really act as defect sinks?
- Are all surfaces and interfaces created equal?