Stability of Implanted Transition Metal Dopants in Rock-salt Oxides

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Transition metals (TMs) implanted in oxides with rock-salt crystal structures (for example MgO and BaO) are assumed to substitute cations (Mg in case of MgO) from the lattice sites. We show that not all implanted TMs substitute cations but can be stable in interstitial sites as well. Stability of TM (Sc–Zn) dopants in various charge states in MgO and BaO has been investigated in the framework of density functional theory. We find that two factors govern the preference for an interstitial site: i) relative ionic radius and ii) oxygen affinity, of cation and the TM dopants. If the radius of the cation is much larger than TM dopant as is the case in BaO, TM atoms always sit at interstitial sites. On the other hand, if the radius of the cation is comparable to that of the dopant TM, as in case of MgO, the transition of the preferred defect site, from substitution of lattice Mg atom (Sc to Mn) to interstitial (Fe to Zn) is observed. This transition can be attributed to the change in the oxygen affinity of the TM atoms from Sc to Zn. Our results explain experiments on Ni and Fe atoms implanted in MgO. This is the first-time we have shown that TM dopants can be stable at interstitial sites in stable compounds, which could potentially give rise to exotic properties. This work provides an attractive computational scheme to predict site preference (interstitial or substitution) of implanted dopants in compounds.

I. INTRODUCTION

Dopants in semiconductors cause significant changes in their electronic and optical properties, as required for their industrial applications. Among various ways available, ion-beam implantation is a very reliable and popular technique to incorporate impurities in a host lattice [1–3] as it provides controllable selective area doping in the target materials [4]. The most widely used implanted defects in semiconductors include O and N in SiC [5], P [6], B [7], Si [8–10] and Er [11, 12] in SiO₂. P [13] and Si⁺ implanted thermal oxide films on crystalline Si [14] as it provides controllable selective area doping in the target materials [4]. The most widely used implanted defects in semiconductors include O and N in SiC [5], P [6], B [7], Si [8–10] and Er [11, 12] in SiO₂; P [13] and Si⁺ implanted thermal oxide films on crystalline Si [14] for photoluminescence, modified refractive index and optical waveguides [15]; Au [16], Cu [17] in SiO₂, Pd in Si [18] and As in GaAS [19] for tuning optical and physical properties.

Defects in rock-salt oxides (for example MgO) have been studied extensively [20–31] for its application in optical and magnetic sensors, switching devices and for application as dilute magnetic semiconductors [32–34]. Apart from various chemical routes available for creating defects in MgO [34–37], there have been instances where MgO is implanted with different ions. These include, Au for modifying refractive index of MgO and creating quantum antidots [38,39]; Cu and Ni for modifying optical properties [40,41], He, Ar, Ne, Fe, Cr for photoluminescence [42,43], Ne, Ar, Zr, Ru, Si, Cr and Fe for enhancing secondary electron emission yield [44–47] and MgO implanted with various magnetic impurities like Fe, Cr, Ni, Co have also been reported to exhibit giant magneto resistance (GMR), super-paramagnetism [18,21] and ferromagnetic ordering [22,54].

To our surprise, studies on ion-implanted rock-salt oxides assume that the dopants occupy only the substitutional sites replacing host lattice cations without any exploration of the other possible sites including interstitials. Possibility of dopant occupying interstitial sites has also been ignored in cases like Li intercalation in rock-salt-structured entropy stabilized oxide [54], citing empirical rules like Pauling’s rule [55]. Although there has not been any previous study on the thermodynamic stability of implanted transition metals sitting at interstitial position in rock-salt oxides, an experimental work shows that Fe can be stable in interstitial [56], and one of our recent works [57] showed Fe atoms preferring interstitial positions in MgO. Here we carry out a systematic investigation of the thermodynamic stability of implanted transition metals (TMs) in MgO. TMs having partially filled d-orbitals [58] can give rise to some fascinating properties in the host lattice. Our work explores the (i) stability of dopants in MgO in both neutral and charged states, (ii) preferred defect sites in the host lattice, and (iii) relation between stability, local distortion and changes in the electronic structure of the host lattice caused by the dopants, for Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn. Besides MgO, we have also studied TM dopants in BaO which has similar crystal structure but larger lattice parameter than MgO. The reason for choosing two oxides is to perform a comparative study in order to understand the effect of interstitial volume on the stability of TM defects. Here we have used density functional theory (DFT) which has long been used efficiently for studying the stability of charged and neutral defects in oxides [59,60] by calculating defect formation energies [55,61,62]. This paper is organized as follows. Section II describes the state-of-the-art computational methodology to calculate stability of TM dopants in semiconductors. In Section III, we report and discuss the results we have ob-

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tained from our DFT calculations and finally we conclude in section IV.

II. METHODOLOGY

A. Formation energy of implanted defects

The focus of the present study is to explore the possibility of implanted TM being stable at the interstitial sites or substituting the host cations from the lattice sites. To do so, we calculate the dopant formation energies by placing TM in two positions: (1) TM is placed at host cation site (wyckoff 4a(0.5,0,0.5)) and host atom is pushed to the center of the tetrahedra formed by oxygen atoms as shown in Fig. 1a, (here onwards we would refer this configuration as substitutional site) and (2) TM is at the center of the tetrahedra formed by oxygen atoms (wyckoff 8c(0.25,0.25,0.25)) as shown in Fig. 1b (we would refer this configuration as interstitial site). If the first configuration is more stable, then the implanted TM atom substitutes host cation and the host cation goes into the interstitial site, which then can migrate out of the oxide thus forming substitutional doping. If the second configuration is more stable then TM will not substitute host cation and will be stable as an added atom in the interstitial site. It should be noted that often when substitutional formation energy is calculated, substituted atom is removed from the host lattice, this maintains overall stoichiometry of the host lattice. Such approach is a good representation of the system when doping is achieved by mixing compounds so that overall stoichiometry is maintained. But in case of implanting TMs in oxide, there could be more metal in the oxide if TM atom prefers to occupy interstitial site.

The stability of the TM in the oxide is assessed by calculating formation energy $E_f^q$ of the dopant in various charge states using following equation [61, 63–65],

$$E_f^q = E_D^q - E_B - \eta + q(\mu + E_{ref} + \Delta V) + E_{corr}^q \quad (1)$$

where $E_D^q$ and $E_B$ are the total energies of the defect supercell with charge q and the defect free host supercell, respectively. $\eta$ is the chemical potential of the transition metal atom species. The '-' sign before $\eta$ refers to addition of defect in the host. We take both gaseous and crystalline metal energy as chemical potential of transition metal. Choice of gaseous metal as reference is to represent TM ion implanted in host materials. $E_{ref}$ is a suitable reference energy which is generally taken to be the valence band maximum (VBM), the energy of the highest occupied level. $\mu$ corresponds to the electronic chemical potential. $\Delta V$ is the correction to realign the reference potential in the defect supercell with that in the defect free supercell [29]. $E_{corr}^q$ is the correction to the electrostatic interaction and the finite size of the supercell. Here we have taken only the first-order monopole correction into account.

B. First-principles method

Formation energy of transition metal dopants, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn, in charge states 0, +1, +2, +3 and +4 have been calculated using cubic super cell containing 32 formula units of MgO or BaO. This results in dopant concentration of 3.1%. Density functional theory (DFT) as implemented in Vienna Ab initio Simulation Package (VASP) [66, 67] was used for all calculation, employing projector-augmented wave (PAW) method [68]. For all cases, spin-polarized calculations were performed. A plane wave cut-off of 500 eV and a k-point mesh of 5x5x5 were used for achieving converged results within $10^{-4}$ eV per atom. All the structures were fully relaxed using the conjugate gradient scheme and relaxations were considered converged when force on each atom was smaller than 0.02 eV/Å. For calculating the energy of TM atoms in bulk, the most stable structures were considered and sufficient k points were taken to reach the convergence. The density of states (DOS) is calculated by the linear tetrahedron method with Blochl corrections [69].

Generalized gradient approximation (GGA) was used to treat the exchange correlation interaction using the Perdew, Burke, and Ernzerhof (PBE) [70] functional. Although the defect formation energy varies with the choice of functional [63], GGA is known to provide good results for qualitative studies [71]. The use of GGA here is justified by the fact that, focus of this paper is restricted to study the general physiochemical trends related to transition metal dopants in stable oxides, and the results should be taken as qualitative. Performing advanced calculations like HSE to get the accurate values of band gaps and defect formation energies are beyond the scope of the present paper. The lattice parameter and the band gap values obtained from our calculation are 4.2 Å and
III. RESULTS AND DISCUSSION

A. Site preference

To explore whether a dopant prefers to sit at interstitial site or substitute host cation, we calculate dopant formation energy with the dopant placed at host lattice or in interstitial as shown in Fig. 1(a) and Fig. 1(b) respectively. In MgO we find that while Sc, Ti, V, Cr and Mn prefer to substitute lattice Mg atoms and push them into the interstitial sites; Fe, Co, Ni, Cu and Zn prefer to be at the interstitial sites. This preference does not depend on their charge states. However, some TM atoms in their neutral state seem to deviate from the observed trend. For neutral Ni, which is expected to sit as interstitial site prefers a corner of the tetrahedral void available in MgO (wyckoff 32f (0.81,0.688,0.688)). Neutral Mn also prefers the corner of the tetrahedra. On the other hand, Fe \(_0\) chooses neither the middle nor the corner of the tetrahedra, but prefers to sit in between two lattice oxygen atoms as shown in Fig. 1(d) (wyckoff 48g (0.25,0.9,0.25)). This seemingly unusual position is in agreement with previously reported observation employing Mossbauer spectroscopy \([56]\). We find that, preference for a substitutional site increases (difference in formation energy of substitutional and interstitial site) with dopants Mn, Cr, V, Ti and Sc, thus Sc has a very strong preference for substitutional site. Similarly preference for interstitial site increases with dopants Fe, Co, Ni and Cu. Transition from interstitial site to substitutional site occur from Fe to Mn.

Unlike MgO, no change in the preferred defect site has been observed in BaO for the entire range of TM atoms studied (Sc–Zn). All the stable defects, neutral or charged, prefer to sit at interstitial. However, an interesting trend in the interstitial defect position has been observed as the atomic radius of the defect changes. TM atoms with relatively larger atomic radii (Sc–Mn) occupy the middle of the tetrahedral void (Fig. 1(b)), however Fe–Cu prefer to sit at one corner of the tetrahedra (Fig. 1(c)).

B. Stability of TM dopants

Dopant formation energy at preferred defect site as a function of electronic chemical potential \(\mu\) for all the TM atoms in stable charge states is shown in Fig. 2 and Fig. 3 for MgO and BaO, respectively. \(\mu\) varies from VBM up to the band-gap of the host oxide, obtained from our DFT calculation. TM dopant formation energies, with gaseous and crystalline metal energy as references are shown in both the figures. Formation energy of a TM dopant is lower when gaseous metal is considered, hence it is energetically favorable to implant metal ions than TM being intercalated from crystalline metal. Formation energy of dopants in MgO is relatively higher than BaO for all TMs at all electronic chemical potentials. Formation energy is lower for BaO compared to MgO at CBM because DFT predicted band gap is smaller for BaO compared to MgO. A careful observation of the formation energy at VBM for the crystalline metal energy reference reveals that forma-
As a function of electronic chemical potential $\mu$; here $\mu$ is referenced to the valence band maximum (VBM). Dashed and solid lines represent the TM dopant formation energies, with gaseous and crystalline metal energy as references, respectively. The formation energy is lowest for Sc, followed by Ti, V, Cr, Mn, Fe, Zn, Co, Ni and that of Cu is highest. This trend can be understood if we consider the oxygen affinity of TMs. We define oxygen affinity of TMs as enthalpy of formation per oxygen atom of TMs oxides; it is listed in Table I. Here we have considered the TM oxide showing the highest enthalpy of oxide formation per oxygen atom. Higher the oxygen affinity of TM, more the stability of the dopant. If we consider formation energy of dopant at VBM with bulk metal energy as reference, we find that Co, Ni, Cu and Zn are unstable and Sc, Ti, V, Cr, Mn and Fe are stable.

Elements like Sc, Zn that are known to show only one valency, assume only one charge state as dopant for the whole range of electronic chemical potential studied. Those that take multiple valencies like Ti, V, Cr, Mn, Fe, Co, Ni and Cu, do not prefer all the charge states. For example, Ti, V and Cr in BaO take only one charge state. Preferred charge state for a given electronic chemical potential would depend on various factors like pressure exerted on the cell and position of the Fermi level. We will discuss these factors in greater detail in subsequent sections.

C. Charge on dopants

Excess charges in the charged supercell should be confined to TM atom alone as both Mg and Ba does not take multiple valency. We calculate atomic charges on Mg, Ba and TM atoms in defected and defect free supercells using Bader decomposition scheme, and the results are listed below in Table II. Bader charge of Mg atom in a defect free MgO supercell is 1.66e and of Ba atom in a defect free BaO supercell is 1.37e. From the calculation it is evident that charge states of Mg and Ba atoms remain almost unaltered irrespective of the TM atom and their preferred defect site (interstitial or substitution) in the oxide. Maximum change in the charge state of Mg due to incorporation of dopant is 0.09e (in case of Sc$^{3+}$ and Ti$^{4+}$). However, for a given TM in a particular charge state, change in the charge state of Ba is more than that of Mg, which is in agreement with the fact that Mg shows higher affinity for oxygen than Ba.

D. Role of stress induced by dopant on its stability

To understand the role of stress induced by dopant (on the host oxides) on its stability, we calculate hydrostatic pressure exerted by dopant on the supercell. Fig. 4 and Fig. 5 show, the hydrostatic pressure exerted by the TM dopants on MgO and BaO supercells respectively in their most stable charge states at $\mu=\text{VBM}$, and the corre-
TABLE II: Bader charge ($q$) of TM atoms in most stable charge states and Mg and Ba atoms in defect supercell. When TM is in interstitial site we report average charge on four Mg or Ba atoms surrounding TM, but when TM substitute Mg atom in MgO, charge on substituted Mg is reported.

| TM atom | q(e) | TM atom | q(e) | BaO | q(e) |
|---------|------|---------|------|-----|------|
| Sc$^{3+}$ | 1.87 | Ti$^{4+}$ | 2.03 | Sc$^{3+}$ | 1.76 |
| Mg | 1.57 | Mg | 1.57 | Ba | 1.43 |
| V$^{4+}$ | 1.86 | Cr$^{3+}$ | 1.59 | V$^{4+}$ | 0.96 |
| Mg | 1.58 | Mg | 1.58 | Ba | 1.30 |
| Mn$^{4+}$ | 1.66 | Fe$^{3+}$ | 1.12 | Mn$^{4+}$ | 1.73 |
| Mg | 1.58 | Mg | 1.66 | Ba | 1.51 |
| Co$^{3+}$ | 0.89 | Ni$^{3+}$ | 0.93 | Co$^{3+}$ | 0.90 |
| Mg | 1.69 | Mg | 1.66 | Ba | 1.47 |
| Cu$^{3+}$ | 0.64 | Zn$^{2+}$ | 0.82 | Cu$^{3+}$ | 0.69 |
| Mg | 1.69 | Mg | 1.66 | Ba | 1.46 |

sponding defect formation energies. If size of the added dopant is larger than available space at interstitial site then it exerts positive pressure and if it is smaller then it exerts negative pressure. For TM atoms substituting lattice Mg atoms, we find that when the lattice Mg atoms are being pushed to the interstitial sites, there is almost no change in the oxygen tetrahedra surrounding Mg ion, compared to the same in a defect free MgO supercell. The change in the tetrahedral volume varies from 0.21% (for Ti$^{4+}$) to a maximum of 1.79% (for V$^{4+}$). Change in the octahedral volume with TM ions at lattice Mg sites dictates the pressure developed on the supercell.

Clearly pressure alone does not explain dopant formation energy and hence the site preference for the dopants. Cu$^{3+}$ is relatively unstable compared to Cr$^{3+}$ and Fe$^{3+}$, while all of them exert very small pressure on the supercell. Although Mn$^{4+}$ in interstitial site exerts very small pressure compared to Mn$^{4+}$ at substitutional site, still Mn prefers substitutional site. Similarly, very large pressure created by Zn$^{2+}$ does not help to substitute Mg atom. In case of BaO, all the dopants sit at interstitials, and the pressure exerted by defects are mostly negative in nature. This observation is expected as interstitial space available in BaO is relatively larger than the size of dopants. As dopants get more charged, their size decreases, and hence pressure exerted on the supercell becomes more and more negative.

E. Electronic structure

As pressure exerted by a dopant is not sufficient to explain its stability, we consider the electronic structure of pure and doped MgO and BaO to get a better insight of the stability of dopants. We calculated density of states (DOS) for the defected and defect free MgO and BaO supercells. In Fig. 6 we plot DOS along with the Fermi level for few cases: Sc at substitutional site, and Fe and Zn at interstitial site in MgO, with an aim to provide rationale for preferred charge states. Position of Fermi level with respect to VBM and CBM is a good indicator of relative stability of various charge states of a system. Closer the Fermi level is to VBM, more stable is the system [81].

For Sc$^{0}$, Sc$^{1+}$ and Sc$^{2+}$ in MgO, the Fermi level is in the anti-bonding region of the density of states while for Sc$^{3+}$, it is in the bonding region. Hence, Sc is most stable in 3+ charge state in MgO. It is interesting to note that for both the cases no defect state appears in the band gap. Both of them are known to take only one valency and they are found to be stable in that valency alone. In contrast, Fe can take multiple charge states and as dopant it is found to be stable in multiple charge states. This could be attributed to defect states appearing in the
FIG. 6: Total density of states plots of TM doped MgO in their neutral and most stable charged states and pure MgO. The vertical dashed line corresponds to the Fermi level, obtained by alignment of electrostatic potentials of the defect supercell and pure MgO.

TABLE III: Ionic radii for TM atoms, Mg and Ba in 6C environment [82]

| Atom | Ionic radius (Å) | Atom | Ionic radius (Å) |
|------|------------------|------|------------------|
| Mg$^{2+}$ | 0.72 | Ba$^{2+}$ | 1.35 |
| Sc$^{3+}$ | 0.745 | Fe$^{3+}$ | 0.645 |
| Ti$^{4+}$ | 0.605 | Fe$^{2+}$ | 0.78 |
| Ti$^{3+}$ | 0.67 | Co$^{3+}$ | 0.61 |
| Ti$^{2+}$ | 0.86 | Co$^{2+}$ | 0.745 |
| V$^{4+}$ | 0.58 | Ni$^{3+}$ | 0.6 |
| V$^{3+}$ | 0.64 | Ni$^{2+}$ | 0.69 |
| Cr$^{3+}$ | 0.615 | Cu$^{3+}$ | 0.54 |
| Mn$^{4+}$ | 0.53 | Cu$^{2+}$ | 0.73 |
| Mn$^{3+}$ | 0.645 | Cu$^{1+}$ | 0.77 |
| Mn$^{2+}$ | 0.83 | Zn$^{2+}$ | 0.74 |

F. Predicting site preference

Based on our results, we propose an empirical rule for site preference of dopants in rock-salt oxides. It states that site preference is governed by both ionic radius and oxygen affinity of TM; if ionic radius of host cation is large (approximately twice), then TM occupies interstitial site as in case of BaO. But if ionic radius of host cation is similar to that of TM as in case of MgO, then TM replaces cation provided oxygen affinity of TM is similar to that of the host cation, otherwise it occupies interstitial site. This is in contrast to Pauling’s rule that takes only ionic radius of oxygen into account. To explain the empirical rule, we have taken Shannon ionic radii [82], and the oxide formation energy per oxygen is taken as the oxygen affinity. As cations (Mg and Ba) in host oxides are coordinated by 6 oxygen atoms, Shannon ionic radii with 6 coordination are considered and are listed in Table III. Enthalpy of oxide formation per oxygen atom of TM oxides are listed in Table I.

Ionic radius of Ba$^{2+}$ is 1.35 Å, which is significantly larger (almost twice) than the ionic radius of Sc$^{3+}$ (0.75 Å), the largest dopant among all the TM dopants considered in our computation. Hence in case of BaO all the dopants prefer interstitial sites. However, ionic radius of Mg$^{2+}$ (0.72 Å) is comparable to all the dopants considered, as listed in Table III. It should be noted that ionic radius of a TM dopant depends on the charge state, but it still prefers substitutional site. On the other hand, both Fe$^{2+}$ and Fe$^{3+}$ prefer to occupy the interstitial sites although ionic radius of Fe$^{2+}$ (0.65 Å) is smaller and Fe$^{3+}$ (0.78 Å) is larger than the ionic radius of Mg$^{2+}$. In such cases ionic radius has minimal role in dictating the site preference, but oxygen affinity (already defined as enthalpy of formation of oxide per oxygen atom) serves as a better indicator for site preference. It is not possi-
nable to predict which of the TMs will prefer substitutional site, as Mn, V and Ti have smaller oxygen affinity compared to Mg but prefer to substitute lattice Mg atoms. However, increase in the preference for substitutional site with increasing oxygen affinity, does point to the efficacy of oxygen affinity in determining the trend.

G. Ni and Fe implanted MgO

Our results explain experimental observation on Fe and Ni ions implanted in MgO. Experiment shows that Ni atoms implanted in MgO at room temperature get uniformly distributed but on annealing it tends to segregate at grain boundary [83]. This could be possible only if implanted Ni occupies interstitial site and not the substitutional site. This is in agreement with our calculations. Although, Ni prefers interstitial site, formation energy of the dopant with bulk as reference (shown by the solid line in Fig. 2) is always positive for the entire range of chemical potential studied. This suggest that Ni could occupy interstitial site but it is unstable in MgO. This explains why Ni form metallic precipitate when annealed. Ni can precipitate out of MgO by hopping from one interstitial site to other. We have calculated the barrier of transition from one interstitial site to the other using nudged elastic band (NEB) method, details of which will be discussed somewhere else [84]. Barriers for transition of Ni in MgO is very low for all its charge states. Hence substantial diffusion of Ni in MgO can be achieved by annealing.

Ni presents an interesting case to compare our way of calculating interstitial dopant formation energy (where number of Mg atoms in the lattice remains the same after doping), with the one where Mg atom is replaced with Ni atom in the supercell [85], we call it replacement formation energy for convenience. We consider neutral Ni as a defect in a 32 formula unit of MgO. Replacement formation energy is defined as

\[
E_f = E_D + \mu_{Mg} - E_B - \eta
\]  

(2)

Here \(E_D\) and \(E_B\) are total energies of the supercell containing Ni defect, and defect free MgO supercell respectively. \(\eta\) refers to the chemical potential of Ni and \(\mu_{Mg}\) is the chemical potential of Mg; both are taken as respective crystalline metal energies. Replacement formation energy came out to be 4.42 eV which is nearly 3.81 eV lower than the interstitial formation energy of Ni in interstitial in MgO. This points towards the importance of calculating interstitial and substitutional formation energies as defined in this work and establishes interstitial being a possible defect site for the TM atoms. Existing experiments [1] show that Fe implanted in MgO is stable in Fe\(^{3+}\), Fe\(^{2+}\) and Fe\(^0\) charge states, but does not comment on where Fe ions sit in the host lattice. We show conclusively that Fe occupies interstitial site. We calculated the dopant formation energies of Fe in both substitutional and interstitial sites as shown in Fig. 7. Here we have taken the bulk energy references for calculating the chemical potential of Fe atoms. Fe in interstitial site is always more stable than in substitutional site. Stable charge states for Fe in interstitial site are +3, +2 and 0, while in substitutional site they are +3, +2, +1 and 0. Experiments [1] suggest that +3, +2 and 0 are the stable states for Fe in MgO, hence it is evident that Fe occupies interstitial sites in MgO and not the substitutional sites. Another justification behind this finding is that, if Fe does not occupy interstitial position, it will not migrate out of MgO to form metallic precipitate. Although our calculations suggest that Fe in interstitial position is preferred over substitutional position, but difference in energy between two positions is small, specially when electronic chemical potential is high. Hence, Fe could occasionally occupy substitutional position as well, which has also been shown experimentally [56].

IV. CONCLUSIONS

In this work, we have carried out a systematic investigation of stability of 10 TM dopants in the rock-salt crystal structure oxides namely MgO and BaO, under the purview of density functional theory. We calculated the TM dopant formation energies in various charge states as a function of the electronic chemical potential. We show that TM dopants can occupy interstitial site, contrary to the common belief that TM dopants will invariably substitute cations in the oxide. In case of BaO, all the TM dopants prefer interstitial site. However, for MgO, Fe, Co, Ni, Cu and Zn prefer interstitial sites while Sc, Ti, V, Cr and Mn prefer to substitute Mg. Our results suggest that the site preference of TM atoms in rock-salt oxides depends on relative ionic radii and oxygen affinity of the host lattice and the dopant. If ionic radius of the host lattice is significantly bigger (approximately twice of that of dopant), then the dopants prefer interstitial sites. However, if ionic radius of the dopant is comparable to that of the host lattice, it can substitute lattice cations.
only if its oxygen affinity is similar to that of the host lattice. Stability of dopants in oxides depends on the electronic chemical potential; lower electronic chemical potential leads to higher stability. For given electronic chemical potential, higher the affinity of the TM to oxygen, greater the stability of the dopant. Our result on Ni occupying interstitial site explains experimentally observed phenomena of implanted Ni ions migrating out of MgO after annealing. Experimentally reported charge states of implanted Fe in MgO was found to be stable only when Fe is in interstitial site, which further points to the possibility of intercalating dopants at interstitial sites. Similarly, various experiments on ions implanted in stable oxides, for example Al$_2$O$_3$ [83, 86–89] could be explained based on our findings. Computational scheme presented here can be applied to other stable oxides like CaO, ZnO and various perovskites to explore the possibilities of stabilizing dopants at interstitial sites. Stabilizing defects at interstitial sites can result in novel properties. Hence, our results provide guidelines to design new ion implant experiments to stabilize ions in interstitial sites of stable compounds.

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[1] C. White, C. McGharge, P. Sklad, L. Boatner, and G. Farlow, “Ion implantation and annealing of crystalline oxides,” Materials Science Reports, vol. 4, no. 2, pp. 41–146, 1989.
[2] V. Markevich, “A comparative study of ion implantation and irradiation-induced defects in ge crystals,” Materials Science in Semiconductor Processing, vol. 9, no. 4, pp. 588–596, 2006. Proceedings of Symposium T E MRS 2006 Spring Meeting on Germanium based semiconductors from materials to devices.
[3] A. Perez, “Ion implantation effects in crystalline inorganic insulators,” Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, vol. 1, no. 2, pp. 621–627, 1984.
[4] S. O. Kucheyev, J. S. Williams, C. Jagadish, J. Zou, C. Evans, A. J. Nelson, and A. V. Hamza, “Ion-beam-produced structural defects in zno,” Phys. Rev. B, vol. 67, p. 094115, Mar 2003.
[5] M. Pomaska, J. Mock, F. Khler, U. Zastrow, M. Perani, O. Astakhov, D. Cavalcoli, R. R. Alfano, F. Finger, and K. Ding, “Role of oxygen and nitrogen in n-type microcrystalline silicon carbide grown by hot wire chemical vapor deposition,” Journal of Applied Physics, vol. 120, no. 22, p. 225105, 2016.
[6] K. Murakami, R. Shirakawa, M. Tsujimura, N. Uchida, N. Fukata, and S.-i. Hishita, “Phosphorus ion implantation in silicon nanocrystals embedded in sio2,” Journal of Applied Physics, vol. 105, no. 5, p. 054307, 2009.
[7] M. Fujii, S. Hayashi, and K. Yamamoto, “Photoluminescence from b-doped si nanocrystals,” Journal of Applied Physics, vol. 83, no. 12, pp. 7953–7957, 1998.
[8] C. E. Chryssou, A. J. Kenyon, T. S. Iwayama, C. W. Pitt, and D. E. Hole, “Evidence of energy coupling between si nanocrystals and er3+ in ion-implanted silica thin films,” Applied Physics Letters, vol. 75, no. 14, pp. 2011–2013, 1999.
[9] T. ShimizuIwayama, K. Fujita, S. Nakao, K. Saitoh, T. Fujita, and N. Itoh, “Visible photoluminescence in si+ ion-implanted silica glass,” Journal of Applied Physics, vol. 75, no. 12, pp. 7779–7783, 1994.
[10] S. Guha, “Characterization of si+ ion-implanted sio2 films and silica glasses,” Journal of Applied Physics, vol. 84, no. 9, pp. 5210–5217, 1998.
[11] R. G. Elliman, M. J. Lederer, and B. Luther-Davies, “Optical absorption measurements of silica containing si nanocrystals produced by ion implantation and thermal annealing,” Applied Physics Letters, vol. 80, no. 8, pp. 1325–1327, 2002.
[12] A. J. Kenyon, C. E. Chryssou, C. W. Pitt, T. ShimizuIwayama, D. E. Hole, N. Sharna, and C. J. Humphreys, “Luminescence from erbium-doped silicon nanocrystals in silica: Excitation mechanisms,” Journal of Applied Physics, vol. 91, no. 1, pp. 367–374, 2002.
[13] S. Ruffell, I. V. Mitchell, and P. J. Simpson, “Annealing behavior of low-energy ion-implanted phosphorus in silicon,” Journal of Applied Physics, vol. 97, no. 12, p. 123518, 2005.
[14] T. ShimizuIwayama, S. Nakao, and K. Saitoh, “Visible photoluminescence in si+ implanted thermal oxide films on crystalline si,” Applied Physics Letters, vol. 65, no. 14, pp. 1814–1816, 1994.
[15] A. P. Knights, P. J. Simpson, L. B. Allard, J. L. Brebner, and J. Albert, “Si ion implantationinduced damage in fused silica probed by variableenergy positrons,” Journal of Applied Physics, vol. 79, no. 12, pp. 9022–9028, 1996.
[16] R. H. Magruder, L. Yang, R. F. Haglund, C. W. White, L. Yang, R. Dorsinville, and R. R. Alfano, “Optical properties of gold nanocluster composites formed by deep ion implantation in silica,” Applied Physics Letters, vol. 62, no. 15, pp. 1730–1732, 1993.
[17] R. H. Magruder, R. F. Haglund, L. Yang, J. E. Wittig, and R. A. Zuhr, “Physical and optical properties of cu nanoclusters fabricated by ion implantation in fused silica,” Journal of Applied Physics, vol. 76, no. 2, pp. 708–715, 1994.
[18] D. K. Sood, P. K. Sekhar, and S. Bhansali, “Ion implantation based selective synthesis of silica nanowires on silicon wafers,” Applied Physics Letters, vol. 88, no. 14, p. 143110, 2006.
[19] M. Erman, J. B. Theeten, P. Chambron, S. M. Kelso, and D. E. Aspnes, “Optical properties and damage analysis of gas single crystals partly amorphized by ion implantation,” Journal of Applied Physics, vol. 56, no. 10, pp. 2664–2671, 1984.
[20] D. O. Scanlon, A. Walsh, B. J. Morgan, M. Nolan, J. Fearon, and G. W. Watson, “Surface sensitivity in lithium-doping of mgo: a density functional theory study with correction for on-site coulomb interactions,” *The Journal of Physical Chemistry C*, vol. 111, no. 22, pp. 7971–7979, 2007.

[21] J. W. Lee and J.-H. Ko, “Defect states of transition metal-doped mgo for secondary electron emission of plasma display panel,” *Journal of Information Display*, vol. 15, no. 4, pp. 157–161, 2014.

[22] H. Schut, A. V. Veen, F. Labohm, A. Fedorov, E. Neef, and R. Konings, “Annealing behaviour of defects in helium implanted mgo,” *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, vol. 147, no. 1, pp. 212–215, 1999.

[23] Y. Chen, H. T. Tohver, J. Narayan, and M. M. Abraham, “High-temperature and ionization-induced effects in lithium-doped mgo single crystals,” *Phys. Rev. B*, vol. 16, pp. 5535–5542, Dec 1977.

[24] R. Llusar, M. Casarrubios, Z. Barandiaran, and L. Seijo, “Ab initio model potential calculations on the electronic spectrum of n2+ doped mgo including correlation, spinorbit and embedding effects,” *The Journal of Chemical Physics*, vol. 105, no. 13, pp. 5321–5330, 1996.

[25] B. P. Uberuaga, X.-M. Bai, P. P. Dholabhai, N. Moore, and D. M. Duffy, “Point defect-grain boundary interactions in mgo: an atomistic study,” *Journal of Physics: Condensed Matter*, vol. 25, no. 35, p. 355001, 2013.

[26] B. P. Uberuaga, R. Smith, A. R. Cleave, F. Montalenti, G. Henkelman, R. W. Grimes, A. F. Voter, and K. E. Sicakfus, “Structure and mobility of defects formed from collision cascades in mgo,” *Phys. Rev. Lett.*, vol. 92, p. 115505, Mar 2004.

[27] H.-S. Ahn, T.-E. Kim, E. Cho, M. Ji, C.-K. Lee, S. Han, Y. Cho, and C. Kim, “Molecular dynamics study on low-energy sputtering properties of mgo surfaces,” *Journal of Applied Physics*, vol. 103, no. 7, p. 073518, 2008.

[28] H. Wu, A. Stroppa, S. Sakong, S. Picozzi, M. Scheffler, and P. Kratzer, “Magnetism in c- or n-doped mgo and zn: A density-functional study of impurity pairs,” *Phys. Rev. Lett.*, vol. 105, p. 267203, Dec 2010.

[29] N. A. Richter, S. Sicolo, S. V. Levchenko, J. Sauer, and M. Scheffler, “Concentration of vacancies at metal-oxide surfaces: Case study of mgo(100),” *Phys. Rev. Lett.*, vol. 111, no. 4, p. 045502, Jul 2013.

[30] C. A. Gilbert, S. D. Kenny, R. Smith, and E. Sanville, “Ab initio study of point defects in magnesium oxide,” *Phys. Rev. B*, vol. 76, p. 184103, Nov 2007.

[31] G. Henkelman, B. P. Uberuaga, D. J. Harris, J. H. Harding, and N. L. Allan, “Mgo addimer diffusion on mgo(100): A comparison of ab initio and empirical models,” *Phys. Rev. B*, vol. 72, p. 115437, Sep 2005.

[32] S. Ramachandran, J. Narayan, and J. T. Prater, “Magnetic properties of ni-doped mgo diluted magnetic insulators,” *Applied Physics Letters*, vol. 90, no. 13, p. 132511, 2007.

[33] B. M. Maoz, E. Tirosh, M. Bar Sadan, and G. Markovich, “Defect-induced magnetism in chemically synthesized nanoscale sheets of mgo,” *Phys. Rev. B*, vol. 83, p. 161201, Apr 2011.

[34] S. Azzaza, M. El-Hilo, S. Narayanan, J. J. Vijayan, N. Mamouni, A. Benyoussef, A. E. Kenz, and M. Bououdina, “Structural, optical and magnetic characterizations of mn-doped mgo nanoparticles,” *Materials Chemistry and Physics*, vol. 143, no. 3, pp. 1500 – 1507, 2014.

[35] C. Martínez-Boubeta, J. I. Beltrán, L. Balcels, Z. Konstantinović, S. Valencia, D. Schmitz, J. Arbiol, S. Estrade, J. Cornil, and B. Martínez, “Ferromagnetism in transparent thin films of mgo,” *Phys. Rev. B*, vol. 82, p. 024405, Jul 2010.

[36] D. Mishra, B. P. Mandal, R. Mukherjee, R. Naik, G. Lawes, and B. Nadgorny, “Oxygen vacancy enhanced room temperature magnetism in al-doped mgo nanoparticles,” *Applied Physics Letters*, vol. 102, no. 18, p. 182404, 2013.

[37] E.-H. Choi, H.-J. Oh, Y.-G. Kim, J.-J. Ko, J.-Y. Lim, J.-G. Kim, D.-I. Kim, G. Cho, and S.-O. Kang, “Measurement of secondary electron emission coefficient () of mgo protective layer with various crystallinities,” *Japanese Journal of Applied Physics*, vol. 37, no. 12S, p. 7015, 1998.

[38] C. M. Wang, S. Thevuthasan, V. Shuttahanand, A. Cavanagh, W. Jiang, L. E. Thomas, and W. J. Weber, “Microstructure of precipitated au nanoclusters in mgo,” *Journal of Applied Physics*, vol. 93, no. 10, pp. 6327–6333, 2003.

[39] J. Xu, J. Moxom, S. H. Overbury, C. W. White, A. P. Mills, and R. Suzuki, “Quantum antidot formation and correlation to optical shift of gold nanoparticles embedded in mgo,” *Phys. Rev. Lett.*, vol. 88, p. 175502, Apr 2002.

[40] J. Xu, A. P. Mills, A. Ueda, D. O. Henderson, R. Suzuki, and S. Ishibashi, “Vacancy clusters on surfaces of au nanoparticles embedded in mgo,” *Phys. Rev. Lett.*, vol. 83, pp. 4586–4589, Nov 1999.

[41] R. Zimmerman, D. Ilia, E. Williams, S. Sarkisov, D. Poker, and D. Hensley, “Fabrication of copper and gold nanoclusters in mgo (100) by mev ion implantation,” *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, vol. 141, no. 1, pp. 308 – 311, 1998.

[42] X. Xiang, X. Zu, S. Zhu, C. Zhang, and L. Wang, “Effect of annealing on the optical absorption of ni nanoparticles in mgo single crystals,” *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, vol. 250, no. 1, pp. 229 – 232, 2006. Radiation Effects in Insulators.

[43] J. R. Crawford and R. D. Dragsdorff, “Photoluminescence from he, fr, ces, and cr ionimplanted mgo,” *Journal of Applied Physics*, vol. 44, no. 1, pp. 385–388, 1973.

[44] V. Skvortsova and L. Trinkler, “The optical properties of magnesium oxide containing transition metal ions and defects produced by fast neutron irradiation,” in *Proceedings of the 3rd WSEAS International Conference on Advances in Sensors, Signals and Materials, SENSIG '10/MATERIALS'10*, (Stevens Point, Wisconsin, USA), pp. 150–154, World Scientific and Engineering Academy and Society (WSEAS), 2010.

[45] R. S. Averbuck, P. Ehgart, A. I. Popov, and A. v. Sambeek, “Defects in ion implanted and electron irradiated mgo and al2o3,” *Radiation Effects and Defects in Solids*, vol. 136, no. 1–4, pp. 169–173, 1995.

[46] J. W. Lee and J.-H. Ko, “Defect states of transition metal-doped mgo for secondary electron emission of plasma display panel,” *Journal of Information Display*, vol. 15, no. 4, pp. 157–161, 2014.

[47] J. W. Lee, “Defect states of zn-, ru-, si- and ge-doped mgo calculated by using first-principles method for auger
neutralization,” New Physics: Sae Multi, vol. 66, no. 11, pp. 1354–1358, 2016.

[48] G. M. A. Perez, J. A. S. B. D. Sawicka, and T. Tyliszczak, “Iron-ion implantation effects in mgo crystals,” Phys. Rev. B, vol. 28, no. 3, pp. 1227–1238, 1983.

[49] S. Zhu, X. Xiang, X. Zu, and L. Wang, “Magnetic nanoparticles of ni in mgo single crystals by ion implantation,” Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, vol. 242, no. 1, pp. 114 – 117, 2006. Ion Beam Modification of Materials.

[50] Y. C. J. Narayan and H. M. Moon, “Nickel colloids in reduced nickel-doped magnesium oxide,” Phys. Rev. Lett., vol. 46, no. 22, pp. 1491–1494, 1981.

[51] H. N., S. I., O. T., T. H., W. H., and T. T., “Nano-clustering of iron and magnetic properties of the iron implanted in mgo,” physica status solidi (a), vol. 189, no. 3, pp. 775–780, 2002.

[52] J. Narayan, S. Nori, D. K. Pandya, D. K. Avasthi, and A. I. Smirnov, “Defect dependent ferromagnetism in mgo doped with ni and co,” Applied Physics Letters, vol. 93, no. 8, p. 082507, 2008.

[53] V. Sharma, G. Pilania, and J. E. Lowther, “Ferromagnetism in iv main group element (c) and transition metal (mn) doped mgo: A density functional perspective,” AIP Advances, vol. 1, no. 3, p. 032129, 2011.

[54] A. Sarkar, L. Velasco, D. Wang, Q. Wang, G. Talasila, L. de Biasi, C. Kbel, T. B. S. S. Bhattacharya, H. Hahn, and B. Breitung, “High entropy oxides for reversible energy storage,” Nature Communications, no. 9, pp. 1 – 9, 2018.

[55] Y.-M. Chiang, D. P. Birnie, and W. D. Kingery, “Ceramics: Principles for ceramic science and engineering,” John Wiley & Sons, Inc., New York, 1997.

[56] T. E. Mhlolt, R. Mantovan, H. P. Gunlaugeon, A. Svane, H. Masenda, D. Naidoo, K. Bharuth-Ram, M. Fanciulli, H. P. Gislon, K. Johnston, G. Langouche, S. lasson, R. Sielemann, and G. Weyer, “Interstitial fe in mgo,” Journal of Applied Physics, vol. 115, no. 2, p. 023508, 2014.

[57] Y. Xu, S. K. Yadav, J. A. Aguiar, O. Anderoglu, J. K. Baldwin, Y. Wang, A. Misra, H. Luo, B. P. Uberuaga, and N. Li, “Irradiation-induced formation of a spinel phase at the fcc/mgo interface,” Acta Materialia, vol. 93, pp. 87 – 94, 2015.

[58] V. Ivady, I. A. Abrikosov, E. Janzén, and A. Gali, “Role of screening in the density functional applied to transition-metal defects in semiconductors,” Phys. Rev. B, vol. 87, p. 205201, May 2013.

[59] C. G. Van de Walle and J. Neugebauer, “First-principles calculations for defects and impurities: Applications to iii-nitrides,” Journal of Applied Physics, vol. 95, no. 8, pp. 3851–3879, 2004.

[60] A. Janotti and C. G. Van de Walle, “Native point defects in zno,” Phys. Rev. B, vol. 76, p. 165202, Oct 2007.

[61] C. Freysoldt, B. Lange, J. Neugebauer, Q. Yan, J. L. Lyons, A. Janotti, and C. G. Van de Walle, “Electron and chemical reservoir corrections for point-defect formation energies,” Phys. Rev. B, vol. 93, p. 165206, Apr 2016.

[62] S. Lany and A. Zunger, “Assessment of correction methods for the band-gap problem and for finite-size effects in supercell defect calculations: Case studies for zno and gaas,” Phys. Rev. B, vol. 78, p. 235104, Dec 2008.

[63] R. Ramprasad, H. Zhu, P. Rinke, and M. Scheffler, “New perspective on formation energies and energy levels of point defects in nonmetals,” Phys. Rev. Lett., vol. 108, p. 066404, Feb 2012.

[64] C. Freysoldt, B. Grabowski, T. Hickel, J. Neugebauer, G. Kresse, A. Janotti, and C. G. Van de Walle, “First-principles calculations for point defects in solids,” Rev. Mod. Phys., vol. 86, pp. 253–305, Mar 2014.

[65] S. Bajaj, G. S. Pomrehn, J. D. Doak, W. Gierlotka, H. Jay Wu, S.-W. Chen, C. Wolverton, W. A. Goddard, and G. J. Snyder, “Ab initio study of intrinsic point defects in pbel: an insight into phase stability,” Acta Materialia, vol. 92, pp. 72 – 80, 2015.

[66] G. Kresse and J. Furthmüller, “Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set,” Physical Review B, vol. 54, no. 16, p. 11169, 1996.

[67] G. Kresse and J. Furthmüller, “Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set,” Computational Materials Science, vol. 6, no. 1, pp. 15 – 50, 1996.

[68] P. E. Blöchl, “Projector augmented-wave method,” Physical Review B, vol. 50, no. 24, p. 17953, 1994.

[69] P. E. Blöchl, O. Jepsen, and O. K. Andersen, “Improved tetrahedron method for brillouin-zone integrations,” Phys. Rev. B, vol. 49, pp. 16223–16233, Jun 1994.

[70] J. P. Perdew, K. Burke, and M. Ernzerhof, “Generalized gradient approximation made simple,” Physical review letters, vol. 77, no. 18, p. 3865, 1996.

[71] V. Sharma, G. Pilania, G. A. Rossetti, K. Slencs, and R. Ramprasad, “Comprehensive examination of dopants and defects in bo3 from first principles,” Phys. Rev. B, vol. 87, p. 134109, Apr 2013.

[72] E. Ertékin, L. K. Wagner, and J. C. Grossman, “Point-defect optical transitions and thermal ionization energies from quantum monte carlo methods: Application to the f-center defect in mgo,” Phys. Rev. B, vol. 87, p. 155210, Apr 2013.

[73] A. Schleife, F. Fuchs, J. Furthmüller, and F. Bechstedt, “First-principles study of ground- and excited-state properties of MgO, ZnO, and CdO polymorphs,” Phys. Rev. B, vol. 73, p. 245212, Jun 2006.

[74] F. Tran and P. Blaha, “Accurate band gaps of semiconductors from quantum monte carlo methods: Application to the f-center defect in mgo,” Phys. Rev. B, vol. 77, p. 134109, Apr 2013.

[75] A. I. Smirnov, “Defect dependent ferromagnetism in mgo doped with ni and co,” Applied Physics Letters, vol. 93, no. 8, p. 082507, 2008.

[76] R. F. Bader, “Atoms in molecules: Principal for ceramic science and engineering,” New Physics: Sae Multi, vol. 66, no. 11, pp. 1354–1358, 2016.
[80] W. Tang, E. Sanville, and G. Henkelman, “A grid-based bader analysis algorithm without lattice bias,” J. Phys.: Condens. Matter, vol. 21, p. 084204, 2009.

[81] J.-H. Xu and A. J. F. T. Oguchi, “Solid-solution strengthening: Substitution of v in ni3a1 and structural stability of ni3(al,v),” Phys. rev. B, vol. 36, no. 8, pp. 4186 – 4189, 1987.

[82] R. D. SHANNON, “Revised effective ionic radii and systematic studies of interatomic distances in halides and chaleogenides,” Acta Crystallographica, vol. A32, pp. 751–767, 1976.

[83] E. Alves, C. Marques, R. da Silva, T. Monteiro, J. Soares, C. McHargue, L. Ononye, and L. Allard, “Structural and optical studies of co and ti implanted sapphire,” Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, vol. 207, no. 1, pp. 55 – 62, 2003. Symposium: Ion Beam Processing and Modification of Glasses and Ceramics.

[84] D. Misra and S. K. Yadav, “Precipitation of ni and fe from rock-salt structured oxides,” in preparation.

[85] S. Prada, L. Giordano, and G. Pacchioni, “Li, al, and ni substitutional doping in mgo ultrathin films on met-}

als: Work function tuning via charge compensation,” The Journal of Physical Chemistry C, vol. 116, no. 9, pp. 5781–5786, 2012.

[86] X. Xiang, X. T. Zu, S. Zhu, and L. M. Wang, “Optical properties of metallic nanoparticles in ni-ion-implanted -al2o3 single crystals,” Applied Physics Letters, vol. 84, no. 1, pp. 52–54, 2004.

[87] A. Stepanov, C. Marques, E. Alves, and et. al., “Nonlinear optical properties of gold nanoparticles synthesized by ion implantation in sapphire matrix,” Tech. Phys. Lett., vol. 31, no. 8, pp. 702 – 705, 2005.

[88] C. McHargue, S. Ren, and J. Hunn, “Nanometer-size dispersions of iron in sapphire prepared by ion implantation and annealing,” Materials Science and Engineering: A, vol. 253, no. 1, pp. 1 – 7, 1998.

[89] P.-E. Mota-Santiago, A. Crespo-Sosa, J.-L. Jimnez-Hernndez, H.-G. Silva-Pereyra, J.-A. Reyes-Esqueda, and A. Oliver, “Size characterisation of noble-metal nano-crystals formed in sapphire by ion irradiation and subsequent thermal annealing,” Applied Surface Science, vol. 259, pp. 574 – 581, 2012.