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Ordered structures of defect clusters in gadolinium-doped ceria

Zhi-Peng Li,1,a) Toshiyuki Mori,1 Fei Ye,2 Dingrong Ou,3 Jin Zou,4,5 and John Drennan5

1 Global Research Center for Environment and Energy based on Nanomaterials Science, National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan
2 Key Laboratory of Materials Modification, School of Materials Science and Engineering, Dalian University of Technology, 2 Linggong Road, Dalian, Liaoning 116024, People’s Republic of China
3 Laboratory of Fuel Cells, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, Liaoning 116023, People’s Republic of China
4 School of Engineering, The University of Queensland, St. Lucia, Brisbane, Queensland 4072, Australia
5 Centre for Microscopy and Microanalysis, The University of Queensland, St. Lucia, Brisbane, Queensland 4072, Australia

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The nano-domain, with short-range ordered structure, has been widely observed in rare-earth-doped ceria. Atomistic simulation has been employed to investigate the ordering structure of the nano-domain, as a result of aggregation and segregation of dopant cations and the associated oxygen vacancies in gadolinium-doped ceria. It is found that the binding energy of defect cluster increases as a function of cluster size, which provides the intrinsic driving force for the defect cluster growth. However, the ordered structures of the defect clusters are different from the chain model as previously reported. Adjacent oxygen vacancies prefer to locate along (110)/2 lattice vector, which results in a unique stable structure (isosceles triangle) formation. Such isosceles triangle structure can act as the smallest unit of cluster growth to form a symmetric dumbbell structure. This unique dumbbell structure is hence considered as a building block for the development of larger defect clusters, leading to nano-domain formation in rare-earth-doped ceria. © 2011 American Institute of Physics. [doi:10.1063/1.3599089]

I. INTRODUCTION

A solid oxide fuel cell (SOFC) is a highly efficient device which can electrochemically convert the chemical energy of various fuels to electricity and heat with little pollution.1,2 The traditional ceramic material used as electrolyte in SOFC is yttria-stabilized zirconia (YSZ), which generally works at 800–1000 °C. However, the high operating temperature will usually result in serious degradation and sealing problems which add to the cost. As a result in recent years, lowering the operating temperature to intermediate level (500 °C–700 °C) has become an urgent task and thus triggers the development of intermediate-temperature SOFCs (IT-SOFCs). One critical issue of IT-SOFCs development is to improve the ionic conductivity of solid electrolyte since lowering operating temperature will subsequently lower ions migration in SOFC components. Rare-earth-doped ceria is considered as a promising candidate material for use at intermediate or even lower temperatures, due to their higher oxygen ion conductivity compared with the traditional YSZ within similar temperature range.3,4 Enhancement of ionic conductivity in doped ceria used in IT-SOFCs has thereby attracted intense interests. The doped aliovalent cations, associated with the charge-compensation oxygen vacancies, will lead to defect structure formation in ceria fluorite lattice, which permits high oxygen ion conduction.5 It was elucidated that higher dopant concentration would lead to higher conductivity, as a result of additional dopants that give rise to lower activation energy for oxygen vacancy migration in doped ceria.6 However, it was also established that ionic conductivity did not unitarily increase with the dopant concentration. Generally, a maximum conductivity can be observed at a doping level between 10 and 20 at.% in doped ceria.7,8 Nevertheless, the conductivity will decrease as the dopant concentration further increases, even though it is still far less than the solubility level. One possible reason is the interactions among the defect clusters.9,10 Such strong interactions will significantly reduce the mobility of oxygen vacancies, which are the charge carries in ionic conductor, and thus decrease the ionic conductivity of the material.11–13 Recently, our group reported that nano-domains can be widely observed in La,14 Sm,15 Y,16 Yb,17 Ho,18 Dy,19 Tb,20 and Gd (Refs. 21 and 22) doped ceria. It was evaluated that such nano-domain formation was attributed to the aggregation and segregation of dopant cations and associated oxygen vacancies. It is believed to enhance the ordering structure of charge compensating defects, block the migration of oxygen vacancies, and correspondingly reduce the concentration of freely mobile oxygen vacancies. Alternately, the appearance of nano-domains in doped ceria can lead to the decrease of ionic conductivity with increased dopant concentration.

Based on these experimental results, Ye et al. simulated the ordered structures of charge compensating defects in gadolinium-doped ceria (GDC), which is one of the most frequently used electrolytes among rare-earth doped ceria in IT-SOFCs.23,24 It was suggested that the oxygen vacancies tended to form curved chains in the defect clusters and related dopant cations preferred to locate at the second nearest
behavior of defect cluster in doped ceria. This simulation is on the basis of Born model description of an ionic crystal, in which the lattice energy stems from three sources: long-range Coulombic forces, short-range interactions, and polarizations. The Coulombic forces are summed using Ewald’s method to provide convergence. The short-range interactions were captured by Buckingham pair potential in the form of $E(r_{ij}) = A \exp(-r_{ij}/\rho) - C_{ij}r_{ij}^{-6}$, where $r_{ij}$ is the atomic distances, and $A$, $\rho$, and $C$ are adjustable parameters (see Table I). Since short-range interactions decrease quickly with increasing atomic distances, it is necessary to consider that those ions are separated less than a certain cut-off distance (20 Å in this study). The polarizability of ions is expressed by means of the shell model. This consists of a massless shell with charge $|e|$ that is allowed to move to a massive core with charge $X|e|$, resulting in the overall charge state of each ion equal to $(X + Y)|e|$. The shell is bound to the core by an isotropic harmonic spring with force constant $k$, and the displacement of the shell relative to the core gives a good description of electronic polarization. In this study, $O^{2-}$ and $Ce^{4+}$ ions are treated as polarizable and their shell parameters are listed in Table II. To calculate the intrinsic defect energy in bulk lattice, Mott-Littleton two-region method was applied, which is coded in GULP program. To approach simulation of the accommodation of the defect clusters in perfect crystal, the lattice around defect center is divided into two spherical regions (I and II) together with an interfacial region Ia. Ions in region I are allowed to be explicitly relaxed related to the defect, which is introduced to the center of region I, while ions in region Ia are assumed to be weakly perturbed and thereby vary via the Mott-Littleton approximation. Meanwhile, the interaction between region I and II ions are explicitly calculated. In order to ensure that the defect energy is sufficiently converged with respect to the region radii, an inner region I with a radius $3a_0$ ($a_0 = 5.411$ Å, the lattice constant of ceria) and the interfacial region Ia with a radius $6a_0$ were used for calculation.

Explicitly, the positive defect energy means the energy required to form the defect. Therefore, defects with the lowest energy are preferred as stable in the crystal lattice. On the other hand, for defect clusters with different number of defect components, binding energy $\Delta E_{b}$ is calculated to investigate the preference and stability of defect clusters.

### II. EXPERIMENTAL AND METHODOLOGY

GDC nanopowders were synthesized by ammonium carbonate co-precipitation method. After calcined at 800°C for 2 h under flowing $O_2$ gas (200 ml/min), nanopowders were isostatically pressed under 200 MPa. Then compact pellets were sintered at 1400°C for 6 h in air. To characterize microstructure evolution as a function of dopant concentration, high resolution transmission electron microscopy (HRTEM) imaging, selected area electron diffraction (SAED), and electron energy loss spectroscopy (EELS) were performed separately in a JEOL JEM-2000EX and a FEI Tecnai-F30 field emission gun TEM equipped with a Gatan imaging filtering system. GDC sintered tablets were mechanically cut, thinned, dimpled, and then ion-milled with a precisely controlled accelerating voltage (4.0 kV) and beam current (10 µA) in an ion polisher, to produce electron-transparent thin areas for TEM observations.

Atomic computer simulation, based on energy minimization techniques, was employed to investigate the formation of defect clusters, detailed structural evolution pathway of defect clusters and related structure formation of nano-domain still remains unclear. Additionally, interesting questions also come out based on the chain model put forward. For instance, since the curved chain is a typical non-convergent structure, it is difficult to predict the evolutionary pathway of defect cluster growth corresponding to the increasing dopant concentration. This is because the defect clusters cannot grow infinitely along one direction without any structural restriction. Moreover, the linearly elongated chain structure is restricted in one specific direction, which will significantly enhance the anisotropic structure of the defect clusters. However, from experimental observations, all nano-domains observed in rare-earth-doped ceria have neither specific orientation nor anisotropic microstructure features. On the other hand, the examined defect clusters in previous investigations are mostly less than four oxygen vacancies, which are not large enough to analyze the ordered structure as well as to predict the evolution of defect clusters. Therefore, it is essential to study the ordered structure of larger defect clusters to fully exploit the mechanism of defect cluster formation and evolution, as well as to gain fundamental insights into the nano-domain formation and related influence on conduction phenomena in doped ceria.

In this study, the defect clusters formation and evolution in doped ceria were validated by experimental observations, and more detailed analysis of such defect clusters were conducted from an atomist perspective. Large defect clusters in GDC containing up to six oxygen vacancies and twelve associated dopant cations were investigated by atomistic simulation calculations. These results were then compared with the chain model as previously reported and a more stable unique structure was established. Finally, ordered defect cluster structure was determined and the nano-domain formation was rationalized in terms of this unique structure.

### Table I. Short-range pair potential parameters.

<table>
<thead>
<tr>
<th>Species</th>
<th>A (eV)</th>
<th>$\rho$ (Å)</th>
<th>C (eV Å$^6$)</th>
<th>References</th>
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<tr>
<td>Ce$^{4+}$–$O^{2-}$</td>
<td>1986.8</td>
<td>0.3511</td>
<td>20.40</td>
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<td>Gd$^{3+}$–$O^{2-}$</td>
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<td>20.34</td>
<td>31</td>
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<tr>
<td>$O^{2-}$–$O^{2-}$</td>
<td>22764.3</td>
<td>0.149</td>
<td>45.83</td>
<td>32</td>
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</tbody>
</table>

### Table II. Shell parameters.

<table>
<thead>
<tr>
<th>Species</th>
<th>Y (el)</th>
<th>K (eV Å$^{-2}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$^{4+}$</td>
<td>7.7</td>
<td>291.8</td>
<td>32</td>
</tr>
<tr>
<td>$O^{2-}$</td>
<td>–6.1</td>
<td>419.9</td>
<td>35</td>
</tr>
</tbody>
</table>
with the following formula:

\[ \Delta E_0 = \Sigma E_{\text{isolated}} - E_{\text{cluster}}. \] (1)

\( \Sigma E_{\text{isolated}} \) refers to the sum of defect energies of all components in the defect cluster, and \( E_{\text{cluster}} \) is the defect energy of the cluster itself. From Eq. (1), it can be noticed that a positive binding energy implies a preference of the formation of defect cluster over its individual components. Therefore, the higher binding energy indicates greater stability of defect cluster. Combining the exact defect and binding energy, we can thus predict the formation and evolution of defect clusters in bulk materials.

III. RESULTS

Figure 1(a) is a typical HRTEM image of 10 at.% GDC (10GDC) observed from [110] zone axis. Corresponding SAED pattern is represented in Fig. 1(c). By comparing another GDC sample with higher dopant concentration (i.e., 25GDC), a nano-domain (denoted by dashed line in Fig. 1(b)) can be observed. The corresponding SAED pattern of the nano-domain region demonstrates extra diffuse scattering (i.e., denoted by white arrows in Fig. 2(d)), which is attributed to nano-domain intergrow ing in ceria fluorite matrix. Such nano-domain and peculiar diffuse scattering features have been widely observed in the heavily doped ceria. The appearance of short-range ordered structure in 25GDC is not only detected by SAED, but also verified by EELS analyses. As shown in Fig. 1(e), the EELS spectrum of oxygen K adsorption edge displays fine structures of peaks A, B, and C. Correspondingly, the related EELS result of 25GDC (Fig. 1(f)) represents significant enhancement of B peak. Such fine structure evolution of EELS spectra is usually designated as the fingerprint to analyze crystalline microstructural change.\(^{35}\) In accordance with the previous reports,\(^{37}\) this EELS result indicates that the nano-domain formation is accompanied with ordered vacancy structures in 25GDC. In order to clarify the ordered structure of defect clusters as well as newly appeared nano-domain in doped ceria, atomistic simulation was consequently performed.

Figure 2(a) shows possible relations between one Gd\(^{3+}\) cation and related oxygen vacancy in a fluorite unit cell. Generally, an oxygen vacancy can be located at the first, second, or third neighbor site (marked by solid lines in Fig. 2(a)) to its corresponding substitutional ion, with the separation lattice vector of \( 111/4 \), \( 113/4 \), and \( 133/4 \), respectively. Kröger-Vink notation is used in this study to simplify the expression of defect cluster, e.g., a defect cluster consisting of one oxygen vacancy and one Gd\(^{3+}\) cation is designated as \( 1V_0\ 1Gd\ 1Ce \). To classify spatial relationships among constituents in defect clusters, lattice vectors between two adjacent oxygen vacancies \( \langle V_0 - V_0 \rangle \), and vectors between an oxygen vacancy and its corresponding dopant cations \( \langle V_0 - Gd\Ce \rangle \) are used for notification. Comparing binding energies of one oxygen vacancy and one associated dopant cation located at the first, second, and third neighbor sites \( (0.87, 0.65, \text{and } 0.45 \text{ eV, respectively}) \), it suggests that Gd\(^{3+}\) prefers to occupy the first neighbor site related to its corresponding \( V_0 \), separated by \( 111/4 \). However, based only on the slight difference between the binding energy of dopant cations located at the first neighbor sites with that at the second sites, it is imprudent to conclude that the dopant cations will only occupy the nearest neighbor site. Since the substitution of trivalent dopant cations for Ce\(^{4+}\) is accompanied with the formation of a charge-compensation oxygen vacancy for every two Gd\(^{3+}\) ions, binding energies were studied of the simplest neutralized defect clusters consisting of one oxygen vacancy and two dopant cations. Figure 2(b) is the defect cluster \( 1V_0\ 2Gd\) with two dopant cations located at the first neighbor sites. If one Gd\(^{3+}\) occupies the second neighbor site instead of the first one (Fig. 2(c)), the binding energy will decrease from 1.49 eV (Fig. 2(b)) to 1.21 eV. When both substitutional ions are at the second neighbor sites, the related binding energy will further decrease to 1.17 eV (Fig. 2(d)). The decrease of the binding energy will be attributed to nano-domain intergrowth in ceria fluorite matrix.
energy as a function of relative positions between dopant cations and oxygen vacancies indicates that Gd$^{3+}$ prefers to occupy the first neighbor sites to minimize the defect energy rather than being separated far away from their corresponding oxygen vacancies. When considering ordered structure of two VO$^-$, it is believed that VO$^-$ - VO$^-$ interaction usually occurs along (110)/2 or (111)/2 directions. Among all the possible atomic structures of 2VO$^-$ 4Gd$^{3+}$, the defect cluster shown in Fig. 3(a) has the lowest defect energy (158.30 eV) as well as the highest binding energy ($\Delta E_b = 3.35$ eV), with two VO$^-$ separated by (110)/2 and corresponding Gd$^{3+}$ located at the first neighbor sites. Similar to the result represented in Fig. 2, if all Gd$^{3+}$ are located at the second neighbor sites, the related binding energy will decrease to 2.20 eV, even though two VO$^-$ remain at the same positions. In order to compare with the chain model of ordered defect clusters, the curved chain structure with the highest binding energy among all possible structures investigated in previous report are also displayed. Figure 3(c) is the most stable atomic structure of 2VO$^-$ 4Gd$^{3+}$ in chain model, where VO$^-$ - VO$^-$ is separated by (111)/2 and Gd$^{3+}$ are situated at the second neighbor sites. These three atomic structures shown in Fig. 3 have higher binding energies than the other different structures investigated in our simulations (others are not shown here). Note that the chain structure actually has lower binding energy ($\Delta E_b = 2.07$ eV) than structures in Figs. 3(a) and 3(b), implying that the previous chain structure may not be the most stable structure of defect cluster embedded in fluorite ceria matrix. When the number of VO$^-$ increases to three, a unique defect structure begins to appear, as shown in Fig. 4(a). Such unique structure has the highest binding energy ($\Delta E_b = 5.21$ eV) among all possible arrangements in 3VO$^-$ 6Gd$^{3+}$. Oxygen vacancies in this structure are separated along (110)/2 lattice vectors. The three VO$^-$ defects can also construct an isosceles triangle ($\Delta ABC$ in Fig. 4(a)) with two adjacent equal edges along (110)/2 and a corresponding interior angle 120°, while the subtense vector of this isosceles triangle is (112). All Gd$^{3+}$ occupy the first neighbor sites with respect to the corresponding VO$^-$.

Similarly, this isosceles triangle structure has much higher binding energy than the chain structure ($\Delta E_b = 3.47$ eV) (Fig. 4(b)). Taking into account the defect cluster that consists of four VO$^-$ (4V$O^- 8Gd^{3+}$), the defect structure with the highest binding energy ($\Delta E_b = 7.06$ eV) has a tetrahedron configuration (Fig. 5(a)). Interestingly, the three faces of this tetrahedron are constructed by three congruent isosceles triangles as shown in Fig. 4(a). Similar to the defect clusters in Figs. 3(a) and 4(a), all Gd$^{3+}$ occupy the first neighbor sites with respect to the corresponding VO$^-$, Note that the chain structure of 4VO$^-$ 8Gd$^{3+}$ (Fig. 5(b)) has much lower binding energy ($\Delta E_b = 4.30$ eV) compared to the tetrahedron structure. This symmetric tetrahedron structure suggests that the unique isosceles triangle (Fig. 4(a)) may be the smallest unit to construct ordered structure of the larger defect clusters. In other words, we can predict the growth pathway of defect clusters through the formation of such unique isosceles triangle structure. For the interaction between the existing defect cluster and another individual defect, it can be suspected that the newly enrolled oxygen vacancy will occupy the specific site which can form the unique isosceles triangle with respect to the existing defects. This hypothesis can be validated by further investigating 5VO$^-$ 10Gd$^{3+}$ and 6VO$^-$ 10Gd$^{3+}$ defect clusters.

Figure 6(a) represents the defect structure of 5VO$^-$ 10Gd$^{3+}$ with the highest binding energy ($\Delta E_b = 8.84$ eV). Based upon the defect structure of 4VO$^-$ 8Gd$^{3+}$, the newly enrolled VO$^-$ is located along (110)/2 related to

FIG. 3. Defect cluster of 2VO$^-$(4Gd$^{3+}$). (a) two VO$^-$ are separated by (110)/2 and all Gd$^{3+}$ ions locate at first neighbor sites with respect to their VO$^-$; (b) the same VO$^-$ - VO$^-$ structure to (a), while all Gd$^{3+}$ are at second neighbor sites. (c) The chain model structure of 2VO$^-$(4Gd$^{3+}$), where two VO$^-$ are separated by (111)/2 while all Gd$^{3+}$ occupy second neighbor sites.

FIG. 4. Defect cluster of 3VO$^-$(6Gd$^{3+}$). (a) nearest two VO$^-$ are separated by (110)/2 and all Gd$^{3+}$ ions are located at first neighbor sites, and such three VO$^-$ can construct an isosceles triangle with the highest binding energy among all possible defects arrangements; (b) the corresponding chain model structure with the same number of defects.

FIG. 5. Defect cluster of 4VO$^-$(8Gd$^{3+}$). (a) the most stable structure, the tetrahedron can be divided into three congruent isosceles triangles as shown in Fig. 4(a); (b) the corresponding chain model structure with the same number of defects.
its nearest $V_O$ in the existing $4V_O^- 8Gd^{3+}$ defect cluster. Particularly, this new $V_O$ can form the unique isosceles triangle together with other two nearby $V_O$ in the tetrahedron structure. Therefore, the $5V_O^- 10Gd^{3+}$ cluster can be considered as a combination of four congruent isosceles triangles as shown in Fig. 4(a), and every two adjacent $V_O$ are separated by $(110)/2$. The chain structure of $5V_O^- 10Gd^{3+}$ cluster (Fig. 6(a)), however, has much lower binding energy ($\Delta E_b = 5.79$ eV) and is thus not as stable as the structure shown in Fig. 6(a). Similarly, when the defect cluster grows up to $6V_O^- 12Gd^{3+}$, the newly enrolled $V_O$ will be located at the site followed by the same criterion as aforementioned (Fig. 7(a)). The $6V_O^- 12Gd^{3+}$ defect cluster formed by such criterion has the highest binding energy ($\Delta E_b = 10.94$ eV) among all possible arrangements of defect clusters with the same number of $V_O$ and $Gd^{3+}$. Comparatively, it is more stable than the chain structure, which has much lower binding energy ($\Delta E_b = 7.10$ eV, Fig. 7(b)). Moreover, such defect structure is highly symmetric: it can be not only considered as the symmetric combination of six congruent isosceles triangles as shown in Fig. 4(a), but also assigned as two congruent tetrahedrons, the same structure as that in Fig. 5(a), symmetrically integrated together by sharing one common edge. Besides energy considerations, such highly symmetric structure shown in Fig. 7(a) is also convergent as a better optimum structure than the non-convergent chain structure for the development of large defect clusters from the geometry point of view.

IV. DISCUSSION

According to the above calculations, the unique isosceles triangle constructed by $V_O$ can be regarded as the smallest unit to develop large defect clusters with ordered structure. Moreover, such triangle structure will further evolve into more symmetric and stable dumbbell structure represented in Fig. 7(a). Therefore, we designated the defect structures discussed in this study as the dumbbell model, in contrast to the chain model as previously reported. Since oxygen vacancy ordering is generally accompanied with dopant cations ordering, the enhanced ordering of all oxygen vacancies will also increase the ordering level of associated cations, difficult to be directly verified by the experimental techniques though. Therefore, the ordered structure of the dopant cations should not be neglected. Calculation results in Figs. 2 and 3 illustrate that $Gd^{3+}$ cations prefer to occupy the first neighbor sites related to their associated $V_O$. Nevertheless, for one pair of $Gd^{3+}$ and associated $V_O$, there are four different orientations while being separated by the same $(111)/4$ lattice vector. In order to determine the exact site that $Gd^{3+}$ will occupy, different sites of $Gd^{3+}$ location have been detected with the same $V_O$ structure. Take the $6V_O^- 12Gd^{3+}$ cluster, for example. The defect structure with the highest binding energy is shown in Fig. 8(a), where all $Gd^{3+}$ ions occupy the first neighbor sites related to the corresponding $V_O$. As long as we change one $Gd^{3+}$ (the highlighted cation in Fig. 8) from $Gd_1$ site (Fig. 8(a)) to $Gd_2$ (Fig. 8(b)), the relative binding energy will decrease from 10.94 to 10.84 eV. This implies that the $Gd_1$ site is more energetically favorable than $Gd_2$, even though both sites actually are the first neighbor with respect to the associated $V_O$ site A. The only site difference between $Gd_1$ and $Gd_2$ is that $Gd_1$ is the second neighbor site with respect to the nearby $V_O$ B site, while $Gd_2$ is the third neighbor one. As discussed in Fig. 2, the second neighbor site is more energetically favorable than the third one. It, hence, indicates that for the location of dopant cations depends not only on its nearest neighbor $V_O$, but also on the second nearest neighbor $V_O$. Comparing all possible arrangements of dopant cations, it reveals that the dopant cation prefers to occupy the site that is not only the
first neighbor site related to associated $V_O$, but also the first or second neighbor site with respect to the second nearest neighbor $V_O$. For larger clusters (more than three $V_O$), one Gd$^{3+}$ cannot be the first or second neighbor to all $V_O$ in the same cluster. In this case, our systematical calculations suggest that Gd$^{3+}$ will occupy the first neighbor site to its associated $V_O$, and try to share the most first or second neighbor sites to other nearby $V_O$. Moreover, note that when one Gd$^{3+}$ position changes while the $V_O$ structure remains the same, as shown in Figs. 8(a) and 8(b), the difference of binding energy (0.1 eV) is not significant. Nevertheless, other systematical calculations (not shown here) illustrate that changing $V_O$ positions while keeping the same Gd$^{3+}$ relative locations will lead to a significant change in the binding energy. This phenomenon can be elucidated by the fact that oxygen vacancies are highly mobile whereas dopant cations are relatively immobile in fluorite structure. Additionally, it illustrates that in oxygen-deficient oxides, such as the nonstoichiometric cerium oxides, oxygen vacancies are the predominating defects. Therefore, the ordered structure of oxygen vacancies has more significant effects on minimizing the total defect energy of clusters. Contrarily, relative dopant cations positions are not as sensitive as those of oxygen vacancies.

Figure 8(c) is the defect cluster that has the same $V_O$ structure as shown in Fig. 8(a), while with all Gd$^{3+}$ ions located at the second neighbor sites the binding energy ($\Delta E_b = 8.00$ eV) is lower. This comparison confirms that Gd$^{3+}$ prefer to occupy the first neighbor site with respect to their corresponding $V_O$ rather than the second neighbor site as discussed in previous report. More detailed comparison is shown in Fig. 9. The line connected by solid square points represents defect clusters with all Gd$^{3+}$ located at first neighbor sites, while the line connected by open square points stands for clusters with Gd$^{3+}$ located at the second neighbor sites. Both have the same $V_O$ structures constructed by isosceles dumbbell model. Figure 9 clearly illustrates that Gd$^{3+}$ cations prefer to occupy the first neighbor site with respect to the corresponding $V_O$. The bifurcate feature displayed in the same figure indicates that as the defect cluster grows, first neighbor sites are more energetically favorable than second neighbor sites and hence more significantly enhance the ordering level of dopant cations in defect clusters.

Quantitatively, Fig. 10 exhibits the binding energy evolution as a function of the number of $V_O$ for both the dumbbell model and chain model. Noted that the binding energy in both models is positively related to the number of $V_O$, implying that there is an intrinsic driving force for defect clusters growth. It also reflects that the induced defects (oxygen vacancies and dopant cations) are not randomly distributed in fluorite ceria lattice. On the contrary, all induced defects prefer to aggregate and form ordered structure, which is in accordance with the experimental observations. Moreover, Fig. 10 clearly reveals that the dumbbell model has higher binding energy than chain model. Particularly, as the number of oxygen vacancies increases, the binding energy difference between these two models becomes more significant. This suggests that when defect clusters are small, they may have several possible structures and orientations related to each other. With dopant concentration increasing, more defects will be induced in ceria matrix, which will subsequently drive the growth of defect clusters and enhance their ordered structures.

According to the experimental observations, it can be realized that the nano-domain has a short-range ordered structure, which can be interpreted as diffuse scattering in the diffraction pattern. Even though ordering level of dopant cations cannot be directly detected by the experimental techniques, enhanced ordering level of oxygen vacancy can be detected by EELS. Such short-range ordered structure can be elucidated by the atomistic simulation technique as discussed above. Therefore, the nano-domain formation in doped ceria can be rationalized as follows. The dopant cations will introduce associated charge-compensation oxygen vacancies. Initially defects (dopant cations and oxygen vacancies) in the ceria matrix are randomly distributed. High temperature sintering process (1400°C in this case) will boost defects movement and migration. In order to minimizing the defect energy, oxygen vacancies prefer to stay along (110)/2 and associated dopant cations will occupy the first neighbor sites related to their corresponding oxygen vacancies. Three adjacent oxygen vacancies will form a unique isosceles triangle structure, which is validated as the most stable structure among different defects arrangements. Such isosceles triangle structure can be considered as the smallest unit for larger defect cluster development. For instance, when four oxygen vacancies aggregate, a symmetric tetrahedron will be formed, which is actually constructed by three congruent isosceles triangles. When more defects are enrolled, they will occupy the sites that can form the unique isosceles triangle structure as shown in Fig. 8(b).
triangle and ordered structure is consequently developed. A more symmetric and stable dumbbell structure will appear, constructed by six oxygen vacancies, with a combination of six congruent isosceles triangles. Such unique stable structure can be deemed as the building block for larger defect cluster formation. Existed ordered defect structure will also act as the trapping/sinking center for randomly distributed defects, and such defect clusters will continuously grow in terms of the unique dumbbell structure formation. This will subsequently enhance the total ordering level of defect clusters, and thus lead to nano-domain formation in doped ceria.

V. CONCLUSIONS

In summary, HRTEM, SEAD, and EELS analyses comprehensively demonstrate nano-domain formation in Gd-doped ceria with short-range ordered structure. Atomistic simulation technique was applied to investigate defect clusters formation and determine related ordered structures in fluorite crystal structure. It is revealed that the binding energy of defect cluster in doped ceria will increase as a function of cluster size. Induced charge-compensation oxygen vacancies prefer to form a unique isosceles triangle which has been validated as the most stable structure. Such unique triangle can be considered as the smallest unit for larger defect clusters formation. Correspondingly, associated dopant cations will occupy the first neighbor sites with respect to their related oxygen vacancies. As defect clusters grow up to six oxygen vacancies, a more symmetric and stable dumbbell structure comes into being, which can be interpreted as a combination of six isosceles triangles. Defect clusters will grow in terms of the formation of such dumbbell structure and subsequently enhance the total ordering level of clusters, leading to nano-domain formation with ordered structure in rare-earth-doped ceria. These results would further advance our knowledge of the microstructure evolution in nonstoichiometric oxides and related influence to ionic conductivity in oxygen-deficient material systems.

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