X-ray line broadening analysis in $(Gd_{0.1}Y_{0.9})_2O_3$ and $(Yb_{0.135}Y_{0.865})_2O_3$ nanopowders

B. Antic[1], A. Kremenovic[1,2] , A. Meden[3] and B. Jancar[4]

[1] Institute of Nuclear Sciences "Vinca", Solid State Physics Laboratory, P. O. Box 522, 11001 Belgrade, Serbia

[2] Faculty of Mining and Geology, Laboratory for Crystallography, University of Belgrade, Djusina 7, 11000 Belgrade, Serbia

[3]University of Ljubljana, Faculty of Chemistry and Chemical Technology, 1000 Ljubljana, Slovenia

[4]Jozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

Mixed sesquioxide $(Gd_{0.1}Y_{0.9})_2O_3$ and $(Yb_{0.135}Y_{0.865})_2O_3$ have been synthesized by thermal decomposition of complex compounds with acetilacetonato ligands and high energy ball milling, respectively. The as-prepared sample $(Gd_{0.1}Y_{0.9})_2O_3$ (U1) was annealed at 500 °C (U2) and 700 °C (U3) while $(Yb_{0.135}Y_{0.865})_2O_3$ (S1), was also annealed at 650 °C (S2) and 950 °C (S3). HR-TEM photographs show that the particle size is 5 nm in Gd,Y mixed oxide (U1) and 15-20 nm in Yb,Y mixed oxide (S1). Particles were nearly spherical in shape.

The corresponding diffraction patterns were indexed in space group *Ia3* . X-ray powder diffraction data were used to refine crystal structures and microstructure. Size/strain analyses have been done by the refinement of regular TCH-pV function parameters (isotropic effects) and the refinement of multipolar functions, i.e., symmetrized cubic harmonics (anisotropic effects). The average apparent crystallite size of the U1-U3 was 10-64 nm. The values for S1-S3 were from 3.6-8.5 nm. These results indicate that one average particle is composed of one or a few crystallites.

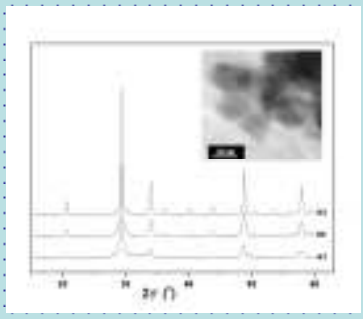
Changes of microstructure parameters with annealing were analysed. The X-ray line broadening anisotropy due to a strain effect decreases from U1 to U3 (average apparent strain and estimated degree of anisotropy in parentheses: 31(2) 10^4 for U1, 30(3) 10^4 for U2 and 19.57(2) 10^4 for U3), while the crystallite size anisotropy increases from U1 to U3 (average apparent crystallite size and estimated degree of anisotropy in parentheses: 98(21) Å for U1, 127 (31) Å for U2 and 642 (357) Å for U3).

Obtained results for S1-S3 indicate that average apparent crystallite size increases and average maximal microstrain decrease with temperature increase. Small anisotropic XRPD line broadening only due to crystallite size effect could be noticed. As the annealing temperature increases anisotropy of XRPD line broadening slightly decreases.

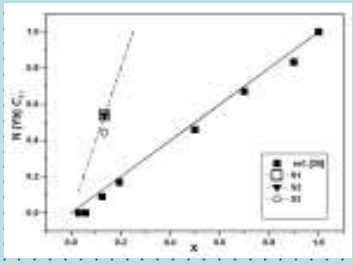
By refinement of occupation numbers, it was found that Gd^{3+} preferentially occupies C_{3i} sites in host Y_2O_3, forming a metastable cation distribution. Also, a variable cation distribution in Y,Yb mixed oxide depending on particle size was found.

The magnetic susceptibility of nanosized Er_2O_3 indicates the antiferromagnetic ↔ paramagnetic transition at 1.8 K or lower, while in ultrafine such as in a bulk counterpart the transition was observed at noticeably higher temperature of ~ 3.4 K.

Crystal structure of Y_2O_3:Yb

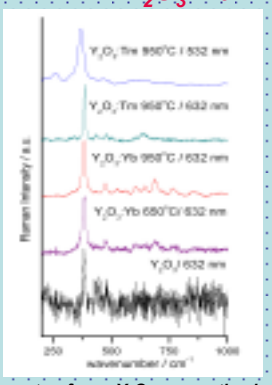


X-ray powder diffraction patterns of the Yb:Y_2O_3 samples: as-prepared (S1), annealed at 650 °C (S2) and annealed at 950 °C (S3). The inset: TEM micrograph for S1.

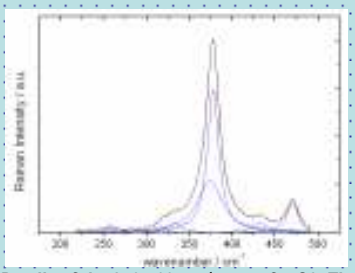


Occupation number values (N) of Yb^{3+} for the C_{3i} site versus composition (x) for $(Yb_xY_{1-x})_2O_3$. The straight line denotes N values for random Yb^{3+} distribution, while the dash-dot-dot line denotes N values for Yb^{3+} exclusively distributed in C_{3i} sites.

Raman spectra of Y_2O_3:Yb

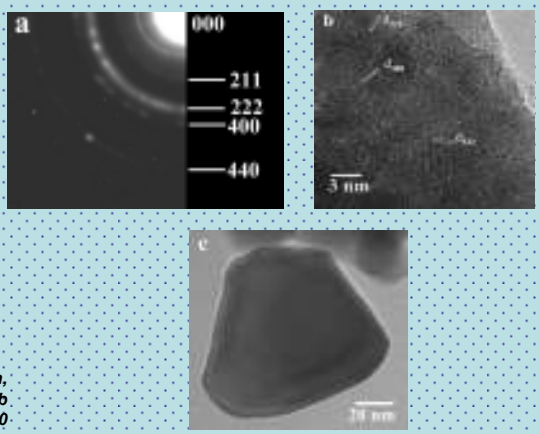


Raman spectra for : Y_2O_3 as-synthesised / 632nm, Y_2O_3:Yb annealed at 650 °C / 632 nm, Y_2O_3:Yb annealed at 950 °C / 632 nm, Y_2O_3:Tm annealed at 950 °C / 632 nm and Y_2O_3:Tm annealed at 950 °C / 532 nm.



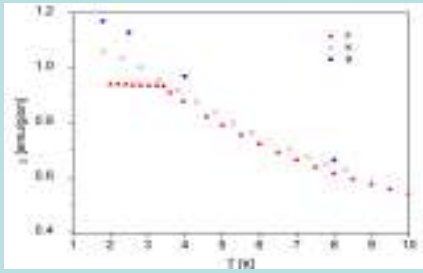
Details of the 250-500 cm^{-1} range for S3. The main 378 cm^{-1} peak is asymmetric and can be decomposed in different components, a rather narrow Lorentzian peak (characteristic for the cubic phase) and a broader one (characteristic for the distorted monoclinic phase).

Microstructure of Er_2O_3



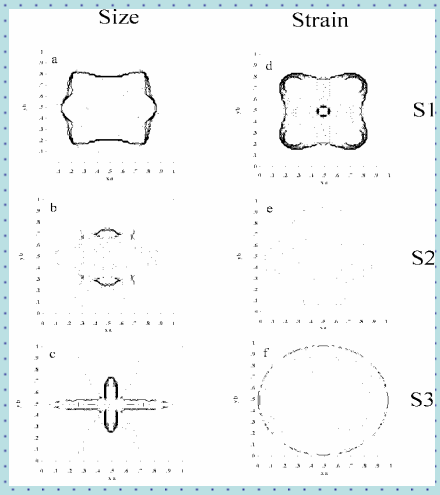
a) Electron diffraction pattern of the cubic form of 5 nm- Er_2O_3 particles
b) HRTEM image of 5 nm - Er_2O_3 particles
c) HRTEM image of ultrafine - Er_2O_3 particles

Néel temperature vs. particle size



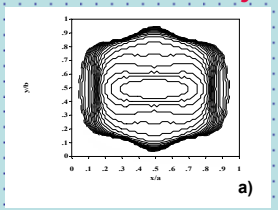
The low temperature susceptibility of (▲)-ultrafine - Er_2O_3 and (○)-5 nm - Er_2O_3 . (■)-susceptibility of 5 nm - Er_2O_3 from linear fit of M(H) in weak magnetic field.

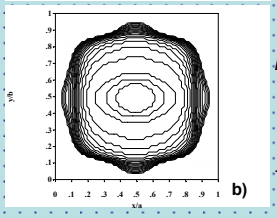
Size/strain analysis in Y_2O_3:Yb

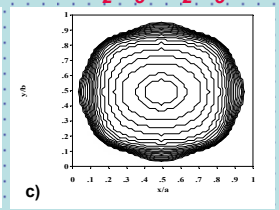


Average apparent size (a-c) and strain (d-f) for S1-S3, respectively.

Size/strain analysis in Gd_2O_3 / Y_2O_3

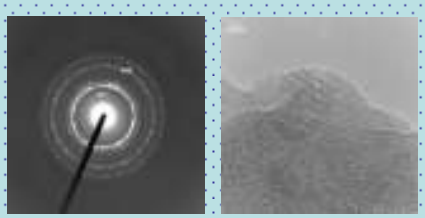






Gd_2O_3/Y_2O_3

Projections of the three-dimensional body that represents "apparent ctystallite size" in the (001) crystallographic plane; As-prepared sample (a), annealed at 500 °C (b), annealed at 700 °C (c)



SAED pattern and HRTEM image of as-prepared $(Y_{0.9}Gd_{0.1})_2O_3$