Electronic Supplementary Material (ESI) for CrystEngComm.

CCs.

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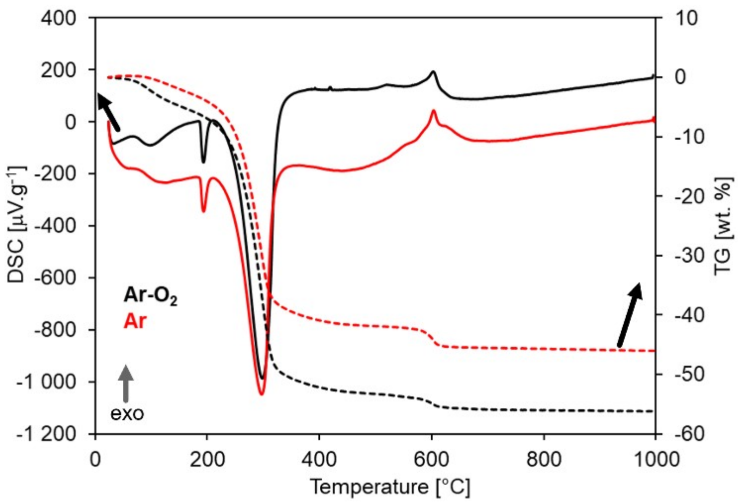

Fig S1 - DSC-TG curves (solid lines and dotted lines, respectively) of untreated HfO_2 under Ar (red lines) and Ar-20mol%O_2 (black lines) atmosphere.

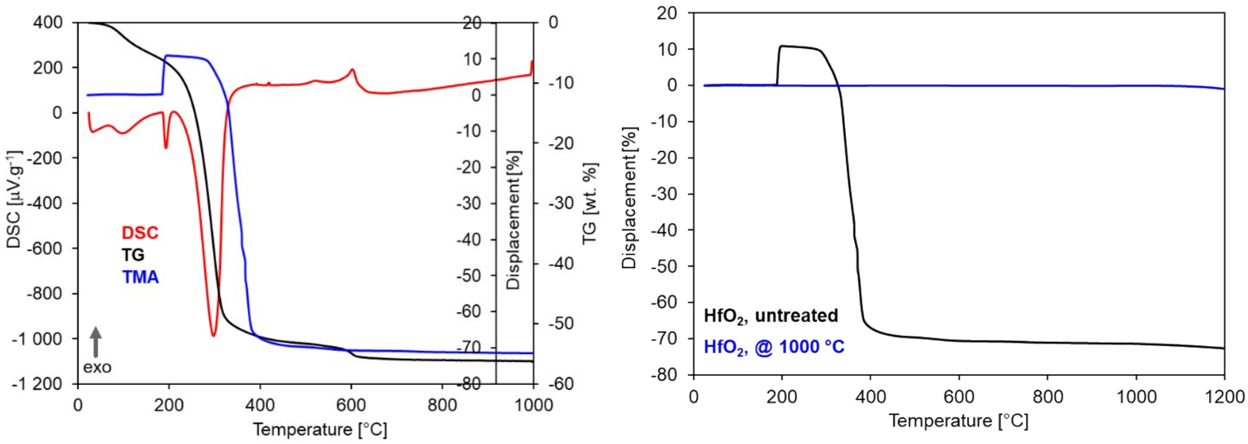

Fig S2 – DSC-TGA-TMA curves of HfO_2 untreated samples (left) and TMA curves of HfO_2 untreated and HfO_2 annealed at 1000 °C (right).

MS (amu)	Fragment	T_{onset} (°C)
15	CH_3	134, 271, 385, 535
17	OH, NH_3	54, 151, 256, 372, 538, 574
18	H_2O	53, 184, 240, 356, 465, 537, 586
28	N_2, CO	158, 413
30	NO	110, 231, 289, 363, 461, 538
32	O_2	35, 144, 409
44	CO_2	77, 151, 211, 314, 408, 568
45	$HCOO^-$	172, 303, 410, 571
46	NO_2	30, 131, 237, 303, 368, 521, 577

Table S1 – Summary of fragments detected by MS at displayed onset temperatures accompanying DSC-TGA effects.

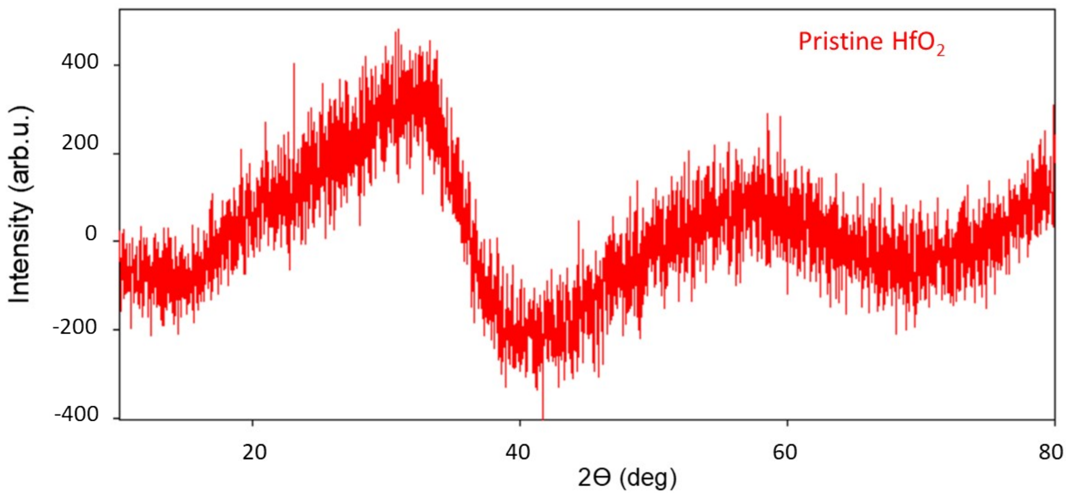

Fig S3 – XRD analysis performed on untreated solid product after photo-induced synthesis suggesting amorphous nature of NPs.

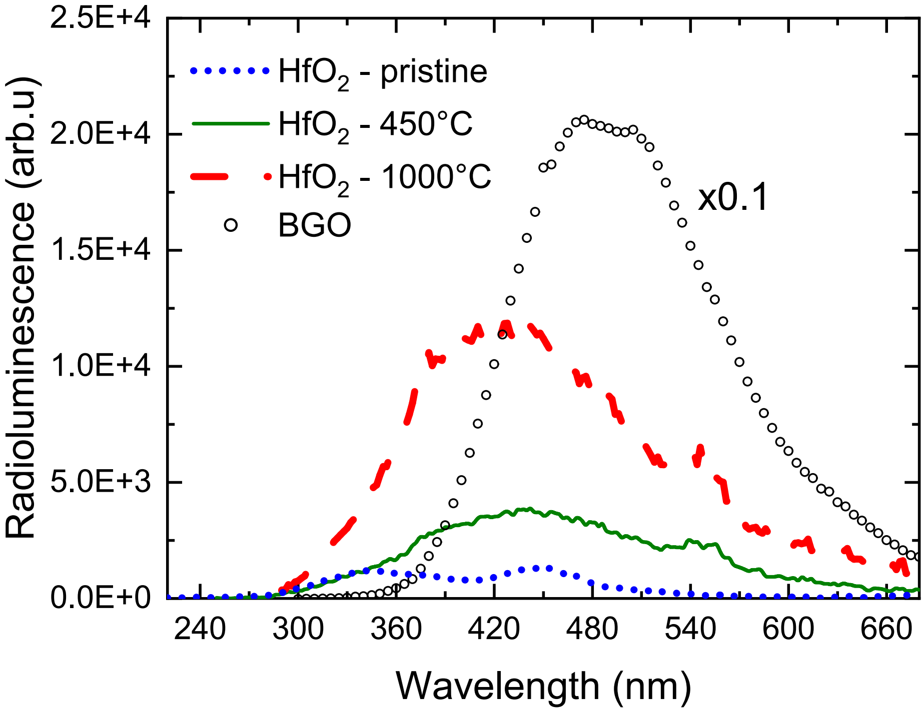

Fig S4– RL at RT of pristine HfO_2 NPs, NPs annealed at 450 °C (amorphous- blue small dots and the green line respectively) and HfO_2 annealed at 1000 °C (crystalline-red dotted line) in comparison with the powder of standard BGO - $Bi_4Ge_3O_{12}$ scintillator (black empty dots). RL of BGO has been acquired with reduced slit of ¼ with respect to the case of HfO_2 NPs and RL amplitude and the light output has been divided by a

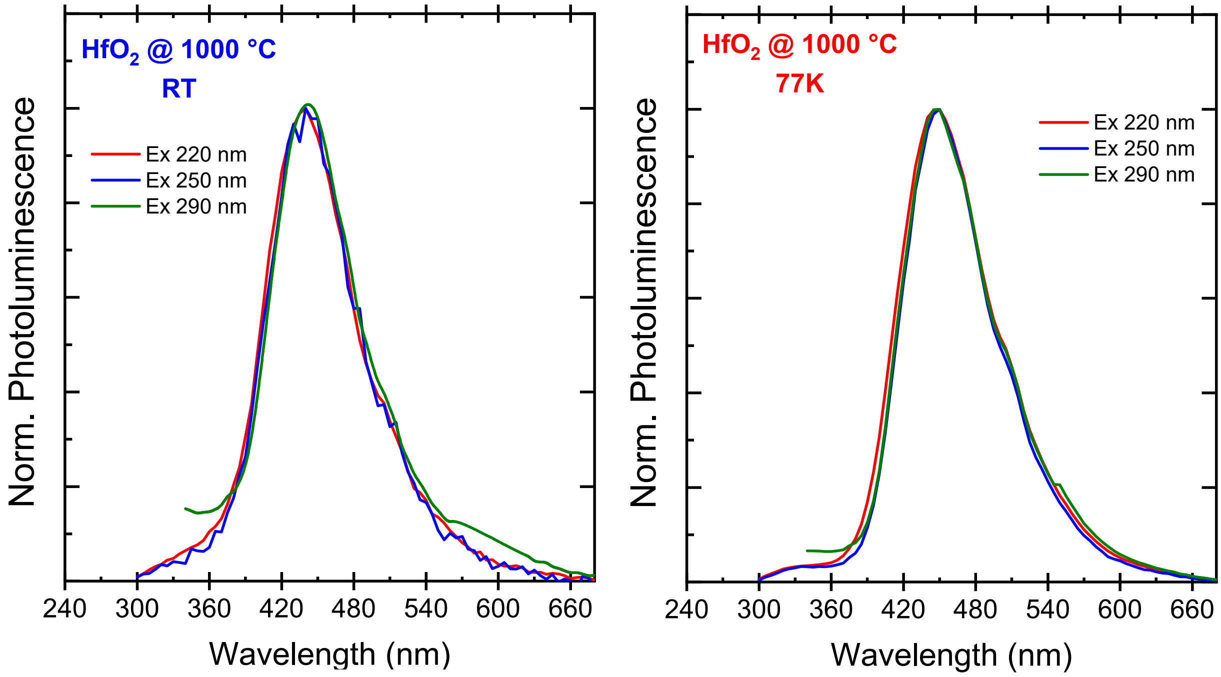

Fig S5 – PL under diverse excitation wavelengths for NPs annealed at 1000 °C at room temperature (left)

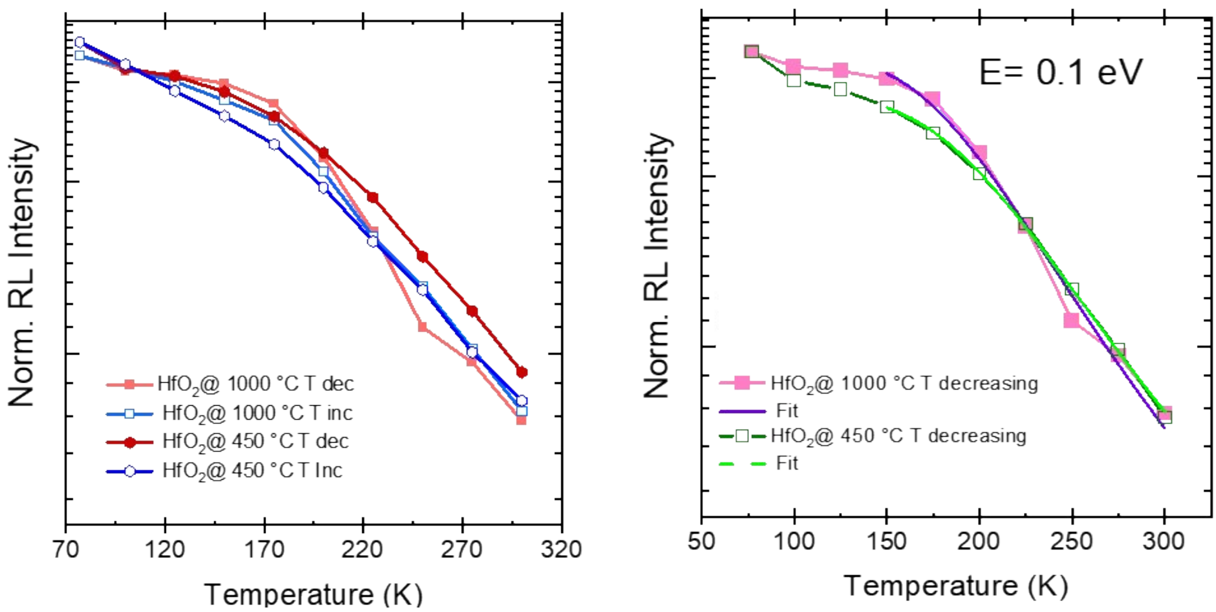

Fig. S6. - Normalized RL intensity as a function of temperature of NPs annealed at 450 °C and 1000 °C (integration of the RL spectra within 400-600 nm). RL spectra of HfO_2 NPs have been recorded by decreasing (T- dec) and increasing (T – inc) the temperature (left). RL intensity on the same NPs (light green and pink lines with markers) together with fit curves obtained from equation eqn(1) from 150 K to 300 K (dark green and violet lines) (right).

where

k_b is the Boltzmann's constant.

α is a constant parameter.

I_0 is the luminescence intensity at 77K (here).

eqn (1)	I(T)= I0/1+α(exp(-E(k$_B$T)))
α	(450°C) 130 ± 15 (1000°C) 160 ± 16
E	(450°C) 0.10 ± 0.01 (1000°C) 0.10 ± 0.01

Table S2 -Thermal quenching parameters α and E of the RL intensities in HfO_2 annealed at 450 °C and 1000°C, obtained by numerical fits of the experimental data with eqn (1)

TRPL data analysis.

The time resolved PL and scintillation spectra reported in Figure 6 show a complex behavior. The signal decay has been reproduced with an analytical multi-exponential function:

$$I_{PL/Scint}(t) \propto y_0 + \sum_i A_i e^{-\left(t/\tau_i\right)} \quad . \qquad \text{Eq. S1}$$

Y_0 parameter has been added to consider the instrumental background and the contribution of any additional slower components.

The parameters used for the fitting procedure are reported in Table 2. The emission lifetime τ_{avg} has been calculated as the weighted average of the characteristic decay time for each i-exponential function using:

$$\tau_{avg} = \frac{\sum_i A_i \tau_i}{\sum_i A_i} \quad . \qquad \text{Eq. S2}$$

	A_1, τ_1	A_2, τ_2	A_3, τ_3	y_0
TR-PL HfO_2 @ 1000°C	1440 ± 220, 1.5 ± 0.2ns	280 ± 30, 2.7 ± 0.3 ns	12 ± 1.8, 90 ± 15 ns	9.0
Scint. HfO_2 @ 1000°C	113 ± 20, 0.2 ± 0.01ns	15 ± 2, 3.2 ± 0.4 ns	4.0 ± 0.6, 60 ± 10 ns	9.0

Table S3 -Results of the fit analyses performed on the experimental data of TR-PL and scintillation decay.