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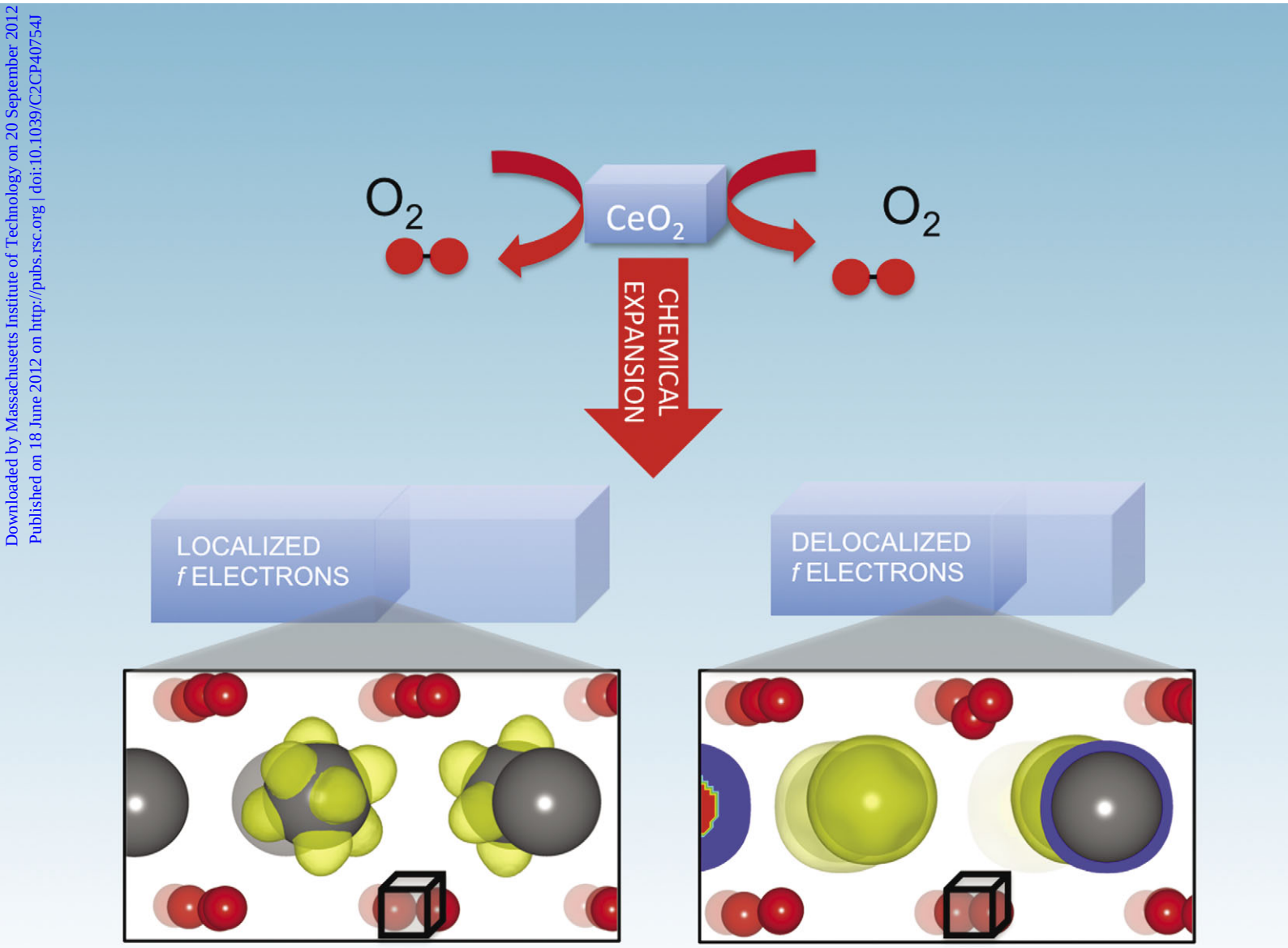

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COMMUNICATION

Charge localization increases chemical expansion in cerium-based oxides†

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In this work, we demonstrate the mechanism by which electronic charge localization increases the chemical expansion coefficient in two model systems, $CeO_{2-\delta}$ and $BaCeO_{3-\delta}$. Using Density Functional Theory calculations, we predict that this coefficient is increased by more than 70% when charge is fully localized, consistent with the observation that materials with a smaller degree of charge localization have smaller chemical expansion coefficients. This finding has important consequences for devising materials with smaller chemical expansion coefficients and for the reliability of the widely-used Shannon's ionic radii.

In solid state ionic materials, formation of point defects due to changes in temperature, composition, and surrounding environment, often results in significant lattice contraction or dilation,[1–3] known as chemical expansion. If not accounted for, chemical expansion can lead to significant stresses and ultimately mechanical failure. Examples are solid oxide fuel cell (SOFC) components[4,5] – exposed to reducing and oxidizing atmospheres at elevated temperatures – or electrodes in Li-ion batteries during Li intercalation.[6,7] Additionally, chemical expansion leads to strain-induced metallic to insulator transitions in superconductors[8] with rearrangement of ions around point defects. A chemical expansion coefficient,[2,9] α_C, is often defined (assuming a linear behaviour) by relating chemical expansion, ε, to changes in defect concentration, δ, analogous to the thermal expansion coefficient:

$$\varepsilon = \frac{a - a_0}{a_0} = \alpha_C \delta, \qquad (1)$$

where, in the example of reduced ceria, a and a_0 are the lattice parameters of $CeO_{2-\delta}$ and CeO_2, respectively (see ref. 10 for further information). Despite the importance of this phenomenon, a detailed understanding of the factors affecting α_C is still to emerge. The main goal of this work is to show quantitatively, using atomistic modeling, that charge localization is a key factor that increases chemical expansion, and we demonstrate this using model oxides, $CeO_{2-\delta}$ and $BaCeO_{3-\delta}$, from two different crystal classes.

Doped and undoped cerium oxide ($CeO_{2-\delta}$) adopts the fluorite structure and is a widely used compound in oxygen storage materials for heterogeneous gas catalysis.[11] This is due to its large variation in oxygen non-stoichiometry (δ), facilitated by the Ce^{4+}/Ce^{3+} redox couple.[12] Additionally, doped ceria is being investigated as the solid electrolyte in intermediate to low temperature SOFCs, where the non-stoichiometry induced chemical expansion can lead to mechanical failure.[13] Recently, we studied the origin of chemical expansion in $CeO_{2-\delta}$[10,14] (relying on Shannon's ionic radii, a valid assumption for this system[15]), and found that upon reduction (increase in δ), chemical expansion arises from two competing mechanisms: (1) an increase in lattice volume upon increase in Ce radius (*i.e.* $Ce^{4+} \rightarrow Ce^{3+}$) and (2) a decrease in lattice volume with the formation of charge compensating oxygen vacancies.[10] The cation radius change upon reduction is significantly larger than the contraction from oxygen vacancy formation, resulting in a net expansion of the lattice (or contraction upon oxidation). Like other low electron mobility oxides, electrons formed during reduction of ceria are localized in the Ce 4f orbital, forming small polarons within the narrow conduction band.[16] In this paper we show that this localization contributes to the large observed α_C in ceria.

Another strategic material expected to exhibit similar defect induced chemical expansion (predicted here) is $BaCeO_{3-\delta}$. It is a perovskite-structured material[17] with considerable proton conductivity at intermediate temperatures,[18] making it a candidate electrolyte material in proton-conducting fuel cells.[19] Its use as a semiconducting ferroelectric in solar-energy conversion devices (when doped with Ti) has also been recently suggested.[20] As in ceria, the 4f electrons, formed during reduction, are expected to be strongly localized, thus forming Ce^{3+} cations[18,21,22] and leading to chemical expansion.

In other non-stoichiometric oxides, such as the perovskites $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ and $Nd_{0.6}Sr_{0.4}Co_{1-y}Fe_yO_{3-\delta}$, electrons exhibit less localization, as exemplified by their metallic-like conductivities for small y.[23,24] Unlike the case of ceria,

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† Electronic supplementary information (ESI) available: Density of states, lattice parameters, Ce cation projected spin density and Ce ionic radii for different U values. See DOI: 10.1039/c2cp40754j

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the delocalized nature of the excess electrons should preclude the use of Shannon ionic radii in quantitatively determining the relative contribution to chemical expansion of cation radius change *versus* oxygen vacancy formation. Other uses of Shannon radii, for example, the Goldschmidt tolerance factor calculation to determine perovskite structural stability or the lattice free volume, as defined by Sammels and co-workers[25] to predict conducting properties, are also expected to be less reliable. In fact, electron delocalization was identified by Shannon as a limitation in determining ionic radii of compounds containing transition elements.[15] Previously, one of the authors of this paper suggested charge localization could explain the difference in α_C observed for different non-stoichiometric perovskites, using the enthalpy of electron migration as an indicator of localization.[26] Additionally, charge delocalization may explain part of the reason why α_C is typically much smaller for non-stoichiometric perovskites than fluorites,[27] though other factors might also have to be taken into account (*i.e.* lattice structure, relaxations and composition). It is thus useful to understand the effect of charge localization on α_C in non-stoichiometric oxides with the results then applied towards development of materials with reduced chemical expansion.

Here we use Density Functional Theory (DFT) calculations to elucidate and quantify the effect of charge localization on the chemical expansion process. This is achieved by systematically varying the Hubbard term, U, which alters the electronic structure and extent of charge localization. The results clearly show that the level of charge localization in $CeO_{2-\delta}$ and $BaCeO_{3-\delta}$ correlates well with α_C in these materials. Our findings are consistent with the observation that materials with less electron localization, such as $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ and $Nd_{0.6}Sr_{0.4}Co_{1-y}Fe_yO_{3-\delta}$, exhibit smaller chemical expansion coefficients. Our results also suggest that charge localization can be used to tune chemical expansion in these oxide materials, thus expanding their range of applicability. Finally, we discuss the consequences of our findings for the reliability of Shannon's ionic radii and all those parameters relying on them, such as Goldschmidt tolerance factors, used for determining perovskite structural stability.

The DFT and DFT + U calculations were performed on $2 \times 2 \times 2$ supercells (96 and 160 atoms for stoichiometric CeO_2 and $BaCeO_3$, respectively) with the Vienna *Ab initio* Simulation Package (VASP),[28,29] using the Projector Augmented Wave (PAW) method. A Generalized Gradient Approximation (GGA) with the Perdew-Wang 91 (PW91) exchange–correlation function and an energy cut-off of 500 eV were used. A Hubbard parameter, U, was used for Ce, employing the Dudarev approach,[30] and this was varied from 0 to 8.0 eV. The calculations were carried out using the Brillouin zone sampled with a $(2 \times 2 \times 2)$ and $(1 \times 1 \times 1)$ Monkhorst–Pack mesh k-points grid for CeO_2 and $BaCeO_3$, respectively. These settings are in line with those previously used in the literature[31] and tests were performed to confirm that the results are well converged with respect to these parameters. We calculated the lattice parameters of six ($\delta = 0$, 0.0312, 0.0625, 0.125, 0.1875, and 0.25) $CeO_{2-\delta}$ and four ($\delta = 0$, 0.0312, 0.0625, 0.125) $BaCeO_{3-\delta}$ compositions, by performing a full structure minimization, followed by extraction of α_C using eqn (1). The employed energy cut-off ensures that Puley stresses are negligible. This approach is preferred over others,[32]

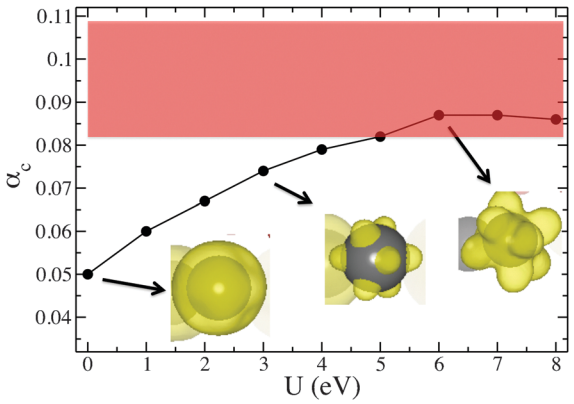

Fig. 1 Chemical expansion coefficients (α_C) for $CeO_{2-\delta}$ *vs.* Hubbard term, U. The red shaded area indicates the experimentally determined range for α_C, showing consistency with our predictions for $U \geq 5$ eV. The three inset figures show the 4f electron charge density (yellow) around a Ce cation (grey sphere) for $U = 0$, 3 and 5 eV. The contour level used is 0.05 electrons/Å^3.

because it is quick and intuitive and it has been recently shown to accurately predict α_C in several compounds.[10]

Standard DFT functionals are known to fail to describe the localized nature of the 4f electrons in ceria, due to the failure to cancel the Coulomb energy leading to a self-interaction error.[31] Consequently, standard DFT calculations predict a metallic ground state for reduced ceria, in clear contradiction to the experimental evidence (see Fig. S1 in Supporting Information†). To correct for this shortcoming, a Hubbard term, U, is usually added to force the 4f electrons to localize on the Ce^{3+} cations[31,33,34] (see Fig. 1). The addition of this term recovers the correct insulating behaviour of this material and this approach has been widely and successfully used over the past years.[31,33–35] *The key idea of this work is to use the above-mentioned limitation of DFT calculations to our advantage to elucidate the mechanism by which charge localization affects chemical expansion.* We calculate the chemical expansion coefficient as a function of U to assess the role of charge localization on this coefficient. It is known that the addition of the U term alters the lattice parameter of CeO_2 itself. Indeed a linear trend is observed for the lattice parameter *vs.* the U value, as shown in the Supplementary Material.† However, this needs not be a cause of concern since, in this work, we discuss the evolution of lattice parameter as a function of non-stoichiometry, δ, and not its absolute value (see eqn (1)). Finally, by selecting two separate model crystal structures, which have the same critical cation, Ce, this unique computational methodology isolates the effect of charge localization from other factors such as variations in chemical composition and/or crystal structure, unavoidable with experimental approaches.

In Fig. 1 we show the predicted chemical expansion coefficient, α_C, for $CeO_{2-\delta}$, extracted from Fig. 3 in the Supporting Material.† This clearly increases with U, saturating above about $U = 5$ eV where electrons are completely localized, as expected from the DOS in Fig. S1 in the Supporting Material.† The three insets in Fig. 1 show visually the increase in localization of 4f electron charge density around a Ce cation (with one neighbour vacancy) with increasing U. Charge localization was also confirmed by the projected spin density,[14] which is close to one for the Ce^{3+}

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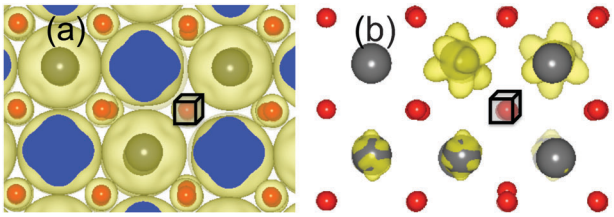

Fig. 2 Charge density for $U = 0.0$ eV (a) and 5.0 eV (b) in $CeO_{2-\delta}$. The contour level for the isosurfaces is 0.005 electrons/A^3. Color code as above. Blue indicates high charge density, typical of an area very close to the center of a Ce cation.

cation when $U \geq 5$ eV (see Table I in Supporting Material†). It is clear that charge localization strongly affects the chemical expansion coefficient, with a 74% increase from delocalized ($U = 0$ eV) to completely localized ($U = 6$ eV). Additionally, the simulated α_C values for $U \geq 5$ eV agree well with the range of experimental data, indicated by the shaded red area in Fig. 1.[10,36,37] This indicates that a U value in the 5–7 eV range must be used to obtain a good agreement with the experimental evidence, in accordance with previous investigations.[14,31,34,38]

Fig. 2 shows, in more detail, the 4f electron charge density isosurfaces in reduced ceria, using, on purpose, a very small contour level of 0.005 electrons/Å^3 for $U = 0.0$ eV and $U = 5.0$ eV. As expected, the 4f electrons are strongly localized on top of two Ce^{3+} when $U = 5.0$ eV, apparent by almost no charge density anywhere else in the crystal, even for such low contour levels. On the other hand, when $U = 0.0$ eV, charge density is delocalized and thus, more spread throughout the crystal lattice, filling vacant spaces between the atoms. This even distribution of charge means that all the Ce cations slightly increase their size upon reduction, resulting in a less distorted short range structure than in the localized case, and, hence, a lower α_C. This is confirmed by the fact that the Ce–O distances, in the vicinity of a vacancy, are all very similar (2.32–2.38 Å) in the delocalized system, whereas they vary more significantly (2.32–2.46 Å) in the localized case.

To show that our finding is generalizable beyond its applicability to a specific material/crystal structure, we have also calculated α_C for perovskite-structured $BaCeO_{3-\delta}$. In Fig. 3 we report the lattice

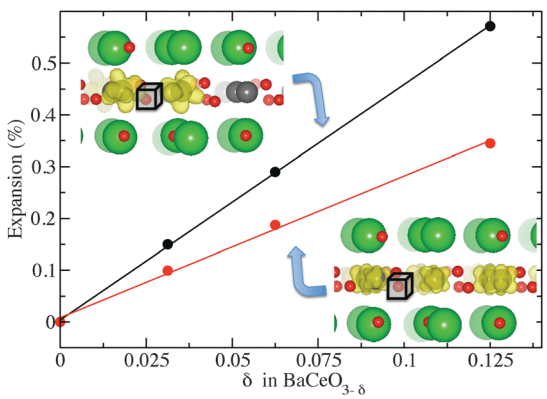

Fig. 3 Lattice parameter expansion (%) *vs.* δ for $BaCeO_{3-\delta}$ with $U = 5.0$ eV (black points) and $U = 0.0$ eV (red points). Black and red lines are linear fits. The two insets show the 4*f* charge density for $U = 5.0$ eV (top) and $U = 0.0$ eV (bottom). Color code and contour level as in Fig. 1; barium atoms are green.

parameter of this material for different levels of electron localization, as a function of the non-stoichiometry parameter, δ. The chemical expansion coefficients, extracted from the figure, are 0.027 and 0.045 for $U = 0$ and 5 eV, respectively. Unfortunately, to the authors' knowledge, no experimental chemical expansion coefficients are available for this material. However, the success of DFT + U (with $U \geq 5$) in describing the chemical expansion of several CeO_2-based oxides[10] makes us confident of its accuracy in this case.

Charge localization (confirmed by the cation projected spin density, as explained above) significantly increases α_C by the same amount as in $CeO_{2-\delta}$, proving that this behaviour is mainly determined by the cation, which localizes the electrons upon loss of oxygen from the lattice. However, it is worth noting that α_C in $CeO_{2-\delta}$ is about twice that in $BaCeO_{3-\delta}$, showing that structure and/or composition also play a key role in determining the value of α_C, and this is currently being investigated by the authors. These calculations confirm that charge localization plays an important role in the chemical expansion of these systems.

The obtained result has important consequences for the values of Shannon's ionic radii often used to predict α_C and other structural parameters. The effect of charge localization can be quantified using the following equations (used in our previous work[10]) to calculate a radius for Ce.

$$\alpha_M = \frac{r_s - r_h}{r_h + r_O} \text{ and } \alpha_V = \frac{1}{4}\frac{r_V - r_O}{r_h + r_O}. \quad (2)$$

where r_s, r_h, r_O and r_V are the radii of the trivalent cation (Ce^{3+}), host cation (Ce^{4+}), oxide ion, and oxygen vacancy respectively and $\alpha_C = \alpha_M + \alpha_V$. Rearranging these equations results in a solution for the Ce^{3+} radius shown below.

$$r_{Ce^{3+}} = r_h + (\alpha_C - \alpha_M)(r_h + r_O). \quad (3)$$

Using Shannon's radii for O^{2-} and Ce^{4+} (1.38 and 0.97 Å), the value for the radius of a vacancy (1.169 Å) from our previous work, and α_C as obtained from Fig. 1 for $U = 7$ eV,[39] we estimate $r(Ce^{3+}) = 1.125$ Å for ceria, in good agreement with Shannon ionic radii for Ce^{3+} (1.143 Å). To illustrate the effect of charge delocalization, we estimate an *effective radius* for Ce^{3+} equal to 1.082 Å (by using in eqn (3) the value of α_C for $U = 0$ eV), a substantial reduction (~4%) over the charge-localized case. Calculated radii for all the U values are reported in Supplementary Material.† It is clear that eqn (3) cannot be applied to metallic ceria, since, in this case, the 4f electrons are delocalized around all the Ce ions present in the simulation, and therefore it is not correct to differentiate between Ce^{4+} and Ce^{3+} cations. However, this approach gives an indication of the change to be expected in the Shannon radius of a certain element when charge becomes delocalized. To this end, we consider the Goldschimdt tolerance factor, discussed earlier and defined by the following equation.[40,41]

$$t = \frac{(r_A + r_O)}{\sqrt{2}(r_B + r_O)} \quad (4)$$

where r_A, r_B are the radii of the A-site, B-site cations and r_O the oxygen radius. We note that a 4% change in the ionic radius of either the A or B cation will yield a change of approximately

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2% in the tolerance factor. This is larger than the 1% variation typically defining stability domains of crystal structures,[41] thus resulting in potentially erroneous estimations of crystalline phases. Similar considerations can be made for other parameters, such as the free volume, which are even more sensitive to changes in ionic radii.[25] We therefore conclude that *Shannon's radii can be used reliably only when the studied system has the same degree of charge localization as the one used to obtain the value of the Shannon radius*.

Our results have important consequences for chemical expansion in these materials. Indeed, the fact that charge delocalization leads to a smaller chemical expansion coefficient, suggests that a strategy based on our findings could be used to minimize chemical expansion. In our previous work, we suggested doping ceria with transition metal elements such as V, Ti and Fe, since these present a smaller radius change (based on Shannon's radii) when changing their valence. Since these elements are also expected to introduce a certain degree of metallicity (Mn addition to ceria, for instance, is believed to result in mixed ionic electronic conductive behaviour at relatively high oxygen partial pressure[42]), we anticipate that the radius change of these elements could actually be smaller than predicted from Shannon's radii (due to less than complete charge localization), thus leading to materials with even further reduced α_C. Our group is currently investigating the validation of these predictions.

Conclusions

In summary, charge localization was computationally shown to result in a significant increase of the chemical expansion coefficient, in $CeO_{2-\delta}$ and $BaCeO_{3-\delta}$, taken as model materials. Our unique method, taking advantage of a limitation of DFT calculations, allowed the insulating nature of ceria to be switched to metallic (by systematically reducing the Hubbard U term), with consequent delocalization of electrons. The chemical expansion coefficient was found to increase, in $CeO_{2-\delta}$, from 0.050 in the "metallic" case to 0.087 for the charge-localized case, an increase of 74%, with the ionic α_C in good agreement with experiments.[10,36,37] A similar behaviour was observed for $BaCeO_{3-\delta}$, showing that this result does not depend on a specific crystal structure and/or chemical composition, but rather depends on the extent of electron localization on the critical cation, that is Ce in this case. This is consistent with the observation that materials with smaller degree of charge localization have smaller α_C[26,27] and shows how charge localization can be used, in principle, to tune chemical expansion in non-stoichiometric oxides. Our findings draw caution to the wide-spread use of Shannon ionic radii – these values become unreliable if the studied system does not have the same degree of charge localization as the one used to obtain the radius. This also has important implications for the use of Goldschmidt tolerance factors (which strongly rely on Shannon radii) and which we show depend significantly on the degree of charge localization in the system.

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