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Comment on "Unusual Photoluminescence of CaHfO3 and SrHfO₃ 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 "CaHfO₃" nanoparticles (reported in Figure 1S) perfectly matches to cubic stabilized HfO₂ 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 HfO₂ 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 ABX₃ type perovskite structure. The formation of the orthorhombic (Pnma space group) perovskite CaHfO3 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)TiO₃ and BaZrO3 can be taken from Niederberger et al. [4,5] It should also be noted that the cubic (perovskite) modification of CaHfO₃ and SrHfO₃, which was used for the assignment of the reflections

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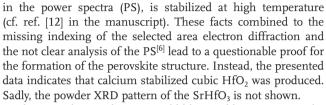
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The second point that we would like to address concerns the chemical characterization of the as-synthesized samples. Thermogravimetric analysis shows a large weight loss between 450 and 550 °C (Figure 2S) which can be attributed to the combustion of organic species. In fact, a weight loss of around 15% for the "CaHfO₃" and 30% for the "SrHfO₃" 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 RE2O3 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 RE₂O₃benzoate 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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