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Hole trapping properties of germanium in α-quartz

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Abstract. We present the first calculation of the self-trapping properties of germanium in α-quartz using the classic defect simulation technique. Our calculation suggests that it is easier for a hole to be self-trapped at oxygen ions next to a Ge^{3+} ion than a Ge^{4+} ion, which is in agreement with the experimental results. The hole self-trapping next to Ge^{3+} is accompanied by a large network distortion. Our results indicate that the most favourable hole trapping site is the next-nearest-neighbour oxygen to the Ge^{3+} ion, rather than the nearest-neighbour oxygens. Examining the most favourable hole trapping sites, we suggest that the distortion in the Si–O–Si bond angle plays a more important role in hole self-trapping than that in the Si–O bond length.

1. Introduction

Self-trapping in α-quartz is a challenging problem. Experimentally, neither self-trapped holes (STHs) nor self-trapped electrons (STEs) have been observed [1–7]. Results from our recent Mott–Littleton shell model calculations [8] suggested that it is possible for an STH to be weakly trapped in an oxygen ion with populations of both small and large polarons. Nevertheless, additional stabilization from other factors such as structural variations in amorphous silica are important contributing factors. On the other hand, both STEs and STHs have been observed experimentally in germanium doped silica samples. Hagon *et al* [9] gave a theoretical discussion on the STE and attributed the stabilization factor to the electron correlation effects in the GeO_4 tetrahedron. However, the origin of the trapping mechanism is complex and is not fully understood.

In the present study, we aim to study the properties of STHs in germanium doped α-quartz. There are three possible forms in which germanium can exist in the silica lattice, namely (i) a Ge^{4+} ion, (ii) a Ge^{3+} ion with a compensating alkali metal ion e.g. Na^{+}, (iii) a Ge^{3+} ion, i.e. Ge^{4+} capturing an electron. We perform the Mott–Littleton calculation for the first two cases and discuss the STH mechanisms.

2. Computational method

In the Mott–Littleton calculation, the defective lattice is treated by using a two-region strategy [10]. In this approach the crystal is formally divided into an inner region (region I) and an outer region (region II). In the inner region the lattice configuration is evaluated explicitly while the outer region can be viewed from the defect as a continuum. The displacements within the outer region are due solely to the electric field produced by the total charge of the defect centred at the defect origin. Detailed discussion of this simulation

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technique can be found in [11]. Many of the key ideas and applications are given in the papers honouring 50 years of the Mott–Littleton method [12].

Basically, our simulation is based on the shell model generalization of the Born model of the solid with additional three-body, angle dependent terms. The short-range two-body interactions used in this classic simulation are described by the Born–Mayer potential supplemented by an attractive r^{-6} term:

$$V(r) = A\exp(-r/\rho) - Cr^{-6} \tag{1}$$

where A, ρ and C are constants. The polarizability of individual ions and its dependence on local atomic environment is treated by the shell model [13], in which the outer valence cloud of the ion is simulated by a massless shell of charge Y and the nucleus and inner electrons by a core of charge X. The total charge of the ion is thus $X + Y$, which indicates the oxidation state of the ion. The interaction between core and shell of any ion is treated as being harmonic with a spring constant k and is represented by

$$V(r) = \tfrac{1}{2}kd^2 \tag{2}$$

where d is the relative displacement of the core and shell of ion i. The electronic polarizability of the free ion is thus given by

$$\alpha = Y^2/k. \tag{3}$$

The three-body interactions are expressed as

$$V = \tfrac{1}{2}k_3(\theta - \theta_0)^2 \tag{4}$$

where θ is the angle between the three ions and θ_0 the equilibrium angle.

In this work, the oxygen ions are treated using the shell model while the silicon ions are treated using a rigid model (without a shell). We used the potential parameters A, ρ and C and shell parameters Y and k derived for the α-quartz by Sanders and coworkers [14]. This potential includes a three-body interaction, and it reproduced the structure of α-quartz in good agreement with the experimental data which is successfully applied to calculation of the energies of point defects in quartz [15]. The germanium ions are also treated using a rigid model and sodium ions are treated using the shell model. Their potential parameters were taken from [16] and [15] respectively. All the potential parameters used in this work are given in table 1. We used a radius of the inner region of 10.3 Å, which includes 630 species, and a radius of the interfacial region of 22.3 Å, which includes 6000 species. All the ions in the two regions are fully relaxed in our calculation.

3. Results and discussion

3.1. Hole self-trapping in Ge^{4+} doped α-quartz

Our model system of Ge^{4+} doped α-quartz was made by substituting Ge^{4+} for one of three basis silicon atoms in α-quartz and the system was then run using CASCADE until the system reached equilibrium. This equilibrium system was used as the model system for Ge^{4+} doped α-quartz. The coordinates of atoms in Ge^{4+} doped α-quartz at equilibrium are given in table 2, and the structure of this model system is shown in figure 1(a) (in all the figures

Table 1. Potential parameters.

Shell model parameters			
Ion	k (eV Å^{-2})	Y ($\|e\|$)	
Si	rigid ion		
Ge	rigid ion		
O	74.92	−2.848	
Na	96.44	2.128	
Two-body potential parameters			
Interaction	A (eV)	ρ (Å)	C (eV Å)
O–O	22 764.0	0.1490	27.88
Si–O	1283.9073	0.3205	10.6616
Ge–O	1980.02	0.3172	53.66
Na–O	1226.80	0.3065	0.0
Three-body potential parameters			
Interaction	k_3 (eV rad^{-2})	θ_0 (°)	
O–Si–O	2.097	109.47	
O–Ge–O	0.5861	109.47	

Table 2. The coordinates of atoms in Ge^{4+} doped α-quartz.

Lattice vectors:

$x_1 = 4.819\,15i$

$x_2 = -2.409\,58i + 4.415\,79j - 0.041\,72k$

$x_3 = 5.459\,90k$

Basis positions:

Atom	X	Y	Z
O1	−1.554 90	−1.316 40	−3.827 78
O2	0.362 48	−1.807 80	−1.909 93
O3	−0.006 72	−0.002 42	−0.008 00
O4	−3.964 47	0.707 86	−2.398 30
O5	−2.047 10	1.199 43	−4.316 14
O6	−2.416 30	−0.658 01	−0.758 17
Si	−3.927 46	−0.444 47	−1.282 88
Si	−1.517 89	−0.215 95	0.516 70
Ge^{4+}	−0.624 45	−2.512 16	−3.092 18

shown in this paper, the atoms with interatomic distance less than 2.30 Å are connected by a 'bond' for convenience of showing the structural changes). The substitution of silicon with Ge^{4+} changes the structure slightly. The SiO_4 tetrahedron is almost unchanged but the GeO_4 tetrahedron has a larger Ge–O bond length of about 1.69 Å compared with the Si–O bond length of 1.60–1.61 Å in the SiO_4 tetrahedron.

The defect energy is defined as the energy to create a hole in our model system. We use the experimental fact that the hole is localized on an oxygen atom. Two energy terms are involved in the self-trapping mechanism. The first is elastic energy and the other is electronic energy. The elastic energy is contributed by lattice distortion as well as lattice polarization. Again, the polarization energy is composed of displacement and electronic components. We made an estimate of the two components of polarization energy arising from the localized hole on the oxygen atom by performing two calculations: (i) a 'thermal' calculation in which a full equilibrium of the lattice surrounding the defect is

performed and (ii) an 'optical' calculation in which only relaxation of the shells is allowed. The defect energies corresponding to the 'thermal' and 'optical' calculations in the model system are listed in table 3. We may equate the result of the second calculation to the partly electronic polarization energy surrounding the defect, while the difference between the 'optical' and 'thermal' calculations gives the displacement polarization energy. We note that the displacement polarization is substantial, with a value of about 7.9 eV, while the electronic polarization has a large value of about 2.2–2.4 eV. We have also estimated the formation energy of a hole on an oxygen atom to be about 12.43–12.59 eV, indicating that a large energy is needed to form a hole on an oxygen atom.

Table 3. The calculated defect energies in Ge^{4+} doped α-quartz.

O^- substituting position	Energy (eV)		Displacement polarization energy (eV)	Electronic polarization energy (eV)	Hole formation energy (eV)	Hole trapping energy (eV)
	Thermal	Optical				
O1	21.48	29.15	7.67	2.07	12.73	$0.5E_v - 9.69$
O2	21.47	29.19	7.70	2.06	12.72	$0.5E_v - 9.62$
O3	21.62	29.30	7.68	2.23	12.87	$0.5E_v - 9.97$
O4	21.48	29.17	7.69	2.05	12.73	$0.5E_v - 9.69$
O5	21.47	29.09	7.62	2.03	12.72	$0.5E_v - 9.62$
O6	21.62	29.40	7.68	2.24	12.87	$0.5E_v - 9.97$

We next proceed to calculate the total defect energy E_{vk} arising from a lattice distortion caused by a hole localized on the oxygen atom. In examining the stability of the self-trapped oxygen hole relative to a hole in its lowest-energy state in the valence band of an undistorted crystal, we follow the criteria proposed by Norgett and Stoneham [17] that the hole is self-trapped if the energy

$$E_s = \tfrac{1}{2}E_v + E_{vk} - E_M \tag{5}$$

is negative. Here E_{vk} is the calculated 'thermal' defect energy of the hole, E_v is the width of the valence band in the undistorted crystal, and E_M is the anion Madelung energy. In our case of O^- substituting for O3, E_{vk} is 21.34 eV and E_M is 31.59 eV. The value of E_s can thus be estimated by

$$E_s = \tfrac{1}{2}E_v - 10.25\ \text{eV}. \tag{6}$$

The available experimental and calculated values of E_v for α-quartz are in the range of 20–21 eV [18–21]. We used the smallest value of E_v for the calculation in formula (6) and obtained E_s to be −0.25 eV. The negative value of E_s indicates that self-trapping of a hole on O3 in our model system is energetically favourable. We have also calculated the hole trapping energy E_s for the other hole configurations (see table 3) and found that self-trapping of a hole on O6 is also favourable with an E_s of about −0.23 eV, but self-trapping of a hole on O1, O2, O4 and O5 ions is not favourable.

Figures 1(*a*) and (*b*) shows core positions of some selected ions around the hole site (O3) before and after hole trapping respectively. It is observed that trapping a hole on the oxygen ion gives rise to the displacement of the oxygen ion O^-/O3 itself by 0.15 Å. However, the two nearest silicon ions Si1 and Si3 show large displacements of 0.43 Å and 0.58 Å, respectively. It is noted that both Si1 and Si3 shift away from the oxygen ion O^-/O3

and that the Si3 ion shifts more than Si1 ion. The other three oxygen ions surrounding the Si3 ion (O8, O9 and O10) also show a larger displacement compared with the three oxygen ions surrounding the Si1 ion (i.e. O1, O6 and O7). We calculated the equilibrium geometries (see table 4) for the neutral charged cluster and for the positively charged cluster, which correspond to the structure before and after oxygen O^- substitutes for O3, respectively. We found that both Si1–O3 and Si3–O3 bond lengths change significantly from 1.61–1.62 Å for a neutral configuration to 2.14–2.18 Å for the positively charged configuration, but bond angle Si1–O3–Si3 undergoes only a small change of about 2°, from 136.97° for a neutral configuration to 134.87° for a positive charged configuration. We found that except for the elongation of Si1–O3 and Si3–O3, all the other silicon–oxygen bonds in $Si1O_4$ and $Si3O_4$ tetrahedra are shortened by about 0.5 Å. We also calculated the bond angles in $Si1O_4$ and $Si3O_4$ tetrahedra. We found that bond angles of O1–Si1–O3, O3–Si1–O6 and O3–Si1–O7 decrease by 8–13° whereas the other three angles in the $Si1O_4$ tetrahedron increase by 6–11°. The bond angles of the $Si3O_4$ tetrahedron have similar changes to those in the $Si1O_4$ tetrahedron. All the other bond lengths and bond angles in this model system have smaller changes compared to those mentioned above. Comparing the structure of Ge^{4+} doped α-quartz before and after hole trapping (see figure 1(*a*) and (*b*)), we observed only a small structural difference. This explains why self-trapping energy in Ge^{4+} doped α-quartz is so small: the distortion caused by the hole trapping is not very large.

3.2. *Hole self-trapping in Ge^{3+} doped α-quartz*

Our model system of Ge^{3+} doped α-quartz was made by substituting Ge^{3+} for one of three basis silicon atoms in α-quartz ion with a charge compensating alkali metal ion Na^+. The system was run using CASCADE until it reached equilibrium and the equilibrium system was then used as the model system. The coordinates of atoms in Ge^{3+} doped α-quartz at equilibrium are given in table 5 and the structure of this model system is shown in figure 2(*a*). Table 6 shows the calculated defect energies in Ge^{3+} doped α-quartz. Unlike the case in Ge^{4+} doped α-quartz, O^- substituting for O3 causes a huge displacement polarization energy of 15.39 eV and a large electronic polarization energy of 2.52 eV. The calculated hole formation energy at the O3 site is small, with a value of 4.82 eV. The hole trapping energy E_s is $0.5E_v - 18.03$ eV. No matter what value of E_v for α-quartz (20–21 eV [18–21]) we use, the hole trapping energy E_s will be negative, indicating that an oxygen hole can be self-trapped at the O3 site in Ge^{3+} doped α-quartz. For the other five oxygen hole configurations, we found similar results, that an oxygen hole can be self-trapped in Ge^{3+} doped α-quartz (see table 6). It is surprising to find that the most favourable oxygen hole self-trapping site is not the nearest oxygen site to the Ge^{3+} ion (O1, O2, O4 and O5 sites), but the O3 site, the next-nearest neighbour oxygen to the Ge^{3+} ion with a Ge–O3 distance of 3.77 Å.

Compared with the structure of Ge^{3+} doped α-quartz before oxygen hole trapping (see figure 2(*a*)), the structural change caused by oxygen hole trapping is apparent (see figure 2(*b*)). The O^-/O3 is found to have a large displacement of 1.40 Å. Both Si1 and Si3 have large displacements of about 1 Å as well. The Si1–O3 bond length increases from 1.62 Å before hole trapping to 2.17 Å after hole trapping. The Si3–O3 bond seems to be broken: the distance of Si3–O3 increases significantly from 1.63 Å before hole trapping to 3.04 Å after hole trapping. We found that most atoms have a displacement greater than 0.5 Å, and some even have larger displacements, for example, Na1 has a displacement of 2.43 Å and Na3 has a displacement of 1.56 Å. These large atom displacements cause the large structural changes shown in table 7. The most obvious changes are the changes of coordination number. For example, before hole trapping the Si1 and Ge^{3+} ions have a

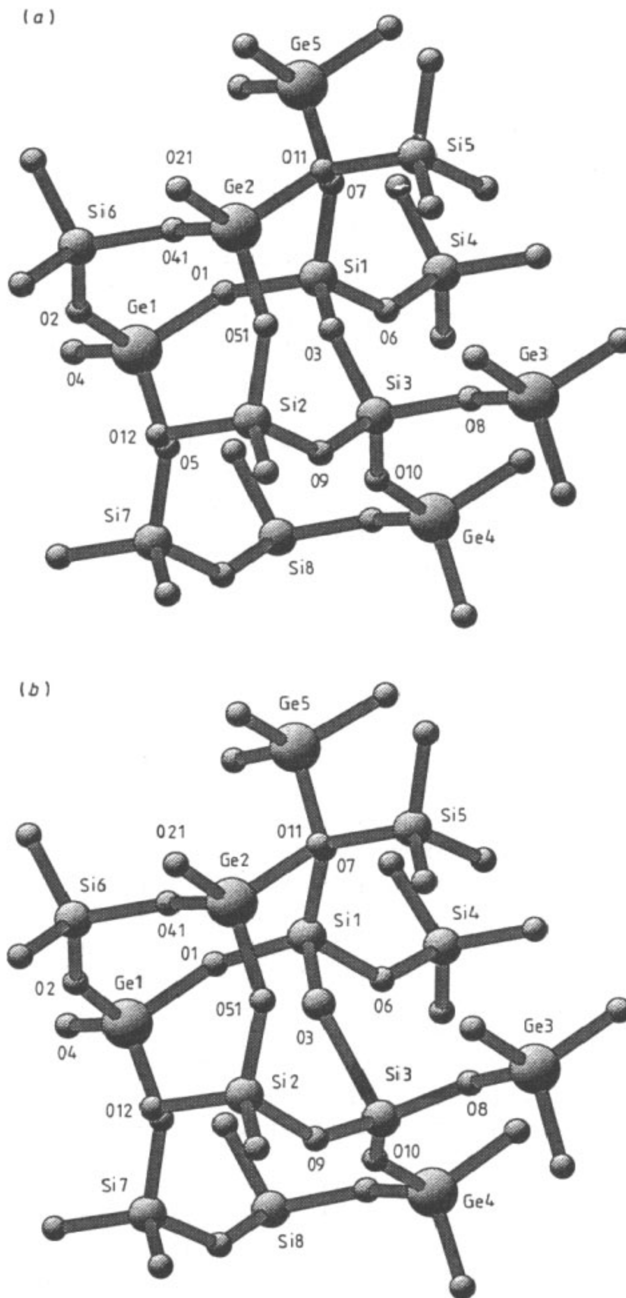

Figure 1. The structure of Ge^{4+} doped α-quartz (*a*) before and (*b*) after oxygen hole trapping at the O3 site. (Note that the atoms with interatomic distance less than 2.30 Å are connected by a 'bond' for convenience of showing the structural changes.)

coordination of four and the O1 ion has a coordination of two, but after hole trapping, the Si1 has a coordination of six, the Si3 has a coordination of five and the O1 has a coordination

Table 4. Equilibrium geometry for the neutral and positively charged cluster (O hole at O3 site) in Ge^{4+} doped α-quartz. Bond lengths are given in units of ångströms and bond angles are given in units of degrees.

Bond length	Neutral	Positive	Bond angle	Neutral	Positive
Ge1–O1	1.6842	1.7220	O1–Ge1–O2	109.37	108.35
Ge1–O2	1.6934	1.6729	O1–Ge1–O4	112.93	108.66
Ge1–O4	1.6842	1.6683	O1–Ge1–O5	108.20	107.19
Ge1–O5	1.6934	1.6820	O2–Ge1–O4	108.20	111.21
			O2–Ge1–O5	108.70	110.58
			O4–Ge1–O5	109.37	110.71
Si1–O1	1.6042	1.5516	O1–Si1–O3	109.87	96.53
Si1–O3	1.6182	2.1363	O1–Si1–O6	109.76	117.89
Si1–O6	1.6211	1.5790	O1–Si1–O7	109.50	119.27
Si1–O7	1.5913	1.5483	O3–Si1–O6	107.75	96.84
			O3–Si1–O7	108.88	100.55
			O6–Si1–O7	111.05	117.16
Ge2–O11	1.6842	1.6808	O11–Ge2–O21	109.37	109.01
Ge2–O21	1.6934	1.6912	O11–Ge2–O41	112.93	112.82
Ge2–O41	1.6842	1.6818	O11–Ge2–O51	108.20	108.44
Ge2–O51	1.6934	1.7069	O21–Ge2–O41	108.20	107.86
			O21–Ge2–O51	108.70	109.23
			O41–Ge2–O51	109.37	109.42
Si3–O3	1.6238	2.1770	O3–Si3–O8	109.86	98.66
Si3–O8	1.6042	1.5586	O3–Si3–O9	107.08	93.65
Si3–O9	1.6139	1.5648	O3–Si3–O10	111.29	98.56
Si3–O10	1.5913	1.5466	O8–Si3–O9	110.04	119.03
			O8–Si3–O10	109.50	116.33
			O9–Si3–O10	109.03	121.13
Si2–O51	1.5913	1.5799	Si1–O3–Si3	136.97	134.87
Si4–O6	1.6139	1.6592	Ge1–O1–Si1	143.22	151.61
Si5–O11	1.6042	1.6057			
Si6–O2	1.5931	1.5945			
Si7–O5	1.5913	1.5977			
Ge3–O8	1.6842	1.7295			
Ge4–O10	1.6934	1.7455			
Ge5–O7	1.6934	1.7415			

of six. This shows that some new bonds are formed (in this paper we define two atoms with an atom–atom distance less than 2.30 Å as bound atoms), for example, Si3–O1, Si3–O5, O3–O8, O1–O8 and Na3–O41. The large displacement polarization energy of 15.39 eV can be attributed to this large lattice distortion caused by oxygen hole trapping. We noted that other oxygen hole configuration also caused similar large lattice distortions (which are not shown in this paper). This large lattice distortion causes the displacement polarization to be greater than the hole formation energy, leading to the oxygen hole self-trapping.

4. Discussion

The difference in response to oxygen hole trapping in Ge^{4+} and Ge^{3+} doped α-quartz may be attributed to their different structural environment. Table 8 shows the comparison of

Table 5. Coordinates of atoms in Ge^{3+} doped α-quartz.

lattice vectors:
$x_1 = 4.8707i$
$x_2 = -2.4353i + 4.2181j$
$x_3 = 5.37780k$

Basis positions:

Atom	X	Y	Z
O1	−1.585679	−1.13536	−3.75842
O2	0.25670	−2.19229	−1.60377
O3	−0.00060	0.00313	0.00047
O4	−4.32446	0.16291	−2.47493
O5	−2.31496	1.12834	−4.48427
O6	−2.473630	−0.84795	−0.81445
Si	−4.05993	−0.73713	−1.21068
Si	−1.57105	−0.14340	0.38305
Ge^{3+}	−0.91859	−2.60259	−2.93260
Na	−3.67577	−1.42715	−3.09016

calculated equilibrium neutral geometry of α-quartz, Ge^{4+} doped α-quartz and Ge^{3+} doped α-quartz (note that the Si site in α-quartz is equivalent to the Ge1 site in germanium doped α-quartz). For our calculated α-quartz, there are only two different Si–O bonds with the bond lengths of 1.6048 Å and 1.6109 Å. The O–Si–O bond angles in the SiO_4 tetrahedron range from 108.49° to 110.94°, and the Si–O–Si bond angle is 141.56°. In Ge^{4+} doped α-quartz, the Si ion is substituted by the Ge1 ion. The bond lengths in the GeO_4 tetrahedron increase by 0.08 Å each compared with the bond lengths in the SiO_4 tetrahedron. The Ge1–O bond lengths range from 1.6842 Å to 1.6934 Å. The O–Ge1–O bond angles also change, ranging from 108.20° to 112.93°. Comparing the $Si1O_4$ tetrahedron in α-quartz and in Ge^{4+} doped α-quartz, the difference is found to be small, but the Si1–O3–Si3 bond angle in Ge^{4+} doped α-quartz decreases by about 4.5° to a value of 136.97°, whereas the Ge1–O1–Si1 bond angles in Ge^{4+} doped α-quartz change little, increasing only by about 1.5° to a value of 143.22°. We found large structural changes in Ge^{3+} doped α-quartz. The Ge1–O bond lengths are 1.8122–1.9299 Å, 0.2–0.3 Å increments compared with the Si–O bond lengths in α-quartz. The O–Ge1–O bond angles change significantly, ranging from 92.8° to 124.70°. The bond lengths in the $Si1O_4$ tetrahedron in Ge^{3+} doped α-quartz are in the range of 1.5593–1.6564 Å; the difference in the bond lengths is much more than that in α-quartz and in Ge^{4+} doped α-quartz. The O–Si1–O bond angles also change a great deal, ranging from 104.37° to 117.83°. The most significant changes occur in the Si–O–Si bond angles. We observed that the Si1–O3–Si3 bond angle decreases down to 127.99° and Ge1–O1–Si increases to 149.33°.

Comparing the changes in the Si–O3 bond length and the Si1–O3–Si3 bond angle in α-quartz, Ge^{4+} doped α-quartz and Ge^{3+} doped α-quartz, shows that the changes in the Si–O3 bond length in Ge^{4+} doped α-quartz and in Ge^{3+} doped α-quartz are 0.84% and 1.17% respectively, whereas the changes in the Si1–O3–Si3 bond angle in Ge^{4+} doped α-quartz and in Ge^{3+} doped α-quartz are 3.25% and 9.59% respectively. We noted that the structural change in Ge^{3+} doped α-quartz is much larger than that in Ge^{4+} doped α-quartz, and the change in the Si1–O3–Si3 bond angle is much larger than the change in the Si1–O3 bond length. It appears that the greater ease of trapping an oxygen hole in Ge^{3+} doped α-quartz than in Ge^{4+} doped α-quartz is due to the fact that Ge^{3+} doped α-quartz has a larger lattice distortion than Ge^{4+} doped α-quartz. We also noted that in Ge^{3+} doped α-quartz O1 has a larger change in bond length but a smaller change in bond angle (the Ge1–O1 bond length

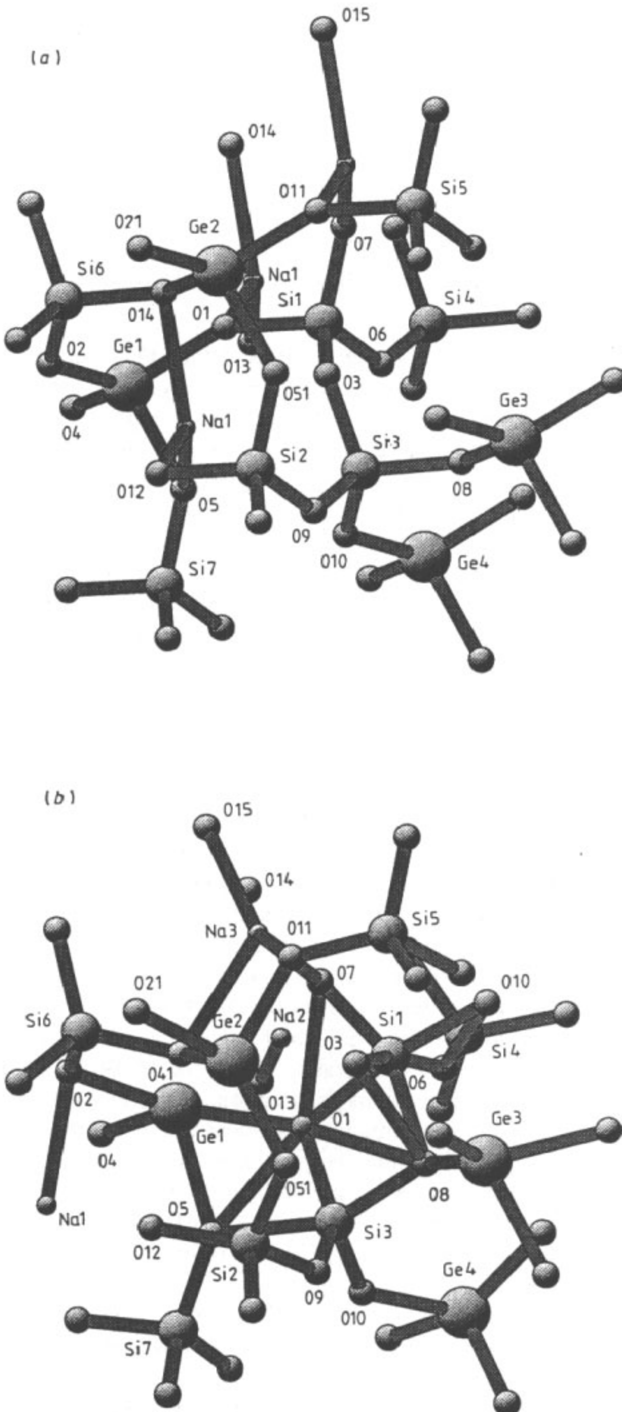

Figure 2. The structure of Ge^{3+} doped α-quartz (*a*) before and (*b*) after oxygen hole trapping at the O3 site. (Note that the atoms with interatomic distance less than 2.30 Å are connected by a 'bond' for convenience of showing the structural changes.)

Table 6. The calculated defect energies in Ge^{3+} doped α-quartz.

O^- substituting position	Energy (eV) Thermal	Energy (eV) Optical	Displacement polarization energy (eV)	Electronic polarization energy (eV)	Hole formation energy (eV)	Hole trapping energy (eV)
O1	15.29	26.79	11.50	2.36	6.54	$0.5E_v - 13.71$
O2	17.04	26.61	9.57	2.85	8.29	$0.5E_v - 12.85$
O3	13.57	28.96	15.39	2.52	4.82	$0.5E_v - 18.03$
O4	17.94	27.45	9.51	2.76	9.19	$0.5E_v - 12.57$
O5	16.35	26.63	10.28	2.76	7.60	$0.5E_v - 13.28$
O6	14.59	28.25	13.66	2.38	5.84	$0.5E_v - 16.02$

is 1.8122 Å and the Ge1–O1–Si1 bond angle is 149.33°) than O3 (the Si1–O3 bond length is 1.6235 Å and the Si1–O3–Si3 bond angle is 127.99°). Hence, O3 traps an oxygen hole more easily than O1 as our results revealed. It appears that the change in bond angle plays a more important role in trapping an oxygen hole than the change in bond length.

Hayes and Jenkin [2, 3] identified a hole trap in α-quartz where the hole is localized on a bridging oxygen with one nearest-neighbour germanium ion. We found that in Ge^{3+} doped α-quartz the O3 and O6 sites are the most favourable hole trapping sites, which are the next-nearest neighbours to the germanium ion. However, the other four nearest-neighbour oxygen sites to Ge^{3+} (O1, O2, O4 and O5) can also trap the oxygen hole, but these sites are not the most favourable ones. For example, the hole trapping energies at O3 and O6 sites are $0.5E_v - 18.03$ eV and $0.5E_v - 16.02$ eV respectively, whereas the hole trapping energies at the other four oxygen sites range from $0.5E_v - 12.57$ eV to $0.5E_v - 12.71$ eV. Although O3 is not the nearest neighbour to the germanium ion, we found that it moves closer to the Ge2 and Ge3 ions after hole trapping on O3. The Ge2–O3 distance changes from 3.69 Å before hole trapping to 2.56 Å after hole trapping, and the Ge3–O3 distance changes from 4.08 Å before hole trapping to 2.58 Å after hole trapping. It seems that the most favourable hole trapping site is an oxygen near to two Ge^{3+} ions. This result is in line with the experimental finding [3] that a hole trapped on an oxygen bonded to two nearest germanium ions provides a deeper hole trap than a single germanium ion. We noted that both O3 and O6 are the oxygens bridging a silicon rather than a germanium ion. The reason O3 and O6 are more favourable to trap the hole may be attributed to the large lattice distortion. For example, in Ge^{3+} doped α-quartz the Si1–O3–Si3 bond angle changes by 9.59% whereas the change in the Ge1–O1–Si1 bond angle is 5.49%. The hole trapping on the O3 causes the larger displacement polarization energy of 15.39 eV compared with the hole trapped on the O1, with a displacement polarization energy of 11.50 eV. Even for the four nearest-neighbour oxygens to germanium, the O1 and O5 are more favourable to trap a hole than the O2 and O4. The hole trapping energies at the O1 and O5 are $0.5E_v - 13.71$ eV and $0.5E_v - 13.28$ eV respectively, whereas the O2 and O4 have the respective lower hole trapping energies of $0.5E_v - 12.85$ eV and $0.5E_v - 12.57$ eV. We found a similar result in Ge^{3+} doped α-quartz: the O3 and O6 ions are slightly more favourable to trap an oxygen hole than the other four oxygen ions.

It is noted that the STH self-trapping energy at O3 in Ge^{4+} doped α-quartz (−0.25 eV) is similar to our calculated STH self-trapping energy at oxygen ions in pure α-quartz (−0.41 eV) [8]. However a STH is not observed experimentally in α-quartz whereas it is observed in germanium doped α-quartz. This is probably due to the fact that all the nearest-neighbour oxygen sites to Si are equivalent in terms of hole trapping ability. This means that the STH jumps more easily to the next trapping site, leading to ease of migration of the STH in α-quartz. So the STH in α-quartz is very mobile and not easy to observe. In Ge^{4+} doped

α-quartz the trapping abilities of different neighbour oxygens are different. Some oxygen sites are able to trap an STH (e.g. O3 and O6) but others are not. This reduces the ease of migration of the STH to the next trapping site, i.e. the STH may stay in some site for a longer time. This implies that the STH in Ge^{4+} doped α-quartz appears more 'localized', so it is easier to observe by experiment.

Table 7. Equilibrium geometry for the neutral and positively charged clusters in Ge^{3+} doped α-quartz. Bond lengths are given in units of ångströms and bond angles are given in units of degrees.

Bond length	Neutral	Positive	Bond angle	Neutral	Positive
Ge1–O1	1.8122	1.9774	O1–Ge1–O2	113.20	151.53
Ge1–O2	1.8869	1.8951	O1–Ge1–O4	124.70	126.10
Ge1–O4	1.8060	1.9207	O1–Ge1–O5	92.08	65.92
Ge1–O5	1.9299	2.0868	O2–Ge1–O4	111.08	82.37
Ge1–Na1	2.6054	2.6772	O2–Ge1–O5	104.91	116.32
			O4–Ge1–O5	106.86	95.23
Si1–O1	1.5852	1.7533	O1–Si1–O3	104.37	86.51
Si1–O3	1.6235	2.1726	O1–Si1–O6	107.04	99.47
Si1–O6	1.6564	1.6437	O1–Si1–O7	104.52	86.23
Si1–O7	1.5593	1.5976	O3–Si1–O6	113.22	161.48
Si1–O8		1.9690	O3–Si1–O7	117.83	89.46
Si1–O10		1.7575	O6–Si1–O7	108.86	108.32
Ge2–O11	1.8100	1.8438	O11–Ge2–O21	113.20	91.76
Ge2–O21	1.8869	1.9173	O11–Ge2–O41	124.70	97.11
Ge2–O41	1.8060	1.9433	O11–Ge2–O51	92.08	124.14
Ge2–O51	1.9299	1.8307	O21–Ge2–O41	111.08	97.82
			O21–Ge2–O51	104.91	134.43
			O41–Ge2–O51	106.86	103.60
Si3–O3	1.6329	3.0365	O3–Si3–O8	104.71	47.91
Si3–O8	1.5742	1.7307	O3–Si3–O9	109.37	84.77
Si3–O9	1.6387	1.6789	O3–Si3–O10	117.34	156.44
Si3–O10	1.5742	1.5568	O8–Si3–O9	113.28	98.18
Si3–O1	3.7297	1.7038	O8–Si3–O10	106.23	109.06
Si3–O5	3.2310	1.9305	O9–Si3–O10	106.12	106.40
O1–O5	2.6940	2.2120	Si1–O3–Si3	127.99	61.61
O1–O8	6.2826	2.2597	Ge1–O1–Si1	149.23	131.16
O1–O7	2.4866	2.2931			
O3–O8	5.2621	2.2738			
Na2–O1	2.1152	2.6211			
Na2–O13	2.0636	2.1397			
Na2–O14	2.2327	2.3566			
Na3–O11	2.1152	2.1273			
Na3–O7	2.0636	2.2926			
Na3–O15	2.2327	2.2920			
Na3–O41	3.4835	2.2184			

Table 8. A comparison of the calculated equilibrium neutral geometry of α-quartz, Ge^{4+} doped α-quartz and Ge^{3+} doped α-quartz. (Note that the Si site in α-quartz is equivalent to the Ge1 site in germanium doped α-quartz.)

	Bond length (Å)		Bond angle (°)	
α-quartz	Si–O1	1.6048	O1–Si–O2	110.94
	Si–O2	1.6109	O1–Si–O4	108.55
	Si–O4	1.6048	O1–Si–O5	108.49
	Si–O5	1.6109	O2–Si–O4	108.49
			O2–Si–O5	109.42
			O4–Si–O5	110.94
	Si1–O1	1.6109	O1–Si1–O3	110.94
	Si1–O3	1.6048	O1–Si1–O6	109.42
	Si1–O6	1.6109	O1–Si1–O7	108.49
	Si1–O7	1.6048	O3–Si1–O6	108.49
			O3–Si1–O7	108.55
			O6–Si1–O7	110.94
			Si1–O3–Si3	141.56
			Si–O1–Si1	141.56
Ge^{4+} doped α-quartz	Ge1–O1	1.6842	O1–Ge1–O2	109.37
	Ge1–O2	1.6934	O1–Ge1–O4	112.93
	Ge1–O4	1.6842	O1–Ge1–O5	108.20
	Ge1–O5	1.6934	O2–Ge1–O4	108.20
			O2–Ge1–O5	108.70
			O4–Ge1–O5	109.37
	Si1–O1	1.6042	O1–Si1–O3	109.87
	Si1–O3	1.6182	O1–Si1–O6	109.76
	Si1–O6	1.6211	O1–Si1–O7	109.50
	Si1–O7	1.5913	O3–Si1–O6	107.75
			O3–Si1–O7	108.88
			O6–Si1–O7	111.05
			Si1–O3–Si3	136.97
			Ge1–O1–Si1	143.22
Ge^{3+} doped α-quartz	Ge1–O1	1.8122	O1–Ge1–O2	113.20
	Ge1–O2	1.8869	O1–Ge1–O4	124.70
	Ge1–O4	1.8060	O1–Ge1–O5	92.08
	Ge1–O5	1.9299	O2–Ge1–O4	111.08
			O2–Ge1–O5	104.91
			O4–Ge1–O5	106.86
	Si1–O1	1.5852	O1–Si1–O3	104.37
	Si1–O3	1.6235	O1–Si1–O6	107.04
	Si1–O6	1.6564	O1–Si1–O7	104.52
	Si1–O7	1.5593	O3–Si1–O6	113.22
			O3–Si1–O7	117.83
			O6–Si1–O7	108.86
			Si1–O3–Si3	127.99
			Ge1–O1–Si1	149.33

5. Conclusion

We have made the first calculation of the self-trapping hole in germanium doped α-quartz using the classic defect simulation technique. Our results show that a hole is easier to self-trap at oxygen ions next to a Ge^{3+} ion than a Ge^{4+} ion, because Ge^{3+} substitution for silicon causes a larger lattice distortion than Ge^{4+} substitution. Our results indicate that the

most favourable hole trapping site is the O3 site, next-nearest neighbour to Ge^{3+}, rather than the nearest-neighbour oxygens to the Ge^{3+} ion. Our results also show that the distortion in the Si–O–Si bond angle plays a more important role in hole self-trapping than that in the Si–O bond length.

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