

On the ionic conductivity of some zirconia-derived high-entropy oxides

Elise Bonnet, Jean-Claude Grenier, Jean-Marc. Bassat, Alain Jacob, Bruno Delatouche, Stéphane Bourdais

► To cite this version:

Elise Bonnet, Jean-Claude Grenier, Jean-Marc. Bassat, Alain Jacob, Bruno Delatouche, et al.. On the ionic conductivity of some zirconia-derived high-entropy oxides. Journal of the European Ceramic Society, 2021, 41 (8), pp.4505-4515. 10.1016/j.jeurceramsoc.2021.03.021 . hal-03197157

HAL Id: hal-03197157 https://hal.science/hal-03197157

Submitted on 13 Apr 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

On the ionic conductivity

of some Zirconia-derived High-Entropy Oxides

Bonnet E. ⁽¹⁾, Grenier J.C. ⁽¹⁾, Bassat J.M. ⁽¹⁾

and Jacob A.⁽²⁾, Delatouche B.⁽²⁾, Bourdais S.⁽²⁾

¹CNRS, Univ. Bordeaux, Bordeaux INP, ICMCB, UMR 5026, F-33600 PESSAC Cedex, France

² IMRA Europe S.A.S., 220 rue Albert Caquot, BP 213, 06904 Sophia Antipolis, France

ABSTRACT

The reported High Entropy Oxides (HEOs) up to now exhibit lower ionic conductivity values than those of classical SOFC electrolytes. Multi-cations oxides, stabilized with the fluorite-type structure are investigated here in order to examine whether the high entropy is relevant to enhance the anionic conductivity of such HEOs, or not. The two synthesis routes that are used do not show significant impact on material properties. Based on configurational entropy ($\geq 1.5 \text{ k}_B/f.u.$ for HEOs) and ionic radius difference calculations, new compositions are designed and prepared: *i*) the (Hf_{1/3}Ce_{1/3}Zr_{1/3})_{1-x}(Gd_{1/2}Y_{1/2})_xO_{2-x/2} series in which the x ratio is increased so as to promote a high vacancy concentration, *ii*) the (Hf_xCe_yZr_{1-x-y})_{0.85}Yb_{0.15}O_{1.93} series based on the critical radius concept. The ionic conductivity of these HEOs is slightly improved compared to previously reported data but does not exceed 4 x 10⁻⁴ S.cm⁻¹ at 600 °C. Possible causes of such a low ionic conductivity value are discussed.

Keywords: high-entropy oxide; fluorite oxide; ionic conductivity; SOFC; sintering

1. INTRODUCTION

In solid state chemistry, the most usual way to synthesize new materials is to study solid solutions between a limited number of components (usually 2 or 3). Stable compounds with high enthalpy formation are generally obtained [1]. New compositions can also be predicted using density functional theory calculations or combinatorial chemistry, for instance [2]–[4].

However, as detailed below it is also sometimes very interesting to prepare metastable compounds using alternative synthesis routes. For instance, in the field of oxides, the so-called "soft chemistry" including chemical reactions at low temperatures or even electrochemical reactions at room temperature has been widely developed with a proven efficiency [5]. Corresponding materials with original compositions and interesting advanced physical properties have been obtained.

Based on fundamental thermodynamics principles, high configurational entropy (ΔS_{config}) can be used to stabilize metastable single phases using high temperature sintering. For instance, attractive properties were found for metal alloys, so-called high entropy alloys (HEAs) [6]–[8]. Murty *et al.* [9] showed that the ΔS_{config} reaches a maximum value when all the different metals, and at least five, are present in equiatomic amount.

Following these research activities, Rost *et al.* in 2015 extended the high entropy concept to multicomponent oxides, the so-called High Entropy Oxides (HEOs), and prepared new mixed oxides truly entropy-stabilized [10]. Studying an equimolar mixture of simple oxides (MgO, CoO, NiO, CuO and ZnO), they showed that a configurational disorder promotes the transition from multiple phases (at low temperature) to single phase (at high temperature) upon a cyclic heat treatment.

In parallel, improved properties compared to binary or doped oxides were sometimes observed, as for instance dielectric properties, Li⁺ superionic conductivity, which provided motivation for extending researches to various classes of compounds [11], [12]. Rare earth oxides and even more complex structures such as perovskites were investigated [13], [14]. Similarly, new high-entropy compounds have been found in various classes of materials, including borides [15], carbides [16], nitrides [17], silicides [18], chalcogenides [19] fluorides [20], [21] or layered hydroxides [22]. High Entropy Alloys (HEAs) and Compounds are defined by an entropy of mixing ΔS_{mix} higher than $\approx 1.5 \text{ k}_{\text{B}}$ /f.u. [23], corresponding typically to an equimolar mixing of 5 elements randomly distributed in the prototype structure. More recently, a multi-atomic substitution at the anionic site was reported to enable the stabilization into single phase of carbo-nitrides [24], oxy-carbo-nitrides [25], boro-carbo-nitrides [26], while a dual phase segregation was always seen in boro-carbides in [27]. The design can be generalized

by multiple elements substitution on all and any (cationic and anionic) sites of the considered prototype crystal structure.

Among this literature, we noticed the pioneering work by Gild *et al.* who investigated fluorite-type High Entropy Oxides derived from the zirconia ZrO_2 , hafnia HfO₂ or ceria CeO₂ used as a base mixture with the addition of various oxides (Y₂O₃, Yb₂O₃, La₂O₃, Gd₂O₃, TiO₂, CaO, MgO), all of them being in equal molar fractions [28]–[30]. In the same way, Chen *et al.* synthesized an equimolar ZrO_2 -HfO₂-CeO₂-SnO₂-TiO₂ composition [31] and Wright *et al.* non-equimolar ($Zr_{1/3}Hf_{1/3}Ce_{1/3}$) based compositions [32].

Such materials could be interesting as electrolytes for Solid Oxide Fuel Cells (SOFCs). However only a few ionic conductivity data were reported, with values of the order of 10^{-4} S.cm⁻¹ at 600 °C (by Gild *et al.* [28], [31]) and of 5 x 10^{-8} S.cm⁻¹ at 600 °C in the undoped ZrHfCeSnTiO₁₀) [31].

For comparison, the commercial electrolyte materials used in SOFCs are the yttria stabilized zirconia (namely 8YSZ - $Zr_{0.852}Y_{0.148}O_{1.93}$), and the gadolinium doped ceria (Ce_{0.9}Gd_{0.1}O_{1.95}, 10GDC), with ionic conductivities at 600 °C, 9.2 x 10⁻³ S.cm⁻¹ and 2.37 x 10⁻² S.cm⁻¹, respectively, and the oxygen vacancy amounts of 3.7 % and 2.5 %, respectively) [33].

In the present study, we investigated the stability and ionic conductivity of high-entropy oxides stabilized in the fluorite crystal structure. Compounds showing some oxygen deficiency are more especially considered with the aim to induce ionic conduction. Their unit formula is $AO_{2-\delta} \square_{\delta}$, where A is a mixture of ≥ 4 metals on the cationic site, while both oxygen (O) and oxygen vacancies (\square or $V_{O^{2-}}^{...}$) are distributed on the anionic sites. In the following, the simple notation $AO_{2-\delta}$ will be used. Both cationic and anionic entropic terms were varied by compositional adjustments, with a view to answer the following basic question: "Is the high entropy a relevant parameter to likely enhance the anionic conductivity of such oxides?"

In a first part, the synthesis and characterization of these materials are described using two synthesis routes with the aim to possibly identify a preferred preparation mode, in terms of homogeneity of cation distribution at the nanoscale and of the pellet morphology. The two routes are compared through the preparation of $(Hf_{1/3}Ce_{1/3}Zr_{1/3})_{0.6}(Gd_{1/2}Y_{1/2})_{0.4}O_{1.80}$, one of the best HEOs reported in ref. [28]. Then, new compositions of fluorite-type oxides are designed with configurational entropy, ΔS_{config} , being higher than 1.5 k_B/f.u. [23].

In a second part, we adjust compositions based on entropy and ionic size difference considerations. We thus design, synthesize and characterize 13 new compounds, among which 7 compounds are found stable and sorted in two composition families. In a third part, we report on the first family of compositions, the $(Hf_{1/3}Ce_{1/3}Zr_{1/3})_{1-x}(Gd_{1/2}Y_{1/2})_xO_{2-x/2}$ series, in which the dopant cation ratio, x, is increased so as to promote a high oxygen vacancy concentration. The stability of the corresponding compounds is checked using X-ray diffraction (XRD) and their ionic conductivity measured as a function of x. The fourth part is dedicated to the second family of compositions $(Hf_xCe_yZr_{1-x-y})_{0.85}Yb_{0.15}O_{1.93}$, which is designed based on the concept of critical ionic radius applied to the Yb dopant cation. Then, in the final discussion, using available results from literature and our present work, we examine the possible causes that explain the ionic conductivity evolution in high-entropy fluorite oxides so far reported.

2. EXPERIMENTAL

2.1. Sample preparation

Pellet samples were prepared by using a solid-state reaction or a wet chemical synthesis, respectively called S1 and S2 routes. The S1 route combined ball milling and Spark Plasma Sintering (SPS), while S2 route used co-precipitation followed by annealing in a furnace.

2.1.1. Sample preparation through S1 route

Dry powders with typical 1 to 10 μ m grain sizes, of Y₂O₃, ZrO₂, HfO₂ and rare earth oxides (La₂O₃, CeO₂, Gd₂O₃, Yb₂O₃, purchased from Thermo Fischer Scientific, REactonTM grade 99.9 % pure, or Sigma Aldrich, 99 % pure for ZrO₂) were used as raw materials. The powders were mixed in appropriate amounts according to the designed composition. The blend powder (20 g) and ethanol (10-15 ml) were ball-milled in a Pulverisette 6 equipment (Fritsch FRANCE) using ZrO₂ bowl (80 ml) and 100 g of ZrO₂ balls (3 mm diameter). A milling at 460 rpm rotation speed was applied during 20 h, with one third of the time in off position. After milling, the blend was extracted with additional ethanol and dried under vacuum at 70 °C.

The solid residue was sieved through a 150 μ m sieve and then, a ~1.6 g fraction was densified into Ø15 mm pellets by Spark Plasma Sintering (FDC Dr Sinter SPS machine, Japan) under vacuum in graphite molds at 1500 °C for 5 min with a heating ramping rate of 100 °C/min and a uniaxial pressure of 50 MPa. Prior, the chamber was pumped down to 10⁻³ Pa. The relative density of the prepared pellets was not lower than 95 %. The SPS processing conditions are a severely reducing environment, resulting in black-colored pellets, which were then oxidized to white or light-grey colored pellets by an oxidation annealing, *e.g.* during the firing step in air at 800 °C (see below).

2.1.2. Sample preparation through S2 route

Nitrate salts, Ce(NO₃)₃·6H₂O, Gd(NO₃)₃·6H₂O, Y(NO₃)₃·4H₂O, Yb(NO₃)₃·xH₂O (Alfa Aesar, \ge 99.5 %), an oxynitrate solution of Zr (ZrO(NO₃)₂ .xH₂O, 4N, Rhodia raw materials, 2.16 mol/l) and an oxychloride salt of Hf⁴⁺ (HfOCl₂·8H₂O, Alfa Aesar, 98.5 %; Zr < 1.5 %) were used as precursors. They were mixed in appropriate proportions and dissolved under stirring in de-ionized water (15 MΩ) for 15 min, to finally obtain a concentration of metal cations of 0.58 mol/l. This solution was then added drop-by-drop in a stirred basic solution of ammonia, 1.4 mol/l (prepared from NH₄OH solution, Alfa Aesar, ACS, 28 – 30% NH₃) with a controlled pH at 10.8 (ammonia 30 wt% added drop by drop). Precipitation immediately occurred. The slurry was kept under stirring for 4 h, at room temperature.

The precipitate was then centrifuged (5000 rpm) and washed with 1.4 mol/l ammonia and finally with ethanol. The powder was dried on a sand bath at 50 °C and grinded with a mortar. After that, it was calcined at 600 °C for 1 h with a heating ramp of 1 °C/min and then, grinded by attrition with 2 mm diameter zirconia balls in ethanol medium. After drying, \approx 1 g of powder was compacted into pellets of 25 mm diameter and 1 mm thickness by uniaxial pressing at 20 MPa. The pellets were then sintered in ambient air (in a Carbolite BLF 1700 furnace model) at 1500 °C for 6 h with a heating ramp of 2.5 °C/min and finally air quenched. The relative density of the prepared pellets was not lower than 91 %.

2.2. Characterization

The samples were characterized by X-Ray Diffraction (XRD using a PANalytical X'Pert Pro diffractometer) with copper radiation and X'Celerator detector. The lattice parameters were determined using the Fullprof profile matching program [34]. The sample density was calculated with the measured mass and geometric parameters of the pellet. The relative density was obtained by dividing the experimental density by the theoretical density that was determined with the corresponding lattice parameters (Fm-3m cubic symmetry) and the formula unit.

The Scanning Electron Microscopy (SEM S2000 from Hitachi at IMRA and SEM 6700F from Jeol at ICMB) using secondary or back-scattered electrons, coupled to an Energy-Dispersive X-ray microanalysis (EDX) Noran System SIX, was used to examine the microstructure and the distribution of the elements. The observations were performed on pellet surface (or pellet cross-sections obtained with a manual fracture). For back-scattering mode observation and for EDX analysis, samples were polished and coated with 0.5 nm sputtered Pt layer before analysis. The measurements were performed with an electron beam voltage of 15 kV. The grain size was determined by a counting over 100 grains, the median being taken into consideration.

The ionic conductivity of the samples was measured by Electrochemical Impedance Spectroscopy (EIS) using a Solartron analytical-AMETEK impedance analyzer. To perform the measurements, the sintered pellets were polished, first, with silicon carbide papers in water media, then, with diamond paste (3 µm

 \emptyset) and, finally, cleaned with ethanol to obtain two mirror surfaces. A Pt ink was then deposited with a paintbrush on the two surfaces, then, sintered at 800 °C for 2 h. This preparation is required to optimize the electrical contact with the gold grids of the EIS setup. The measurements were performed in potentiostatic mode with a 10 mA amplitude around the open circuit voltage in the frequency range of 1 MHz to 100 mHz, from 400 °C up to 800 °C. The electrical conductivities were determined by fitting the Nyquist curves thanks to Zview[®] software [35] with an equivalent circuit made of a series resistance and a combination of R-CPE equivalent elements. As the measurements were performed in air, all the cations are in their highest valences, which prevents any electronic conductivity contribution, so that the electrical conductivities are purely ionic conductivities. The Arrhenius plot was used to compare ionic conductivity values of the samples in the temperature range 400 - 800 °C.

After EIS experiments, the samples were polished to remove the Pt film and again analyzed by XRD in order to check whether the microstructure had changed or not.

3. RESULTS

3.1. Comparison of the S1 and S2 synthesis routes

Samples with the composition $(Hf_{1/3}Ce_{1/3}Zr_{1/3})_{0.6}(Gd_{1/2}Y_{1/2})_{0.4}O_{1.80}$ (HEFO7B) – the composition with the highest ionic conductivity in Gild *et al.* paper [28] - were prepared by both S1 and S2 preparation routes and noted HEFO7B#1 and HEFO7B#2, respectively. Both types of samples had a \geq 96 % relative density (**Table 1**). For comparison, the reference ionic conductor 8YSZ (Zr_{0.852}Y_{0.148}O_{1.93}) was also prepared using S2 route, with a relative density close to 100 %. It is labelled 8YSZ#2.

XRD analysis

The XRD patterns of all these four samples exhibit a single phase with a cubic fluorite-type structure (SG: 225; Fm-3m symmetry). The slight offset of the lattice parameters reported in **Table 1** between as sintered HEFO7B#1 and #2 samples, can be explained by the SPS severe reducing conditions, which induce an increase in lattice parameter (as part of Ce^{+4} is reduced to Ce^{3+} with ionic radius of 0.097 and 0.114 nm, respectively) [36]. Indeed, the lattice parameter of HEFO7B#1 sample is decreased after its re-oxidation at 800 °C (from 0.531 to 0.526 nm, **Table 1**), being finally equal to that of HEFO7B#2.

SEM observations

As illustrated in **Figure 1** and reported in **Table 1**, the grain size of the SPS sample HEFO7B#1 is significantly smaller (about one order of magnitude) than that of the HEFO7B#2 sample: the S1 route

leads to smaller grain size than the S2 route. The shorter duration of the SPS technique in S1 route could explain this difference.

Using EDX analysis, the mappings of both HEFO7B#1 and #2 samples (**Supplementary Information 1**) show a uniform dispersion of Ce, Zr, Hf, Y and Gd cations: both S1 and S2 preparation routes are adapted to prepare HEOs. Furthermore, the resolution of the analysis cannot distinguish the routes in terms of cation distribution.



Figure 1. Cross-section SEM observations of (a) HEFO7B#1, (b) HEFO7B #2 and (c) 8YSZ#2 ceramics.

Ionic conductivity measurements

The ionic conductivities of 8YSZ#2, HEFO7B#1 and HEFO7B#2 samples measured in the 400 - 800 °C temperature range are shown in **Figure 2**. The ionic conductivities of samples HEFO7B#1 (2.8×10^{-4} S.cm⁻¹ at 600°C) and #2 (1.8×10^{-4} S.cm⁻¹ at 600°C) are of the same order of magnitude. They are also similar to that reported for #HEFO7B in ref. [28] (1.1×10^{-4} S.cm⁻¹ at 600 °C, extrapolated data by linear fitting); this compound was prepared from oxide powders mixed using high-energy ball milling, grinded, densified via SPS at 1800 °C, annealed at 1500 °C for 24 h and air-quenched. Therefore, both synthesis routes yield similar materials and all HEFO7B samples are characterized by significantly lower conductivities than that of the 8YSZ#2 sample (a difference of one order of magnitude). Furthermore, and surprisingly, using the S2 preparation route does not improve the ionic conductivity, even if a larger grain size is obtained.



Figure 2. Arrhenius plots of ionic conductivities measured by EIS, for High-Entropy Fluorite Oxide HEFO7B#1, HEFO7B#2 and for 8YSZ#2 reference sample. Data from Gild *et al.* for HEFO7B are reported for comparison from 800 °C to 650 °C.

Table 1. Main results for comparison of the preparation routes for the HEFO7B composition.

Sample	Prepa- ration	Lattice parameter (nm)		i- Lattice parameter n (nm)		Lattice parameter (nm)		Lattice parameter (nm)		Lattice parameter (nm)		Lattice parameter (nm)		Lattice parameter (nm)		Lattice parameter (nm)		Lattice parameter (nm)		Relative density	Grain size (μm) (median	Ionic c	onductivity	v (S.cm⁻¹)
		Before EIS	After EIS		SEM count)	800 °C	600 °C	400 °C																
HEFO7B [28]	-	0.528	-	95.8 %	-	1.5 x 10 ⁻³	-	-																
HEFO7B #1	S1	0.531	0.527	100 %	0.3	4.0 x10 ⁻³	2.8 x 10 ⁻⁴	2.9 x 10 ⁻⁶																
HEFO7B #2	S2	0.526	0.526	96 %	1.5	3.0 x10 ⁻³	1.8 x 10 ⁻⁴	1.4 x 10 ⁻⁶																
8YSZ #2	S2	0.514	0.514	100 %	> 5	4.6 x10 ⁻²	5.2 x 10 ⁻³	8.3 x 10 ⁻⁵																

To conclude, whatever the synthesis route S1, S2 or Gild *et al.* the same order of magnitude of the ionic conductivity (3×10^{-4} S.cm⁻¹ at 600 °C) is obtained for this high entropy compound (HEFO7B) and this value is significantly lower than the classical one (8YSZ#2).

3.2. New compositions: Mixing entropy calculations

The objective of this work was to design new compositions of high entropy oxides with a fluorite structure and to implement previous reported results. These new compositions were designed by substitution at the cationic sites and by calculating the resulting mixing entropy, or configurational entropy of the material (ΔS_{config}), defined as the sum of the cationic and anionic entropies (ΔS_{cat} and ΔS_{anio} respectively), *i.e.* $\Delta S_{config} = \Delta S_{cat} + \Delta S_{anio}$. Regarding the high entropy condition [23], the value of ΔS_{config} is targeted to be $\geq 1.5 \text{ k}_{B}/f.u.$.

Considering the oxide $A\alpha_A B\alpha_B...N\alpha_N O_{2-\delta}$, with α_N the ratio corresponding to the Nth cation and δ corresponding to the oxygen deficiency amount, *i.e.* to half of the 3+ cations fraction, the cationic entropy is defined as follows [13], [37], [38]:

$$\Delta S_{cat} = -k_B \sum_{i=A}^{N} \alpha i. \ln(\alpha i) \quad \text{with } \sum_{i=A}^{N} \alpha i = 1$$
 Equation 1

and the anionic entropy as:

 $\Delta S_{anio} = -k_B \left[(2-\delta) ln(2-\delta) + \delta ln(\delta) - 2 ln(2) \right]$ Equation 2

To cover a large range of entropy values, new compositions were designed, prepared and characterized, as reported in the selected list of **Table 2**. Some literature compounds are also mentioned for comparison and a full list can be found in **Supplementary Information 2**. To use as SOFC electrolyte, the interesting compositions are those obtained as cubic single-phase and, more important, those stable over the temperature range 400 – 800 °C. In **Table 2**, eight prepared compositions fulfill these conditions: HEFO7B from [28] and the HEFO7-x as well as HEFOYb-15(1), HEFOYb-15(2) and HEFOYb-15(3) designed in this work. Therefore, the following studies will focus on the characterization of these two stable compound families, namely HEFO7 and HEFOYb.

Table 2. Calculated entropies of	compounds newly desi	gned (this work). HEFO7E	6 from Gild et al [28] is included
		,	

Notations	Compositions	ΔS_{config}	ΔS_{cat}	ΔS_{anio}	$V_{0^{2-}}$	Cubic lattice pa	rameter (nm)***	σ _{ion} at 600 °C	δr_{cat}
		(k _B /f.u.)	(k _B /f.u.)	(k _B /f.u.)	(%)	As sintered	After annealing at 800°C	(S.cm ⁻¹)	(%)
HEFOYb-15(3)	$(Hf_0Ce_{0.429}Zr_{0.571})_{0.85}Yb_{0.15}O_{1.93}$	1.32	1.00	0.32	3.8	0.52334(5)	0.52323(9)	3.8 x 10 ⁻⁴	7.41
HEFOYb-15(2)	$(Hf_{0.163}Ce_{0.442}Zr_{0.395})_{0.85}Yb_{0.15}O_{1.93}$	1.61	1.29	0.32	3.8	0.5233(1)	0.52337(3)	4.7 x 10 ⁻⁴	7.56
HEFOYb-15(1)	$(Hf_{0.327}Ce_{0.456}Zr_{0.217})_{0.85}Yb_{0.15}O_{1.93}$	1.64	1.32	0.32	3.8	0.52411(1)	0.52394(9)	3.1 x 10 ⁻⁴	7.72

HEFO10A	$Hf_{0.267}Ce_{0.267}Zr_{0.267}La_{0.2}O_{1.90}$	1.78	1.38	0.40	5.0	No s.p.**	No s.p.	-	13.4
HEFO2-25	$Hf_{0.25}Zr_{0.25}Ce_{0.25}Yb_{0.25}O_{1.87}$	1.85	1.39	0.47	6.3	0.52053(2)	0.5207(1)	-	7.89
HEFO9A	$Hf_{0.168}Ce_{0.168}Zr_{0.168}Ti_{0.168}Sn_{0.168}Y_{0.08}Yb_{0.08}O_{1.92}$	2.24	1.90	0.34	4.0	0.51768(6)	No s.p.	-	10.1
HEFO7-60	$Hf_{0.13}Ce_{0.13}Zr_{0.13}Y_{0.3}Gd_{0.3}O_{1.70}$	2.36	1.52	0.85	15.0	0.53240(2)	0.53041(2)	0.25 x 10 ⁻⁴	8.90
HEFO7-50	$Hf_{0.17}Ce_{0.17}Zr_{0.17}Y_{0.25}Gd_{0.25}O_{1.75}$	2.35	1.60	0.75	12.5	0.53206(3)	0.52905(2)	0.62 x 10 ⁻⁴	9.55
HEFO7-40*	$Hf_{0.2}Zr_{0.2}Ce_{0.2}Y_{0.2}Gd_{0.2}O_{1.8}$	2.26	1.61	0.65	10.0	0.5308(1)	0.52648(5)	3.7 x 10 ⁻⁴	9.73
HEFO7-30	$Hf_{0.23}Ce_{0.23}Zr_{0.23}Y_{0.15}Gd_{0.15}O_{1.85}$	2.12	1.58	0.53	7.5	0.531	0.5245(1)	2.6 x 10 ⁻⁴	9.64
HEFO7-25	$Hf_{0.25}Ce_{0.25}Zr_{0.25}Y_{0.125}Gd_{0.125}O_{1.875}$	2.03	1.56	0.47	6.3	0.529	0.52334(4)	3.5 x 10 ⁻⁴	9.54
HEFO7-16	$Hf_{0.28}Ce_{0.28}Zr_{0.28}Y_{0.08}Gd_{0.08}O_{1.92}$	1.81	1.47	0.34	4.0	No s.p.	No s.p.	1.7 x 10 ⁻⁴	9.07
HEFO11B	$Hf_{0.16}Ce_{0.16}Zr_{0.16}Sn_{0.16}Ti_{0.16}Y_{0.05}Gd_{0.05}Yb_{0.05}La_{0.05}O_{1.90}$	2.46	2.07	0.40	5.0	No s.p.	No s.p.	-	17.6

* (HEFO7B in ref. [28]) ** No s.p. = no single phase. ***The estimated standard deviations were calculated using correlated residuals : [39], [40].

3.3. New compositions: influence of 3+ cation content in the HEFO7 compound family

The anionic entropy is directly correlated to the presence of oxygen vacancies (introduced by 3+ cation substitution), which are well known as mandatory to induce the ionic conduction. The amount of oxygen vacancy $V_{O^{2-}}^{"}$ is generally optimized for each composition to maximize the ionic conductivity. The ideal $V_{O^{2-}}^{"}$ value is around 2 to 4 % for the classical fluorite-type ionic conductors AO_{2-δ} [33]. It is also well known that for too large $V_{O^{2-}}^{"}$ values, oxygen vacancies interact with each other to form clusters, which decreases the ionic conductivity [33]. Applying this knowledge to the HEFO7B high entropy oxide, its poor ionic conductivity measured in previous section **3.1** could be explained by its comparatively large amount of $V_{O^{2-}}^{"} = 10$ %.

Here, the objective was to study the influence of the oxygen vacancy content in high entropy oxides, $\delta = x/2 = V_{O^{2-}}^{..}/50$, defined as the number of oxide ions missing in the prototype fluorite structure AO₂₋ δ . For this purpose, the x value of 3+ cation content was varied in HEFO7B-derived family of compounds $(Hf_{1/3}Ce_{1/3}Zr_{1/3})_{1-x}(Gd_{1/2}Y_{1/2})_xO_{2-\delta}$, with x ranging from 0.16 to 0.60. The corresponding samples were named HEFO7-16 (x = 0.16), up to HEFO7-60 for x = 0.60. This x range was selected to cover a large range of $V_{O^{2-}}^{..}$, varying from 4 % (corresponding to the value of the classical ionic conductor 8YSZ) up to 15 %. As shown in **Figure 3**, the cationic entropy ΔS_{cat} is almost constant, which allows considering ΔS_{anio} to be the main contribution to the increase in ΔS_{config} .



Figure 3. Dependence of the anionic, cationic and configurational entropies on the oxygen vacancy content $\delta = x/2$ in $(Hf_{1/3}Ce_{1/3}Zr_{1/3})_{1-x}(Gd_{1/2}Y_{1/2})_xO_{2-\delta}$.

The six HEFO7 samples were prepared by S1. The color of the pellets was dark after the SPS-quenching and became lighter (light yellow) after being annealed at 800 °C in air.

The characterization results of these six samples are detailed in the following sections and gathered in **Table 2**.

XRD analysis

The XRD results show that a minimum value of the 3+ dopant amount, *i.e.* $x \ge 0.25$, is needed to stabilize the cubic fluorite-type single phase in the $(Hf_{1/3}Ce_{1/3}Zr_{1/3})_{1-x}(Y_{1/2}Gd_{1/2})_xO_{2-\delta}$ solid solution. Indeed, for x = 0.16 (HEFO7-16), two cubic phases were obtained (**Figure 4a**). As expected, the lattice parameter increases with x (as indicated by a shift towards larger 2 θ angles in **Figure 4a**, which agrees with the larger ionic radii of the Gd³⁺ and Y³⁺ dopants with respect to those of the 4+ host cations (**Table 2**) [34]. Furthermore, from **Figure 4b**, the five compositions obtained as cubic single-phase, remained stable after being annealed in air at 800 °C. We also noticed that this oxidation treatment was accompanied with a slight decrease of the lattice parameters, especially for small x values, which is likely related to a smaller ionic radius of Ce⁴⁺ ions, when fully oxidized.



Figure 4. X-ray diffraction patterns of $(Zr_{1/3}Hf_{1/3}Ce_{1/3})_{1-x}(Y_{1/2}Gd_{1/2})_xO_{2-\delta}$ samples with x ranging from 0.16 to 0.60 prepared by S1 route (a) as prepared and (b) after annealing at 800 °C and EIS from 800 to 400 °C.

* The additional reflection in the pattern for the HEFO7-25 is attributed to the tungsten diffraction, present on the copper anti-cathode at the end-of-life tube.

Ionic conductivity measurements

As shown in **Figure 5**, the ionic conductivity is the lowest (*e.g.* 2.5 x 10^{-5} S.cm⁻¹ at T = 600 °C) for the highest value of x (x = 0.60); it increases upon decreasing x down to 0.40 and remains of the same order of magnitude for x ranging from 0.40 down to 0.25 (*i.e.* 6.3 % < $V_{O^{2-}}^{..}$ < 10.0 %). The highest ionic conductivity values are obtained in the dopant range of 0.25 < x < 0.4 (*i.e.* for 6.3 % < $V_{O^{2-}}^{..}$ < 10.0 %), and are never exceeding 3.7 x 10^{-4} S.cm⁻¹ (at T = 600 °C).



Figure 5. Arrhenius plots of the ionic conductivity of the $(Hf_{1/3}Ce_{1/3}Zr_{1/3})_{1-x}(Y_{1/2}Gd_{1/2})_xO_{2-\delta}$ samples with x ranging from 0.16 to 0.60 prepared by S1 route. In the insert, the composition dependence of σ_{ion} at 600 °C.

Unfortunately, for this particular compound family, the $V_{O^{2-}}^{..}$ content cannot be decreased down to the classical ionic conductor value of 4 % because of the instability of the cubic phase (**Figure 4a**) with x = 0.16). Therefore, lower $V_{O^{2-}}^{..}$ values could not be evaluated for the HEFO7 series.

In addition, the ionic conductivity of these $(Hf_{1/3}Ce_{1/3}Zr_{1/3})_{1-x}(Y_{1/2}Gd_{1/2})_xO_{2-\delta}$ compounds is still significantly lower than the 3 x 10⁻³ S.cm⁻¹ (at 600 °C) achieved for 8YSZ#2 reference fluorite ionic conductor.

3.4. New compositions regarding the ΔS_{cat} (HEFOYb-15(1), (2) and (3))

In the following, we expose the design rules and the characterization results of the HEFOYb-15 compounds family. Three compositions were investigated: The $(Hf_{0.327}Ce_{0.456}Zr_{0.217})_{0.85}Yb_{0.15}O_{1.93}$ (labelled HEFOYb-15(1)), the $(Hf_{0.163}Ce_{0.442}Zr_{0.395})_{0.85}Yb_{0.15}O_{1.93}$ (labelled HEFOYb-15(2)) and the $(Hf_0Ce_{0.429}Zr_{0.571})_{0.85}Yb_{0.15}O_{1.93}$ (labelled HEFOYb-15(3)) samples.

As a first design rule for these three compounds, a 3+ cation substituent content of 15 % was selected, then setting an oxygen vacancy amount at 3.5 % of anionic sites, *i.e.* in the typical range of classical ionic conductors (4 %) was chosen; thus, the variation of ΔS_{cat} could be evaluated. A second design rule

for this family was to select host 4+ cations as non-radioactive, non-toxic, relatively abundant and having close ionic radii, which resulted in Hf, Ce anf Zr elements. In order not to significantly disturb the structure with the increase of the ΔS_{cat} , an additional feature was to select a 3+ cation with an ionic radius as close as possible to the so-called "critical ionic radius". This consideration originates from D.J. Kim [41], who defined the critical radius (r_{crit}) of the 3+ dopant for which the host structure formed by $Zr^{4+}/Ce^{4+}/Hf^{4+}$ would be not disturbed. By selecting such a 3+ cation, the stress brought by the size difference between 3+ and 4+ cations is minimized. D.J. Kim's experimental fittings lead to the linear relation: $r_{crit} = p + q$. $r_{ion host}$ with p = 0.034, q = 0.72 and $r_{cat host}$ (in nanometer) corresponding to the ionic radius average of the cations host (Ce, Hf, Zr)O₂. For instance, considering the equimolar oxide host $Hf_{1/3}Ce_{1/3}Zr_{1/3}O_2$, and the cationic radii of Ce⁴⁺(VIII), Zr⁴⁺(VIII) and Hf⁴⁺(VIII) (0.097, 0.084, 0.083 nm, respectively [36]), a r_{crit} can be calculated as 0.0974 nm. As a result of this 3rd design rule, we selected Yb³⁺ as the substituting cation dopant, being the 3+ cation with the closest ionic radius (0.0985 nm).

To perfectly match the critical radius and the Yb³⁺ radius, the ratio between Hf/Ce/Zr was adjusted:

$$r_{Yb3+} = r_{crit} = r_{cat host} = [r_{Yb3+} - p] / q$$

The obtained relation results in multiple possible compositions, which were discriminated using a final rule consisting in reducing the cationic size difference (among the three host 4+ cations only), defined as

$$\delta r_{cat} = \sqrt{\sum_{i=1}^{N} \alpha i \left(1 - \frac{ri}{\sum_{j=1}^{N} \alpha j \cdot rj}\right)^2}$$
 Equation 3

Where ri corresponds to the ionic radius of the *i*th cation with cationic fraction αi [42]. Thus, α_{Hf} was set equal to 0.327, leading to the host structure ratio: (Hf_{0.327}Ce_{0.456}Zr_{0.217})O₂ and the resulting (Hf_{0.327}Ce_{0.456}Zr_{0.217})O₂ and the resulting compound (noted HEFOYb-15(1). Afterwards, in order to evaluate the possible influence of Hf⁴⁺ cation on the ionic conductivity, the Hf⁴⁺ cation ratio α_{Hf} was first reduced by half, leading to the (Hf_{0.163}Ce_{0.442}Zr_{0.395})Yb_{0.15}O_{1.93} compound (HEFOYb-15(2)), and finally eliminated, leading to the (Hf₀Ce_{0.429}Zr_{0.571})Yb_{0.15}O_{1.93} compound (HEFOYb-15(3)).

These compounds prepared by the S2 route, were dark colored after the 1500 °C air-quenching and became light yellow after annealing at 800 °C in air. The obtained relative density was > 87 %. **Table 2** summarizes the characteristic properties of the samples.

XRD analysis

All three HEFOYb-15(1), (2) and (3) compounds were found single-phase with the fluorite cubic structure and, as expected, each being characterized by almost identical lattice parameter (a = 0.524

nm, a = 0.523 nm, a = 0.523 nm, respectively). These compositions designed in accordance with the critical ionic radius theory allowed forming the cubic fluorite-type single-phase for a low value of $V_{O^{2-}}^{...}$ (3.8 %) (**Figure 6**). These HEOs phases occurred even with noticeably smaller entropic contributions (both ΔS_{cat} , ΔS_{anio} and ΔS_{config}) than those of the not-stable HEFO7-16 compound. Furthermore, the phase was still stable after an annealing at 800°C, despite the lower ΔS_{config} (esp. for *e.g.* HEFOYb-15(3) with Hf₀Ce_{0.364}Zr_{0.485}Yb_{0.15}O_{1.93} composition).



Figure 6. X-Rays Diffractograms of the HEFOYb-15(1), HEFOYb-15(2) and HEFOYb-15(3) samples (a) as sintered and (b) after annealing at 800 °C and EIS measurements from 800 to 400 °C. * Some Pt remains after polishing on the surface of the HEFOYb-15(3) sample.

Ionic conductivity measurements

The measured ionic conductivity is similar for the three samples of the HEFOYb series (**Figure 7**) and is similar to that measured for the HEFO7 series (**Figure 5**); it is not significantly improved and is of the same order of magnitude as that of the high entropy oxides previously reported [28].



Figure 7. Arrhenius plots of the ionic conductivity of the HEFOYb-15(1), HEFOYb-15(2) and HEFOYb-15(3) samples prepared by S2 route compared to that of HEFO7-40 prepared by S1.

To conclude on these results, taking into account the critical radius of the host structure allows the thermal stabilization of the cubic fluorite-type single phase, Hf⁴⁺ presence being irrelevant. Furthermore, neither improvement nor degradation of the ionic conductivity was evidenced by respecting the critical ionic radius and by decreasing Hf⁴⁺ cation amount.

4. DISCUSSION

Regarding the cubic fluorite-type phase formation of the HEOs, based only on the composition of a given HE compound, one can easily calculate the above parameters δr_{cat} and ΔS_{config} ($\Delta S_{cat} + \Delta S_{anio}$) (*cf.* **Table 2**). Compounds considered in this work are displayed in **Figure 8** depending on their ΔS_{config} as a function of their δr_{cat} . A similar plot can be found in **Supplementary Information 3**, which includes all

data points for the HE fluorite compositions reported in the literature as stable (or not) in the bulk form (*i.e.* pellets with micrometer-size grains, and excluding nanopowders prone to metastability).



Figure 8. Representation of the ΔS_{config} as a function of the cationic size difference (δr_{cat}), which defines the HE fluorite bulk single-phase formation criteria.
 (•) single phase, after annealing at 800 °C; (•) not single phase, after annealing at 800 °C.

Introducing a new cation by partial substitution on a given cationic site results in two opposite effects: 1) an expected increase in configurational entropy ΔS_{config} - *a priori* favorable to stabilize a new phase (stable only above a given temperature and metastable below- see HEFO9A) and 2) a correlated increase in cationic size differences δr_{cat} because the choice is limited and extended towards extreme sizes (as nearest neighbors were first selected). As a result, and based only on both δr_{cat} and ΔS_{config} criteria, High-Entropy Fluorite oxides that one can design, are found roughly along a diagonal dotted line in **Figure 8**. Among them, the stable ones are found mainly in a narrow range of the cationic size difference, 7 < δr_{cat} < 10 %. Nevertheless, some exceptions can be found not stable, as some relevant factors, such as thermodynamic enthalpy terms, are missing in the present simple picture.

To evaluate the effect of high entropy on ionic conductivity, compounds with small δr_{cat} and with $\Delta S_{config} > 1.5 k_B/f.u.$ (in the upper-left area, directly above classical ionic conductors in **Figure 8**) would be most suitable, but such compounds do not exist, yet. The closest-related ones in this work are the HEOYb-15(1), (2) and (3) compounds. Obviously, compounds with the highest ΔS_{config} cannot be obtained with the cubic fluorite structure, likely because of δr_{cat} is too large (**Table 2**).

Concerning the ionic conductivity of the HEOs, based on our results as well as on those previously reported, it was interesting to try to determine the origin or even possible reasons for the low ionic conductivity, σ_{ion} . Actually, the ionic conductivity of these compounds does not seem to be significantly dependent on the configurational entropies.

Thus, to interpret the results, the average cationic-size difference (δr_{cat}) defined in **equation 3** was considered. The characteristics of the studied samples are reported in **Table 2**.





Figure 9. Dependence of the ionic conductivity on (a) σr_{cat} (b) ΔS_{config} (c) the ΔS_{anio} .

Figure 9 shows the variation of the ionic conductivity of the studied compositions as well as of the classical electrolytes depending on the three relevant parameters δr_{cat} , ΔS_{config} (= $\Delta S_{cat} + \Delta S_{anio}$) and ΔS_{anio} . It is evidenced that the highest values of the ionic conductivity for the HEOs (HEFOYb-15(1),

HEFO7-25, -30 and -40) stand in a rather small range (**Figure 9a-b**); the difference between the HEO Fluorite samples being not significant, one can conclude that the δr_{cat} and ΔS_{config} parameters do not have the expected impact on the ionic conductivity. As already reported in section **3.3**, **Figure 9c** highlights the negative effect of an excess of oxygen vacancy content on the ionic conductivity for the HEFO7-40, -50 and -60 compositions.

Finally, it should be pointed out that the classical ionic conductors exhibit the highest conductivity values, which does not play in favor of HEOs. Therefore, why does the ionic conductivity in HEOs seem to be inhibited? This limitation could be due to oxygen mobility issues. Indeed, the disorder could induce local crystal network perturbations, which would probably lessen the oxygen transport.

Going further in the interpretation should probably imply to carefully consider parameters such as the defects association as well as the migration energies, while the previous discussion takes into account only geometrical factors or thermodynamics. For this purpose, Kinetic Monte Carlo (KMC) or Density Functional Theory (DFT) calculations would be required, as reported for example by Koettgen *et al.* using DFT regarding doped ceria oxides [43]. The association energy between defects on regular lattice sites (trapping) and migration energies for the activation barriers of symmetric jump environments (blocking) could then be discussed on this basis. In particular, the blocking determines the dopant fraction that yields the highest ionic conductivity, while trapping limits the maximum ionic conductivity value. Koettgen defined a general model for the migration energy with a limited number of parameters and only for a two-cations system. With respect to the number of cations and the highly doped oxides considered in this work, this approach could be useful. It could help to better understand the result that the conductivity reaches a maximum for a high dopant content ($x \approx 0.35$), while it usually occurs at much lower content in conventional materials.

In previous publications, mixtures of classical ionic conductors were studied to improve the ionic conductivity. Indeed, Tsoga [44] combined GDC and YSZ (two 3+ cations and two 4+ cations) to obtain multiple stable compositions, including the $Gd_{0.11}Y_{0.04}Ce_{0.40}Zr_{0.45}O_{1.925}$ (called 50YSZ/50GDC in **Figure 9**) with an oxygen stoichiometry close to our designed compounds. Ananthapadmanabhan *et al.* [45] also added Ce⁴⁺ to YSZ to obtain multiple compositions mixing two 4+ cations and one 3+ cation. The Y_{0.18}Ce_{0.41}Zr_{0.41}O_{1.91} composition (called 0.18YSZ/Ce in **Figure 9**) is chosen for comparison, again because of the oxygen stoichiometry. But all these compositions led to poorer ionic conductivities compared to their parent ionic conductors. By comparing their ionic conductivity values (*e.g.* 2.45 x 10⁻⁴ S.cm⁻¹ for 50YSZ/50GDC and 7.95 x 10⁻⁵ S.cm⁻¹ for 0.18YSZ/Ce at 600 °C, *cf.* **Figure 9**) with those

measured for our HEOs, one can conclude that adding more 4+ and 3+ cations does not significantly increase the ionic conductivity but does not degrade it further.

5. CONCLUSION

In previous studies of High Entropy fluorite-type Oxides, reported values of their ionic conductivity were low compared to those of classical ionic conductors (8YSZ and *a fortiori* 10GDC) and useless for applications. Then, on the basis of some relevant parameters such as $V_{O^{2-}}^{..}$, δr_{cat} , ΔS_{config} , we designed new compositions showing high configurational entropy as well as oxygen deficiency. We kept the (Hf/Ce/Zr) basic network substituted by (RE) cations and used two different synthesis routes, which were found to yield the same results.

The challenge was to find a compromise between these three parameters, $\Delta S_{config} \ge 1.5 \text{ k}_{B}/\text{f.u.}$, a minimized value of δr_{cat} (at least < 10 %) to stabilize the cubic fluorite-type phase and, in addition, an oxygen vacancy content, $V_{O^{2-}}^{..}$, close to 3 % (as in the classical electrolytes). The measured values of the ionic conductivity did not currently exceed 4 x 10⁻⁴ S.cm⁻¹ at 600 °C, one order of magnitude lower than the target value of $\sigma = 3 \times 10^{-2}$ S.cm⁻¹ at 600 °C, required for a solid oxide fuel cell application.

The literature reports an increasing number of high entropy oxides, many combinations of cations are possible and this work reports only a few possibilities. The geometric parameters may be not sufficient to be only considered but allows underlining the interdependence of the ionic radius and the entropy regarding the ionic conductivity. It certainly exists a compromise between various parameters; future work will take them into account.

ACKNOWLEDGEMENTS

We acknowledge ICMCB-CNRS and IMRA Europe S.A.S. for providing technical resources (SPS, high temperature furnaces, Scanning Electron Microscopy, electrochemical devices) necessary for the completion of this study, and IMRA Europe S.A.S. for the financial support. We acknowledge Marie-Hélène Delville for her kind scientific contribution.

REFERENCES

- [1] A. R. West, Solid State Chemistry and its Applications. J. Wiley and Sons, 2014.
- [2] A. Jain, Y. Shin, and K. A. Persson, "Computational predictions of energy materials using density functional theory," *Nature Reviews Materials*, vol. 1, no. 1, pp. 1–13, Jan. 2016, doi: 10.1038/natrevmats.2015.4.
- [3] D. Y. Yoon *et al.*, "A Combinatorial Chemistry Method for Fast Screening of Perovskite-Based NO Oxidation Catalyst," *ACS Comb. Sci.*, vol. 16, no. 11, pp. 614–623, Nov. 2014, doi: 10.1021/co5000344.
- [4] X. Xiang *et al.*, "A combinatorial approach to materials discovery," *Science*, vol. 268, no. 5218, pp. 1738–1740, Jun. 1995, doi: 10.1126/science.268.5218.1738.
- [5] J.-C. Grenier, M. Pouchard, and A. Wattiaux, "Electrochemical synthesis: oxygen intercalation. Current Opinion in Solid State & Materials Science," *Ed; J. Rouxel et C.N.R. Rao*, vol. 1 (2), pp. 233–240, 1996, doi: 10.1016/S1359-0286(96)80090-8.
- [6] J.-W. Yeh *et al.*, "Nanostructured High-Entropy Alloys with Multiple Principal Elements: Novel Alloy Design Concepts and Outcomes," *Advanced Engineering Materials*, vol. 6, no. 5, pp. 299– 303, 2004, doi: 10.1002/adem.200300567.
- B. Gludovatz, A. Hohenwarter, D. Catoor, E. H. Chang, E. P. George, and R. O. Ritchie, "A fracture-resistant high-entropy alloy for cryogenic applications," *Science*, vol. 345, no. 6201, pp. 1153–1158, Sep. 2014, doi: 10.1126/science.1254581.
- [8] A. Gali and E. P. George, "Tensile properties of high- and medium-entropy alloys," *Intermetallics*, vol. 39, pp. 74–78, Aug. 2013, doi: 10.1016/j.intermet.2013.03.018.
- [9] B. S. Murty, J. W. Yeh, and S. Ranganathan, "Chapter 10 Applications and Future Directions," in *High Entropy Alloys*, B. S. Murty, J. W. Yeh, and S. Ranganathan, Eds. Boston: Butterworth-Heinemann, 2014, pp. 159–169.
- [10] C. M. Rost et al., "Entropy-stabilized oxides," Nat Commun, vol. 6, Sep. 2015, doi: 10.1038/ncomms9485.
- [11] D. Bérardan, S. Franger, D. Dragoe, A. K. Meena, and N. Dragoe, "Colossal dielectric constant in high entropy oxides," *physica status solidi (RRL) – Rapid Research Letters*, vol. 10, no. 4, pp. 328–333, 2016, doi: 10.1002/pssr.201600043.
- D. Bérardan, S. Franger, A. K. Meena, and N. Dragoe, "Room temperature lithium superionic conductivity in high entropy oxides," *J. Mater. Chem. A*, vol. 4, no. 24, pp. 9536–9541, Jun. 2016, doi: 10.1039/C6TA03249D.
- [13] A. Sarkar *et al.*, "Rare earth and transition metal based entropy stabilised perovskite type oxides," *Journal of the European Ceramic Society*, vol. Volume38, no. Issue5, pp. Pages2318-2327, 2018, doi: 10.1016/j.jeurceramsoc.2017.12.058.
- [14] A. Sarkar *et al.*, "Multicomponent equiatomic rare earth oxides with a narrow band gap and associated praseodymium multivalency," *Dalton Trans.*, vol. 46, no. 36, pp. 12167–12176, Sep. 2017, doi: 10.1039/C7DT02077E.
- [15] Y. Zhang *et al.*, "Dense high-entropy boride ceramics with ultra-high hardness," *Scripta Materialia*, vol. 164, pp. 135–139, Apr. 2019, doi: 10.1016/j.scriptamat.2019.01.021.
- [16] T. J. Harrington *et al.*, "Phase stability and mechanical properties of novel high entropy transition metal carbides," *Acta Materialia*, vol. 166, pp. 271–280, Mar. 2019, doi: 10.1016/j.actamat.2018.12.054.
- [17] T. K. Chen, T. T. Shun, J. W. Yeh, and M. S. Wong, "Nanostructured nitride films of multielement high-entropy alloys by reactive DC sputtering," *Surface and Coatings Technology*, vol. 188–189, pp. 193–200, Nov. 2004, doi: 10.1016/j.surfcoat.2004.08.023.
- [18] Y. Qin, J.-X. Liu, F. Li, X. Wei, H. Wu, and G.-J. Zhang, "A high entropy silicide by reactive spark plasma sintering," J Adv Ceram, vol. 8, no. 1, pp. 148–152, Mar. 2019, doi: 10.1007/s40145-019-0319-3.

- [19] R.-Z. Zhang, F. Gucci, H. Zhu, K. Chen, and M. J. Reece, "Data-Driven Design of Ecofriendly Thermoelectric High-Entropy Sulfides," *Inorganic Chemistry*, vol. 57, no. 20, pp. 13027–13033, Oct. 2018, doi: 10.1021/acs.inorgchem.8b02379.
- [20] X. Chen and Y. Wu, "High-entropy transparent fluoride laser ceramics," *Journal of the American Ceramic Society*, vol. 103, no. 2, pp. 750–756, 2020, doi: 10.1111/jace.16842.
- [21] T. Wang, H. Chen, Z. Yang, J. Liang, and S. Dai, "High-Entropy Perovskite Fluorides: A New Platform for Oxygen Evolution Catalysis," *Journal of the American Chemical Society*, vol. 142, no. 10, pp. 4550–4554, Mar. 2020, doi: 10.1021/jacs.9b12377.
- [22] A. Miura, S. Ishiyama, D. Kubo, N. Rosero Navarro, and K. Tadanaga, "Synthesis and ionic conductivity of a high-entropy layered hydroxide," *Journal of the Ceramic Society of Japan*, vol. 128, pp. 336–339, Jul. 2020, doi: 10.2109/jcersj2.20001.
- [23] A. Sarkar, B. Breitung, and H. Hahn, "High entropy oxides: The role of entropy, enthalpy and synergy," *Scripta Materialia*, vol. 187, pp. 43–48, Oct. 2020, doi: 10.1016/j.scriptamat.2020.05.019.
- [24] F. Li *et al.*, "Synthesis of single-phase metal oxycarbonitride ceramics," *Scripta Materialia*, vol. 176, pp. 17–22, Feb. 2020, doi: 10.1016/j.scriptamat.2019.09.024.
- [25] T. Wen, B. Ye, M. C. Nguyen, M. Ma, and Y. Chu, "Thermophysical and mechanical properties of novel high-entropy metal nitride-carbides," *Journal of the American Ceramic Society*, vol. 103, no. 11, pp. 6475–6489, 2020, doi: 10.1111/jace.17333.
- [26] J. Guan *et al.*, "Synthesis and thermal stability of novel high-entropy metal boron carbonitride ceramic powders," *Ceramics International*, Jul. 2020, doi: 10.1016/j.ceramint.2020.07.126.
- [27] M. Qin et al., "Dual-Phase High-Entropy Ultra-High Temperature Ceramics," Journal of the European Ceramic Society, vol. 40, no. 15, pp. 5037–5050, Dec. 2020, doi: 10.1016/j.jeurceramsoc.2020.05.040.
- [28] J. Gild *et al.*, "High-entropy fluorite oxides," *Journal of the European Ceramic Society*, vol. 38, no. 10, pp. 3578–3584, Aug. 2018, doi: 10.1016/j.jeurceramsoc.2018.04.010.
- [29] X. Q. Cao, R. Vassen, and D. Stoever, "Ceramic materials for thermal barrier coatings," *Journal* of the European Ceramic Society, vol. 24, no. 1, pp. 1–10, Jan. 2004, doi: 10.1016/S0955-2219(03)00129-8.
- [30] J. Cho, J. Park, and J. An, "Low thermal conductivity of atomic layer deposition yttria-stabilized zirconia (YSZ) thin films for thermal insulation applications," *Journal of the European Ceramic Society*, vol. 37, no. 9, pp. 3131–3136, Aug. 2017, doi: 10.1016/j.jeurceramsoc.2017.03.045.
- [31] K. Chen et al., "A five-component entropy-stabilized fluorite oxide," Journal of the European Ceramic Society, vol. 38, no. 11, pp. 4161–4164, Sep. 2018, doi: 10.1016/j.jeurceramsoc.2018.04.063.
- [32] A. J. Wright, Q. Wang, C. Huang, A. Nieto, R. Chen, and J. Luo, "From high-entropy ceramics to compositionally-complex ceramics: A case study of fluorite oxides," *Journal of the European Ceramic Society*, vol. 40, no. 5, pp. 2120–2129, May 2020, doi: 10.1016/j.jeurceramsoc.2020.01.015.
- [33] S. J. Skinner and J. A. Kilner, "Oxygen ion conductors," *Materials Today*, vol. 6, no. 3, pp. 30–37, Mar. 2003, doi: 10.1016/S1369-7021(03)00332-8.
- [34] "Fullprof Suite, Crystallographic tools for Rietveld, profile matiching & integrated intensity refinements of X-Ray and/or neutron data." https://www.ill.eu/sites/fullprof/php/programs8809.html?pagina=FullProf (accessed Jan. 06, 2021).
- [35] "ZView[®] For Windows.," *Scribner Associates*. http://www.scribner.com/software/68-generalelectrochemistr376-zview-for-windows/ (accessed Jan. 06, 2021).
- [36] R. D. Shannon, "Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides," *Acta Cryst.*, vol. 32A, pp. 751–767, 1976, doi: 10.1107/S0567739476001551.

- [37] L. Rogal, P. Bobrowski, F. Körmann, S. Divinski, F. Stein, and B. Grabowski, "Computationallydriven engineering of sublattice ordering in a hexagonal AlHfScTiZr high entropy alloy," *Scientific Reports*, vol. 7, no. 1, Dec. 2017, doi: 10.1038/s41598-017-02385-w.
- [38] B. Ye, T. Wen, M. C. Nguyen, L. Hao, C.-Z. Wang, and Y. Chu, "First-principles study, fabrication and characterization of (Zr0.25Nb0.25Ti0.25V0.25)C high-entropy ceramic," *Acta Materialia*, vol. 170, pp. 15–23, May 2019, doi: 10.1016/j.actamat.2019.03.021.
- [39] J.-F. Bérar and P. Lelann, "E.s.d.'s and estimated probable error obtained in Rietveld refinements with local correlations," J Appl Cryst, vol. 24, no. 1, Art. no. 1, Feb. 1991, doi: 10.1107/S0021889890008391.
- [40] J.-F. Bérar, "Acc. in Pow. Diff. II," NIST Special Publication, vol. 846, pp. 63–67, 1992.
- [41] D.-J. Kim, "Lattice Parameters, Ionic Conductivities, and Solubility Limits in Fluorite-Structure MO2 Oxide [M = Hf4+, Zr4+, Ce4+, Th4+, U4+] Solid Solutions," *Journal of the American Ceramic Society*, vol. 72, no. 8, pp. 1415–1421, 1989, doi: 10.1111/j.1151-2916.1989.tb07663.x.
- [42] J. Gild *et al.*, "High-Entropy Metal Diborides: A New Class of High-Entropy Materials and a New Type of Ultrahigh Temperature Ceramics," *Scientific Reports*, vol. 6, no. 1, p. 37946, Nov. 2016, doi: 10.1038/srep37946.
- [43] J. Koettgen, S. Grieshammer, P. Hein, B. O. H. Grope, M. Nakayama, and M. Martin,
 "Understanding the ionic conductivity maximum in doped ceria: trapping and blocking," *Phys. Chem. Chem. Phys.*, vol. 20, no. 21, pp. 14291–14321, 2018, doi: 10.1039/C7CP08535D.
- [44] A. Tsoga, A. Naoumidis, and D. Stover, "Total electrical conductivity and defect structure of ZrO2–CeO2–Y2O3–Gd2O3 solid solutions," *Solid State Ionics*, vol. 135, no. 1–4, pp. 403–409, Nov. 2000, doi: 10.1016/S0167-2738(00)00477-X.
- [45] P. V. Ananthapadmanabhan, N. Venkatramani, and V. K. Rohatgi, "Structure and Ionic Conductivity of Solid Solutions in the System 0.9{(ZrO2)1-x -(CeO2)x}-0.1(Y2O3)," Journal of the European Ceramic Society, vol. 6, p. 7, 1990.
- [46] S. Kazlauskas, E. Kazakevičius, and A. Kežionis, "Electrical properties of scandia- and ceriastabilized zirconia ceramics," *Solid State Ionics*, vol. 310, pp. 143–147, Nov. 2017, doi: 10.1016/j.ssi.2017.08.008.
- [47] R. Djenadic *et al.*, "Multicomponent equiatomic rare earth oxides," *Materials Research Letters*, vol. 5, no. 2, pp. 102–109, Mar. 2017, doi: 10.1080/21663831.2016.1220433.
- [48] M. Pianassola, M. Loveday, J. W. McMurray, M. Koschan, C. L. Melcher, and M. Zhuravleva, "Solid-state synthesis of multicomponent equiatomic rare-earth oxides," *Journal of the American Ceramic Society*, vol. 103, no. 4, pp. 2908–2918, Apr. 2020, doi: 10.1111/jace.16971.
- [49] M. Anandkumar, S. Bhattacharya, and A. S. Deshpande, "Low temperature synthesis and characterization of single phase multi-component fluorite oxide nanoparticle sols," *RSC Advances*, vol. 9, no. 46, pp. 26825–26830, 2019, doi: 10.1039/C9RA04636D.

SUPPLEMENTARY INFORMATION

Supplementary Information 1: EDX analysis of both HEFO7B#1 and #2 samples.

HEFO7B#1: X-rays mapping (count, voltage: 15.0 kV)



HEFO7B#2: X-rays mapping (count, voltage: 15.0 kV)



SOURCE	Code	Cubic fluorite- type single phase?	Normalized formula	x of O _x	Theo. latt. para.= (4/√3)(rcat+ro	Exp. latt. para. as) sintered	ΔS _{cat}	ΔS _{anio}	ΔS _{confi}	g r _{cat}	δr _{cat}	σ at 600 °C
				-	nm	nm	k₀/f.u	. k _₿ /f.u.	k₀/f.u	nm	%	S.cm ⁻¹
[33]	8YSZ	Υ	Zr0.852Y0.148O1.93	1.93	0.519	0.514	0.42	0.32	0.74	0.087	7.38	9.2 x 10⁻³
[46]	10Sc1CeSZ	Υ	Zr0.809Sc0.182Ce0.009O1.91	1.91	0.514	-	0.52	0.37	0.89	0.084	1.84	2.98 x 10 ⁻²
[33]	GDC10	Υ	Ce0.9Gd0.1O1.95	1.95	0.514	0.542	0.33	0.23	0.56	0.085	1.95	2.37 x 10 ⁻²
[28]	HEFO1	Υ	Hf0.25Zr0.25Ce0.25Y0.25O1.875	1.88	0.530	0.521	1.39	0.47	1.85	0.091	8.96	-
[28]	HEFO2A	N	Hf0.25Zr0.25Ce0.25Y0.125Ti0.125O1.9375	1.94	0.522	-	1.56	0.28	1.84	0.088	10.13	-
[28]	HEFO3A	N	Hf0.25Zr0.25Ce0.25Y0.125Mg0.125O1.812	1.81	0.526	-	1.56	0.62	2.18	0.090	7.99	-
[28]	HEFO4A	Υ	Hf0.25Zr0.25Ce0.25Y0.125Yb0.125O1.875	1.88	0.529	0.523	1.56	0.47	2.03	0.091	8.46	-
[28]	HEFO4B	Υ	Hf0.2Zr0.2Ce0.2Y0.2Yb0.2O1.8	1.80	0.533	0.524	1.61	0.65	2.26	0.093	8.45	-
[28]	HEFO5A	Υ	Hf0.25Zr0.25Ce0.25Y0.125Ca0.125O1.8125	1.81	0.533	0.525	1.56	0.62	2.18	0.093	11.02	-
[28]/[32]	HEFO5B/5H	N	Hf0.2Zr0.2Ce0.2Y0.2Ca0.2O1.7	1.70	0.539	-	1.61	0.85	2.45	0.096	11.51	-
[28]	HEFO6A	N	Hf0.25Zr0.25Ce0.25Y0.125La0.125O1.875	1.88	0.534	-	1.56	0.47	2.03	0.093	12.01	-
[28]	HEFO7A	Υ	Hf0.25Zr0.25Ce0.25Y0.125Gd0.125O1.875	1.88	0.531	0.525	1.56	0.47	2.03	0.092	9.50	-
[28]	HEFO7B	Υ	Hf0.2Zr0.2Ce0.2Y0.2Gd0.2O1.8	1.80	0.536	0.528	1.61	0.65	2.26	0.094	9.67	1.1 x 10 ⁻⁴
[28]	HEFO8A	Υ	Hf0.25Zr0.25Ce0.25Yb0.125Gd0.125O1.875	1.88	0.530	0.525	1.56	0.47	2.03	0.091	9.06	-
[28]	HEFO8B	Υ	Hf0.2Zr0.2Ce0.2Yb0.2Gd0.2O1.8	1.80	0.535	0.527	1.61	0.65	2.26	0.094	9.20	-
[31]	chen2018	Υ	Ce0.2Zr0.2Hf0.2Sn0.2Ti0.2O2.0	2.00	0.512	0.535	1.61	0.00	1.61	0.084	8.91	-
[47]	CeLaPr	Υ	Ce0.33La0.33Pr0.33O	1.83	0.557	0.552	1.10	0.58	1.67	0.103	8.93	-
[47]	CeLaPrY	Υ	Ce0.25La0.25Pr0.25Y0.25O1.75	1.75	0.556	0.550	1.39	0.75	2.14	0.103	7.77	-
[47]	CeLaPrSm	Υ	Ce0.25La0.25Pr0.25Sm0.25O1.75	1.75	0.559	0.553	1.39	0.75	2.14	0.104	7.91	-
[47]	CeLaSmY	Υ	Ce0.25La0.25Sm0.25Y0.25O1.625	1.63	0.563	0.552	1.39	0.97	2.35	0.106	6.69	-
[47]	CeLaPrSmY	N	Ce0.2La0.2Pr0.2Sm0.2Y0.2O1.7	1.70	0.558	-	1.61	0.85	2.45	0.104	7.16	-
[47]	CeLaNdPrSmY	Υ	Ce0.17La0.17Nd0.17Sm0.17Y0.17Pr0.17O1.67	1.67	0.561	0.550	1.79	0.90	2.69	0.105	6.94	-
[47]	CeGdLaNdPrSm	Y N	-	-	-	-	-	-	-	-	-	-
[32]	4L	N	Hf0.314Zr0.314C0.314Y0.029Yb0.029O1.97	1.97	0.524	-	1.30	0.15	1.45	0.089	7.71	-
[32]	4M	Υ	Hf0.284Zr0.284Ce0.284Y0.074Yb0.074OO1.93	1.93	0.526	0.521	1.46	0.32	1.77	0.090	8.18	-
[32]	5L	Υ	Hf0.314Zr0.314Ce0.314Y0.029Ca0.029O1.96	1.96	0.524	0.521	1.30	0.21	1.51	0.089	8.65	-
[32]	5M	Υ	Hf0.284Zr0.284Ce0.284Y0.074Ca0.074O1.89	1.89	0.528	0.522	1.46	0.43	1.89	0.091	10.08	-
[32]	7M	Υ	Hf0.284Zr0.284Ce0.284Y0.074Gd0.074O1.93	1.93	0.527	0.523	1.46	0.32	1.77	0.090	8.95	-

Supplementary Information 2: Compositions and their properties from this work and the literature.

[44]	CGO	Y	Ce0.8Gd0.2O1.90	1.90	0.542	0.50	0.40	0.90	0.099 3.25	-
[44]	YSZ	Y	Zr0.852Y0.148O1.93	1.93	0.514	0.42	0.32	0.74	0.087 7.41	-
[44]	Mix0.1	Y	Ce0.073Zr0.755Gd0.017Y0.155O1.91	1.91	0.516	0.76	0.35	1.12	0.088 8.29	-
[44]	Mix0.25	Y	Ce0.186Zr0.639Gd0.044Y0.131O1.91	1.91	0.521	1.00	0.36	1.36	0.090 8.69	-
[44]	Mix0.5	Y	Ce0.384Zr0.447Gd0.096Y0.073O1.92	1.92	0.528	1.14	0.35	1.49	0.092 8.50	-
[44]	Mix0.75	Y	Ce0.584Zr0.232Gd0.146Y0.038O1.91	1.91	0.535	1.06	0.37	1.43	0.095 7.17	-
[44]	Mix0.9	Y	Ce0.704Zr0.103Gd0.176Y0.017O1.90	1.90	0.540	0.86	0.39	1.24	0.097 5.55	-
[44]	Mix0.95	Y	Ce0.752Zr0.052Gd0.188Y0.008O1.90	1.90	0.541	0.72	0.39	1.11	0.098 4.60	-
[44]	MixR	Y	Ce0.369Zr0.378Gd0.182Y0.072O1.87	1.87	0.530	1.23	0.47	1.71	0.094 8.76	-
[44]	MixR1	Y	Ce0.368Zr0.470Gd0.092Y0.070O1.92	1.92	0.528	1.13	0.34	1.47	0.092 8.55	-
[44]	MixR2	Y	Ce0.420Zr0.505Y0.075O1.96	1.96	0.527	0.90	0.19	1.09	0.091 7.70	-
[44]	MixR3	Y	Ce0.440Zr0.450Gd0.110O1.95	1.95	0.528	0.96	0.25	1.22	0.092 8.30	-
[44]	MixR4	Y	Ce0.424Zr0.437Gd0.106Y0.033O1.93	1.93	0.529	1.08	0.30	1.38	0.092 8.37	-
[44]	MixR5	Y	Ce0.398Zr0.451Gd0.112Y0.039O1.92	1.92	0.528	1.1	0.32	1.42	0.092 8.51	-
[44]	MixR6	Y	Ce0.408Zr0.490Gd0.102O1.95	1.95	0.526	0.95	0.24	1.19	0.091 8.36	-
[45]	x=0	Y	Zr0.818 Y0.182 O1.91	1.91	-	0.47	0.37	0.84	0.087 7.96	-
[45]	x=0.2	Υ	Zr0.656 Ce0.134 Y0.182 O1.91	1.91	-	0.88	0.37	1.25	0.089 8.48	-
[45]	x=0.4	Y	Zr0.491 Ce0.327 Y0.182 O1.91	1.91	-	1.02	0.37	1.39	0.092 8.29	-
[45]	x=0.5	Υ	Zr0.409 Ce0.409 Y0.182 O1.91	1.91	-	1.04	0.37	1.41	0.093 7.95	-
[45]	x=0.6	Υ	Zr0.327 Ce0.491 Y0.182 O1.91	1.91	-	1.02	0.37	1.39	0.094 7.45	-
[45]	x=0.9	Υ	Zr0.082 Ce0.736 Y0.182 O1.91	1.91	-	0.74	0.37	1.11	0.097 4.43	-
[45]	x=1	Y	Ce0.818 Y0.182 O1.91	1.91	-	0.47	0.37	0.84	0.098 1.97	-
[48]	CeLaPr	Y	Ce0.333La0.333Pr0.333O1.833	1.83 0.557	0.551	1.10	0.57	1.67	0.103 8.93	-
[48]	CeGdLaPr	Y	Ce0.25Gd0.25La0.25Pr0.25O1.75	1.75 0.558	0.550	1.39	0.74	2.14	0.104 7.74	-
[48]	CeLaNdPr	Y	Ce0.25Nd0.25La0.25Pr0.25O1.75	1.75 0.561	0.552	1.39	0.74	2.14	0.105 8.26	-
[48]	CeLaPrSm	Y	Ce0.25La0.25Pr0.25Sm0.25O1.75	1.75 0.559	0.551	1.39	0.74	2.14	0.104 7.91	-
[48]	CeLaPrY	Y	Ce0.25La0.25Pr0.25Y0.25O1.75	1.75 0.556	0.548	1.39	0.74	2.14	0.103 7.78	-
[48]	LaPr	Y	La0.5Pr0.5O1.75	1.75 0.563	0.556	0.69	0.75	1.45	0.106 9.43	-
[48]	LaPrY	Y	La0.333Pr0.333Y0.333O1.666	1.67 0.560	0.549	1.10	0.90	2.00	0.105 8.01	-
[49]	CeGdHfLaZr	Y	Ce0.2Hf0.2La0.2Gd0.2Zr0.2O1.8	1.80 0.543	0.534	1.61	0.65	2.26	0.097 12.96	-
[49]	GdHfLaYZr	Y	Zr0.2Hf0.2La0.2Y0.2Gd0.2O1.7	1.70 0.545	0.534	1.61	0.85	2.45	0.098 12.99	-
This work	HEFO2-25	Υ	Hf0.25Zr0.25Ce0.25Yb0.25O1.875	1.88 0.528	0.521	1.39	0.47	1.85	0.091 7.89	2.8 x 10 ⁻⁴
This work	HEFO2-25r	Ν	Hf0.25Zr0.25Ce0.25Yb0.25O1.625	1.63 0.547	-	1.39	0.97	2.35	0.099 15.51	-
This work	HEFOYb-15(1)	Y	Hf0.278Zr0.184Ce0.388Yb0.15O1.93	1.93 0.529	0.524	1.32	0.32	1.64	0.091 7.72	3.1 x 10 ⁻⁴

This work	HEFOYb-15(2)	Y	(Hf0.163Ce0.442Zr0.395)0.85(Yb0.15)O1.93	1.93	0.529	0.523	1.29	0.32	1.61	0.091 7	' .56	4.7 x 10 ⁻⁴
This work	HEFOYb-15(3)	γ	(Hf0Ce0.429Zr0.571)0.85(Yb0.15)O1.93	1.93	0.529	0.523	1.00	0.32	1.32	0.091 7	.41	3.8 x 10 ⁻⁴
This work	HEFO9A	Y	Hf0.168Ce0.168Zr0.168Ti0.168Sn0.168 Y0.08Yb0.08O1.92	1.92	0.513	0.518	1.90	0.34	2.24	0.084 1	.0.12	-
This work	HEF011B	Ν	Zr0.16Hf0.16Ce0.16Sn0.16Ti0.16 Y0.05Yb0.05Gd0.05La0.05O1.9	1.90	0.522	-	2.07	0.40	2.46	0.088 1	.7.62	-
This work	HEFO7-60	Υ	Hf0.13Ce0.13Zr0.13Y0.3Gd0.3O1.70	1.70	0.544	0.530	1.52	0.85	2.36	0.097 8	3.90	0.25 x 10 ⁻⁴
This work	HEFO7-50	Υ	Hf0.17Ce0.17Zr0.17Y0.25Gd0.25O1.75	1.75	0.540	0.529	1.60	0.75	2.35	0.096 9	9.55	0.62 x 10 ⁻⁴
This work	HEFO7-40	Υ	Hf0.2Ce0.2Zr0.2Y0.2Gd0.2O1.80	1.80	0.536	0.526	1.61	0.65	2.26	0.094 9	9.73	3.7 x 10 ⁻⁴
This work	HEFO7-30	γ	Hf0.23Ce0.23Zr0.23Y0.15Gd0.15O1.85	1.85	0.533	0.525	1.58	0.53	2.12	0.093 9	9.64	2.6 x 10 ⁻⁴
This work	HEFO7-25	γ	Hf0.25Ce0.25Zr0.25Y0.125Gd0.125O1.875	1.88	0.531	0.523	1.56	0.47	2.03	0.092 9	.54	3.5 x 10⁻⁴
This work	HEFO7-16	N	Hf0.28Ce0.28Zr0.28Y0.08Gd0.08O1.92	1.92	0.528	-	1.47	0.34	1.81	0.091 9	9.07	1.7 x 10 ⁻⁴

Supplementary Information 3: Representation of the ΔS_{config} as a function of the cationic size difference (δr_{cat}), which defines the HE fluorite bulk single-phase formation criteria. This representation includes all data points for HE fluorite compositions reported in the literature as stable (or not) in the bulk form. (•) single phase; (•) not single phase.

