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Structural transition in rare earth oxide clusters

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Size effects, such as structure transition, have been reported in small clusters of alkali halide compounds. We extend the study to rare earth sesquioxide (Gd_2O_3) clusters which are as ionic as the alkali halide compounds, but have a more complicated structure. In a clean and controlled environment (ultra high vacuum), such particles are well crystallized, faceted and tend to adopt a rhombic dodecahedron shape. This indicates the major role of highly ionic bonds in preserving the crystal lattice even at small sizes (a few lattice parameter). Based on both cathodo-luminescence and transmission electron microscopy, we report the existence of a structural transition from bcc to monoclinic at small sizes. © 2006 American Institute of Physics. [DOI: [10.1063/1.2390693](https://doi.org/10.1063/1.2390693)]

Ionic compounds present huge potential applications as nanoparticles or nanowires, in particular for the design of nano-light sources. Pioneering studies have focused on slightly polar semiconductors (CdSe...).^{1,2} Recent studies concentrate on weakly ionic compounds, doped or not (ZnO, GaN, CdSe).^{3,4} However, another class of ionic materials, the rare earth sesquioxides, is gaining more attention for its potential use as phosphor particles for nanophotonics, or bio-labelling. Few works, as compared to semiconductors, have yet been devoted to investigate the modifications of the fundamental properties of highly ionic particles induced by their size reduction. In particular, the stability of the crystal lattice in ionic nanoparticles has attracted much attention recently. In weakly ionic compounds, such as TiO_2 , it has been reported that reducing the size can help to stabilize either the anatase or the rutile phase, or even to obtain fullerene-like particles.⁵ Highly ionic compounds, such as alkali halides, have been the focus of several studies in clusters physics too.⁶⁻⁹ In highly ionic compounds, the lattice can be regarded as the simplest example of a highly correlated system in the Wigner-Seitz low density limit.¹⁰ One of the fascinating aspects of the theory is the existence of well ordered structures down to sizes as small as a few Angstroms.⁷ Global minima are well described by Coulomb plus Born-Mayer potential.¹¹ For instance, NaCl clusters exhibit a cuboid form in agreement with the solid.^{7,12} Structural transitions between clusters with different cuboidal shapes are reported, but the global symmetry remains cubic as observed in bulk phase. Krückerger *et al.*⁶ reported a phase transition in $(CsI)_nCs^+$

clusters with isomeric structures around $n=32$. In this case, NaCl ($Fm\bar{3}m$) structure dominates for the smallest sizes, CsCl ($Pm\bar{3}m$) being the structure in bulk phase. However, an ultimate conclusion on structure stability versus size for ionic clusters is elusive for several reasons. Since most of the experiments are done with very small ionized clusters, the net charge plays a leading role in the stability. Moreover, the small number of atoms strongly favors magic numbers corresponding to close shell structures. Eventually, the stability of the planes, directly or indirectly controlling the structure of nanoparticles, is an awkward issue as can be understood from the vast literature concerning surfaces of ionic films (see Ref. 13 and references therein). The issue is even more complicated if one considers the possibility of chemical reactions, essentially hydroxylation,¹⁴ on the surface of the particles that can change the stability of a given plane. In this context, the high reactivity of alkali halide clusters forbids to deposit and to study them for a long time even in ultra high vacuum (UHV). This is the reason why all the previous studies have been performed in the gas phase. In this letter, we address the issue of structure stability of highly ionic clusters of practical interest, namely the rare earth sesquioxide clusters. As mentioned above, these clusters are interesting candidates as stable light sources for nanophotonics and bio-labelling. On a fundamental point of view, the experimental limitations encountered with alkali halide clusters mentioned above can be overcome with this class of compounds, and in particular with Gd_2O_3 clusters. Indeed, Gd_2O_3 has a Pauling ionicity f_i comparable to that of alkali halide materials ($f_i > 0.9$). Furthermore, a few percent of Gd^{3+} ions can easily be substituted with Eu^{3+} ions. These latter exhibit a sharp visible (red) luminescence due to transitions between their $4f$

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levels. This kind of radiative transition, normally forbidden, is allowed by Stark effect resulting from the coupling of these levels with the crystal field of Gd_2O_3 . It is therefore a powerful probe of the local symmetry in relation with the lattice structure.^{15,16} However, the rare-earth sesquioxide structure is more complex than that of alkali halide compounds. Under ambient conditions of pressure and temperature, Gd_2O_3 adopts a bcc structure ($Ia\bar{3}$) with 80 atoms per unit cell, while at high pressure or high temperature, it crystallizes in the $C2/m$ monoclinic structure, with 30 atoms per unit cell. Consequently, the benefit in experimental study gained by using such materials is counterbalanced by a more complex description of the material, as compared to alkali halide compounds. Nevertheless, this is interesting if one seeks to generalize the results obtained with simple ionic clusters to more complex ones.

The cluster films have been deposited using the low energy cluster beam deposition (LECBD) technique which has been described in details elsewhere.¹⁷ Two kinds of samples of Gd_2O_3 clusters doped with 10 % of Eu^{3+} ions in substitution of Gd^{3+} ions have been produced by deposition on either amorphous carbon films for subsequent transmission electron microscopy (TEM) analysis or HF-cleaned silicon substrates for both x-ray photoelectron spectroscopy (XPS) and cathodo-luminescence. According to TEM analysis, the samples have a mean size of 3.2 and 2.3 nm, respectively, and a size dispersion less than 1 nm.¹⁸ The composition of the clusters has been investigated by x-ray photoelectron spectroscopy.¹⁹ No carbon contamination has been detected on the deposited clusters. Only a weak OH contamination has been observed. Even though this contamination may influence the luminescence of the clusters (broadening of the peak), it has no effect on the cluster structure. Furthermore, it did not evolve significantly over a period of a few hours in UHV. The analysis confirms that the cluster films have the expected stoichiometry of Gd_2O_3 with 10% of Gd^{3+} ions substituted by Eu^{3+} ions. This is of prime importance since the stoichiometry directly controls all the properties and in the first place the structure. It is worth noticing that Eu^{3+} ions can easily substitute Gd^{3+} ions due to their similar chemical behaviors and ionic radii. This, in addition to the fact that our synthesis process is governed by kinetics, ensures that Eu^{3+} ions are actually embedded in the clusters.

The cluster structure has been directly analyzed by TEM on several hundreds of particles and by high resolution transmission electronic microscopy (HRTEM) on several tens of particles. A major part of the particles observed on each micrograph corresponding to the sample with the largest cluster mean size exhibits at least one atomic plane family ($\approx 60\%$ without tilting the sample, the non diffracting particles being obviously the smallest). In contrast, for the sample with the smallest cluster mean size, surprisingly few particles exhibit diffracting plane families. Figure 1 (middle left) reproduces a typical Gd_2O_3 cluster, with a diameter of 3 nm. For all the clusters showing two diffracting plane families or more, the structure corresponds to bcc with a cell parameter of 10.7 ± 0.1 Å. This is comparable to the bulk value of 10.71 Å for Gd_2O_3 doped with 10 % Eu^{3+} ions. Therefore, we can assert that no cell contraction occurs at this typical size. The

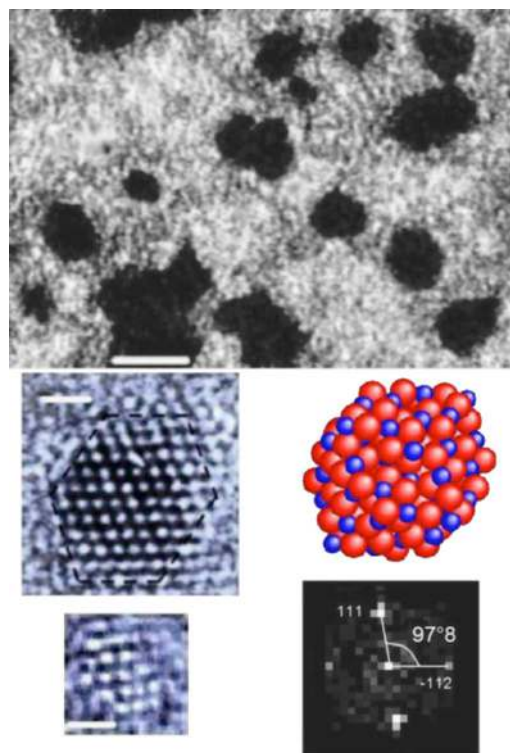


FIG. 1. Top, large TEM view showing several clusters of Gd_2O_3 doped with 10 % of Eu^{3+} ions. The facets of the clusters can be seen. The white bar represents 5 nm; middle left, a typical 3 nm cubic cluster imaged by HRTEM; middle right, ball and stick representation of a rhombic dodecahedron, limited by twelve (110) faces (zone axis [110]) corresponding to the cluster shown on the left; bottom left, a monoclinic cluster. The white bar represents 1 nm; bottom right, corresponding Fourier transform. The angle of $97^\circ 8'$ is the unambiguous signature of the monoclinic structure.

highly ionic bond in rare-earth oxides explains why the crystallization is easily preserved and observed among our clusters. This is in contrast to less ionic clusters where an amorphous phase can be obtained.

Besides, facets can be seen for a major part of the particles in the micrographs (see Fig. 1, top). This fact has not been reported for particles either synthesized by wet chemistry or sol-gel deposition.²⁰ We believe that our observation is made possible by the UHV conditions of synthesis. Moreover, 98 % of the particles showing two or more diffracting plane families point the [110] direction to the observer. This goes to show that they are standing on a (110) face. If the axis distribution of the clusters were isotropic, since there are six [110] directions and three [100] directions, one would expect only 66 % of the particles pointing the [110] axis to the observer. This gives credit to the existence of preferential faces on which the clusters stand. One last argument is the aspect ratio of the clusters. We have measured the ratio between the long and short axes and found a mean value of 1.4. The values range from 1–2.2. For the polyhedron formed with twelve (110) faces, the rhombic dodecahedron shown in Fig. 1 (middle right), the aspect ratio is $\sqrt{2}$. This analysis further supports the fact that Gd_2O_3 clusters produced in UHV tend to adopt a particular geometry: the rhombic dodecahedron. This polyhedron happens to be the first Brillouin zone associated with the bcc ($Ia\bar{3}$) structure of the lattice. It is not straightforward to predict the rhombic dodeca-

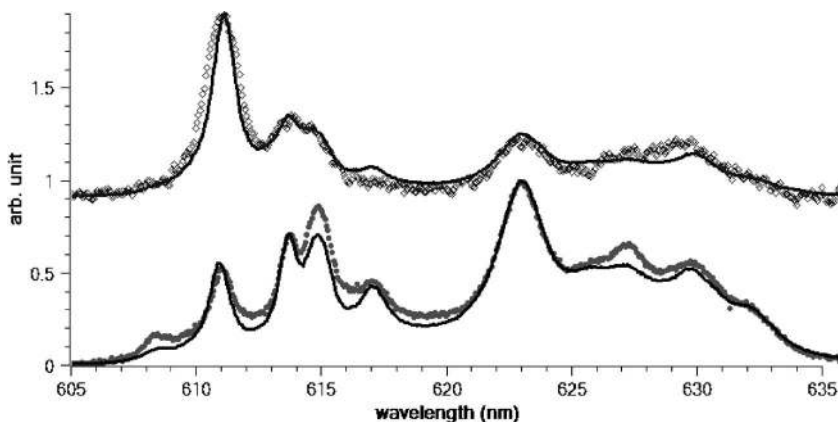


FIG. 2. 5D_0 - 7F_2 transition of Eu^{3+} excited by a 4 keV electron beam in clusters with a mean diameter of 3.2 nm (\diamond top) and of 2.3 nm (\bullet bottom) deposited on HF-cleaned Si substrates. The corresponding fit, obtained from a weighted sum of bulk cubic and bulk monoclinic spectra is shown in each case as a solid line.

hedron as the stable structure for our ionic clusters since there is a balance between the polyhedron with the largest compacity and the destabilizing term arising from the truncation in the Madelung series. However, one can notice that the (110) faces are neutral (no excess of charges) while (100) or (111) faces are not. In particular, the (100) planes contain only anions or cations. Thus, the (100) or (111) faces are not expected to be stable as they are in the NaCl or CsCl structures. Actually, one can imagine a structure more compact, than the rhombic dodecahedron. It is a complex polyhedron made with a set of (110) planes and (210) planes. The shape is intermediate to rhombic and pentagonal dodecahedron. Such a polyhedron has an aspect ratio closer to 1 and we cannot discard the existence of such a polyhedron among our clusters. We only state that it appears in a minority of cases. The reason for this stands in the fact that the surface energy, crudely evaluated with the simple bond breaking model, of a (210) face is 1.22 times higher than that of a (110) face.

The TEM analysis on the cluster structures is further completed by the cathodo-luminescence one. Figure 2 reproduces the luminescence spectra of Eu^{3+} ions in two cluster assembled films (20 nm thick) deposited on a passivated Si substrate and with a mean size of 3.2 and 2.3 nm, respectively. The measurements have been performed by *in situ* cathodo-luminescence. The samples have been excited by a 4 keV electron beam and the emitted light has been collected through an optical fiber to a Jobin-Yvon TRIAX 320 spectrometer and a CCD camera. The electron beam was continuous. Therefore, we did not perform *in situ* luminescence lifetime analysis. We have investigated specially the 605–635 nm range that corresponds to the most intense emission of the materials: the 5D_0 - 7F_2 transition of Eu^{3+} ions. The cluster films reveal two contributions, one from Eu^{3+} ions in a cubic environment, with 6 oxygen neighbors, and a second one from Eu^{3+} in a monoclinic environment, with 6 and 7 oxygen neighbors. We have fitted the measured spectra of both samples with a weighted sum of the spectra from bulk cubic and bulk monoclinic samples. The results are plotted in Fig. 2. The agreement between the fits and the experimental spectra is fairly good. A discrepancy is observed for the spectra from the clusters with the smallest mean size (particularly at 615 and 627 nm). The intensity ratios between the different peaks forming the spectrum are directly linked to the occupancy of the three distinct crystallographic sites avail-

able to the Eu^{3+} ions in bulk monoclinic Gd_2O_3 .²¹ Therefore, the observed difference reveals the modification of the occupancy of these three crystallographic sites compared to the bulk monoclinic phase. This change is likely to come from the increase in the surface ions in the cluster film. It may favor the presence of a certain site to the detriment of the others. Nevertheless, it appears clearly that the contribution from the monoclinic environment is enhanced in the spectrum from clusters with the smallest mean size. In this latter case, the ratio I_c/I_m of the cathodo-luminescence intensities of the cubic and monoclinic environments is 0.507 whereas it increases to 3.579 for the clusters with the largest mean size. Therefore, reducing the cluster size favors the presence of monoclinic environment for Eu^{3+} ions. The question then is to know whether these ions are embedded in particles with a real monoclinic structure or if they are just ions standing on or close to the surface of cubic particles with an excess of oxygen creating a local environment tantamount to a monoclinic one. The answer to this question is rather difficult. Indeed, no x-ray diffraction experiment can be performed satisfactorily on our films. First, the signal is weak because of the small amount of deposited matter. Second, even if we managed to see some diffraction peaks, their width would be too large to unambiguously assign them to a given structure. Raman spectroscopy would also be a mean to distinguish the amount of each structure. However, the Raman cross section of Gd_2O_3 is too weak to allow such a discrimination in very thin films. The only mean left is the HRTEM. As in x-ray diffraction, some main diffraction planes from both the cubic and the monoclinic structures are close. For instance, the (222) planes of the cubic lattice and the (111) or $(1\bar{1}1)$ planes of the monoclinic structure have a 3 % difference of their reticular distances. However, the precision of our HRTEM analysis is $\pm 1\%$ on reticular distances. This accuracy has allowed us to discriminate the monoclinic structure from the cubic one in clusters exhibiting one plane family. Even more convincing is the observation of a monoclinic cluster showing two plane families. The cluster shown in Fig. 1 (bottom) can unambiguously be attributed to the monoclinic structure. The angle of $97^\circ 8'$ between the diffraction spots of Fig. 1 (bottom right) is the signature of the monoclinic structure (the angle between the (222) and (-222) plane in the cubic structure is $70^\circ 53'$). The presence of entirely monoclinic clusters is therefore established. Eventually, the existence of

Eu³⁺ ions in a monoclinic environment embedded in a cubic cluster can further be discarded according to theoretical calculations by U. Landman and co-workers²² which have shown that the coexistence in ionic compound clusters (NaCl) of the high and low temperature phases is difficult among the same cluster. This, along with the TEM observation is strong hint that the luminescence signal from monoclinic environment effectively comes from monoclinic particles and not from monoclinic-like environment on the surface of the clusters.

The increase in the monoclinic signal with the size reduction reveals the appearance of some structure transition from cubic to monoclinic at small sizes. Such a transition is known for metallic clusters,²³ for alkali halide clusters,⁶ as well as for ionic oxide compounds such as TiO₂⁵ and ZnO²⁴ at the nanometer lengthscale. The structure transition is often explained as a consequence of the Gibbs' pressure induced by the surface. At ambient pressure, the temperature for the phase transition of Gd₂O₃ from cubic to monoclinic appears at 1450 °C. However, this transition needs a pressure of 3 GPa at room temperature.²⁵ For a diameter of the order of 3 nm, this leads to a surface tension γ of 2.25 N.m⁻¹. Such a value is in the typical range for oxide materials.^{13,26} The existence of such a phase transition is of importance since it seems to generalize the one observed on more simple alkali halide ionic clusters. Unfortunately, since the exact value of γ is unknown for the (110) faces, it is not possible to give an accurate value of the particle diameter for this transition at room temperature from this argument. However, a good estimate can be obtained. The ratio I_c/I_m depends on both the mass ratio m_c/m_m and the ratio α_c/α_m of the cathodoluminescence cross sections of the two crystallographic phases: $\alpha_c/\alpha_m = I_c/I_m \times m_m/m_c$. For the sake of accuracy, we have measured this last ratio for a mixture made of powders of both phases in equal quantity. The mixture constitution has been checked by x-ray diffraction analysis. The value, measured for an electron beam accelerated at 4 keV, is $\alpha_c/\alpha_m = 6.53$. This value is in agreement with the only previously published measurement.²⁷ Assuming that this ratio does not evolve when the size of the clusters is reduced, we deduce a mass ratio m_m/m_c equal to 93 % and 36 % for the distributions with a mean diameter of 2.3 and 3.2 nm, respectively. Based on the log-normal shape of the size distributions of the clusters, characteristic to accretion processes, and assuming that the structural transition appears abruptly at a particular size, the critical diameter corresponding to the structural transition is estimated to be 2.8 nm for both distribution. In this context, the observed reduction of the photoluminescence efficiency of rare earth oxide clusters with size²⁸ can be explained by their structure change, the cross section of the monoclinic phase being less than that of the cubic phase.²⁷

We have investigated the structure transition of highly ionic clusters (Gd₂O₃), doped with 10 % of Eu³⁺ ion. The TEM and cathodoluminescence analyses reveal that the particles are crystallized in the bcc (*Ia3*) structure for sizes down to 3 nm in diameter. This emphasizes the role of a highly ionic bond in the preservation of the crystal lattice at small sizes, in accordance with what is observed for alkali

halide clusters. Furthermore, we have observed that the particles, deposited in UHV, are faceted and tend to adopt a rhombic dodecahedron shape, which favors the neutral (110) planes. Eventually, reducing the mean size of the cluster distribution to 2.3 nm enhances the presence of monoclinic particles. This observation reveals the existence of a structure transition at small sizes (≈ 2.8 nm) from the cubic phase to the monoclinic phase. This transition is compatible with a crude estimate of the Gibbs' pressure undergone by the smallest clusters. The structure transition towards the high temperature or high pressure structure should hold for all rare earth sesquioxides M₂O₃ which adopt the cubic structure at ambient conditions (namely all of them but Ce₂O₃, and Pr₂O₃ and Nd₂O₃ which crystallize in the hexagonal P32/m structure). It generalizes a phenomenon previously reported for alkali halide clusters.

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