Response to "Comment on 'Unusual Photoluminescence of $CaHfO_3$ and $SrHfO_3$ Nanoparticles'"

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The comment from Clavel et al. on our paper entitled "Unusual photoluminescence of $CaHfO_3$ and $SrHfO_3$ nanoparticles" raises questions on the synthesis, the photoluminescence, and the structure of these perovskite nanoparticles. The comment is based on several references used as support; most of which are self-citations. It surprisingly seems to miss the key point of our report, i.e., no luminescence from regular hafnia perovskite nanoparticles is expected under the experimental conditions described in our work, as there are no energy levels available for any radiative processes in contrast to many lanthanide and rare earth (RE) compounds. This is the reasoning behind entitling the observed strong visible luminescence as "unusual" and suggesting a surface-related effect as its plausible origin. We find the comment rather dubious, and at times unrealistic and inconsistent. More specifically, the authors open their comment by claiming that the photoluminescence (PL) studied in our paper is not a surface-related effect. However, in their conclusion, they self-contradictorily suggest that the PL observed in our study is related to benzoate species adsorbed on the surface of the nanoparticles, which in our opinion is a surface related effect. If the authors had contacted us directly, we would have been equally glad to answer their concerns.

With respect to the perovskite phase: The structure of these hafnia perovskites was studied using Cs corrected TEM and synchrotron measurements. An X-ray diffraction (XRD) pattern of $CaHfO_3$ sample fitted with Rietveld refinement (**Figure 1**a) highlights the XRD peaks of the perovskite structure and provides sizes <2 nm for the perovskite particles (smallest perovskites ever synthesized in the literature) and 6 nm for the HfO_2.[1] A size decrease induces peak broadening for the perovskite phase; the secondary cubic HfO_2 phase (nanoparticles of average size ≈5–6 nm) then becomes more prominent on the XRD pattern. This explains why, the authors had incorrectly considered the XRD pattern to correspond to the HfO_2 cubic phase. The authors have expressed disappointment in not seeing the XRD pattern of $SrHfO_3$ in our paper; we have therefore included a synchrotron XRD pattern, in Figure 1b, which validates the formation of the $SrHfO_3$ perovskite cubic phase (Figure 1). A Cs corrected high-resolution transmission electron microscopy (HRTEM) image of $CaHfO_3$ has been provided along with an indexed selected area diffraction pattern in **Figure 2**.[2] The comparison of the XRD patterns with the corresponding electron diffraction patterns in self-cited references (numbered [4], [5] in the comment) used as support are equivocal as they appear to be two different structures. Thermogravimetric analysis (TGA) is unfortunately not provided in ref. [4] and [5] of the comment and would have certainly highlighted the presence of probable secondary phases such as carbonates and TiO_2. From our experience, perovskite synthesis using the non-aqueous route has, more often than not, created secondary phases such as carbonates, easily revealed by TGA.

In our study a 325 nm (3.8 eV) wavelength photoexcitation was employed in PL experiments. A photon energy of 3.8 eV is lower than the safely attributed benzoate species bandgap of 4.2 eV mentioned in the comment; this, in consequence, is insufficient to induce any interband excitation and emission from these organic species. However, W. Chen et al. have demonstrated that surface states can lower the adsorption energy compared to the ban gap of the compound and these states are size dependent.[3] This might be a possible explanation as to how the hafnia perovskite nanoparticles were excited with a wavelength of 325 nm.

Our manuscript clearly illustrates different PL behaviors for $SrHfO_3$ and $CaHfO_3$ upon changing the ambient (vacuum/air); the effect is considerably more pronounced for $CaHfO_3$ than for $SrHfO_3$. The time evolution of the PL spectra under UV exposure for both compounds is also dissimilar. If the PL had indeed originated from benzoate species, no difference should have been observed at all in any aspect of the emission. In addition, PL temperature dependencies also show differences between $SrHfO_3$ and $CaHfO_3$ that have never been observed in benzoate species to the best of our knowledge, not even in the references provided in the comment. Thereupon, the tentative model that sheds light on the nature of the observed PL based on luminescent centers located at the surface of the nanoparticles is the only available explanation. TGA in our manuscript clearly gives an indication of the organic species originating from the synthesis route, but our materials cannot be considered as "nanohybrid" compounds, as suggested in the comment considering the HRTEM images where monodispersed particles are displayed

RE oxycarbonates are luminescent structures;[4–6] they organize themselves as lamellae as shown by HRTEM[7] and are very easily formed. Their TGA curves show a "bump" at 450–500 °C, indicating combustion of these species,[5] at much lower temperatures than other carbonates viz. calcite. As already mentioned, the non-aqueous route easily forms carbonate species and similar TGA tendencies are visible in the

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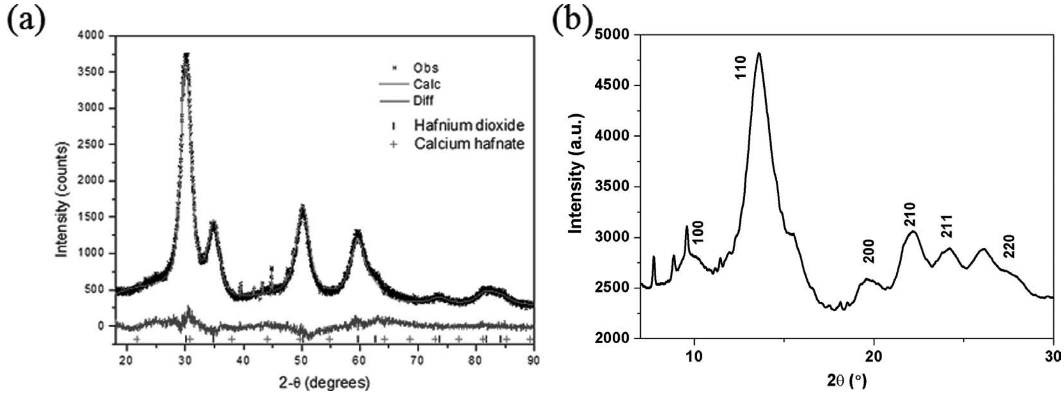

Figure 1. a) XRD pattern of $CaHfO_3$ sample fitted with Rietveld refinement. b) Synchrotron X-ray diffraction pattern of $SrHfO_3$ nanoparticles (Pattern: 00-044-0991) ($\lambda = 0.69776$ Å).

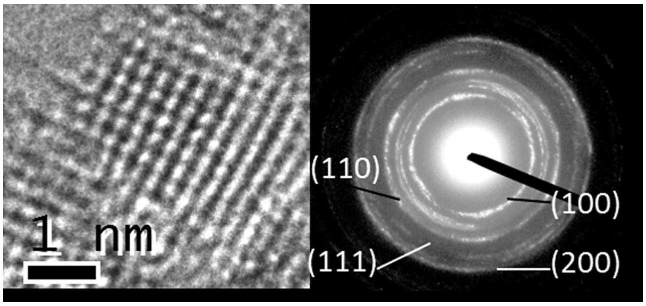

Figure 2. Cs corrected HRTEM of a $CaHfO_3$ perovskite nanoparticle along <001> and selected area diffraction pattern indexed to the cubic perovskite reflections.

supporting information of papers[8,9] cited in the comment. On careful reading of the self-cited reference[8] used as support in the comment, we notice that the authors were very surprised to not observe any contribution of the benzoate species in the PL emission, consequently attributing this absent emission to the complete energy transfer from benzoates to RE lanthanides. In our opinion, this is an unconvincing interpretation of the results as no benzoate species are emitting; instead, a plausible explanation for the emission spectra in ref. [8,9] could be the emission of lamellar RE oxycarbonates doped with lanthanides,[5] i.e., the lamellar RE oxycarbonates are separated by benzoate ligands in their case.[7] The PL properties may therefore be misleading and consequently cannot be considered to be an explanation for our observed photoluminescence, as our emission does not emanate from carbonates nor benzoates.

To conclude, we have synthesized Hf perovskites without any sort of doping, as tiny as 1.6 nm, exhibiting nanosize related photoluminescence.

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[1] In order to confirm the presence of $CaHfO_3$ and the validity of using a fixed lattice parameter determined from TEM analysis the Rietveld refinement was repeated using the same model without this phase. There is a clear indication that the unusual background shape between 38 and 48° 2θ is due to the broad (002) and (021) peaks of $CaHfO_3$. There are no overlapping reflections from HfO_2 in this region of the pattern.

[2] The comment has suggested that the HRTEM images in our work correspond to the <112> zone axis for both $CaHfO_3$ and $SrHfO_3$. Taking into account the point-to-point resolution of our microscope we can completely eliminate the <112>.

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[5] K. Koyabu, Y. Mayama, T. Masui, N. Imanaka, *J. Alloys Compd.* **2006**, *418*, 230.

[6] S. Lechevallier, P. Lecante, R. Mauricot, H. Dexpert, J. Dexpert-Ghys, H.-K. Kong, G.-L. Law, K.-L. Wong, *Chem. Mater.* **2010**, *22*, 6153.

[7] H. Dexpert, G. Schiffmacher, P. Caro, *J. Solid State Chem.* **1975**, *15*, 301.

[8] M. Karmaoui, R. A. Sá Ferreira, A. T. Mane, L. D. Carlos, N. Pinna, *Chem. Mater.* **2006**, *18*, 4493.

[9] M. Karmaoui, L. Mafra, R. A. Sá Ferreira, J. Rocha, L. D. Carlos, N. Pinna, *J. Phys. Chem. C* **2007**, *111*, 2539.

[10] The comparison of the PL emission spectra and TGA measurements from ref. [5,6] show similarities with the ones published by the authors in ref. [8,9], respectively.