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Effect of Electrostatic and Size on Dopant Occupancy in Lithium Niobate Single Crystal

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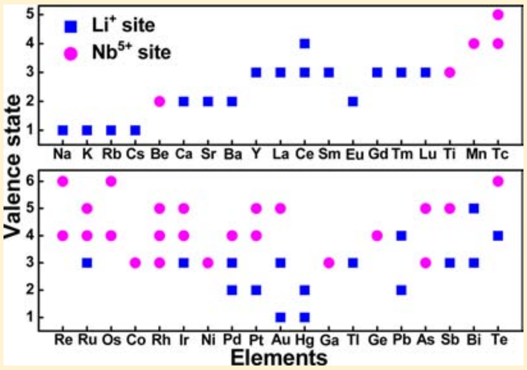
ABSTRACT: We proposed a simple and an effective method to predict the site occupancy and threshold concentration of metal ions in lithium niobate ($LiNbO_3$, LN) single crystal. The ionic energy parameter E_i, defined by the ionic electronegativity and ionic radius, was proposed to describe the electrostatic and size effects of cations on the structural stability of LN. The dopant location can be easily identified by comparing the E_i deviation of dopant from those of host cations Li^+ and Nb^{5+}, and the dopant prefers to occupy the lattice site with the smaller deviation of E_i. Our calculated occupancies agree well with those experimental results, which demonstrate the predictive power of our present method. We in this work predicted the preferred occupancies of 60 metal ions in LN single crystal. Further, the threshold concentrations of some frequently used dopants were calculated on the basis of the assumption that all doped LN crystals can endure the same variation of E_i.



1. INTRODUCTION

Lithium niobate ($LiNbO_3$, LN), a versatile synthetic crystal, combines many amazing physical properties such as electro-optic, acousto-optic, piezoelectric, pyroelectric, and nonlinear optic properties and thus has wide potential applications in waveguide devices, holographic storage, and nonlinear optics.[1,2] LN is a typical nonstoichiometric crystal and has a wide solid solution region.[3] The Li_2O deficiency, and consequently excess Nb_2O_5, leads to a large concentration of intrinsic defects, including an antisite defect (a Nb^{5+} ion at a Li^+ site, expressed as Nb_{Li}^{4+}) and four lithium vacancies (V_{Li}^-).[4] The change of composition results in significant changes in the physical properties of the system including Curie temperature, photorefractive properties, and ferroelectric coercive field.[5] Moreover, various extrinsic defects including optical damage-resistant ions,[6] photorefractive ions,[7] and rare earth (RE) ions[8] also can be introduced into the LN crystallographic frame for fitting the requirements of different applications, which depend on the dopant type and concentration. Among these applications, dopants are always responsible for modification of various physical properties of LN matrix. Since the occupancy site of dopants determines the microscopic crystal structure and electronic structure, e.g., the local structure distortion, nature of defects, and impurity energy levels in LN single crystal, and thus strongly influences its physical properties, the site selectivity of dopants should be clarified to deeply understand their roles in modification of functional properties of LN single crystal.

However, it is very difficult to determine the lattice position of diffused ions in LN matrix, which is owing to the similarity of the chemical environment of lattice sites of Li^+ and Nb^{5+}. To date, considerable experimental and theoretical work has been carried out to determine the site occupancy of various dopants in LN matrix. Much progress has been achieved on account of the use of advanced characterization techniques;[9−11] however, these experimental characterization methods are relatively expensive, and the results sometimes are controversial. For theoretical prediction of the dopant occupancy, Kling et al. proposed that dopants with a normal valence state lower than that of Nb^{5+} ions occupy Li^+ sites; otherwise, they replace Nb^{5+} ions.[12] On the other hand, Rebouta et al. developed a way to identify the dopant occupancy by comparing the lengths of dopant−O, Li−O, and Nb−O bonds.[13] They suggested that all dopants with a dopant−O bond length exceeding the mean Nb−O bond length occupy Li^+ sites or shifted Li^+ sites if the bond length also exceeds the mean Li−O bond length, while dopants with a bond length smaller than or equal to the mean Nb−O bond length can occupy either Li^+ or Nb^{5+} sites. Recently, Xue et al. developed empirical models from the viewpoint of chemical bonds to determine the dopant occupancy in LN single crystal.[14−16] Although the predicted occupancy results of some frequently used dopants are quite satisfactory, the doping behaviors of ions in the whole periodic table have not been systematically investigated.

In a doped oxide, electrostatic interactions between ions with different charges and strain-mediated interactions due to the size mismatch between host and dopant atoms are general in

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nature.[17] From previous work of Kling et al.,[12] Rebouta et al.,[13] and Xue and He,[14] we find that dopant occupancy in LN single crystal is closely related to such parameters as valence state and bond length, indicating that occupancy selectivity of dopants in LN matrix is controlled by a combination of charge and size effects. The concept of electronegativity (EN), which was defined by Pauling as "the power of an atom in a molecule to attract electrons to itself",[18] is a widely used parameter to describe the interaction between atoms and electrons in condensed matters and further to predict the structure and physical properties of crystal materials. Recently, we proposed an ionic EN scale on the basis of effective electrostatic potential at the boundary of an ion, by which the EN values of 82 elements with different oxidation states, coordination numbers, and spin states were quantitatively scaled.[19] The electrostatic potential of an ion in a particular chemical environment can be well reflected by this comprehensive EN scale, which gives us a good opportunity to systematically investigate the doping behaviors of various metal ions in LN crystals. In this work, we explored the underlying driving force of the site selectivity of various dopants in LN matrix by considering the electrostatic and size effects of cations on the structural stability of doped LN crystals. Besides, the threshold concentrations of some frequently used ions were successfully estimated.

2. THEORETICAL METHOD

The crystallographic structure of LN single crystal possesses distorted hexagonal close-packed oxygen octahedra by sharing their common faces (along the *c* axis) or edges (at the *ab* plane), which forms a trigonal lattice. Li^+ and Nb^{5+} cations are six coordinated to O^{2-} anions, and the O^{2-} anion is four coordinated to two Li^+ cations and two Nb^{5+} cations. The stacking sequence of consequent cations is Li^+, Nb^{5+}, and an empty octahedron along the +*c* axis direction, which form a helix. The vacant space (vacant oxygen octahedra and tetrahedra) in LN single crystal can be regarded as an important buffer for Nb^{5+} and Li^+ cations to balance their strong repulsions.[20] Since the vacant space is not available for any dopant,[20] we just need to determine the introduced cations occupying the Li^+ or Nb^{5+} site. According to the Buckingham energy model,[21] the energy of ionic materials includes an electrostatic energy part and ionic size effects and the structural stability of an oxide is determined by the charge and size of cations. Both effects of electrostatic interactions and size can be well reflected by ionic EN and ionic radius. However, what roles ionic EN and ionic radius play and how they determine the site occupancy of dopants are not clear. According to the available occupancies of dopants in LN matrix (as shown in Figure 1), we can find that a dopant occupies Li^+ sites if its ionic EN is smaller than that of Nb^{5+} and its ionic radius is larger than that of Nb^{5+} while it occupies Nb^{5+} sites when its ionic radius is smaller than that of Nb^{5+} and its ionic EN is larger than that of Nb^{5+}. To describe the combined effect of electrostatic interactions and size of a cation and qualitatively reflect the matching degree between the dopant and the substituted ion, we defined the ionic energy parameter E_i using ionic EN and ionic radius as

$$E_i = \chi^{\alpha} r^{\beta} \tag{1}$$

where χ and r are the ionic EN and ionic radius of a cation, respectively, and α and β are constants. The ionic energy parameter E_i reflects effects of both electrostatic interactions and size of a cation on the energy and thus the structural stability of an ionic crystal. We assume that substitution will occur at the site where the doped and the substituted ions have a smaller difference of E_i, which denotes the smaller change of the system's energy, and the deviation of E_i can be obtained by the following equation

$$D_{\mathrm{M}}^{\mathrm{Li(Nb)}} = |E_{i(\mathrm{M})} - E_{i(\mathrm{Li\ or\ Nb})}| \tag{2}$$

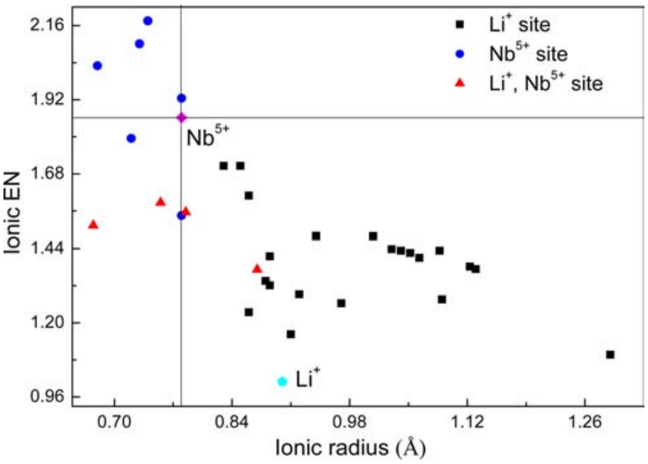

Figure 1. Identification of dopant location in LN matrix according to the scales of both ionic EN and ionic radius. Horizontal and vertical lines represent the ionic EN and ionic radius equal to those of Nb^{5+} ion, respectively.

where $D_{\mathrm{M}}^{\mathrm{Li(Nb)}}$ denotes the deviation of E_i of a cation M^{z+} from that of Li^+ or Nb^{5+}. Larger $D_{\mathrm{M}}^{\mathrm{Li(Nb)}}$ indicates an unsuited dopant that will lead to serious structural instability in the LN crystallographic frame.

In order to determine the values of α and β in eq 1, we give Mg^{2+} and Zn^{2+} ions incorporated into LN matrix as examples. Experimentally, Mg^{2+} and Zn^{2+} ions occupy Li^+ sites undoubtedly. According to eq 2, we get the following relationship as

$$|\chi_{\mathrm{Mg(Zn)}}^{\alpha} r_{\mathrm{Mg(Zn)}}^{\beta} - \chi_{\mathrm{Li}}^{\alpha} r_{\mathrm{Li}}^{\beta}| < |\chi_{\mathrm{Mg(Zn)}}^{\alpha} r_{\mathrm{Mg(Zn)}}^{\beta} - \chi_{\mathrm{Nb}}^{\alpha} r_{\mathrm{Nb}}^{\beta}| \tag{3}$$

If the correct occupancies of Mg^{2+} and Zn^{2+} ions in LN matrix are obtained, the relation between α and β should satisfy $\alpha/\beta < 0.23$. For simplification, we suppose that $\alpha = 0.2$ and $\beta = 1.0$, which indicates that the electrostatic effect is a subordinate factor while the size effect is an uppermost factor determining the dopant occupancy in LN matrix. As to doped LN crystals, the absolute discrepancy $D_{\mathrm{M}}^{\mathrm{Li(Nb)}}$ arising from the cation mismatching can be regarded as the driving force for lattice substitution.

3. RESULTS AND DISCUSSION

Using eq 1, we calculated the ionic energy parameter E_i of various metal ions with different valence states. Throughout this work, ionic EN values are taken from ref 19 and the ionic radii are from ref 22. All calculated values of the absolute deviation $D_{\mathrm{M}}^{\mathrm{Li(Nb)}}$ and the predicted occupancies of some frequently used metal ions are listed in Table 1, and the corresponding experimental occupancies[15,16,23−34] of these dopants are also listed for comparison. The predicted dopant locations correspond well with the available experimental ones except for Ti^{4+} and Ni^{2+}, which demonstrates the predictive power of our method. The dopants preferentially replace Li^+ sites before replacing Nb^{5+} sites if $D_{\mathrm{M}}^{\mathrm{Li}} < D_{\mathrm{M}}^{\mathrm{Nb}}$, while they preferentially occupy Nb^{5+} sites before replacing Li^+ sites if $D_{\mathrm{M}}^{\mathrm{Li}} > D_{\mathrm{M}}^{\mathrm{Nb}}$. For instance, all optical damage-resistant ions (such as Mg^{2+}, Zn^{2+}, Sc^{3+}, In^{3+}, Hf^{4+}, Zr^{4+}, and Sn^{4+}) and RE ions have experimentally been proven to occupy Li^+ sites undoubtedly in congruent LN crystals at low doping concentration,[16,33,34] which agree well with our calculations. Some transition metal (TM) ions such as Mn^{2+}, Fe^{2+}, and Co^{2+} also occupy Li^+ sites. In the case of Mo^{6+}, Ta^{5+}, and W^{6+}, they occupy Nb^{5+} sites due to $D_{\mathrm{M}}^{\mathrm{Li}} > D_{\mathrm{M}}^{\mathrm{Nb}}$.

However, the occupancies of some TM ions are still of controversy to date.[16] For example, Fe^{3+} and Cr^{3+} ions preferentially occupy Nb^{5+} sites according to our predictions,

Table 1. Theoretically and Experimentally Determined Occupancies of Some Frequently Used Metal Ions as the Dopant in LN Crystallographic Frame

metal ions	E_i	$D_{\mathrm{M}}^{\mathrm{Li}}$	$D_{\mathrm{M}}^{\mathrm{Nb}}$	calculated occupancies	experimental occupancies
Mg^{2+}	0.897	0.005	0.014	Li	Li[a]
Al^{3+}	0.733	0.169	0.150	Nb	Li,[b] Nb[b]
Sc^{3+}	0.949	0.047	0.066	Li	Li[a]
Ti^{4+}	0.831	0.071	0.052	Nb	Li[c]
V^{3+}	0.851	0.051	0.032	Nb	Nb[d]
V^{4+}	0.809	0.093	0.074	Nb	Nb[d]
V^{5+}	0.783	0.119	0.100	Nb	Nb[d]
Cr^{3+}	0.828	0.074	0.055	Nb	Li,[a] Nb[a]
Mn^{2+}	1.016	0.114	0.133	Li	Li[a]
Fe^{2+}	0.968	0.066	0.085	Li	Li[e]
Fe^{3+}	0.858	0.044	0.025	Nb	Li,[f] Nb[g]
Co^{2+}	0.936	0.034	0.053	Li	Li[a]
Ni^{2+}	0.884	0.018	0.001	Nb	Li[a]
Cu^{+}	0.938	0.036	0.055	Li	Li[h]
Cu^{2+}	0.927	0.025	0.044	Li	Li,[i] Nb[i]
Zn^{2+}	0.932	0.030	0.049	Li	Li[a]
Zr^{4+}	0.946	0.044	0.063	Li	Li[a]
Mo^{6+}	0.847	0.055	0.036	Nb	Nb[j]
Ag^{+}	1.314	0.412	0.431	Li	Li[k]
Cd^{2+}	1.144	0.242	0.261	Li	Li[b]
In^{3+}	1.017	0.115	0.134	Li	Li[a]
Sn^{4+}	0.924	0.022	0.041	Li	Li[l]
Pr^{3+}	1.204	0.302	0.321	Li	Li[a]
Nd^{3+}	1.198	0.296	0.315	Li	Li[a]
Eu^{3+}	1.168	0.266	0.285	Li	Li[a]
Tb^{3+}	1.139	0.237	0.256	Li	Li[m]
Dy^{3+}	1.129	0.227	0.246	Li	Li[m]
Ho^{3+}	1.119	0.217	0.236	Li	Li[a]
Er^{3+}	1.108	0.206	0.225	Li	Li[a]
Yb^{3+}	1.090	0.188	0.207	Li	Li[a]
Hf^{4+}	0.946	0.044	0.063	Li	Li[n]
Ta^{5+}	0.889	0.013	0.006	Nb	Nb[a]
W^{6+}	0.864	0.038	0.019	Nb	Nb[a]

[a] Reference 16. [b] Reference 15. [c] Reference 23. [d] Reference 24. [e] Reference 25. [f] Reference 26. [g] Reference 27. [h] Reference 28. [i] Reference 29. [j] Reference 30. [k] Reference 31. [l] Reference 32. [m] Reference 33. [n] Reference 34.

while they can also occupy Li^+ sites in congruent LN crystals at low doping concentration; Cu^{2+} ion preferentially occupies Li^+ sites according to our prediction, while it can also occupy Nb^{5+} sites. The departure of experimental results from our predictions may be ascribed to the existing antisite defects ($\mathrm{Nb_{Li}}^{4+}$). LN crystals are usually grown with a congruent, nonstoichiometric composition possessing excess Nb^{5+} ions at Li^+ sites in the crystallographic frame. The deviation $D_{\mathrm{Nb}}^{\mathrm{Li}}$ of an antisite is 0.019, indicating the very similar chemical environments of Li^+ and Nb^{5+} and the ease of formation of antisite defects in LN single crystal, that is, the variation of the system's energy is small, and correspondingly the crystal is relatively stable when a Nb^{5+} ion substitutes for Li^+ ion. This deviation is close to the deviation values of $D_{\mathrm{M}}^{\mathrm{Nb}}$ or $D_{\mathrm{M}}^{\mathrm{Li}}$ of Fe^{3+} and Cr^{3+} ions. In other words, these ions have a strong tendency to occupy $\mathrm{Nb_{Li}}^{4+}$ site, i.e., these ions occupy Li^+ sites. As for Cu^{2+} ion, its location in the LN lattice depends on the method of doping. Jabłonski et al. suggested that Cu^{2+} ions occupy Li^+ sites in the LN lattice in the case of doping by a diffusion process, while incorporation of Cu^{2+} ions into the LN lattice during crystal growth may lead to their location at Nb^{5+} sites.[29]

The lattice location of RE ions may have their own characters due to their relatively large $D_{\mathrm{M}}^{\mathrm{Li(Nb)}}$ values. As shown in Table 1, all $D_{\mathrm{M}}^{\mathrm{Li}}$ values of RE ions are smaller than $D_{\mathrm{M}}^{\mathrm{Nb}}$ but larger than other ions (optical damage resistant ions or some TM ions), and both $D_{\mathrm{M}}^{\mathrm{Li}}$ and $D_{\mathrm{M}}^{\mathrm{Nb}}$ decrease with increasing atomic number. The radii of RE ions are larger than those of host lattice ions Li^+ and Nb^{5+} and thus have a larger size effect. Since $D_{\mathrm{M}}^{\mathrm{Li(Nb)}}$ reflects the mismatching degree of dopant and substituted ion, a larger $D_{\mathrm{M}}^{\mathrm{Li(Nb)}}$ indicates a greater structural instability when a dopant incorporates into LN matrix. Therefore, it may be difficult to actualize the doping of RE ions at high concentration in LN crystallographic frame.

According to eqs 1 and 2, we predicted dopant occupancies of 60 metal ions with different valence states in LN matrix, as shown in Figure 2. It was found that monovalent group IA and divalent group IIA ions except for Be^{2+} prefer to occupy Li^+ sites; most of group IIIA, IVA, VA, and VIA ions with the valence state lower than their group numbers preferentially occupy Li^+ sites; all RE ions are predicted to occupy Li^+ sites; most of the TM ions, especially group VIIB and VIIIB ions, preferentially substitute for Nb^{5+} sites. Generally speaking, the dopants with valence state lower than three have a tendency to occupy the Li^+ sites, the dopants with valence state higher than three preferentially occupy Nb^{5+} sites, whereas it is branching for trivalent ions when the doping concentration is lower than the threshold concentration. For group IA and IIA ions, both $D_{\mathrm{M}}^{\mathrm{Li}}$ and $D_{\mathrm{M}}^{\mathrm{Nb}}$ are larger than other ions, even RE ions. These dopants that have equal or similar valence to Li^+ have more tendency to occupy Li^+ sites. However, little attention has been paid to the occupancy of group IA and IIA dopants experimentally or theoretically. It should be noted that a larger $D_{\mathrm{M}}^{\mathrm{Li(Nb)}}$ value means greater structural instability. When group IA and IIA dopants are introduced into the LN lattice, this doping process would lead to large lattice relaxation. Therefore, it is likely to be inappropriate to choose these ions as dopants. For group IIIA, IVA, VA, and VIA ions, since there are few reports about the site selectivity in LN crystallographic frame, the occupancy behaviors of group IIIA, IVA, VA, and VIA ions should be systematically investigated.

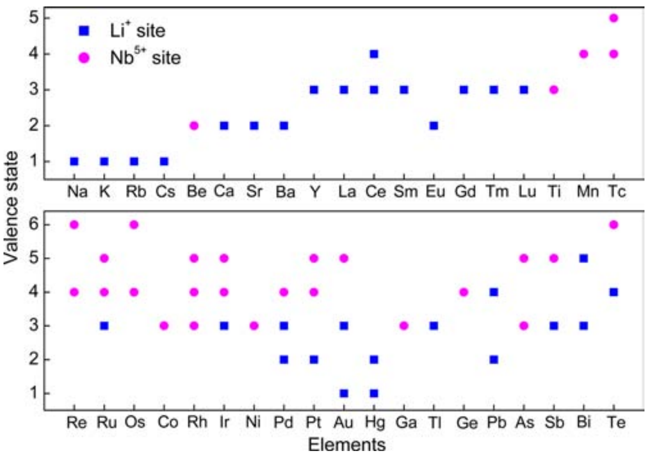

Figure 2. Predicted occupancies of 60 dopants in LN crystallographic frame, which are those metal ions with different valence states.

Further, we developed a mathematical method on the basis of ionic energy parameter to predict the dopant threshold. For an undoped LN single crystal, the crystal is stable and the sum of the ionic energy parameter of cations is a constant. When a dopant incorporates into LN crystal, the energy of the system will change and the whole crystal structure becomes unstable with the increase of doping concentration. Since the contribution of a cation on the system's energy can be reflected by its ionic energy parameter, the variation of total ionic energy parameter reaches an extreme value at the threshold value of a dopant. There are two kinds of constituent cations in each stoichiometric molecular formula: Li^+ and Nb^{5+} ions, and the ionic energy parameter ΣE_{i0} of one LN formula can be regarded as a sum of E_i of all constituent cations

$$\sum E_{i0} = \chi_{Li}^{0.2} r_{Li} + \chi_{Nb}^{0.2} r_{Nb} \qquad (4)$$

In this way, the total ionic energy parameter ΣE_{i0} of LN single crystal is calculated to be 1.785.

According to the restriction of local charge balance, several intrinsic defect models in congruent LN crystals have been proposed, including oxygen vacancy model, niobium vacancy model, and lithium vacancy model.[9,35,36] When a dopant is introduced into LN crystal, the incorporation mechanism has been generally discussed on the basis of a defect model in undoped crystals. Among these models, the lithium vacancy model has been accepted by most researchers. On the basis of the lithium vacancy model, the Mg^{2+} substitution formula at the threshold concentration is $[Li_{1-2x}Mg_xV_x][Nb][O_3]$. The total ionic energy parameter of Mg^{2+}-doped LN crystals at the threshold value can be described as

$$\sum E_{iMg} = (1 - 2x)\chi_{Li}^{0.2} r_{Li} + x\chi_{Mg}^{0.2} r_{Mg} + \chi_{Nb}^{0.2} r_{Nb} \qquad (5)$$

The threshold concentration of 5 mol % of Mg^{2+} in congruent LN crystals has been determined by experimental observation,[15] and ΣE_{iMg} of 5 mol % Mg^{2+}-doped LN crystals is 1.740.

In this regard, it is convenient to measure the variation of ionic energy parameter by the following expression

$$\Delta \sum E_{iMg} = \left| \sum E_{iMg} - \sum E_{i0} \right| \qquad (6)$$

where $\Delta\Sigma E_{iMg}$ is the variation of the ionic energy parameter when Mg^{2+} occupies Li^+ sites and the total ionic energy parameter of Mg^{2+}-doped LN crystals changes 0.045 compared to undoped LN crystals. For doped LN crystals grown from congruent melt, it is assumed that they all have the same variation of ionic energy parameter when their doping concentrations reach their threshold values. Therefore, the theoretical threshold values of some frequently used dopants were calculated and are listed in Table 2, which are highly consistent with the available threshold concentrations. Certainly, there are different threshold values for a dopant in LN crystals, which result from different compositions and growth conditions. It should be noted herein that threshold concentration means the extreme value of doping when the dopant occupancy changes from Li^+ to Nb^{5+} sites, and thus, only dopants that can occupy both Li^+ and Nb^{5+} sites are expected to have the threshold concentration.

Table 2. Calculated and Reported Threshold Concentration (in mol %) of Some Frequently Used Dopants in Congruent LN Crystal

	threshold concentration			threshold concentration	
metal ions	present work	available reports[a]	metal ions	present work	available reports[a]
Mg^{2+}	5.00%	5.00%	Hf^{4+}	1.70%	1.91%
Sc^{3+}	2.58%	2.62%	Fe^{2+}	5.43%	
Mn^{2+}	5.76%	5.03%	Cu^{2+}	5.17%	
Zn^{2+}	5.20%	5.30%	Sn^{4+}	1.69%	
Zr^{4+}	1.70%	1.91%	Er^{3+}	2.84%	
In^{3+}	2.68%	2.73%	Yb^{3+}	2.81%	

[a] Reference 15.

4. CONCLUSIONS

We established an empirical method to predict the dopant occupancy in the LN crystallographic frame by comparing the absolute discrepancy $D_M^{Li(Nb)}$ of the ionic energy parameter of a cation M^{z+} from those of Li^+ and Nb^{5+}. The ionic energy parameter, defined by ionic EN and ionic radius, reflects the electrostatic and size effects of an ion, and $D_M^{Li(Nb)}$denotes the mismatching degree of dopant and substituted ion, which reflects the degree of structural instability for a doped LN crystal. The close agreement between our predictions and the available experimental reports suggests that $D_M^{Li(Nb)}$ is a reasonable parameter to assign the site occupancy of metal ions in LN crystallographic frame. Additionally, we predicted the occupancies of 60 metal ions with different valence states in LN matrix and found that monovalent group IA and divalent group IIA ions except for Be^{2+}, most of group IIIA, IVA, VA, and VIA ions with the valence state lower than their group numbers, and all RE ions preferentially occupy Li^+ sites; TM ions with valence state higher than +3 preferentially substitute for Nb^{5+} sites. Further, the threshold concentrations of some dopants were also estimated in light of the same variation of total ionic energy parameter of Mg^{2+}-doped LN crystals with the experimental threshold value of 5 mol %, and the results also agree well with available reports. The current work provides important insight into the driving force of dopant occupancy in LN matrix and reveals its fundamental doping rules, which gives us useful guidance in practical doping of LN single crystal to control both intrinsic and extrinsic defects so as to tailor it for various applications.

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Notes

The authors declare no competing financial interest.

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