LATTICE PARAMETERS AND DEFECT STRUCTURE OF THE FLUORITE- AND C-TYPE OXIDE SOLID SOLUTIONS BETWEEN MO₂ AND M₂O₃

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ABSTRACT

Lattice parameter data of a wide range of oxide solid solutions M₁₋₂M'₂O₂₋₃/₂ formed between the fluorite dioxides MO₂ (y=0) and the C-type sesquioxides M'+O₁.₅ (y=1) are compiled and critically reviewed. Due to the formation of oxygen vacancy in the anion sublattice, the lattice parameters of these solid solutions exhibit a marked deviation from Vegard's law: the trend of this deviation is significantly positive (convex) for systems of larger tetravalent cations (Th⁴⁺, Ce⁴⁺) and even slightly negative (concave) for systems of smaller cations (Zr⁴⁺, Hf⁴⁺). A new crystal-chemical representation, which can give a straightforward description of such systematic variations of lattice parameters in these systems, is proposed. In this representation the lattice parameter of a given solid solution is evaluated using only one well-defined crystal-chemical parameter, rᵣ, the average cationic radius at the average oxygen coordination number (CN) of (8-2y) at that composition y. The numerical evaluation of this representation demonstrates its practical applicability for a variety of oxide solid solutions over the whole composition range between MO₂ (y=0) and M'+O₁.₅ (y=1).

INTRODUCTION

In this paper the authors propose a new concise crystal-chemical representation applicable to the lattice parameters (a₀) of a wide variety of oxide solid solutions M₁₋₂M'₂O₂₋₃/₂ predominantly formed between the fluorite dioxides MO₂ (y=0) of actinide (An) and lanthanide (Ln) tetravalent cations (M⁺⁺⁺ = Th, U, Ce, Zr, Hf, etc) and the C-type sesquioxides M'+O₁.₅ (y=1) of lanthanide trivalent cations (M⁺⁺ = Ln⁺⁺). Analogous solid solutions of MO₂ with monoxides M'O of divalent alkali-earth cations (M⁺⁺⁺ =Mg, Ca, Sr, Ba, etc) are not dealt with here directly, for, as shown later, these systems need a different approach. The lattice parameter of the fluorite-type oxide solid solutions such as doped thoria and stabilized zirconia is one of the most important basic parameter which largely determines various physicochemical properties of these systems such as ionic conductivity, phase stability, etc. Thus, many lattice parameter data are now available on these solid solutions, and in numerous reports their physicochemical properties are discussed in connection with the behavior of their lattice parameters. It is therefore of prime value to develop a reliable theoretical and/or calculation model (method), whether microscopic or...
phenomenological (empirical), which can properly describe the variations of their lattice parameters with reasonable accuracy. In the usual solid solutions between the isostructural systems (e.g., those between the fluorite dioxides) Vegard's law (linear $a_0$ vs. $y$ relationship) is a good first approximation. In contrast, in these solid solutions the substitution of aliovalent oxides $M'O_u$ ($u=1$ or $1.5$) for $MO_2$ inevitably introduces the fixed amount of oxygen vacancies ($V_o$) into the anion sublattice; $M_{1-y}M'_yO_{2-x}V_x$ $(x = y$ or $y/2)$. The gross mutual solubility of the structurally similar fluorite $MO_2$ and C-type $M'O_{1.5}$ ($u=1.5$) (in fact this is a superstructure of the former), together with quite a wide span of covered ionic-radii ratios of the constitute cations, $r_{M^4+}/r_{M^3+}$, makes these systems most suitable for examining how the lattice parameters of grossly defective solid solutions change with the cation- and oxygen compositions, the ionic radii of the constitute cations, etc, and how one can successfully model their behavior. This is our first approach toward this goal focussing on the $MO_2-M'O_{1.5}$ ($u=1.5$) type systems, and this could be regarded as an extension and/or improvement of many previous attempts along this line represented by that of Kim (1).

**CRYSTAL-CHEMICAL REPRESENTAION**

Lattice Parameter Data and Formulation of the Present Representation

Figures 1 and 2 show the reported lattice parameter ($a_0$) data of several representative solid solutions $M_{1-y}M'_yO_{2-y/2}$ as $a_0$ vs. $y$ plots over the entire composition range including both the fluorite- and C-type solid solution phases in the $MO_2$- and $M'O_{1.5}$-rich sides, respectively; those of relatively large $M^4+$ cations (Th, Ce) are shown in Fig. 1 and those of relatively small $M^4+$ cations (Zr, Hf) in Fig. 2. As was briefly mentioned above, the C-type (solid solution) phase is the superstructure with its lattice parameter double of the parent fluorite (solid solution) phase. So, for the C-type phase one half (1/2) of the lattice parameters are plotted in these Figures. This superstructure formation in the C-type phase results from the oxygen-vacancy ordering in the anion sublattice. However, except for this doubling of the lattice parameter, this ordering seems to have little effect on their lattice parameters; that is, the lattice parameters of the fluorite- and C-type solid solution phases, irrespective of the existence of the miscibility gap in between, can be connected almost smoothly using a single curve as a good first approximation. This fact is important and is used as the basis for the present modeling of their lattice parameters. As is also well known, in systems of relatively small $M^4+$ cations (Zr, Hf) shown in Fig. 2 the ‘stabilized’ cubic-fluorite phase appears first after about 10 to 20 mole % substitution of $M'O_{1.5}$ is attained.

It is clearly seen in these Figures that the lattice parameters of these solid solutions exhibit quite diverse but systematic variations depending on both the ionic radii of the respective constitute cations ($M^{4+}, M^{3+}$) and their various combinations: A marked deviation from simple Vegard’s law (linear $a_0$ vs. $y$ relationship) is evident for all of these solid solutions: The mode of this deviation changes from significantly positive (convex) for systems of relatively large $M^{4+}$ cations (Th, Ce) in Fig. 1 to even slightly negative (concave) for those of relatively small $M^{4+}$ cations (Zr, Hf) in Fig. 2. It is also apparent in Fig. 2 that the Zr and Hf systems exhibit a hump in their $a_0$ vs. $y$ plots extending over 0.4<$y$<0.8 region, which the authors will discuss later in some detail.
The main aim of the proposed model is to reproduce these experimental lattice parameter data of various solid solutions shown in Figs. 1 and 2 in a quantitative manner over the entire composition range between MO$_2$($y$=0) and M'Oi.5 ($y$=1.0) consistent with the physical reality of the system. This attempt relies on the above-mentioned basis derived from the experimental fact that oxygen vacancies in both the fluorite- and C-type phases can be handled as the same entity as for their lattice parameters, whether they are disordered or ordered. In Kim's model (1) (the hitherto reported the most representative and almost exclusively used model) the description only of the fluorite solid solution phase on the MO$_2$-rich side was intended. It is certain that due to this limitation, his model, using the linear $a_0$ vs. $y$ approximation, allows to reproduce the experimental lattice parameter data of these systems inside the relatively narrow fluorite solid solution phase with reasonable accuracy. As is apparent in Figs. 1 and 2, however, the higher level approximation is necessary to extend the model to the entire composition range. This extension of the model to the entire composition range, in turn, bears a direct merit on the present representation that the lattice parameter of the other end member at $y$ = 1, i.e., M'Oi.5, can be fixed with sufficient accuracy, in addition to those of the one end member at $y$ = 0, i.e., MO$_2$. This is the main reason that the authors focus here their treatment only on the MO$_2$- M'Oi.5 type solid solutions excluding the MO$_2$- M'O type; that is, in the latter systems where M'O has different crystal structure (the rock-salt type) some ambiguity always remains in choosing this other proper end member, e.g., MM'O$_3$ or what? Then, the main problem here is reduced to finding out the appropriate way.

Figure 1. Lattice parameter ($a_0$) vs. composition ($y$) plots for ThO$_2$-YO$_1.5$ (2), CeO$_2$-GdO$_{1.5}$ (3,4), and CeO$_2$-NdO$_{1.5}$ (3-5) solid solutions.

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(method) how to connect the theoretical curve over the entire composition range (0<y<1) in between these two fixed end members, MO\(_2\) (y=0) and M'\(\text{O}_{1.5}\) (y=1).

As the first step in formulating the present crystal-chemical representation, it is essential to know the lattice parameters of these two end members, MO\(_2\) (y=0) and M'\(\text{O}_{1.5}\) (y=1), as precise as possible. Fig. 3 shows the reported lattice parameter data of the both systems compiled over the wide range of the ionic radii (r\(_c\)) of the respective constitute cations. (Throughout the present paper, Shannon’s ionic radii (9) are used.)

In this Figure, the lattice parameters (a\(_0\)) of the four fluorite dioxides MO\(_2\) shown in Figs. 1 and 2 (M = Th, Ce, Zr, Hf) are plotted against the ionic radii of the respective M\(^{4+}\) cations, r\(_{M^{4+}}\), at the oxygen coordination number (CN) of 8 in the ideal (stoichiometric) fluorite lattice. Here, for ZrO\(_2\) and HfO\(_2\) their extrapolated values to the respective y=0 composition from the stabilized cubic fluorite phase in Fig. 2 are used (0.512nm for ZrO\(_2\) and 0.5095nm for HfO\(_2\)). The least square fit of these lattice parameters, including also those of other MO\(_2\) s of tetravalent actinides (An\(^{4+}\)) (UO\(_2\), PuO\(_2\), NpO\(_2\), AmO\(_2\), BkO\(_2\), etc) (10) (not shown in this figure, for the sake of clarity), gives;

Figure 2. Lattice parameter (a\(_0\)) vs. composition (y) plots for ZrO\(_2\)-DyO\(_{1.5}\) (6), HfO\(_2\)-ErO\(_{1.5}\) (7, 8) solid solutions.
Figure 3. Lattice parameter ($a_0$) vs. cation ionic radii ($r_c$) plots for MO$_2$ and MO$_{1.5}$ Systems: $r_c$ at CN=8 and 6 are used for MO$_2$ and MO$_{1.5}$, respectively.

$$f_F = a_{0F} = 0.3572 + 1.48 \cdot r_c + 4.3 \cdot r_c^2 \text{ (nm)}$$ [1]

Also in this Figure, one half (1/2) of the lattice parameters of the C-type M'O$_{1.5}$'s, $a_{0C}/2$ (11), are plotted against the ionic radii of the respective M$^{3+}$ constitute cations, $r_{M^{3+}}$, at the oxygen coordination number of 6 (CN=8-2y at y=1). Their least square fit gives;

$$f_C = a_{0C}/2 = 0.40693 + 0.03741 \cdot r_c + 14.7973 \cdot r_c^2 \text{ (nm)}$$ [2]

In Eqs. [1], [2] and in Fig. 3 their lattice parameters, $a_{0F}$ and $a_{0C}/2$, are redefined as $f_F$ and $f_C$, respectively, to use below as functionals representing the respective lattice parameters.

On the other hand, according to the most standard hard-sphere (ion packing) model (11-13), the lattice parameter of the ideal fluorite dioxide is expressed by the following equation;

$$a_{0F} = a_{0C}/2 = (4/\sqrt{3}) \cdot (r_c + r_{O^{2-}})$$ [3]

where $r_{O^{2-}}$ denotes the ionic radius of the oxide ion (~0.138nm) (9) at the cation coordination number(CN) of 4 in the fluorite lattice. It is instructive to see in Fig. 3 (Eqs.
that the experimental lattice parameters of the both end members, \(\text{MO}_2\) and \(\text{M'O}_{1.5}\), themselves, when arranged over the respective wide \(r_c\) range, do not necessarily follow this most standard form of their lattice parameters, Eq. [3] based on the hard sphere (ion packing) model. This seems to be more so for the oxygen-vacancy (Vo) containing defective C-type \(\text{M'O}_{1.5}\), plausibly having more structural flexibility and therefore extending over the wider \(r_c\) range as the stable phase. In fact, the calculated \(a_{0F}\) line according to Eq. [3] using \(r_{O2^-}=0.138\)nm lies only slightly above that of \(f_{F}\) (Eq. [1]) for \(0.085 < r_c < 0.105\)nm.

The length of the perpendicular straight line connecting in between the two lattice parameter curves \((f_c\) and \(f_{F}\)) at constant \(r_c\) shown in Fig. 3, is nothing but the difference of the lattice parameters \(\Delta f(C-F)\) (= \(f_c - f_{F}\)) between the two oxygen-vacancy containing C-type phase with the oxygen coordination number (CN) of 6 and the ideal fluorite phase with its CN of 8, having the same \(r_c\). That is, the introduction of full oxygen vacancies from 0 (at \(y=0\)) to 2 (at \(y=1.0\)) at constant \(r_c\) causes the full change of its lattice parameter \(\Delta f(C-F)\) (= \(f_c - f_{F}\)). No change other than that of the oxygen vacancy (Vo) content exists here between the both systems at constant \(r_c\). Then, it is reasonable to assume that the introduction of 2y oxygen vacancy at any \(y\) at constant \(r_c\) causes the proportional change \((2y/2=y)\) of its lattice parameter, \(y \cdot \Delta f(C-F)\). Consequently, the lattice parameter of a given solid solution with its composition \(y\) on this line is calculated as; \(a_{0(ss)}(y) = f_{F} + y \cdot \Delta f(C-F) = f_{F} + y \cdot (f_c - f_{F}) = (1-y) \cdot f_{F} + y \cdot f_c\), i.e., one reaches a simple conclusion given by the following expression;

\[
a_{0(ss)}(y) = (1-y) \cdot f_{F} + y \cdot f_c \tag{4}
\]

This is the basic equation in the present crystal-chemical representation to evaluate the lattice parameter of the solid solution \(\text{M}_{1-y}\text{M'}_y\text{O}_{2-y/2}\) (0\(<y<1\)). Eq. [4] says that the lattice parameter \(a_{0}(ss)\) of a given solid solution with its composition \(y\) and average cationic radius \(r_{C}(ss)\) is expressed by the average lattice parameter of the (hypothetical) solid solution between \(\text{MO}_2\) and \(\text{MO'}_{1.5}\) both having the same \(r_{C}(ss)\). To make sure, note here that those \(\text{MO}_2\) and \(\text{MO'}_{1.5}\) having the same \(r_{C}(ss)\) are naturally different from the actual end members \(\text{MO}_2\) and \(\text{MO'}_{1.5}\) of the solid solution having the respective different \(r_{M4+}\) and \(r_{M3+}\), (also different from \(r_{C}(ss))\). In other words, one can say that this is given by the internal dividing point of this perpendicular straight line connecting the lattice-parameter functionals of the two (hypothetical) end members, \(f_{F}\) and \(f_c\), at that \(r_{C}(ss)\) by the composition ratio of the respective end members, \((1-y) : y\), according to the well-known lever rule. It is also apparent from the above derivation procedure of Eq. [4] that it is basically the oxygen-vacancy effect (more specifically the term related to the ionic-radius difference between the oxygen vacancy and the oxide ion) that is actually evaluated here. (Otherwise both lines \(f_{F}\) and \(f_c\) should coincide with each other. But this idea is not pursued here further). Thus, it is judged that this causes the unique non-Vegard’s law behavior of these solid solutions.

The actual procedure to evaluate the lattice parameters of the present solid solutions using Eq. [4] is illustrated in the below for several systems shown in Figs. 1 and 2, (especially for ThO\(_2\)-Y\(_2\)O\(_3\) system having the widest lattice-parameter difference between
Figure 4. Lattice parameter \( a_0 \) vs. the average cation ionic radius \( r_c \) plots for several systems shown in Figs. 1 and 2.

For this purpose, their experimental lattice parameter \( a_0 \) data shown in Figs. 1 and 2 are now re-plotted as \( a_0 \) vs. \( r_c \) plots as in Fig. 3; the results are shown in Fig. 4 in the extended scale for the concerned region. Here, \( r_c \) denotes the average cationic ionic radius of the solid solution, \( M_{1-y}M'_yO_{2-y/2} \), at the average oxygen coordination number \((8-2y)\) at composition \(y\);

\[
r_c = (1-y) r_{M^4^+} + y r_{M^3^+} \quad \text{(at } CN=8-2y) \tag{5}
\]

where \( r_{M^4^+} \) and \( r_{M^3^+} \) are the ionic radii of the constitute cations at the average oxygen coordination number \( CN \) of \((8-2y)\), and can be easily evaluated from the aforementioned Shannon’s ionic-radii table in which \( r_c \) of various ions are given at several coordination numbers (e.g., \( CN = 4, 5, 6, 8, 10, 12 \), etc.) For example, \( r_{Y^3^+} \) and \( r_{Th^4^+} \) in the \( ThO_2-Y_2O_3 \) system are well approximated by the respective following expressions between \( 4<CN<12 \);

\[
r_{Y^3^+} = 0.1014 + 0.00553 \cdot (CN-8) - 0.00035 \cdot (CN-8)^2 + 0.00022 \cdot (CN-8)^3 \quad \text{(nm)} \tag{6}
\]

\[
r_{Th^4^+} = 0.105 + 0.00488 \cdot (CN-8) - 0.00023 \cdot (CN-8)^2 \quad \text{(nm)} \tag{7}
\]
In general, $r_C$ of any cation increases with increase of the coordination number (CN) of oxygen around them due to an increase of the repulsion between the coordinating oxygens. As seen in Eqs. [6] and [7], the linear interpolation is usually sufficient for small CN range.

In this $a_0$ vs. $r_C$(ss) representation, the experimental lattice parameters of the four solid solutions (ThO$_2$-Y$_2$O$_3$, CeO$_2$-Nd$_2$O$_3$, CeO$_2$-Gd$_2$O$_3$, ZrO$_2$-Dy$_2$O$_3$) exhibit remarkably diverse behavior due to different $r_{M^{3+}}$/$r_{M^{4+}}$ ratios between them. At every $r_C$(ss) calculated by Eq. [5], the evaluation of its lattice parameter using Eq. [4] is quite simple. For example, as shown in Fig. 4, consider the ThO$_2$-Y$_2$O$_3$ system at three different compositions of $y = y_1$, $y_2$ and $y_3$ at which their calculated $r_C$(ss) in Eq. [5] (using Eqs. [6] and [7]) are $r_Cn$ ($n=1,2,3$), respectively. From Eq. [4] it immediately follows that the lattice parameter of each solid solution, $a_0$(ss) at the composition $y_n$ is given by, $a_0$(ss)($y_n$) =$1-y_n$ $\cdot$ $f_F + y_n$ $\cdot$ $f_C$ on each perpendicular straight line as depicted there; one can quite clearly understand what was mentioned above that this is the internal dividing point of each straight line connecting the lattice-parameter functionals of the two end members, $f_F$ and $f_C$, at that $r_Cn$ by the composition ratio of the respective end members, ($1-y_n$) : $y_n$. Or, this is the average lattice parameter $a_0$(ss) of the hypothetical solid solution between MO$_2$ and MO$_{1.5}$, (1-$y$) MO$_2$ + $y$ MO$_{1.5}$, both having the same $r_Cn$ and the respective lattice parameters $f_F$ and $f_C$.

RESULTS AND DISCUSSION

The calculated $a_0$(ss) vs. $r_C$(ss) curves thus obtained for the four systems are shown in Fig. 4 as the respective solid curves and give good fit to their respective experimental plots. Also in Figs. 1 and 2, the calculated curves of the present representation are shown in the form of the more usual $a_0$ vs. $y$ curves for all these systems. In these Figures, for comparison, curves according to the so far most widely and exclusively used Kim’s empirical formula (1) are also shown for some systems. To the authors’ knowledge, Kim’s formula is the hitherto proposed the only one with which one can readily calculate the lattice parameters of these various fluorite-type solid solution phases. It is apparent that the present representation can give overall better fit to the lattice parameter data than Kim’s empirical formula. This is especially so in the higher $y$ regions ($y>0.4$) of relatively large M$^{4+}$ cations (Th, Ce) shown in Fig. 1, where due to the strong convex shape of the experimental $a_0$ vs. $y$ curves, the linear $a_0$ vs. $y$ approximation adopted in Kim’s model does not hold well. In Figs. 3 and 4, one can easily understand that this is due to the increased oxygen-vacancy effects for larger M$^{4+}$ systems (larger difference between $f_F$ and $f_C$). However, as mentioned previously, Kim’s formula was originally intended to apply only for the fluorite-type solid solution phase on the MO$_2$-rich side, and in this region Kim’s formula gives reasonably good fit to all these systems. This fact seems remarkable in view of the ‘user-friendly’ simple form of Kim’s empirical formula;

$$a_0$(ss) = $a_0$(0) + $y$ ($\sum a_h \Delta z_k$ + $b_h \Delta r_k$) \hspace{1cm} [8]

where $a_0$(0) denotes the lattice parameter of the host fluorite dioxide, the coefficients $a_h$ and $b_h$ are numerical parameters in the valence-difference term ($\Delta z_k = z_k-z_h$) and the ionic-radii difference term ($\Delta r_k = r_k-r_h$ at CN = 8) between the k-th dopant ($z_k$=2 or 3) and the host cations ($z_h$=4), respectively, to be determined by the numerical fitting of Eq. [8] to the
experimental lattice parameter data. The difference in the formulation between Kim's and the present model is obvious; in the former the second $\Delta Z_k$ term uses the ionic radii of the host- and dopant cations $r_k$ and $r_l$ only at the oxygen coordination number (CN) of 8 in the ideal fluorite lattice, and therefore the resultant first $\Delta Z_k$ term inevitably involves the direct and indirect oxygen-vacancy effects, i.e., the one arising from the ionic-radii difference between the oxygen vacancy and the oxide ion (Eq. [4]), and the other arising from the variations of $r_k$ and $r_l$ with change of the oxygen coordination number (CN) with $y$ (Eqs. [5]-[7]). Whereas in the latter those are evaluated in an explicitly separate but consecutive manner.

It is appropriate to make here some mention also on the hard-sphere based model proposed by Ohmichi, et al (13): There, the extension of Eq. [3] was made to apply for solid solutions by introducing the concept of effective ionic radius of oxygen vacancy, $r_{Vo}$; $a_0(ss) = (4/\sqrt{3}) \cdot (r_C(ss) + r_{O2-}(ss))$, where $r_C(ss)$ is given by Eq. [5] and $r_{O2-}(ss)$ is the average ionic radius of oxygen in the solid solution defined by $r_{O2-}(ss) = (1 - y/4)r_{O2-} + (y/4)r_{Vo}$. Applying this expression of $a_0(ss)$ to a number of urania-based fluorite-type solid solutions (UO$_2$-LnO$_{1.5}$), they showed that $r_{Vo} = 0.150$nm gives good fit to their experimental lattice parameter data. Actually, the present model is a straightforward extension and elaboration of this Ohmichi, et al's model rather than Kim's model. However, here, the authors tried to avoid the usage of the hard sphere-based lattice-parameter expression and the introduction of $r_{Vo}$. Instead, here, the author used the experimentally derived lattice-parameter expressions of the fluorite- and C-type oxides (Fig. 3 and Eqs. [1], [2]) and the difference term between them ($\Delta f(C-F) = f_C - f_P$). This is due to the authors' intention to keep the present representation as 'model independent' as possible and also free from any numerically adjustable parameters, i.e., assessable using only the experimental data and the directly experimentally derivable parameters.

This attempt seems to succeed to some extent: One remarkable point of the present crystal-chemical representation is that this can describe the lattice parameter data of almost any MO$_2$-M'$_{1.5}$ type solid solution with reasonable accuracy over the entire composition range in a consistent and systematic manner in combination of the simple lattice-parameter expression, Eq. [4] with its clear physical meaning and the only one well defined crystal-chemical parameter of the average cationic ionic radius, $r_C(ss)$ defined by Eq. [5] (i.e., without any arbitrary numerical parameter). Utilizing the $a_0(ss)$ vs. $r_C(ss)$ representation shown in Fig. 4 the numerical evaluation of the present model can be performed in a visible straightforward manner both graphically and analytically. Immediately on this graphic representation, one can reproduce and understand the remarkable basic features of their lattice parameters such as strong deviation from Vegard' law, the mode of which systematically changes from the significantly positive (convex) to even slightly negative (concave) with decreasing the ionic radius of the constituent M$^+$ cations (Th$^{4+}$→Ce$^{4+}$→Zr$^{4+}$→Hf), i.e., with diminishing the oxygen-vacancy effects. Though in treating the MO$_2$-M'O type solid solutions, as mentioned previously, some ambiguity exists in properly fixing the end member on the M'O side, it is reasonable as a rough first approximation to fix this at MM'O$_3$ with its average valence of 3+ and average cationic ionic radius $r_c$ of $(r_c(M^{4+})+r_c(M^{2+}))/2$ as the simulate of M'O$_{1.5}$ in the MO$_2$-M'O$_{1.5}$ type solid solutions.
It is to be noted, however, that in the intermediate composition range (0.4<\textit{y}<0.8) for the smaller M\textsuperscript{4+} (Zr, Hf) systems shown in Fig. 2, a hump in their experimental \textit{a}_0 vs \textit{y} plots is observed, and such behavior could not be reproduced in the present representation. The \textit{a}_0 vs \textit{y} plots of both Zr and Hf systems exhibit in fact a more complex slightly sigmoidal shape due to the existence of this hump, though the overall deviation from Vegard’s law seems considerably smaller than the larger M\textsuperscript{4+} systems shown in Fig. 1 (as understood well in Fig. 4). This reflects the significant change of their defect structure from that assumed in the present model, most probably due to the formation of the pyrochlore-type microdomains (Zr\textsubscript{2-x}Ln\textsubscript{x}O\textsubscript{7+z}) in the parent fluorite phase (or more appropriately the pyrochlore-type local structure) around this composition range (0.4<\textit{y}<0.8) in these smaller M\textsuperscript{4+} systems (14). In fact, in the larger Ln\textsuperscript{3+} (=La, Sm, Nd, etc)-containing Zr (and Hf) systems this pyrochlore-type compounds (Zr\textsubscript{2-x}Ln\textsubscript{x}O\textsubscript{7+z}) is known to appear as an intermediate nonstoichiometric phase around this composition range. In the ideal (stoichiometric) pyrochlore compound Zr\textsubscript{2}Ln\textsubscript{2}O\textsubscript{7} (\textit{y}=0.5) the simultaneous ordering of constituent cations and oxygen vacancies occurs from the parent fluorite lattice, and as a result here the smaller M\textsuperscript{4+} cations and the larger Ln\textsuperscript{3+} are coordinated not by the average 7 (=8-2\textit{y}) oxide ions but by the six and eight oxide ions, respectively. This kind of stronger ordering of both cations and oxygen vacancies is judged to be the reason for the discernable hump in \textit{a}_0 vs \textit{y} plots in these systems. Such situation is quite different from that in the C-type phase and obviously inconsistent with the basic assumption of average oxygen coordination in the present model. The extension of the present representation is necessary in order to incorporate properly such stronger ordering effects in the pyrochlore-type phase (and/or local structure).

In addition to the application for the fluorite-type solid oxide electrolytes for the electrochemical technology, a lot of usage of the present representation will also be found for the fluorite-based nuclear fuels and nuclear waste forms, etc, in the field of the nuclear technology. Especially here, many multi-components oxide solid solutions containing simultaneously a variety of actinides (An\textsuperscript{3,4,5,6,7+}), lanthanides (Ln\textsuperscript{3,4+}), alkali and alkali-earth elements (Ae\textsuperscript{1,2+}), etc, are occasionally encountered. For those systems it is often almost impossible to distinguish which are the hosts or dopants. Then, the authors recommend; just know their compositions (An\textsuperscript{3,4,5,6,7+}, Ln\textsuperscript{3,4+}, Ae\textsuperscript{1,2+}), calculate their average cationic ionic radii \textit{r}_C(ss) and average (mean) valence \textit{Z}_C (usually 3<\textit{Z}_C<4) (the latter gives the oxygen composition (\textit{Z}_C/2 = (2-\textit{y}/2)). Then, go on to the \textit{a}_0(ss) vs. \textit{r}_C(ss) representation shown in Figs. 4, draw a perpendicular straight line at that \textit{r}_C(ss) in between the two curves, \textit{f}_1 and \textit{f}_2, and divide it according to the composition ratio of (1-\textit{y}): \textit{y}, according to the lever rule.

**SUMMARY**

In this paper the authors proposed a concise phenomenological crystal-chemical representation applicable to the lattice parameters (\textit{a}_0) of a wide range of oxide solid solutions M\textsubscript{1-y}M\textsubscript{y}O\textsubscript{2+y/2} formed between the fluorite dioxides MO\textsubscript{2} (\textit{y}=0) of various tetravalent cations (M\textsuperscript{4+} = Th, Ce, Zr, Hf, etc) and the C-type sesquioxides M\textsuperscript{3+}O\textsubscript{1.5} (\textit{y}=1) of various lanthanide trivalent cations (M\textsuperscript{3+} = Ln\textsuperscript{3+}). As was shown in the foregoing, the proposed representation can give a clear and straightforward description of quite diverse but systematic variations of the lattice parameters these systems exhibit (Figs. 1, 2) over
the whole composition range in a consistent and quantitative manner: The most notable basic feature of their lattice parameters is the marked deviation from simple Vegard's law due to the formation of oxygen vacancy in the anion sublattice by substitution of aliovalent oxides $M'O_{1.5}$ for $MO_2$. The mode of this deviation changes from significantly positive (convex) for systems of larger tetravalent cations ($Th^{4+}, Ce^{4+}$) (Fig. 1) to even slightly negative (concave) for systems of smaller cations ($Zr^{4+}, Hf^{4+}$) (Fig. 2), due to the systematic variation of this oxygen-vacancy effects caused by the ionic radii of the respective constitute cations ($M^{4+}, M^{3+}$) and their combinations (Figs. 3, 4). The remarkable feature of the present representation is that the lattice parameter of a given solid solution is evaluated in a straightforward graphical (visible) way utilizing the proposed $a_0(ss)$ vs. $r_c(ss)$ representation (Fig. 4 and Eq. [4]) by using only one well-defined crystal-chemical parameter of $r_c$ (Eq. [5]), the average cationic radius at the average oxygen coordination number (CN) of (8-2y) at that composition y. The numerical evaluation of the present representation indeed demonstrates its practical applicability for a variety of these oxide solid solutions over the whole composition range between $MO_2$ ($y=0$) and $M'O_{1.5}$ ($y=1$). Thus, the present representation is expected to be useful both for evaluating the lattice parameters of other similar oxide solid solutions (not shown in Figs. 1 and 2, and numerous multi-component type) and for constructing new modeling techniques (methods).

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