**Computer modelling of Bi12SiO20 and Bi4Si3O12: intrinsic defects and rare earth ion incorporation**

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**Abstract:** Defect properties of Bi12SiO12 and Bi4Si3O12 compounds were investigated using atomistic computer modelling techniques based on energy minimisation. Interatomic potentials obtained by empirical fitting reproduce the lattice parameters for both materials and the available elastic and dielectric constants with reasonable accuracy. The relative stability of the phases and the intrinsic defects of both phases are predicted. A new methodology is used for calculating solution energies for rare earth doping which takes doping concentration into account.

1. **Introduction**

Bismuth silicon oxides, obtained by crystallisation of the Bi2O3-SiO2 system, such as Bi12SiO20 and Bi4Si3O12, have attracted much interest due to their technological applications [1-3] in medicine, geological exploration, nuclear physics and high energy physics [4-5]. In particular, Bi12SiO20 is used in scintillators and photorefractive materials, in lasers [6-7] and in materials with applications in electrooptics, acoustics, and piezotechnics, where physical properties such as photorefractivity, photoconductivity, optical activity, reflection holography, lensometry, the velocity of ultrasound wave propagation are important [8-16]. Bi4Si3O12 is used as a highly efficient scintillator in gamma ray spectroscopy and high energy physics, and in non-linear optical devices, nuclear medicine, and photorefractive materials [5].

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In general, the physical properties observed in both compounds are directly or indirectly influenced by intrinsic or extrinsic defects. Information about defects, including the dopant ions involved, their valence and local symmetry, mechanisms of charge compensation (when necessary), and the predominance of intrinsic defects is essential information that can help explain the material properties and also help to improve and enhance particular properties. Atomistic computer modelling has been shown to be a powerful method for obtaining detailed information about intrinsic and extrinsic defects. Recently, this method has been employed with success in point defect calculations on other sillenite compounds, such as Bi12GeO20[17-18] and Bi12TiO20 [19], and related compounds in the Bi2O3-MeO2 series (where Me = Ge, Si, Ti and Mn) system [20].

In this paper, atomistic computer modelling based on lattice energy minimisation is applied to study the defect properties in the bismuth silicate compounds. Additional intrinsic defects formed by electron and hole trapping and antisite defects are considered as well as the more familiar Frenkel and Schottky defects. Extrinsic defects are then considered in a study of doping by a range of rare earth ions where solution energies, solution schemes and solubility limits are obtained.

1. **Methodology**

In this work, Buckingham potentials have been used to model the interactions between the ions in the crystal, given by the equation

 (1)

where the index *i* and *j* label the ionic species,  *qi*  is the charge of the ion labelled by *i*  in units of electron charge. The bond-bending terms for O-Si-O, that describe covalent interactions, are also included. For all such bonds, a quadratic energy term is included as follows:

 (2)

Where *kb* is the bond-bending force constant, and *θ0* is the equilibrium bond angle.

Ionic polarisability is modelled using the shell model, which is used to describe the highly polarisable oxygen and bismuth ions. In this model, it is assumed that the ion is formed of a massless shell with charge *Y*, effectively representing the outermost electrons, and a core, representing the inner electrons, connected to the shell by a harmonic spring with a force constant *k*, giving rise to a finite ionic polarisability, i.e.

 (3)

The silicon ion was described as a rigid ion, whose charge is set to the formal value (+4). The calculations, which include energy minimisation and defect substitution, were performed using the GULP code [21]. In order to perform the defect calculations, the Mott–Littleton method [22] was employed, where the lattice surrounding the defect is divided in two regions. Region I, formed by ions in the spherical region close to defect, is treated explicitly with all ion interactions being considered, and region II, formed by more distant ions, being treated using a continuum approach. Consistent cut-off radii of 14 and 18 Å have been used for regions I and II (a) respectively.

1. **Results**
	1. ***Interatomic potentials and structure calculation***

Bi4Si3O12 and Bi12SiO20 were modelled using the set of potential parameters presented in tables 1a and 1b. The Bi-O and Si-O parameters were refitted using an initial parameterisation obtained by Islam et al [23], and Sanders et al [24], respectively. Potentials describing the interaction between rare earth ions and the host framework were obtained by Araújo et al [25]. As can be seen from the difference between the experimental and the calculated structural data, given in Table 2, the derived potential describes the compounds well. The Bi12SiO20 structure adopts the cubic system with space group I23 [26]. The body centre and the corners of the unit cell are occupied by silicon–oxygen tetrahedra. The whole structure consists of seven-oxygen coordinated Bi polyhedra and with the SiO4 tetrahedra [26] with the three no-equivalent oxygen sites. The Bi4Si3O12 structure also has cubic symmetry, space group I-43d [27], where the Bi, Si, and O atoms occupy 16c, 12a and 48e positions, respectively, using Wyckoff notation. Table 3 shows that good agreement is obtained between some physical properties calculated for both compounds.

Calculated lattice energy and the lattice energy per ion for both compounds and the parent oxides are given in Table 4. These values can be used to estimate the relative stability of each phase. It is noted that the lattice energy *per formula unit* of Bi4Si3O12 is lower than the Bi12SiO20 phase. On the other hand, the melting temperatures, which are an indication of the relative stability of the phases, are in the reverse order, with temperatures of 1025oC [30] and 910oC [31] for the Bi4Si3O12 and Bi12SiO20 phases, respectively. This occurs due to the different compositions, and the different number of ions in both phases should be taken into account. Thus, the lattice energies per formula unit are divided by the number of Bi ions, obtaining values of -35.64 eV and -27.97 eV for the Bi4Si3O12 and Bi12SiO20 phases, respectively. The correct trend is therefore obtained.

* 1. ***Intrinsic defects***

Employing the potentials derived in the previous section, and the calculated lattice energies obtained, the energies of formation of the most important point defects in Bi12SiO20 and Bi4Si3O12 have been calculated. The interstitial sites used were (1/2, 0, 0) for Bi12SiO20 and (1/4, 1/4, 1/2) for Bi4Si3O12. The energies have been combined to form Frenkel, Schottky, pseudo-Schottky (Bi2O3, SiO2), and anti-Schottky energies. However, in order to explain the observed bismuth excess mainly in the 12-1-20 composition, it is necessary to consider more complex defects. Historically, one model was proposed to explain the bismuth excess [32-33], i.e. a bismuth antisite defect compensated by a hole. Based on this information, three additional defect reactions have been considered. Their formation process is explained in the following reactions, where the Kröger-Vink notation [34] has been adopted. Scheme (i) involves the substitution of Bi3+ at Si4+ with trapped hole compensation  plus Si4+ at Bi3+ with trapped electron compensation. Scheme (ii) involves a bismuth antisite defect with trapped hole compensation together with bismuth and oxygen vacancy formation. Finally, scheme (iii) involves the bismuth antisite defect with trapped hole compensation together with bismuth and oxygen vacancies, with formation of oxygen vapour.

Scheme (i)

 (4)

For which the formation energy, *Ef*, is given by

 (5)

where the and  terms are the formation of bismuth and silicon antisite defects, respectively, and *Eh* and *Ee* are the energies required to create a trapped hole and a trapped electron, respectively. The model used for the hole state is the 0-ion, while for the electron state it is the Bi2+ and Si3+ species. Electron and hole formation energies are calculated by combining GULP interatomic energies with free-ion intra-atomic energies, i.e., the second electron affinity of oxygen [35], the fourth ionisation potential of silicon, and the third ionization potential of bismuth [36]. Here the simplifying assumption is made that such ionisation energies differ little from the free atom values. These values are given in Table 5.

Scheme (ii)

 (6)

For which the formation energy, *Ef,* is given by

 (7)

where the ,,  terms are the formation energies of bismuth and silicon antisite defects, bismuth and oxygen vacancies respectively, and *Eh* is the energy required to create a hole. is the lattice energy of silicon dioxide in the α-quartz phase. The energy required to create a trapped hole is given by sum of the energy required (in the gas phase) for the process O2-→ O1-+*e*- and the substitutional defect energy required to replace an O- ion on a regular O2- site. This is the model used to describe a trapped hole in an O2- ion nearby the Bi-Si antisite. The energy required to create an electron is given by sum of the energy required (in the gas phase) for the process Si4++ *e*- → Si3+ and the substitutional defect energy required to replace an Si3+ ion on a regular Si4+ site or is given by sum of the energy required (in the gas phase) for the process Bi3++ *e*- → Bi2+ and the substitutional defect energy required to replace an Bi2+ ion on a regular Bi3+. All energies required to calculate the intrinsic defect are given in the table. Following the procedure described above, solution energies are calculated for scheme (iii):

 (8)

For which the formation energy, *Ef*, is given by

 (9)

The calculated formation energies for the basic defects are given in Table 6. Using those values, the solution energies of the intrinsic defects can be calculated, and they are given in Table 7. The solution energies from Table 7 assume the defects to be unbound and normalised per defect.

In the Bi12SiO20 phase, the Frenkel energies are higher than Schottky energies. This is an indicative of the low stability of interstitial defects, since the Frenkel defect is formed by the displacement of ions into interstitial sites. Therefore, the concentration of interstitial ions will be negligible. The formation energies show that the most favourable intrinsic defect is scheme (ii) followed by the Schottky and pseudo-Schottky Bi2O3 defects. In scheme (ii), the Bi3+ ions occupy Si4+ sites compensated by a trapped hole in a neighbouring oxygen ion. The Bi displaces the Si to the surface (accompanied with 2 oxygen to for a silica molecule) leaving a vacancy that is further compensated by oxygen vacancies. This defect can also be seen as a BiSi**`** antisite capturing a hole that is formed close to a pseudo-Schottky Bi2O3 defect, thus lowering the total energy. The pseudo-Schottky Bi2O3 defect is a normal intrinsic disorder associated with a well-stabilised reaction. In the other hand, the  defect is a not a normal defect and is not self consistent due to the fact that the hole has to come from somewhere that, in turn, leaves an electron.

This result is consistent with a series of experimental results. X-ray diffraction studies reported that only 87% of the Si sites were occupied [37], while the rest were occupied by Bi3+ ions, with oxygen vacancies as charge compensating defects [38]. Both types of defect are present in scheme (ii). In other experimental work, neutron diffraction studies [39-40] have suggested the existence of Si ions with an effective charge lower than 4. This also indirectly confirms the existence of Bi3+ antisite defects.

The most energetically favourable intrinsic defects in Bi12SiO20, as reported in the present work, are responsible for a series of properties including the optical absorption shoulder, high photosensitivity and photorefractive behaviour. One possible explanation for the optical absorption shoulder and the high photosensitivity is the presence of local centres formed by the antisite Bi3+ formed close to a hole centre [41]. On the other hand, the photorefractive properties are related to the antisite Bi3+ and hole centre. The light induces charge carrier migration (an electron from the antisite Bi3+ centre) following by consecutive trapping by hole defects [42].

All the intrinsic defect solution energies in the Bi4Si3O12 phase are higher than in the Bi12SiO20 phase. This behaviour is explained by the higher density of atoms in the unit cell of Bi4Si3O12 compared with Bi12SiO20. With a compact lattice, the distance between ions is shorter, and consequently, the formation of interstitials or vacancies causes a large deformation around the defect, leading to a higher energy cost associated with the defect formation.

The most energetically favourable form of disorder in the Bi4Si3O12 phase is the oxygen Frenkel, following by Schottky, anti-Schottky and scheme (ii) defects. A range of possibilities is predicted since the energy differences between them are small, indicating that they may coexist in the matrix, but in much lower concentration as compared to the Bi12SiO20 phase. The Schottky, anti-Schottky and scheme (ii) energies are only around 0*.*2 eV higher than the oxygen Frenkel. On the other hand, intrinsic defects involving Bi3+ and Si4+ in interstitial positions (Frenkel Bi and Ti type defects) all have much higher solution energies than the others.

Previous modelling work on the bismuth germanates (Bi4Ge3O12) [18] reported the most energetically favoured intrinsic defect to be the Bi antisite, followed by the oxygen Frenkel defect, which contrasts with the results for Bi4Si3O12 reported here. One possible explanation is that the Si-O tetrahedra are much more closed packed than the Ge-O tetrahedra due to the ionic size of Si4+ as compared to Ge4+. This, in turn, allows the Bi ion to fit easier in the Ge site of Bi4Ge3O12 than in the Si site of Bi4Si3O12. That effect is not crucial for the 12-1-20 phases because the lattice is not so packed and there is some space for the Si site to relax, accommodating Bi ions.

* 1. ***Incorporation of rare earth dopants***

In this section, extrinsic defects generated by trivalent rare earth ions doped into Bi12SiO20 and Bi4Si3O12 have been considered. In the BSO compounds, the dopant ion can substitute at either the Bi3+ or the Si4+ site, and more than one form of charge compensation is possible, where it is necessary. Four schemes of dopant incorporation are considered: (i) incorporation at the Bi3+ site (), where no charge compensation is required; (ii) incorporation at the Si4+ site with oxygen vacancy compensation (); (iii) incorporation at the Si4+ site with bismuth interstitial compensation (); (iv) incorporation at the Si4+ site with trapped hole compensation (). In order to calculate the energy involved in the incorporation of rare earth ions into both compounds, the formation energies of all defects related to the above mechanisms were obtained and given in the Table 8. The energies (substitution energies) have been calculated from the formation energies of the separate defects. The formation energy is then converted to a solution energy, which is the total energy involved in the doping process, including the terms needed for charge compensation when necessary, using a new method recently reported [43].

In previous papers (see e.g. [25]), solution energies have calculated in the infinite dilute limit. In the new method, the incorporation of a particular dopant concentration into the crystal is considered. Both methods are very useful for providing information about where dopants are incorporated, and with which charge compensation mechanism (if needed), but the second one provides additional information on the solubility of dopants. Both methods have been described in more detail in previous papers (see e.g. [25], [43]), but the new method is described briefly below.

The method used mimics, as far as possible, the experimental procedure involved in carrying out the doping. The reactants will be the oxides Bi2O3, SiO2 and M2O3 (where M is a rare earth element) mixed in the appropriate stoichiometric quantities to form the doped compound. As an example, consider doping Bi12SiO20 with a rare earth dopant, M3+, assuming that it is incorporated at the Bi3+ site. The reaction is:



Where the solution energy is given by the following expression:



And:



In the above expressions, Elatt [Bi12SiO20], Elatt [Bi2O3], Elatt [SiO2] and Elatt [M2O3] are lattice energies, E [MBi] is the defect formation energy, and x is the mole fraction of dopant. In writing the second equation, which is the key part of the method, it is assumed that each one of the x mol% of MBi defects is dissolved in the Bi12SiO20 matrix with no interaction between them. So the total energy of the defective lattice is just the lattice energy of the “perfect” surrounding lattice, represented by the first term in the left hand side of the equation, plus the energetic cost to create each one of the defects (E[MBi ]) multiplied by the concentration of the defect x.

The following reactions represent the doping of mole fraction x of M at the Bi or Si sites in Bi12SiO20:

1. Substitution of M3+at Bi3+ sites.







1. Substitution of M3+at Si4+ sites with oxygen vacancy compensation.







1. Substitution of M3+at Si4+ sites with interstitial bismuth compensation.







1. Substitution of M3+at Si4+ sites with hole compensation (resulting from oxidation).







The following reactions represent the doping of mole fraction x of M at the Bi or Si sites in Bi4Si3O12:

1. Substitution of M3+at Bi3+ sites.







1. Substitution of M3+at Si4+ sites with oxygen vacancy compensation.







1. Substitution of M3+at Si4+ sites with interstitial bismuth compensation.







1. Substitution of M3+at Si4+ sites with hole compensation (resulting from oxidation).







From the set of equations above, the solution energies ion for 1% M2O3 in the Bi12SiO20 and Bi4Si3O12 phases were calculated and presented in Table 9 and 10, respectively. As can be seen, there is an energetic preference for incorporation at the Bi3+ site in both phases. Two factors may be considered to explain this behaviour: (i) the ionic radii and (ii) oxidation number difference between dopant and host sites. The rare earth ion dopants have the same oxidation number and smaller ionic radii than the Bi3+ion (the ionic radii of the rare earth ions varies between 0.861 Å and 1.01 Å, assuming six-fold coordination [44]), and the Bi ion radius is 1.17 Å. On the other hand, the ionic radii differences between the rare earth ions and Si4+ site are around ~0.6-0.8 Å. In addition, the difference in oxidation number creates an additional defect for charge compensation. Thus, the absence of charge compensation contributes to the higher stability of dopants in the matrix. Consequently, there is a lower energy cost in the doping process since fewer defects are involved. It is an interesting point that there is no dependence of the solution energies going along the rare earth series, which suggests that substitution should be independent of the increasing atomic number of the M3+ ion, which is due to the fact that all the rare earth ionic radii are lower than that of the Bi3+ ion. The predominance of incorporation of rare earths at the Bi3+ site is in agreement with the results obtained in previous computational studies on Bi12TiO20 [45] and Bi4Ti3O12 [20]. If incorporation at the Si sites are considered, although not stable, it can be seen that scheme (ii), where the rare earth ions occupy the Si site compensated by oxygen vacancy defects Bi interstitials, is the most energetically favourable, followed by scheme (iii), with compensation by Bi interstitials, and scheme (iv), where compensation is by hole defects.

It can be seen that the incorporation of rare earth dopants in Bi4Si3O12 is more favourable than in Bi12SiO20. This result suggests greater defect solubility in the Bi4Si3O12 phase. Figure 1 shows the solution energy for higher concentrations of M2O3 incorporated at the Bi3+ site in Bi12SiO20 and Bi4Si3O12. It can be seen that the solution energy increases with rare earth concentration in both phases. For 1% and 2% M2O3, in the Bi4Si3O12 phase, all the solution energies are negative, indicating that the rare earth ions are readily soluble in the Bi4Si3O12 lattice. But at concentrations higher than 3% Lu2O3 the solution energies for most rare earth ions are positive, indicating they are not readily soluble at these concentrations. In the Bi4Si3O12 phase, for concentration of 1%, all solution energies are negative, suggesting that defect substitutions are possible up to approximately 2% Lu2O3 concentration. The limit of solubility of rare earth doping in the lattice can be estimate by taking the X values where the solution energies became positive. In Figure 2 the dependence of the concentrations of M2O3 that be incorporated in Bi3+ site as function of the rare earth ionic radii ion for both structures is given. Clearly, the Bi4Si3O12 phase has a higher solubility than Bi12SiO20. Figure 2 leads to the conclusion that the solubility limit for M3+ in Bi12SiO20 is around 1.2 % and around 2.2 % in the Bi4Si3O12 phase.

A range of rare earth doped Bi12SiO20 and Bi4Si3O12 samples have been produced experimentally with dopant concentrations below the solubility limit obtained in the present work. For example, in Bi12SiO20:M3+, the dopant concentration is usually around 0.1 % M3+ [32], and even lower dopant concentrations, around 0.01 % M3+ have also been used [46]. The doping concentration of M2O3 in the melt (Bi4Si3O12 phase) varies from 0.1 to 0.7 % ([30], [47], [48]]. Thus, it can be concluded that it is possible to increase the doping concentration in the melt in both phases. Also, with Bi4Ge3O12 various doping concentrations for Nd (0.3%), Er (1%), Tm (0.4%) and Eu (0.3%) have been used, which are all below the computationally predicted solubility limit [49].

1. **Conclusions**

In this work the Bi12SiO12 and Bi4Si3O12 phases of the Bi2O3-SiO2 system have been investigated using atomistic simulation. Calculated structural and physical properties are in good agreement with experiment. The main intrinsic and extrinsic defects in both phases have been calculated, and the results indicate that the most favourable intrinsic defect in Bi12SiO12 is a Bi3+ ion occupying a Si4+ site compensated by a hole, and the pseudo-Schottky Bi2O3 defect ()), while in the Bi4Si3O12 phase the most stable defect is the oxygen Frenkel. The solubility of rare earth ions was investigated and it was concluded that the incorporation occurs at the Bi3+ site in both phases, with calculated solubility limits of around 1% and 2% for Bi12SiO12 and Bi4Si3O12, respectively.

**Acknowledgements**

The authors wish to acknowledge financial support from CAPES, CNPq, FAPITEC-SE and FAPEMA.

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**Table 1a** – Potential parameters for Bi12SiO20 and Bi4Si3O12.

|  |  |
| --- | --- |
| interaction | Buckingham potential parameters |
| A / eV | ρ / Å | C / eVÅ6 |
| Bi3+ - Bi3+ | 24244.50 | 0.3284 | 0.0 |
| Bi3+ - O2- | 69529.35 | 0.2223 | 0.0 |
| Si4+ - O2- | 1123.907 | 0.32052 | 10.66158 |
| O2- - O2- | 9547.96 | 0.2192 | 32.0 |
|  | three-body parameters |  |
|  | k / eV . rad-2 | θ / degrees |  |
| O2- - Si4+ - O2- | 2.09724 | 109.47 |  |

**Table 1b –** Shell charges and spring constants used to model Bi12SiO20 and Bi4Si3O12.

|  |  |
| --- | --- |
| Parameter | ion |
| Bi3+ | O2- |
| shell charge Y / |e| | -5.51 | -2.04 |
| spring constant k / eV Å-2 | 359.55 | 6.30 |

**Table 2** – Comparison of experimental and calculated lattice parameters

|  |  |  |
| --- | --- | --- |
| Compound | a=b=c / Å | difference / % |
| Experimental | Simulated |
| Bi12SiO20[26] | 10.1040 | 10.2021 | 0.97 |
| Bi4Si3O12[27] | 10.2880 | 10.2130 | -0.72 |

**Table 3 –** Elastic constants and other physical properties for Bi12SiO20 and Bi4Si3O12.

|  |  |  |
| --- | --- | --- |
| Parameter | Bi12SiO20 | Bi4Si3O12 |
| Experimental | Simulated | Experimental | Simulated |
| C11 / GPa | 134.3[28] | 323.8 | 129.8[29] | 356.6 |
| C12/ GPa | 30.6[28] | 26.2 | 29.7[29] | 53.6 |
| C44 / GPa | 26.4[28] | 39.5 | 24.7[29] | 100.2 |
| Bulk Modulus (GPa) | 63.1[29] | 125.4  | - | - |
| n() | - | - | 2.051[29] | 2.34 |

**Table 4 –** Calculated lattice energies for Bi12SiO20 and Bi4Si3O12 and the starting oxides (eV)

|  |  |  |
| --- | --- | --- |
| Compound | ELattice | EL/Bi ion |
| Bi­12­SiO20 | -921.31 | -27.92 |
| Bi4Si3O12 | -672.40 | -35.38 |
| Bi­2­O3 | -129.46 | -25.89 |
| SiO2 | -132.95 | -44.31 |

**Table 5** – Electron-Hole formation in Bi12SiO20 and Bi4Si3O12 (eV)

|  |  |  |
| --- | --- | --- |
| Calculated terms(ES) | Bi12SiO20 | Bi4Si3O12 |
| BiBi=(e´) | 21.35 | 23.87 |
| SiSi=(e´) | 46.23 | 47.13 |
| OO=(h) | 14.43 | 18.97 |
| Intra-atomic terms |  |  |
| Bi2+→e´+Bi3+[36] | 25.56 | 25.56 |
| Si3+→e´+Si4+[36] | 45.14 | 45.14 |
| O-+e´→O2-[35] | 8.199 | 8.199 |
| Equations |  |  |
| e= ESBi+Ee | -4.21 | -1.69 |
| e= ESSi+Ee | 1.09 | 1.99 |
| h=ESO+Eh | 6.23 | 10.77 |
| Egap=h+e | 2.02 | 9.08 |

**Table 6 –** Formation energy of basic defects in Bi12SiO20 and Bi4Si3O12 (eV)

|  |  |  |
| --- | --- | --- |
| Defect | Bi12SiO20 | Bi4Si3O12 |
| VBi | 43.63 | 50.52 |
| VSi | 108.99 | 112.85 |
| VO1 | 16.79 | 23.33 |
| VO2 | 16.75 | - |
| VO3 | 17.62 | - |
| Bii1 | -24.48\* | -24.89\*\* |
| Sii1 | -76.79\* | -71.97\*\* |
| Oi1 | -12.40\* | -12.91\*\* |
| SiBi | -58.59 | -49.85 |
| BiSi | 63.68 | 70.90 |

\*(0.5;0;0)\*\*(0.25;0.25;0.5)

**Table 7 –** Formation energy of intrinsic defects in Bi12SiO20 and Bi4Si3O12 (eV)

|  |  |  |
| --- | --- | --- |
| Defect | Bi12SiO20 | Bi4Si3O12 |
| Frenkel Bi | 9.57 | 12.82 |
| Frenkel Si | 16.10 | 20.44 |
| Frenkel O | 2.18 | 5.21 |
| Schottky | 1.40 | 7.79 |
| Pseudo-Schottky Bi2O3 | 1.61 | 8.31 |
| Pseudo-Schottky SiO2 | 3.18 | 8.85 |
| anti-Schottky | 6.54 | 10.63 |
| Anti-site | 2.55 | 10.53 |
| Scheme (i) | 3.56 | 15.07 |
| Scheme (ii) | 0.57 | 7.78 |
| Scheme (iii) | 3.96 | 11.76 |

**Table 8** – Substitution energies for doping at Si4+ and Bi3+ sites (eV)

|  |  |  |  |
| --- | --- | --- | --- |
| Dopant ion | Bi12SiO20 | Bi4Si3O12 | M2O3 |
| Substitution energy (Bi3+ site) | Substitution energy (Si4+ site) | Substitution energy (Bi3+ site) | Substitution energy (Si4+ site) | Lattice energy of oxides |
| Ce3+ | -0.06 | 63.34 | 2.55 | 67.59 | -129.28 |
| Pr3+ | -0.30 | 62.82 | 2.29 | 66.51 | -130.00 |
| Nd3+ | -0.22 | 62.88 | 2.37 | 66.50 | -129.85 |
| Sm3+ | -0.72 | 62.20 | 1.85 | 65.66 | -131.77 |
| Eu3+ | -1.06 | 61.75 | 1.50 | 65.09 | -132,56 |
| Gd3+ | -1.37 | 61.33 | 1.18 | 64.55 | -133.28 |
| Tb3+ | -1.42 | 61.13 | 1.14 | 64.14 | -133.48 |
| Dy3+ | -1.94 | 60.53 | 0.61 | 63.51 | -134.64 |
| Ho3+ | -2.17 | 60.21 | 0.38 | 63.09 | -135.18 |
| Er3+ | -2.50 | 59.73 | 0.05 | 62.53 | -135.97 |
| Tm3+ | -2.87 | 59.22 | -0.31 | 61.83 | -136.84 |
| Yb3+ | -2.97 | 59.09 | -0.41 | 61.69 | -137.09 |
| Lu3+ | -3.17 | 58.82 | -0.60 | 61.36 | -137.54 |

**Table 9** – The solution energies per defect ion for 1% mol M2O3 in Bi12SiO20 (eV).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Dopant ion |  |  |  |  |
| Ce3+ | -2.483 | -2.462 | -2.410 | -2.391 |
| Pr3+ | -2.482 | -2.463 | -2.412 | -2.393 |
| Nd3+ | -2.482 | -2.464 | -2.412 | -2.393 |
| Sm3+ | -2.477 | -2.461 | -2.409 | -2.390 |
| Eu3+ | -2.476 | -2.461 | -2.410 | -2.391 |
| Gd3+ | -2.476 | -2.462 | -2.411 | -2.391 |
| Tb3+ | -2.475 | -2.463 | -2.412 | -2.392 |
| Dy3+ | -2.475 | -2.463 | -2.412 | -2.392 |
| Ho3+ | -2.474 | -2.464 | -2.412 | -2.393 |
| Er3+ | -2.474 | -2.464 | -2.413 | -2.394 |
| Tm3+ | -2.473 | -2.465 | -2.414 | -2.394 |
| Yb3+ | -2.473 | -2.465 | -2.414 | -2.395 |
| Lu3+ | -2.473 | -2.466 | -2.414 | -2.395 |

**Table 10** – Solution energies per defect ion for 1% mol M2O3 in Bi4Si3O12 (eV).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Dopant ion |  |  |  |  |
| Ce3+ | -8.353 | -8.282 | -8.266 | -8.245 |
| Pr3+ | -8.352 | -8.289 | -8.273 | -8.252 |
| Nd3+ | -8.352 | -8.290 | -8.274 | -8.253 |
| Sm3+ | -8.347 | -8.289 | -8.272 | -8.251 |
| Eu3+ | -8.347 | -8.291 | -8.274 | -8.253 |
| Gd3+ | -8.346 | -8.293 | -8.276 | -8.255 |
| Tb3+ | -8.346 | -8.296 | -8.279 | -8.258 |
| Dy3+ | -8.345 | -8.296 | -8.280 | -8.259 |
| Ho3+ | -8.345 | -8.298 | -8.281 | -8.260 |
| Er3+ | -8.344 | -8.299 | -8.283 | -8.262 |
| Tm3+ | -8.343 | -8.302 | -8.285 | -8.264 |
| Yb3+ | -8.343 | -8.302 | -8.285 | -8.265 |
| Lu3+ | -8.343 | -8.303 | -8.287 | -8.266 |



**Figure 1 –** Solution energies for Lutetium dopant ion as a function of mole fraction of M2O3, assuming incorporation at the Bi site.



**Figure 2 –** Solubility limit of M3+ ions incorporated at the Bi3+ site in Bi4Si3O12 and Bi12SiO20.