

## Dopant occupancy and structural stability of doped lithium niobate crystals

Dongfeng Xue\* and Xiangke He

State Key Laboratory of Fine Chemicals, Department of Materials Science and Chemical Engineering, School of Chemical Engineering, Dalian University of Technology, 158 Zhongshan Road, Dalian 116012, People's Republic of China

(Received 18 August 2005; revised manuscript received 31 October 2005; published 24 February 2006)

On the basis of the bond valence model, an approach is established to determine the dopant occupancy in the lithium niobate (LN) crystallographic frame. The dopant location can be easily assigned by comparing the deviation of its normal and calculated valence states, when such a dopant is arbitrarily placed in both  $\text{Li}^+$  and  $\text{Nb}^{5+}$  sites, respectively. Further, the parameter Global Instability Index is used to characterize the structural instability of doped LN crystals. The dopant occupancy in the LN crystallographic frame and its interaction with the LN matrix are quantitatively understood by the structural stability. Calculated threshold values of various dopants are further obtained in the present work.

DOI: [10.1103/PhysRevB.73.064113](https://doi.org/10.1103/PhysRevB.73.064113)

PACS number(s): 77.84.Dy, 61.72.Ji, 61.72.Ss, 61.72.Ww

### I. INTRODUCTION

Lithium niobate [ $\text{LiNbO}_3$  (LN)] is the most widely used multifunction single crystal materials, due to its excellent electronic, linear and nonlinear optical, and dielectric properties. As a typical nonstoichiometric crystal, LN composition varies in a wide range, and consequently leads to a defect complex including an antisite defect (a  $\text{Nb}^{5+}$  ion in a  $\text{Li}^+$  site, expressed as  $\text{Nb}_{\text{Li}}^{4+}$ ), and four lithium vacancies ( $\text{V}_{\text{Li}}^-$ ).<sup>1</sup> For the charge balance compensated by defects, various dopants can be introduced into the LN crystallographic frame. Most interestingly, doping with suitable cations in LN crystals leads to the optical gain and laser emission, photorefractive activity and waveguiding behavior,<sup>2</sup> LN crystals can thus be tuned to fit various requirements of a manifold of different applications. For instance, doping with the modifier such as  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{In}^{3+}$ , and  $\text{Sc}^{3+}$  in rather high concentrations greatly vary the resistance of LN crystals to optical damage;<sup>3</sup> photorefractive properties are introduced by doping the crystal with transition metal (TM) ions; rare earth (RE) ions such as  $\text{Nd}^{3+}$  are doped into the LN matrix as optically active impurities.<sup>2</sup> In these applications, foreign cations or dopants are always responsible for the modification of physical properties of the LN matrix. Therefore, the lattice location of dopants should be clarified firstly to deeply explain fully their roles in the modification.

Up to now, an enormous amount of work has been carried out on the occupancy of various dopants. Much progress has been achieved because of the use of advanced characterization techniques such as electron nuclear double-resonance, electron paramagnetic resonance, extended x-ray absorption fine structure, x-ray standing wave and particularly ion-beam methods,<sup>4-7</sup> since they essentially rely on geometrical arguments to a large extent. Spectrum-structure correlations are also fully considered in infrared and Raman spectroscopy in determining the dopant occupancy due to the sensitivity of spectrum to the structural change of doped LN crystals.<sup>8-10</sup> In addition, some parameters such as lattice constants, coercive fields, or internal fields, and Curie temperature, which are related to the defect structure of doped LN crystals, are also employed to get indirect information of the dopant

occupancy.<sup>11-13</sup> All these methods have allowed a clear picture of the dopant sites to be obtained, and occupancies of various dopants such as photorefractive inhibiting ions, TM and RE ions have been reliably assigned.

However, many problems still remain in relation to the underlying physical mechanisms and driving forces that determine the location.<sup>6,7,14</sup> As an approach towards the solving of these problems, Kling *et al.* suggested a direct link between the normal valence state of a dopant and its occupancy, i.e., dopants with the normal valence state lower than that of  $\text{Nb}^{5+}$  ions occupy  $\text{Li}^+$  sites; otherwise they replace  $\text{Nb}^{5+}$  ions.<sup>6,7</sup> On the other hand, Rebouta *et al.*<sup>14</sup> took the size effect into account and suggested to identify the dopant occupancy by comparing the lengths of dopant-O, Li-O, and Nb-O bonds. They proposed that all dopants with a dopant-O bond length exceeding the mean Nb-O length occupy  $\text{Li}^+$  sites, otherwise, dopants occupy the off-center sites shifted from the regular  $\text{Li}^+$  sites if the bond length also exceeds the mean Li-O length. Dopants with a bond length smaller than or equal to the mean Nb-O length can occupy  $\text{Li}^+$  or  $\text{Nb}^{5+}$  sites.

Each of the criteria takes into account an important aspect of dopant, normal valence state, or size effect, which are considered as two key factors in determining the dopant occupancy in solid-state chemistry. They can explain most of experimental results of low-doped crystals grown from the congruent melt. However, further investigations have shown that the dopant occupancy is far from invariable, which has an interaction with the LN matrix.<sup>15-18</sup> For instance, photorefractive inhibiting ions change occupancies from  $\text{Li}^+$  to  $\text{Nb}^{5+}$  sites if they are doped in a rather high concentration over a certain threshold value;<sup>15</sup> the variation of these thresholds with the change of the LN stoichiometry<sup>16</sup> indicates that the dopant occupancy is also influenced by the LN stoichiometry; codoping of photorefractive inhibiting ions above their thresholds also change the distribution of  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$  ions (from  $\text{Li}^+$  to  $\text{Nb}^{5+}$  sites).<sup>17,18</sup> Therefore, further criterion should be developed to understand dopant occupancies and their interaction with the LN matrix.

In this work, we study the dopant occupancy from the structural stability of doped LN crystals by the bond valence model (BVM).<sup>19</sup> Although LN crystals are in a single phase

for a low dopant content, the local structure is modified by the incorporation of dopants, i.e., the local chemical bonding state changes, which leads to geometric strains, and thus changes the stability of the whole crystallographic structure. In this regard, the dopant occupancy and the interaction between the dopant and LN matrix may be well understood by the structural stability. In the present work, not only the size effect (in the form of constant parameter,  $d_0$ ) but also the normal valence of atoms are taken into account, which are simply characterized by the deviation of the normal and calculated valence state of atom, and the global instability index. Besides, the chemical environment of the LN matrix (in the forms of bond length and coordination number) is fully considered in our investigation. Therefore, the structural stability study by the BVM method may be a reasonable approach to understand the doping behaviors in the LN crystallographic frame.

## II. THEORETICAL ANALYSIS OF DOPED LN CRYSTALS

BVM is one of modern methods for interpreting observed bond lengths and predicting expected values in crystal structures on the basis of the modified Pauling's second rule, which requires the exact fulfillment of the valence balance with due regard for the empirical bond valence-bond length relations. It provides a useful and quantitative description of inorganic bonding and has gained wide acceptance in inorganic crystal chemistry. More attractively, the applications of BVM are independent of the compound type, including ionic, covalent, and metallic materials.<sup>20</sup> Therefore, this model is a useful tool to understand physical and chemical properties of crystals, in a viewpoint of chemical bonds. Recently, we have successfully used this tool in physical property research and defect structure study of LN crystals.<sup>21-24</sup> In this paper, we propose to use BVM to characterize the structural effects arising from the cation substitution in LN crystals.

In BVM, all atoms are considered to be cations or anions according to the sign of the oxidation state. The empirical correlation of Eq. (1) is used to determine the bond valence ( $s_{ij}$ ) of a chemical bond from its length ( $d_{ij}$ ),

$$s_{ij} = \exp\left(\frac{d_0 - d_{ij}}{B}\right), \quad (1)$$

where  $B=0.37$  and  $d_0$  is a constant characteristic of the cation-anion pair.<sup>25</sup> For most compounds, the bond valence sum rule establishes that the sum of bond valences around any atom  $i$  is equal to its normal valence state ( $V_i$ ), i.e.,

$$\sum_j s_{ij} = V_i. \quad (2)$$

In practice, the difference between the normal valence state and bond valence sum is usually small due to the accuracy of measured bond length data unless chemical bonds are excessively stretched or compressed. In such a case, it is convenient to measure local lattice strains in terms of the discrepancy ( $D_i$ ),

$$D_i = V_i - \sum_j s_{ij}. \quad (3)$$

A positive  $D_i$  value means that the coordination octahedron around the atom  $i$  is too large, the average bond length cannot satisfy the bond valence sum rule, therefore, the sum of bond valences of the atom  $i$  increases by decreasing its bond lengths, and vice versa (i.e., a negative value has an opposite effect). In order to express the deviation degree from the normal state, it may be helpful for us to rewrite formula (3) into a form of absolute values, wherein this quantity can be regarded as a pseudopotential that forces the structure to distort.

$$d_i = \left| V_i - \sum_j s_{ij} \right|. \quad (4)$$

A measurement of  $d_i$  over the whole structure is the global instability index (GII),<sup>19,26</sup>

$$\text{GII} = \sqrt{\frac{\sum_{i=1}^N d_i^2}{N}}. \quad (5)$$

Larger  $d_i$  and GII indicate a strained bond that can lead to serious instabilities in the crystal structure. As to doped LN crystals,  $d_i$  and GII can be regarded as the driving force for the lattice distortion arising from the cation mismatching when the dopants are incorporated into LN crystals. The extent of structural distortion increases with increasing  $d_i$  and GII.

Recently, many satisfactory results have been obtained using quantities (e.g.,  $V_i$ ,  $d_i$ , and GII) mentioned above. Calculations of the bond valence sum  $V_i$  become a standard tool in crystallography to evaluate the plausibility of a proposed crystal structure or to localize light elements (H, Li) from x-ray diffraction data.<sup>27-29</sup> Intrinsic ions apparently locate in the site that matches the valence. Further, the migration pathway for mobile  $\text{Ag}^+$  ions in the ionic conductor  $\alpha\text{-AgI}$  is also modeled, with a basic assumption that the ion transportation from one equilibrium site to the next one follows pathways along which the  $d_i$  value remains as small as possible.<sup>30</sup> It is also indicated that GII less than 0.055 v.u. (valence unit) suggests little or no strain, while GII greater than about 2.0 v.u. indicates a structure that is so strained as to be unstable. The successful application of these quantities gives us a clue to understand the site location of extrinsic ions (i.e., dopants) and their doping mechanism in LN crystals.

In the LN crystallographic frame, only two cation sites ( $\text{Li}^+$  and  $\text{Nb}^{5+}$  octahedron) are available for most dopants; both vacant oxygen octahedron and tetrahedron are important buffers for  $\text{Li}^+$  and  $\text{Nb}^{5+}$  ions to balance their strong repulsions.<sup>31</sup> Therefore, various dopants enter the LN crystallographic frame in ionic form by substituting for  $\text{Li}^+$  or  $\text{Nb}^{5+}$  ions.  $d_i$  values of  $\text{Li}^+$  and  $\text{Nb}^{5+}$  ions in regular sites are zero according to the bond valence sum rule, while the value of the dopant in a substituted site arises due to the cation mismatch in the regular  $\text{Li}^+$  or  $\text{Nb}^{5+}$  lattice environment, which subsequently forces the structure to distort. The quantity  $d_i$  may serve well as the driving force of the distortion, and obviously, dopants preferentially occupy the site with

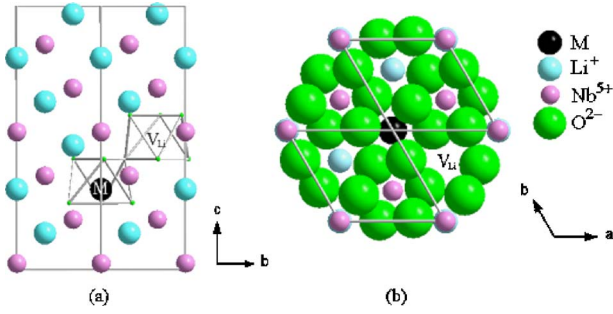


FIG. 1. (Color online) (a) Schematic drawing of the hexagonal unit cell of doped LN crystals. Bonding characteristics around the dopant and Li vacancy are schematically drawing. (b) Microscopic arrangement of constituent atoms projected on the (0001) plane. A solid quadrilateral is unit cell,  $M$  denotes a dopant occupying a Li<sup>+</sup> site and  $V_{Li}$  is a Li vacancy.

smaller  $d_i$ .  $d_i$  values of a dopant in Li<sup>+</sup> and Nb<sup>5+</sup> sites before the distortion can be calculated using Li-O and Nb-O bond lengths in the LN crystal matrix, respectively, irrespective of the original dopant-O bond lengths in dopant oxides (since all the dopant-O bonds in oxides are broken and the dopants enter the LN matrix in an ionic form when the LN crystal is grown from a non-stoichiometric LN melt).

We now consider the calculation of GII over the whole structure. As schematically shown in Fig. 1, if a dopant is incorporated into Li<sup>+</sup> site, corresponding charge compensations ( $V_{Li}^-$ , on the basis of Li vacancy model) emerge arising from the charge mismatching of dopant, and a certain lattice relaxation should occur as a result of replacement. Just considering the situation before the lattice relaxation, we assume that the lattice parameters around dopants and vacancies are unchanged when compared to the ideal LN lattice, which means that dopant-O bonds in doped LN crystals have the same bond lengths as Li-O or Nb-O bonds after the substitution. Therefore,  $d_i$  value of a given dopant can be calculated by Eq. (4) as discussed above, and Li-site vacancies can be treated as the cation with  $d_{V_{Li}} = 1$  v.u. (from  $\sum s_{Li-O} = 1$  to  $\sum s_{V_{Li}-O} = 0$ ).  $d_i$  values of Li<sup>+</sup> and Nb<sup>5+</sup> ions in normal sites are zero according to the bond valence sum rule (i.e.,  $d_{Li} = 0$  v.u.,  $d_{Nb} = 0$  v.u.). In this regard, GII of doped LN crystals can be calculated by Eq. (5).

### III. RESULTS AND DISCUSSION

On the basis of the detailed crystallographic data of pure LN crystals (longer Li-O bonds, 2.260 Å; shorter Li-O bonds, 2.052 Å; longer Nb-O bonds, 2.126 Å; shorter Nb-O bonds, 1.878 Å),<sup>32</sup>  $d_i$  of various dopants on both Li<sup>+</sup> and Nb<sup>5+</sup> sites are calculated, respectively. All calculated  $d_i$  values are listed in Table I. Corresponding occupancies of these dopants are summarized in Table II for comparison. Figure 2 schematically shows the relationship between the dopant occupancy and  $d_i$  values in both Li<sup>+</sup> and Nb<sup>5+</sup> sites. As shown in this figure, dopants preferentially occupy Li<sup>+</sup> sites if  $d_i^{Li} < d_i^{Nb}$  (above the diagonal), while they preferentially occupy Nb<sup>5+</sup> sites if  $d_i^{Li} > d_i^{Nb}$  (below the diagonal). For instance, all photorefractive inhibiting ions (Mg<sup>2+</sup>, Zn<sup>2+</sup>, In<sup>3+</sup>, Sc<sup>3+</sup>) and

TABLE I. Calculated  $d_i^{Li}$  and  $d_i^{Nb}$  values of various dopants when they are arbitrarily placed in Li<sup>+</sup> and Nb<sup>5+</sup> sites, respectively. The unit used here is the valence unit (v.u.). Three kinds of dopants are included in this table, i.e., photorefractive inhibiting ions (Mg<sup>2+</sup>, Zn<sup>2+</sup>, In<sup>3+</sup>, and Sc<sup>3+</sup>), RE ions (Pr<sup>3+</sup>, Nd<sup>3+</sup>, Eu<sup>3+</sup>, Ho<sup>3+</sup>, Er<sup>3+</sup>, and Yb<sup>3+</sup>) and TM ions (Mn<sup>2+</sup>, Al<sup>3+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup>, Ni<sup>3+</sup>, Ti<sup>4+</sup>, Hf<sup>4+</sup>, Ta<sup>5+</sup>, and W<sup>6+</sup>).

Ions	$d_i^{Li}$	$d_i^{Nb}$	Ions	$d_i^{Li}$	$d_i^{Nb}$
Mg <sup>2+</sup>	0.215	0.750	Yb <sup>3+</sup>	0.723	2.737
Zn <sup>2+</sup>	0.161	0.833	Al <sup>3+</sup>	1.535	0.742
Mn <sup>2+</sup>	0.320	1.575	Cr <sup>3+</sup>	1.059	0.009
Sc <sup>3+</sup>	0.279	1.193	Fe <sup>3+</sup>	0.866	0.288
In <sup>3+</sup>	0.140	1.839	Ni <sup>3+</sup>	1.475	0.650
Pr <sup>3+</sup>	2.942	6.157	Ti <sup>4+</sup>	1.518	0.175
Nd <sup>3+</sup>	2.435	5.375	Hf <sup>4+</sup>	0.485	1.416
Eu <sup>3+</sup>	1.998	4.692	Ta <sup>5+</sup>	1.703	0.080
Ho <sup>3+</sup>	1.378	3.747	W <sup>6+</sup>	2.730	0.961
Er <sup>3+</sup>	0.962	3.105			

RE ions have experimentally been proven to occupy Li<sup>+</sup> sites doubtlessly in congruent LN crystals at the low doping concentration,<sup>15,33,35–37,44</sup> which agree well with our present calculation  $d_i^{Li} < d_i^{Nb}$ . Some TM ions such as Mn<sup>2+</sup>, Hf<sup>4+</sup> also occupy Li<sup>+</sup> sites for the same reason.<sup>34,44</sup> In case of Ta<sup>5+</sup> and W<sup>6+</sup>, they occupy Nb<sup>5+</sup> sites due to  $d_i^{Li} > d_i^{Nb}$ .<sup>7,14,44</sup>

However, the occupancies of some TM ions in region I of Fig. 2 are still in controversy up to now.<sup>40–42</sup> For example, Fe<sup>3+</sup> and Cr<sup>3+</sup> ions preferentially occupy Nb<sup>5+</sup> sites accord-

TABLE II. Summary of dopant occupancies in the nonstoichiometric LN crystallographic frame.

Dopant	Dopant occupancy		Dopant occupancy		
	Present work	Other reports	Dopant	Present work	Other reports
Mg <sup>2+</sup>	Li	Li <sup>a</sup>	Yb <sup>3+</sup>	Li	Li <sup>f</sup>
Zn <sup>2+</sup>	Li	Li <sup>b</sup>	Al <sup>3+</sup>	Nb	Nb, Li <sup>h</sup>
Mn <sup>2+</sup>	Li	Li <sup>c</sup>	Cr <sup>3+</sup>	Nb	Nb, Li <sup>i</sup>
Sc <sup>3+</sup>	Li	Li <sup>d</sup>	Fe <sup>3+</sup>	Nb	Nb, <sup>j</sup> Li <sup>k</sup>
In <sup>3+</sup>	Li	Li <sup>e</sup>	Ni <sup>3+</sup>	Nb	Li <sup>l,m</sup>
Pr <sup>3+</sup>	Li	Li <sup>f</sup>	Ti <sup>4+</sup>	Nb	Li <sup>l,m</sup>
Nd <sup>3+</sup>	Li	Li <sup>f</sup>	Hf <sup>4+</sup>	Li	Li, <sup>h</sup> Li, Nb <sup>o</sup>
Eu <sup>3+</sup>	Li	Li <sup>f</sup>	Ta <sup>5+</sup>	Nb	Nb <sup>o,n</sup>
Ho <sup>3+</sup>	Li	Li <sup>f</sup>	W <sup>6+</sup>	Nb	Nb <sup>p</sup>
Er <sup>3+</sup>	Li	Li <sup>g</sup>			

<sup>a</sup>See Ref. 33.

<sup>b</sup>See Ref. 15.

<sup>c</sup>See Ref. 34.

<sup>d</sup>See Ref. 35.

<sup>e</sup>See Ref. 36.

<sup>f</sup>See Ref. 37.

<sup>g</sup>See Ref. 38.

<sup>h</sup>See Ref. 39.

<sup>i</sup>See Ref. 40.

<sup>j</sup>See Ref. 41.

<sup>k</sup>See Ref. 42.

<sup>l</sup>See Ref. 1.

<sup>m</sup>See Ref. 43.

<sup>n</sup>See Ref. 44.

<sup>o</sup>See Ref. 14.

<sup>p</sup>See Ref. 7.

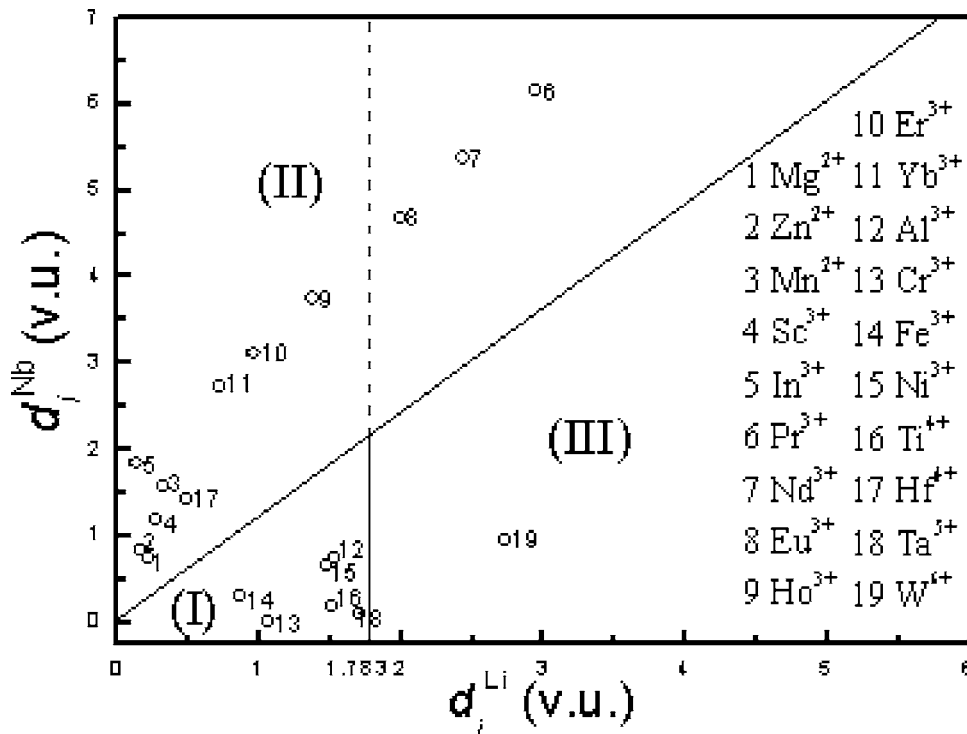


FIG. 2. Theoretical occupancy of various dopants with different  $d_i^{Li}$  and  $d_i^{Nb}$  values in nonstoichiometric LN crystals. Dopants in regions I and II occupy  $Li^+$  sites, while dopants in region III occupy  $Nb^{5+}$  sites.  $d_i^{Li}$  value on diagonal is equal to  $d_i^{Nb}$ .

ing to our criterion; however, they can exclusively occupy  $Li^+$  sites in congruent LN crystals at the low doping concentration.<sup>17,18</sup> The departure of experimental results from our present work may be ascribed to the existing antisite defects ( $Nb_{Li}^{4+}$ ). LN crystals are usually grown with a congruent, nonstoichiometric composition possessing excess  $Nb^{5+}$  ions at  $Li^+$  sites in the crystallographic frame. It means that any dopants in region-I with smaller  $d_i^{Li}$  than that of  $Nb^{5+}$  ions ( $d_{Nb}^{Li}=1.783$  v.u.) can occupy  $Li^+$  sites, regardless of the relative value of  $d_i^{Li}$  and  $d_i^{Nb}$ . However, with increasing the doping concentration,  $Nb_{Li}^{4+}$  are removed gradually and are completely consumed at a certain threshold value, the dopant occupancy then changes from  $Li^+$  to  $Nb^{5+}$  sites. This is the reason why the threshold concentration (which is a limit above which these ions begin to occupy  $Nb^{5+}$  sites) decreases if crystal compositions approach the stoichiometric one. Considering this case from another aspect, the elimination of  $Nb_{Li}^{4+}$  from LN crystals by codoping photorefractive inhibiting ions also changes the dopant occupancy of these ions. This conclusion has been identified in heavily MgO or ZnO codoped Fe:LN and Cr:LN crystals,<sup>17,18</sup> in which all  $Nb_{Li}^{4+}$  are removed by  $Mg^{2+}$  or  $Zn^{2+}$  ions, while  $Fe^{3+}$  and  $Cr^{3+}$  ions occupy both  $Nb^{5+}$  and  $Li^+$  sites due to the charge compensation at  $Li^+$  sites (in this case  $Nb^{5+}$  sites should be firstly occupied and  $Li^+$  sites are later occupied by the charge balance need). It should be noted that the position of the vertical line (corresponding value to  $d_{Nb}^{Li}=1.783$  v.u.) may be slightly changed due to the accuracy of structural measurements.

The occupancies of RE ions may have their own characteristics due to large  $d_i$  values. As shown in Table I and Fig. 2, all  $d_i^{Li}$  values of RE ions are smaller than  $d_i^{Nb}$  but relative larger than other ions (photorefractive inhibiting ions or TM ions), and both  $d_i^{Li}$  and  $d_i^{Nb}$  decrease with increasing the atomic number. For  $Yb^{3+}$ ,  $Er^{3+}$ , and  $Ho^{3+}$  ions,  $d_i$  is relative

smaller than other RE ions and is smaller than  $d_{Nb}^{Li}$ , which means that these dopants preferentially substitute  $Nb_{Li}^{4+}$  firstly when they are incorporated into the LN crystallographic frame. Therefore, they are expected to have the same doping behaviors as these of photorefractive inhibiting ions and their dopant occupancies may also be influenced by the nonstoichiometry. This conclusion has been experimentally proven in  $Er^{3+}$ ,  $Yb^{3+}$  doped LN crystals heavily codoped with MgO and ZnO above their threshold concentrations.<sup>45,46</sup> In these crystals all nonstoichiometric defects are removed and fractional  $Er^{3+}$  and  $Yb^{3+}$  ions change their occupancies from  $Li^+$  to  $Nb^{5+}$  sites. In this regard, it can be deduced that the removal of nonstoichiometric defects by increasing the doping concentration can also change dopant occupancies from  $Li^+$  to  $Nb^{5+}$  sites, when the solid solubility of a dopant in the LN crystal is high enough. Other RE ions such as  $Eu^{3+}$ ,  $Nd^{3+}$ , and  $Pr^{3+}$  ions may have different doping behaviors due to their relative large  $d_i$ . For these ions,  $d_i^{Li}$  is larger than  $d_{Nb}^{Li}$ , which indicates that they substitute  $Li^+$  instead of  $Nb_{Li}^{4+}$  ions, and thus the site location of these ions is insensitive to the nonstoichiometry. Additionally, very high  $d_i^{Nb}$  also indicate that the occupancy of  $Nb^{5+}$  sites is not favorable. Therefore, they exclusively occupy  $Li^+$  sites, irrespective of the stoichiometry of LN matrix and the concentration of codopants ( $Mg^{2+}$ ,  $Zn^{2+}$ , etc.). Up to now, only  $Li^+$  site occupancy has been reported irrespective of the MgO concentration<sup>14</sup> except for  $Er^{3+}$  and  $Yb^{3+}$  ions, which may serve as evidence to support our conclusion.

Our present conclusions give a satisfactory qualitative understanding on the dopant occupancy and the interaction between the dopant and the LN matrix. In order to quantitatively study this interaction, we develop a mathematical method on the basis of BVM and available experimental results. Although numerous studies on the incorporation mechanism of dopants have been carried out, especially on

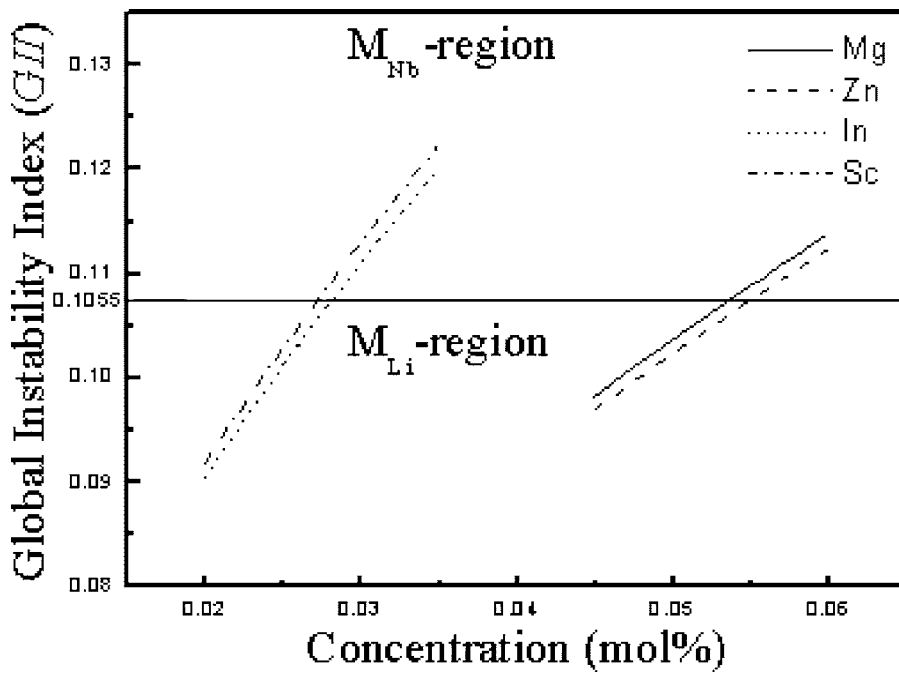
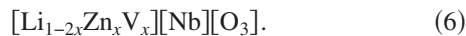


FIG. 3. Global instability index and dopant occupy of photo-refractive inhibiting ions ( $Mg^{2+}$ ,  $Zn^{2+}$ ,  $In^{3+}$ ,  $Sc^{3+}$ ) in a certain doping concentration range. Experimental results of the doping concentration corresponding to the GII value 0.1055 are the so-called threshold concentration, above which these ions change their occupancy from  $Li^+$  to  $Nb^{5+}$  sites.

that of photorefractive inhibiting ions,<sup>15,33,35,36</sup> the mechanism is still an unsolved question and has been generally discussed on the basis of the defect model in undoped crystals. Recent precision x-ray structural study<sup>15</sup> gives reliable results that in a crystal with more than 5.3 mol % ZnO, all  $Nb_{Li}^{4+}$  defects have been removed and all the  $V_{Li}^-$  vacancies disappear at about 7.6 mol % ZnO. The decrease and disappearance of  $V_{Li}^-$  are corresponding to the change of the compensation mechanism, namely a self-compensation process, which requires  $Zn_{Nb}^{3-}$  for the charge compensation. Considering the transition of compensation mechanism, it can be deduced that GII is large enough for fractional  $Zn^{2+}$  ions to change its occupancy when doping concentration is above 5.3 mol %. On the basis of the Li vacancy model, the Zn substitution formula at this concentration is



As discussed above,  $d_{Li}$  and  $d_{Nb}$  in normal  $Li^+$  and  $Nb^{5+}$  sites are zero, respectively, and  $d_{V_{Li}^-} = 1$  v.u. Since each  $O^{2-}$  receives one third of the bond valence formed by Li-site cations

$$d_{O^{2-}} = [xd_{Zn_{Li}} + xd_{V_{Li}^-}]/3. \quad (7)$$

Therefore, the GII expression of ZnO doped LN crystals is

$$GII = [(xd_{Zn_{Li}}^2 + xd_{V_{Li}^-}^2 + 3d_{O^{2-}}^2)/5]^{1/2}. \quad (8)$$

By this way, the GII of 5.3 mol % ZnO doped LN is calculated as about 0.1055. For doped crystals grown from the congruent melt, it is assumed that they all have the same GII value when dopants change their occupancies due to the same melt composition and growth conditions. Therefore, as schematically shown in Fig. 3, calculated doping values of  $Mg^{2+}$ ,  $In^{3+}$ , and  $Sc^{3+}$  ions in the LN crystallographic frame are about 5.20, 2.73, and 2.62 mol %, respectively, which are consistent well with experimental photorefractive threshold

concentrations (for bivalent  $Mg^{2+}$  and  $Zn^{2+}$  are  $\sim 6$  mol % and trivalent  $In^{3+}$  and  $Sc^{3+}$  are  $\sim 3$  mol %<sup>35,47</sup>). This is speculated that they are associated with a site change of the dopant occupancy in the LN crystallographic frame.

The GII may also be used to calculate the threshold value for TM and RE ions, although less attention has been paid on this aspect, since the doping concentrations are always lower than those of the photorefractive inhibiting ions in normal applications. In this work we want to find in which concentration the dopant is able to enter  $Nb^{5+}$  sites. Using the current method, theoretical threshold values of different ions are calculated and listed in Table III. Dopants are expected to occupy  $Li^+$  sites below the calculated threshold (by substituting  $Nb_{Li}^{4+}$  or  $Li^+$  ions in normal  $Li^+$  sites). With increasing the doping concentration, the whole structure becomes unstable and the GII is high enough to force dopant to enter

TABLE III. Theoretical threshold concentrations (in mol %) of various dopants in congruent LN crystals. The numbers in parentheses are experimental data.

Dopants	Threshold concentration	Dopants	Threshold concentration (%)
$Mg^{2+}$	5.20% ( $\sim 6\%$ <sup>a,b</sup> )	$Fe^{3+}$	2.02
$Zn^{2+}$	5.30% ( $\sim 6\%$ <sup>b</sup> )	$Ni^{3+}$	1.74
$Sc^{3+}$	2.62% ( $\sim 3\%$ <sup>b,c</sup> )	$Ti^{4+}$	1.03
$In^{3+}$	2.73% ( $\sim 3\%$ <sup>b,d</sup> )	$Hf^{4+}$	1.69
$Mn^{2+}$	5.03%	$Er^{3+}$	1.90
$Al^{3+}$	1.27%	$Yb^{3+}$	2.20
$Cr^{3+}$	2.60%		

<sup>a</sup>See Ref. 33.

<sup>b</sup>See Ref. 47.

<sup>c</sup>See Ref. 31.

<sup>d</sup>See Ref. 48.

Nb<sup>5+</sup> sites if the doping concentration is above threshold value. However, it should be mentioned that only ions that can occupy both Li<sup>+</sup> and Nb<sup>5+</sup> sites are expected to have the threshold concentration due to the conception of threshold we employed here (the doping concentration above which the dopant changes its occupancy from Li<sup>+</sup> to Nb<sup>5+</sup> sites). For some RE ions such as Nd<sup>3+</sup>, Pr<sup>3+</sup>, and Eu<sup>3+</sup> with very high  $d_i^{\text{Nb}}$  values, they exclusively occupy Li<sup>+</sup> sites irrespective of the doping concentration and codoping of MgO, ZnO, etc.; for W<sup>6+</sup> and Ta<sup>5+</sup>, they always occupy Nb<sup>5+</sup> sites. Therefore, above-mentioned ions do not have the threshold concentration.

#### IV. CONCLUSIONS

We in this work proposed an approach to determine the dopant occupancy in the LN crystallographic frame, using the discrepancy  $d_i$  (between the normal and calculated valence states) as a key parameter. Lattice locations are mainly determined by both the intrinsic characteristics of dopants and the LN matrix (characterized by  $d_i$ ), and they are influenced by the stoichiometry-related defects. The consistent between our present conclusion and available experimental

results suggests that  $d_i$  is a reasonable parameter to assign the dopant occupancy in the LN crystallographic frame. Combining  $d_i$  with the structural stability analysis over the whole structure, the interaction between the dopant and LN matrix (e.g., the site change by codoping, the stoichiometry or doping concentration) are quantitatively understood. In addition, the present method may further function as a guide to realize an effective control of both intrinsic and extrinsic defects, by adjusting the doping concentration, the stoichiometry of the LN matrix, or the codoping concentration. LN crystals can thus be tuned to fit various basic requirements of a manifold of different applications.

#### ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant No. 20471012), the Foundation for the Author of National Excellent Doctoral Dissertation of P. R. China (Grant No. 200322), the Research Fund for the Doctoral Program of Higher Education (Grant No. 20040141004), and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry.

\*Corresponding author. Email address: dfxue@chem.dlut.edu.cn

- <sup>1</sup>N. Iyi, K. Kitamura, F. Izumi, J. K. Yamamoto, T. Hayashi, H. Asano, and S. Kimura, *J. Solid State Chem.* **101**, 340 (1992).
- <sup>2</sup>C. Zaldo, C. Prieto, C. Dexpert, and P. Fessler, *J. Phys.: Condens. Matter* **3**, 4135 (1991).
- <sup>3</sup>T. Volk, M. Wohlecke, N. Rubinina, A. Reichert, and N. Razumovski, *Ferroelectrics* **183**, 291 (1996).
- <sup>4</sup>V. Grachev and G. Malovichko, *Phys. Rev. B* **62**, 7779 (2000).
- <sup>5</sup>M. Vila, A. De Bernabe, and C. Prieto, *J. Alloy, J. Alloys Compd.* **323-324**, 331 (2001).
- <sup>6</sup>A. Kling, J. C. Soares, and M. F. da Silva, in *Insulating Materials for Optoelectronics: New Developments*, edited by F. Agullo-Lopez (World Science, Singapore, 1995).
- <sup>7</sup>A. Kling, C. Valdez, J. G. Marques, M. F. da Silva, and J. C. Soares, *Nucl. Instrum. Methods Phys. Res. B* **190**, 524 (2002).
- <sup>8</sup>M. Hu, C. Chia, J. Chang, W. Tse, and J. Yu, *Mater. Chem. Phys.* **78**, 358 (2002).
- <sup>9</sup>R. Mouras, M. Fontana, P. Bourson, and A. Postnikov, *J. Phys.: Condens. Matter* **12**, 5053 (2000).
- <sup>10</sup>Y. Kong, J. Xu, W. Zhang, and G. Zhang, *J. Phys. Chem. Solids* **61**, 1331 (2000).
- <sup>11</sup>C. Chia, C. Lee, P. Chang, M. Hu, and L. Hu, *Appl. Phys. Lett.* **86**, 182901 (2005).
- <sup>12</sup>F. Abdi, M. Aillerie, M. Fontana, P. Bourson, T. Volk, B. Maximov, S. Sulyanov, N. Rubinina, and M. Wohlecke, *Appl. Phys. B* **B68**, 795 (1999).
- <sup>13</sup>V. Kalinnikov, M. N. Palatnikov, and N. Sidorov, *Russ. J. Inorg. Chem.* **48**, S1 (2003).
- <sup>14</sup>L. Rebouta, P. J. M. Smulders, D. O. Boerma, F. Agullo-Lopez, M. F. da Silva, and J. C. Soares, *Phys. Rev. B* **48**, 3600 (1993).
- <sup>15</sup>T. Chernaya, B. Maksimov, T. Volk, N. Rubinina, and V. Simonov, *JETP Lett.* **73**, 103 (2001).

- <sup>16</sup>Y. Furukawa, K. Kitamura, S. Takekawa, K. Niwa, Y. Yajima, N. Iyi, I. Mnushkina, P. Guggenheim, and J. M. Martin, *J. Cryst. Growth* **211**, 230 (2000).
- <sup>17</sup>J. Diaz-Caro, J. Garcia-Sole, D. Bravo, J. A. Sanz-Garcia, F. J. Lopez, and F. Jaque, *Phys. Rev. B* **54**, 13042 (1996).
- <sup>18</sup>I. W. Park, Y. N. Choi, S. H. Choh, and S. S. Kim, *J. Korean Phys. Soc.* **32**, S693 (1998).
- <sup>19</sup>I. D. Brown, *Acta Crystallogr., Sect. B: Struct. Sci.* **B48**, 553 (1992).
- <sup>20</sup>U. S. Uruson, *Z. Kristallogr.* **218**, 709 (2003).
- <sup>21</sup>D. Xue and K. Betzler, *Appl. Phys. B* **B72**, 641 (2001).
- <sup>22</sup>D. Xue, K. Betzler, and H. Hesse, *Opt. Mater. (Amsterdam, Neth.)* **16**, 381 (2001).
- <sup>23</sup>D. Xue and K. Betzler, *J. Phys.: Condens. Matter* **12**, 6245 (2000).
- <sup>24</sup>X. He, D. Xue, and K. Kitamura, *Mater. Sci. Eng., B* **B120**, 27 (2005).
- <sup>25</sup>I. D. Brown, *Acta Crystallogr., Sect. B: Struct. Sci.* **B41**, 254 (1985).
- <sup>26</sup>A. Salinas-Sanches, J. L. Garcia-Munoz, J. Rodriguez-Carvajal, R. Saez-Puche, and J. L. Martinez, *J. Solid State Chem.* **100**, 201 (1992).
- <sup>27</sup>I. D. Brown, *Acta Crystallogr., Sect. B: Struct. Sci.* **B53**, 381 (1997).
- <sup>28</sup>V. S. Urusov, *Acta Crystallogr., Sect. B: Struct. Sci.* **B51**, 641 (1995).
- <sup>29</sup>K. Waltersson, *Acta Crystallogr., Sect. A: Cryst. Phys., Diff., Theor. Gen. Crystallogr.* **A34**, 901 (1978).
- <sup>30</sup>S. Adams and J. Swenson, *Phys. Rev. B* **63**, 054201 (2000).
- <sup>31</sup>D. Xue, K. Kitamura, and J. Wang, *Opt. Mater. (Amsterdam, Neth.)* **23**, 399 (2003).
- <sup>32</sup>H. Lehnert, H. Boysen, F. Frey, A. Hewat, and P. Radaelli, *Z.*

- Kristallogr. **212**, 712 (1997).
- <sup>33</sup>N. Iyi, K. Kitamura, Y. Yajima, and S. Kimura, *J. Solid State Chem.* **118**, 148 (1995).
- <sup>34</sup>G. Corradi, H. Sothe, J. M. Spaeth, and K. Polgar, *J. Phys.: Condens. Matter* **2**, 6603 (1990).
- <sup>35</sup>S. Shimamura, Y. Watanabe, T. Sota, K. Suzuki, N. Iyi, Y. Yajima, K. Kitamura, T. Yamazaki, A. Sugimoto, and K. Yamagishi, *J. Phys.: Condens. Matter* **8**, 6825 (1996).
- <sup>36</sup>T. Volk and N. Rubinina, *Ferroelectr., Lett. Sect.* **14**, 37 (1992).
- <sup>37</sup>A. Lorenzo, H. Jaffrezic, B. Roux, G. Boulon, and J. Garcia-Sole, *Appl. Phys. Lett.* **67**, 3735 (1995).
- <sup>38</sup>Th. Gog, M. Griebenow, T. Harasimowicz, and G. Materlik, *Ferroelectrics* **153**, 249 (1994).
- <sup>39</sup>V. G. Grachev, G. I. Malovichko, and V. V. Troitski, *Sov. Phys. Solid State* **29**, 349 (1987).
- <sup>40</sup>F. Jaque, J. Garcia-Sole, E. Camarillo, F. J. Lopez, H. Murrieta S., and J. Hernandez A., *Phys. Rev. B* **47**, 5432 (1993).
- <sup>41</sup>M. G. Zhao and M. Chiu, *Phys. Rev. B* **49**, 12556 (1994).
- <sup>42</sup>Th. Gog, P. Schotters, J. Falta, G. Materlik, and M. Grodzicki, *J. Phys.: Condens. Matter* **7**, 6971 (1995).
- <sup>43</sup>C. Zaldo and C. Prieto, *Ferroelectrics* **137**, 47 (1992).
- <sup>44</sup>C. Prieto, C. Zaldo, P. Fessler, H. Dexpert, J. A. Sanz-Garcia, and E. Dieguez, *Phys. Rev. B* **43**, 2594 (1991).
- <sup>45</sup>D. Bravo, A. Martin, and F. J. Lopez, *Solid State Commun.* **112**, 541 (1999).
- <sup>46</sup>C. Bonardi, C. J. Magon, E. A. Vidoto, M. C. Terrile, L. E. Bausa, E. Montoya, D. Braw, A. Martin, and F. J. Lopez, *J. Alloys Compd.* **340**, 323 (2001).
- <sup>47</sup>T. Volk and M. Wohlecke, *Ferroelectr. Rev.* **1**, 195 (1998).
- <sup>48</sup>Y. Kong, J. Wen, and J. H. Wang, *Appl. Phys. Lett.* **66**, 280 (1994).