Comment on “Unusual Photoluminescence of $CaHfO_3$ and $SrHfO_3$ Nanoparticles”

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The manuscript by Rauwel et al.[1] reports the synthesis of hafnium-based perovskite nanoparticles by the “benzyl alcohol route”. The as-synthesized nanoparticles exhibit “unusual” luminescence properties, attributed by the authors to “luminescent centers located at the surface of the nanoparticles”.

The purpose of this comment is to stress that a precise knowledge of the chemical and structural characteristics of the material is the prerequisite for the assessment of structure-properties relationship. This is especially important at the nanometer-scale particularly because surface effects can dramatically influence the final properties of the material. We believe that the conclusions drawn by the authors are based on an incorrect interpretation of the characterization results. Thus, the interpretation of the “unusual” luminescence properties, i.e., “surface-related origin”, would have been different if the presence of organic species absorbed at the surface of the nanoparticles was considered.

The first issue that we want to address regards the structure determination of the samples by Rauwel et al. The powder XRD pattern of the as synthesized “$CaHfO_3$” nanoparticles (reported in Figure 1S) perfectly matches to cubic stabilized HfO_2 nanoparticles (cf. for example Figure 2 in ref. [2]). Indeed, it corresponds to the JCPDS card the authors refer to (N° 00-008-236), which is the one of the cubic HfO_2 phase stabilized by the inclusion from 8 to 40 mol% of calcium (cf. also the original paper this JCPDS card refers to[3]) and not to typical ABX_3 type perovskite structure. The formation of the orthorhombic (Pnma space group) perovskite $CaHfO_3$ structure is generally observed beyond 40 mol% of calcium (cf. for example JCPDS card N° 00-036-1473 and Figure 11 in ref. [3]). The powder XRD patterns of typical cubic or tetragonal perovskite structured nano-sized $(Ba,Sr)TiO_3$ and $BaZrO_3$ can be taken from Niederberger et al.[4,5] It should also be noted that the cubic (perovskite) modification of $CaHfO_3$ and $SrHfO_3$, which was used for the assignment of the reflections in the power spectra (PS), is stabilized at high temperature (cf. ref. [12] in the manuscript). These facts combined to the missing indexing of the selected area electron diffraction and the not clear analysis of the PS[6] lead to a questionable proof for the formation of the perovskite structure. Instead, the presented data indicates that calcium stabilized cubic HfO_2 was produced. Sadly, the powder XRD pattern of the $SrHfO_3$ is not shown.

The second point that we would like to address concerns the chemical characterization of the as-synthesized samples. Thermogravimetric analysis shows a large weight loss between 450 and 550 °C (Figure 2S) which can be attributed to the combustion of organic species. In fact, a weight loss of around 15% for the “$CaHfO_3$” and 30% for the “$SrHfO_3$” nanoparticles speaks for a full coverage of the surface of the nanoparticles. Similar termogravimetric analysis recorded from some oxides synthesized by the “benzyl alcohol route” that contain benzoate species, present exactly the same profile.[7–9] The similarity suggests that the surface of the “perovskite” particles introduced by Rauwel et al. is also terminated by benzoate species. Furthermore, the decomposition of carbonates obtained as secondary phase (e.g., calcite) takes place at temperatures above 600 °C, as also discussed by the authors. In this respect, it cannot be the reason for the large weight loss observed.

The presence of large amounts of benzoate species coordinated to the surface of the Hf-based particles presented in this work is also supported by XPS analysis of the C1s edge (Figure 4S) which shows two main contributions. The most intense one is characteristic of C atoms in aromatic C-C/C-H environment and is centered at a binding energy of around 285 eV. Such a position is usually observed from various carbonaceous species including contamination due to atmospheric exposure. More intriguing is the contribution centered at around 289 eV, which is generally not observed from atmospheric contamination. In the figure, the authors attributed it correctly to carboxylate species, although this is not discussed in the manuscript. A careful analysis of the peak positions and of their relative intensity reveals that the presented spectrum is in good agreement with the one observed for benzoate species (cf. for example ref. [10]). In situ formed benzoate species coming from the oxidation of benzyl alcohol are generally strongly bound to the surface of the oxides and participate in the control of the growth of the nanostructure. They are usually formed at relatively high temperature and can be catalyzed by metal centers. A peculiar example is the formation of rare-earth (RE) oxide-based lamellar organic-inorganic nanostructures under similar conditions.[7,9,11] For example, it was found that carboxylate species were the only organic moieties present between the inorganic RE_2O_3 layers. They form a bridge-like bond with the layer, and are thus responsible for the formation of the hybrid structure. It was

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proven that the metal centers (yttrium and lanthanides) act as catalyst for two subsequent reactions: i) the disproportionation reaction of benzyl alcohol to toluene and benzaldehyde taking place at the surface of the freshly formed rare earth oxide clusters, and ii) a Cannizzaro-like reaction leading to the formation of the rare earth oxide–benzoate nanocomposite under the elimination of toluene. Later on, the formation of benzoate species during the synthesis of metal oxides in benzyl alcohol was found to be more general. For example, benzoate species were found responsible for the morphology control during the formation of alkaline earth aluminates nanostructures.[8]

The two discussed concerns are a result of numerous inconsistencies in the manuscript. As a consequence, the conclusions are also misleading. For instance, the discussion about the "unusual" optical properties of the "perovskite" nanoparticles cannot be made without taking into account the large amount of organic species present at their surface. As a matter of fact, the absorption band with onset at 4.2 eV, which is the main contribution to the spectra presented in Figure 4a, can be safely attributed to the above discussed benzoate species present at the surface of the particles.[12] For example, in the case of RE_2O_3-benzoate hybrid materials, it turned out that de-excitation can lead to a large emission band between 400 and 600 nm.[12]

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[6] The ratio between the d-spacings measured from the PS of the $CaHfO_3$ (Figure 1d) is very different to the one expected for a cubic structure. From the PS one can easily measure $d_{110}/d_{200}=1.62$, which is very different from the expected value ($d_{110}/d_{200}=1.41$). Such a large difference speaks for another orientation and/or structure of the nanoparticle. Furthermore, the same d_{110}/d_{200} ratio is found for the PS of the $SrHfO_3$ nanoparticle (Figure 2d). These PSs agree much better with the [112] zone axis of the cubic-stabilized HfO_2 structure (the reflections would in this case be the 111 and 220 with $d_{111}/d_{220}=1.63$), and also to the cubic perovskites although some intense reflections would be missing in this case. Obviously, there was a problem with the calibration of the microscope during the HRTEM measurements. All in all, the erroneous assignment of the reflections in the PSs does not allow to discriminate between the two structures.

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