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High dielectric constant and capacitance in ultrasmall (2.5 nm) $SrHfO_3$ perovskite nanoparticles produced in a low temperature non-aqueous sol–gel route†

Mohamed Karmaoui,*[ab] E. Venkata Ramana,[c] David M. Tobaldi,[a] Luc Lajaunie,[d] Manuel P. Graça,[c] Raul Arenal,[de] Maria P. Seabra,[a] João A. Labrincha[a] and Robert C. Pullar*[a]

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Strontium hafnium oxide ($SrHfO_3$) has great potential as a high-*k* gate dielectric material, for use in memories, capacitors, CMOS and MOSFETs. We report for the first time the dielectric properties (relative permittivity and capacitance) of $SrHfO_3$ nanoparticles (NPs), as opposed to thin films or sintered bulk ceramics. These monodisperse, ultra-small, perovskite-type $SrHfO_3$ nanocrystals were synthesised through a non-aqueous sol–gel process under solvothermal conditions (at only 220 °C) using benzyl alcohol as a solvent, and with no other capping agents or surfactants. Advanced X-ray diffraction methods (whole powder pattern modelling, WPPM), CS-corrected high-resolution scanning transmission electron microscopy (HRSTEM), dielectric spectroscopy, and optical (UV-vis, Raman) and photoluminescent spectroscopy were used to fully characterise the NPs. These $SrHfO_3$ NPs are the smallest reported and highly monodisperse, with a mean diameter of 2.5 nm, a mode of 2.0 nm and a small size distribution. The formation mechanism of the NPs was determined using NMR and GC-MS analysis of the species involved. Our $SrHfO_3$ nanoparticles had a dielectric constant of 17, which is on par with literature data for bulk and thin film samples, and they also had a relatively large capacitance of 9.5 nF cm^{-2}. As such, they would be suitable for applications as gate dielectrics for capacitors and in metal-oxide semiconductor field-effect transistor (MOSFET) technology.

Of the various classes of inorganic nanoparticles (NPs), perovskite metal oxides NPs are particularly attractive from both the scientific and technological point of view. The unique characteristics of perovskites make them the most diverse class of materials for use in electronics and fuel cells due to their optimal optical, dielectric, ferroelectric, piezoelectric, photoelectric, catalytic or magnetic properties.[1–10] Recently, much interest has been focused on the synthesis and characterisation of multi-metal oxide NPs, and significant progress has been made over the past decade in understanding fundamental aspects of the synthesis of perovskite nanomaterials. Of these functional oxides, extensive work is available on $BaTiO_3$ (BTO) and $SrTiO_3$ (STO) based nanomaterials as their size-induced effects can be used to adjust dielectric and ferroelectric properties. A perovskite-type strontium hafniate ($SrHfO_3$) nanomaterial has also recently attracted a lot of attention due to its promising electrical and optical properties. $SrHfO_3$ doped with various ions (particularly Ce and Cu) is established as a good luminescent material and scintillating material for use in high energy nuclear medical applications.[11] However, to date, little work has been reported on the synthesis and physical properties of $SrHfO_3$ NPs, in contrast to the much-studied BTO and STO nanomaterials.[7–10] What work has been carried out on nanoscale $SrHfO_3$ is nearly all on thin films,[12] for high-*k* gate dielectric transistors[13] and photoluminescent properties.[4]

Alkaline earth hafniates have great potential as near-zero τ_f microwave dielectric ceramics,[14] and in particular $SrHfO_3$ is a very promising candidate for the next generation of capacitors, complementary metal-oxide–semiconductor (CMOS)[10] and

[a]Department of Materials and Ceramic Engineering, CICECO – Aveiro Institute of Materials, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal. E-mail: rpullar@ua.pt; karmaoui@ua.pt; Tel: +351 234 370 041

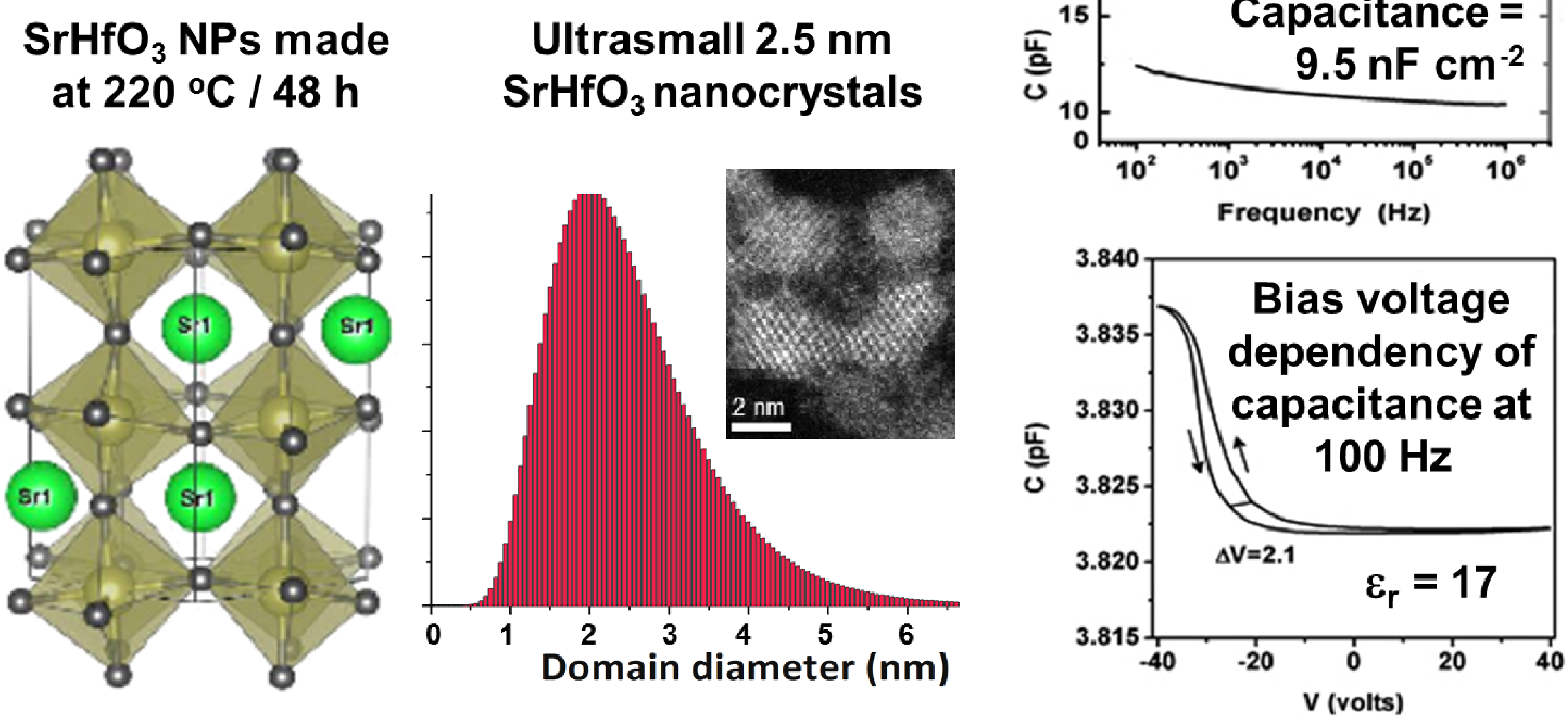
[b]School of Chemistry, College of Engineering and Physical Sciences, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK. E-mail: m.karmaoui@bham.ac.uk; Tel: +44 (0)121 414 8672

[c]I3N-Aveiro, Department of Physics, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

[d]Laboratorio de Microscopias Avanzadas, Instituto de Nanociencia de Aragón, Universidad de Zaragoza, 50018 Zaragoza, Spain

[e]ARAID Foundation, 50018 Zaragoza, Spain

† Electronic supplementary information (ESI) available: ^{13}C NMR spectrum ^{1}H NMR spectrum, gas chromatogram, retention times and structures of relevant organic species and WPPM agreement factors, unit cell parameters, average crystalline domain diameter, and mode of the size distribution. See DOI: 10.1039/c6ra06990h


SrHfO3 NPs made
at 220 oC / 48 h
Sr1
Ultrasmall 2.5 nm
SrHfO3 nanocrystals
2 nm
0 1 2 3 4 5 6
Domain diameter (nm)
Capacitance =
9.5 nF cm-2
C (pF)
15
10
0
Frequency (Hz)
Bias voltage
dependency of
capacitance at
100 Hz
ΔV=2.1
εr = 17
3.840 3.835 3.830 3.825 3.820 3.815
-40 -20 0 20 40
V (volts)