Experiment title: Vibrational spectroscopy of Eu in europium oxide nanoparticles	Experiment number: CH-1564

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Report:

The physical and chemical properties of nanostructured ceramic oxide materials are both of fundamental and technological importance. In particular, the optical properties of rare-earth complexes in sol-gel matrices and of nanosized oxide clusters have been intensively studied, since their luminescence may be used for markers in medical diagnostics [1–3], optical sensors [4], flat-panel displays [5] and many more. The energetically sharp 4f—4f transitions, with wavelengths in the visible range, are particularly suited for that purpose.
It is well known [6] that the luminescence quantum yield of Eu^{3+} complexes is strongly influenced by the chemical environment of the rare-earth ion, since the presence of O–H oscillators may decrease the lifetime of the excited state by vibronic coupling to the $^5D_0$ — $^7F_2$ transition [7].
Recently, the synthesis of surface-capped cubic Eu_2O_3 nanocrystals was reported, whose luminescence quantum yield increased with decreasing size [8] although the electronic transition is strongly localized on the Eu^{3+} ion and therefore should not be very susceptible to quantum size effects. It was speculated that the surface coating would passivate defects within the crystal wandering from the interior to the surface [8].
We have undertaken a detailed study of nanoparticles prepared according to the route described in [8], using

- nuclear inelastic scattering (NIS) to determine selectively the vibrational density of states (VDOS) of the europium atoms,
- EXAFS spectroscopy to determine the local structure around the europium atoms,
- X-ray powder diffraction to assess the degree of crystallinity
- AFM for particle size determination, and
- IR absorption, elementary analysis (EA) and differential thermal analysis (DTA) for further characterization.

Tapping-mode AFM showed that the particles prepared according to [8] had an average size of 15 nm.

The NIS experiment was carried out using a nested high-resolution monochromator (inner crystals: Si (12 12 8), outer crystals: Si (4 4 0) having an overall energy resolution of about 1.2 meV. The powdered samples were pressed into disk shape (8 mm diametre), sealed into copper holders with kapton windows and placed nearly horizontally with 5° inclination to the beam, in order to ensure maximum count rate. Figs. 1 and 2 depict the total and reduced vibrational densities of states of the europium atoms in commercially available bulk and uncoated 58-nm-sized Eu_2O_3, as well as the spectra of four samples prepared under slightly different conditions (different stirring speeds etc.) according to [8]. Fig. 3 shows the VDOS of one of the 15 nm samples for three different temperatures.

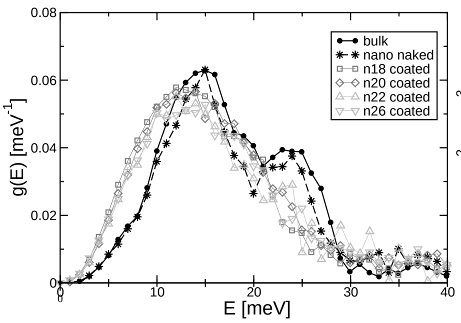

Fig. 1

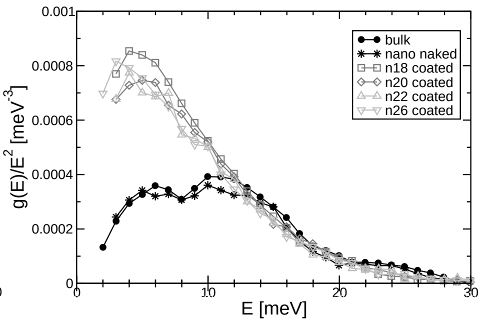

Fig. 2

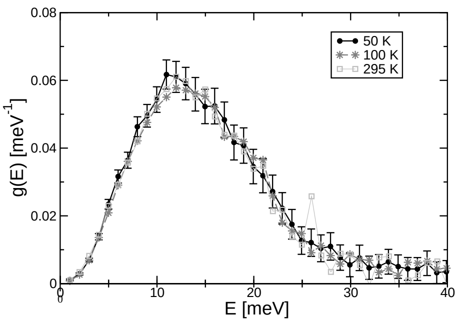

Fig. 3

The following features can be observed:

1. There is no difference of the VDOS of the Eu atoms in bulk and uncoated 58 nm particles, which still exhibit mostly bulk behaviour
2. The high-energy of solid Eu_2O_3 are suppressed in the 15 nm particles in favour of a strong increase of soft modes.
3. The VDOS in all investigated systems is entirely independent of temperature, i.e. we have harmonic behaviour throughout.
4. A pronounced Boson peak in the 15 nm particles points to strong static (structural) disorder

The other characterizations revealed that instead of Eu_2O_3, the 15 nm particles contain predominantly a mixed oxyhydroxide phase. Hence, the quantum size effect, if it exists, is masked by the chemical difference with respect to pure Eu_2O_3.

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