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Effects of additives in α - and θ -alumina: an *ab initio* study

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Abstract

It is of high fundamental and practical importance to be able to control the formation and stability of the different crystalline phases of alumina (Al_2O_3). In this study, we have used density functional theory methods to investigate the changes induced in the thermodynamically stable α phase and the metastable θ phase as one eighth of the Al atoms are substituted for different additives (Sc, W, Mo, Cr, Cu, Si, and B). The calculations predict that the additives strongly affect the relative stability between the two phases. Most tested additives are shown to shift the relative stability towards, and in some cases completely stabilize, the θ phase, while Cu doping is predicted to increase the relative stability of the α phase. The reasons for these effects are discussed, as are possible implications on the growth and use of doped aluminas in practical applications. In addition, the effects of the additives on bulk moduli and densities of states have been investigated.

1. Introduction

Alumina, Al_2O_3 , is a ceramic material that exists in a variety of structural polymorphs [1], which have diverse properties and therefore find applications in different areas. The thermodynamically stable α phase (corundum) is widely used in wear-resistant and protective coatings, due to its chemical inertness, good mechanical properties, and thermal stability [2], whereas the high surface area and fine particle size of some of the metastable (transition) phases make them useful in catalytic applications [1, 3]. In both cases, the formation of undesired phases constitutes a problem. On one hand, when growing the corundum phase conventional techniques require high temperature ($> \sim 800^\circ\text{C}$) in order to avoid formation of metastable phases [4, 5]. This, in turn, limits the choice of substrate materials that can be used. On the other hand, when using transition aluminas the transformation to a more thermodynamically

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stable phase at elevated temperatures is undesired. Thus, finding ways to control the formation of, and transformations between, the different phases of alumina is of great interest.

Consequently, a considerable amount of work has been devoted to experimental investigations of doped aluminas. In these studies, most additives have been found to have a retarding effect on the transformation from the transition phases to the α phase, e.g., Ce [3], La [3, 6], Cr [7, 8], Er [8], Y [8], Ba [9], Sr [9], and Ca [9]. Fe [7] and Cu [10], however, were found to accelerate the transformation to the stable corundum phase. These examples demonstrate that the transformation properties of doped alumina have been thoroughly investigated experimentally, but no studies of the effects of additives on the free energies of different alumina phases have been reported yet.

In the present paper, we report on a systematic study of the effects of Al substitutions on phase stabilities (bulk energies), bulk moduli, and densities of states (DOS) in α - and θ -alumina as calculated within density functional theory (DFT) [11, 12]. The additives used, mainly chosen based on the size of the ions, are primarily transition metal atoms (Sc, W, Mo, Cr, and Cu), with ionic radii ranging from 75 pm (Sc) to 54 pm (Cu) (radii for 3+ ions in octahedral coordination), as compared to 54 pm for Al^{3+} [13]. Si was used in order to examine the effect of an extra valence electron compared to Al, while B, which has the same valence electronic structure as Al, was chosen as it is considerably smaller with a radius of only 27 pm [13].

2. Method

In this section the model used for the calculations is described. The first part deals with the description of the crystal structures of the two phases studied, and the second part with details of the calculations, such as the settings and approximations used.

2.1. Crystal structures

The primitive cell describing the corundum phase is rhombohedral, contains ten atoms, and the lattice parameters are $a = 5.128 \text{ \AA}$ and $\alpha = 55.33^\circ$ [14]. The O^{2-} ions form a distorted hcp lattice, with Al^{3+} cations filling two thirds of the octahedral interstitial positions [1]. All Al positions are equivalent and the shortest Al–O distances are 1.86 and 1.97 Å [14]. The θ phase has, unlike many other transition phases, a well known crystal structure. The conventional unit cell is monoclinic, contains 20 atoms, and has lattice parameters $a = 11.85 \text{ \AA}$, $b = 2.904 \text{ \AA}$, $c = 5.622 \text{ \AA}$, and $\beta = 103.8^\circ$ [15]. The Al ions are equally distributed between tetra- and octahedral interstitial positions in an approximately fcc array of O anions. Thus, two nonequivalent Al positions exist in this structure. The Al–O distances are 1.71–1.81 Å in the tetrahedral positions, and 1.90–2.03 Å in the octahedral positions [15]. The choice of this phase as a representative for the metastable phases is motivated by its well known crystal structure and structural similarity with other commonly found transition aluminas, e.g., δ and γ , which also have a combination of tetra- and octahedrally coordinated Al atoms and an fcc arrangement of the O ions [1]. The combination of tetra- and octahedrally coordinated Al atoms, with an excess of tetrahedrally coordinated ones, also seems to be present in amorphous alumina [16]. In transition sequences, the θ phase frequently occurs as the final step between other metastable phases and corundum [1].

2.2. Computational details

The calculations were carried out using the Vienna *ab initio* simulation package (VASP) [17] in both the local density approximation (LDA) and the generalized gradient approximation

(GGA) [18]. Ultrasoft pseudopotentials (USPP) [19] were used and a conjugate gradient algorithm was employed for the relaxation of ionic positions. Spin-polarization was included in the cases where it was found to affect the results. All calculations on substitutions were performed on $2 \times 1 \times 1$ primitive unit cells for the α phase and a single conventional unit cell for the θ phase. In these 20-atom cells, one Al atom was substituted, yielding compositions of $\text{Al}_{1.75}\text{X}_{0.25}\text{O}_3$. In the LDA calculations the default value (395.7 eV) of the energy cut-off was used, while a higher value (600 eV) was found to be adequate in the GGA case. The number of k points in the irreducible part of the Brillouin zone was 16 for the 20-atom cells and 10 for the ten-atom unit cell used for pure α -alumina. The k points were chosen according to the Monkhorst–Pack method [20]. The convergence criterion for the calculations was that the difference in total energy between consecutive iterations should be $<10^{-3}$ eV. Convergence tests showed that the expected error in total energy using these settings is <20 meV fu $^{-1}$ (fu = chemical formula unit). A smaller error than this is expected for the energy difference between the phases.

To compare energies of formation, calculations on pure metals and the oxygen molecule were also carried out. For these calculations an energy cut-off of 400 eV was normally used, except for the cases of Cr in the GGA (227 eV), Mo in the GGA (300 eV), B with LDA (500 eV), and the O₂ molecule where the cut-off was 395.7 eV (the default value). Computations on Cr (bcc) were performed on a CsCl structure to enable an antiferromagnetic structure. For all other metals, the primitive unit cells of their respective structures were used. The number of irreducible Monkhorst–Pack k points was 56 for the cubic structures, 96 for Sc (hcp), and 20 for α -B (rh). These settings gave an estimated error in total energies of <2 meV atom $^{-1}$. The calculated structural parameters are in good agreement with experiments [21, 22] with an error of $<5\%$, the GGA calculations giving slightly more accurate results.

The computational procedure for all compounds, including the metals, was as follows. First, total energies were calculated for a set of volumes. To the resulting energy–volume curve, a fourth order Birch–Murnaghan equation of state [23, 24] was fitted, yielding predictions of the bulk modulus and the equilibrium volume. Finally, a calculation was made for the predicted equilibrium volume giving the equilibrium energy and the DOS. From the equilibrium VASP energy, the formation energy of an oxide was calculated by subtracting the energies of the corresponding compositions of metals and oxygen molecules.

It is a well known fact that the two main approximations of the exchange and correlation energy occurring in DFT, LDA and GGA, often give slightly different results for a number of material properties. For example, the LDA is known to often underestimate lattice parameters, i.e., overestimate the bonding strength, whereas the GGA typically does the opposite. Also total energy values are often different in the two approximations, a fact that becomes especially important in the case of alumina phase stability, due to the close energy spacing of the different phases in this material. Bearing this in mind, we have chosen to present both LDA and GGA results throughout this paper. It is, therefore, worthwhile to emphasize that even though the two approximations show different absolute numbers for the energy differences between the phases, the shifts with respect to pure alumina occurring for the different dopants are very similar in most cases, as are the DOSs calculated within the two approximations.

3. Results and discussion

This section is divided into four parts, where the first two deal with the specific effects of the additives on the α and θ phases, respectively. Following this, we discuss the relative stability between the two phases and conclude by presenting the effects of additives on the DOS.

Table 1. Lattice parameters of the α phase of Al_2O_3 (fu = chemical formula unit).

$\alpha\text{-Al}_2\text{O}_3$	Present work		Reference [25]		Reference [14]
	LDA	GGA	LDA	GGA	Expt.
a (\AA)	5.099	5.180	5.080	5.161	5.128
α (deg)	55.61	55.65	55.26	55.27	55.33
V ($\text{\AA}^3 \text{fu}^{-1}$)	42.1	44.2	41.3	43.3	42.6

Table 2. Volume changes compared to pure alumina and energies of formation for differently doped α -aluminas. The formation energies are with respect to solid metals and oxygen molecules (fu = chemical formula unit).

	ΔV (%)		E_{for} (eV fu $^{-1}$)	
	LDA	GGA	LDA	GGA
Al_2O_3	0.0	0.0	-17.02	-15.28
$\text{Al}_{1.75}\text{Sc}_{0.25}\text{O}_3$	+4.6	+4.6	-17.05	-15.35
$\text{Al}_{1.75}\text{W}_{0.25}\text{O}_3$	+5.1	+5.2	-15.30	-13.67
$\text{Al}_{1.75}\text{Mo}_{0.25}\text{O}_3$	+5.0	+5.1	-15.54	-13.93
$\text{Al}_{1.75}\text{Cr}_{0.25}\text{O}_3$	+1.5	+1.7	-16.18	-14.59
$\text{Al}_{1.75}\text{Cu}_{0.25}\text{O}_3$	+1.4	+1.7	-15.17	-13.53
$\text{Al}_{1.75}\text{Si}_{0.25}\text{O}_3$	+2.9	+3.4	-15.74	-14.02
$\text{Al}_{1.75}\text{B}_{0.25}\text{O}_3$	-5.0	-4.9	-16.26	-14.58

3.1. Effects of additives in α -alumina

In order to have a reference point for further investigations, calculations on pure alumina were carried out first. The results obtained for the lattice parameters of the α phase, shown in table 1, are in very good agreement with previous theoretical [25, 26] and experimental findings [14].

Table 2 shows the effects of the additives on equilibrium volumes and formation energies. As can be seen, most additives cause an increase in the equilibrium volume compared to pure alumina. This is expected due to the larger ionic radii of most of the foreign ions. The only substitution yielding a decrease in volume is the small B ion. Also, the formation energies are observed to increase for all additives except Sc, for which this quantity is somewhat lower. This effect can in part be explained by comparing oxygen affinities, which are lower than that of Al for all additives except Sc, as indicated from the formation energies of their respective binary oxides [27]. Another probable cause for the raised formation energies is the lattice disturbances caused by the large ionic radii of most additives. The latter effect can be quantified by looking at the distances between the metal ions and the oxygen octahedra surrounding them. In pure α -alumina, the Al–O distances in the distorted octahedra range from 1.85 to 1.97 \AA (LDA results). When a large atom, such as W, is inserted into the lattice, the octahedra become more distorted, with W–O distances of 2.03–2.11 \AA and Al–O distances of 1.82–2.09 \AA . Thus, quite large distortions occur in the lattice as larger ions are added. An increased spread in the distances between the metal and oxygen ions also occurs for the smaller substitutions, such as B, for which some surrounding O ions move significantly closer to the B ion while others keep or even increase their distance. The increased formation energies indicate a decreased chemical stability of these compounds. Consequently, this is an indication that phase separations might become favourable in these cases, even though further calculations are needed to determine the stability of the doped aluminas relative to separation into other substances. However, it can still be possible to form these compounds as metastable phases by non-equilibrium growth

Table 3. Lattice parameters of the θ phase of Al_2O_3 (fu = chemical formula unit).

θ - Al_2O_3	Present work		Reference [25]		Reference [15]
	LDA	GGA	LDA	GGA	Expt.
a (Å)	11.75	11.85	11.66	11.87	11.85
b (Å)	2.900	2.965	2.881	2.929	2.904
c (Å)	5.575	5.664	5.568	5.657	5.622
β (deg)	104.0	103.7	104.1	104.0	103.8
V (Å ³ fu ⁻¹)	46.1	48.3	45.4	47.7	47.0

Table 4. Volume changes compared to pure alumina and energies of formation for differently doped θ -aluminas. Volume changes and energies of formation are for the substitutions (tetrahedral or octahedral) yielding the lowest total energy. The formation energies are with respect to solid metals and oxygen molecules (fu = chemical formula unit).

	ΔV (%)		E_{for} (eV fu ⁻¹)	
	LDA	GGA	LDA	GGA
Al_2O_3	0.0	0.0	-16.84	-15.29
$\text{Al}_{1.75}\text{Sc}_{0.25}\text{O}_3$	+4.9	+5.2	-16.94	-15.43
$\text{Al}_{1.75}\text{W}_{0.25}\text{O}_3$	+3.8	+4.0	-15.45	-13.94
$\text{Al}_{1.75}\text{Mo}_{0.25}\text{O}_3$	+3.8	+4.7	-15.57	-14.09
$\text{Al}_{1.75}\text{Cr}_{0.25}\text{O}_3$	+1.5	+1.9	-16.02	-14.62
$\text{Al}_{1.75}\text{Cu}_{0.25}\text{O}_3$	+1.1	+1.7	-14.97	-13.50
$\text{Al}_{1.75}\text{Si}_{0.25}\text{O}_3$	+0.9	+1.3	-15.86	-14.26
$\text{Al}_{1.75}\text{B}_{0.25}\text{O}_3$	-5.0	-4.9	-16.17	-14.58

techniques. For example, Al_2O_3 - Cr_2O_3 complete solid solutions have been synthesized by thin film growth [28] even though there is a wide miscibility gap at temperatures below about 1500 K [29].

Calculations of the bulk moduli from energy–volume curve fits give values of 243 GPa (LDA) and 221 GPa (GGA) for pure α -alumina, which compare well with the experimental value of 239 GPa [30]. The differences observed in this quantity as additives are added are fairly small in all cases with changes of less than 12%.

3.2. Effects of additives in θ -alumina

As in the case of α -alumina, the lattice parameters of pure θ - Al_2O_3 , shown in table 3, are in good agreement with earlier findings [15, 25, 26]. The effects on the cell volume, shown in table 4, when Al atoms are substituted for different additives are similar to those observed for the α phase, i.e., most additives cause an increase in this quantity due to their larger ionic radii. Consequently, the trends for the formation energies are similar to those observed for the α phase, as seen from table 4. Note that Sc-doped alumina again is the only compound that has a value similar to that of pure alumina. The increments in formation energy for the dopants are, however, generally smaller for this phase than for the α phase, plausibly because the disturbances introduced by ions with deviating size has a smaller effect on this less dense form of alumina.

In the θ phase, the additives can be placed in either tetrahedral or octahedral positions. Figure 1 shows the calculated energy differences between these two possibilities for the different additives. In the figure, a trend where smaller atoms prefer the less commodious

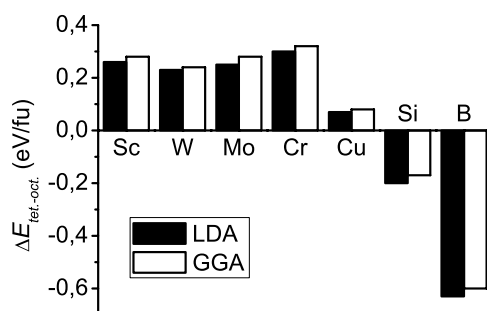


Figure 1. Energy differences between octahedral and tetrahedral substitutions for differently doped θ -aluminas. Values above the zero level indicate that octahedral substitutions are most favourable, whereas values below it indicate that tetrahedral positions are favoured (fu = chemical formula unit).

Table 5. The energy differences between the α and θ phases (differences in formation energies) of differently doped aluminas. Positive values indicate that the α phase is more stable, whereas negative values indicate that the θ phase is more stable (fu = chemical formula unit).

	$\Delta E_{\theta-\alpha}$ (eV fu ⁻¹)	
	LDA	GGA
Al ₂ O ₃	0.18	-0.01
Al _{1.75} Sc _{0.25} O ₃	0.12	-0.08
Al _{1.75} W _{0.25} O ₃	-0.15	-0.27
Al _{1.75} Mo _{0.25} O ₃	-0.03	-0.16
Al _{1.75} Cr _{0.25} O ₃	0.16	-0.03
Al _{1.75} Cu _{0.25} O ₃	0.21	0.02
Al _{1.75} Si _{0.25} O ₃	-0.12	-0.24
Al _{1.75} B _{0.25} O ₃	0.08	0.00

tetrahedral positions can be observed. The effect is particularly strong for the smallest of the tested ions, B. In this compound, the B–O distances in the tetrahedron shrink to 1.47–1.63 Å compared to Al–O distances of 1.74–1.79 Å in pure alumina (LDA results). Such a short bonding length cannot be achieved in the octahedral positions due to the larger number of O ions surrounding the B ion in this case. In fact, as the B atom is placed in an octahedral position in the θ phase, the octahedron is destroyed and only four O atoms are left close to the B atom (B–O distances of 1.51–1.68 Å). For Cu, which has an ionic radius comparable to that of Al, the difference between the two possible configurations is fairly small, while the larger additives prefer the octahedral positions.

The calculated bulk moduli of pure θ -alumina are 198 and 177 GPa with the LDA and GGA, respectively. The effects on this quantity for the doped aluminas are, similarly to the α phase case, relatively small, with changes of less than 8%.

3.3. Relative stability of the α and θ phases

Perhaps the most interesting results of the calculations concern the relative bulk stability of the two phases. The relative stabilities (differences in formation energies) of the studied compounds are shown in table 5. The only experimental value for this quantity that can be found in the literature represents an upper limit for pure alumina. Yokokawa and Kleppa [31] measured the enthalpy difference between the α and δ phases as 0.12 eV fu⁻¹ and, since the δ

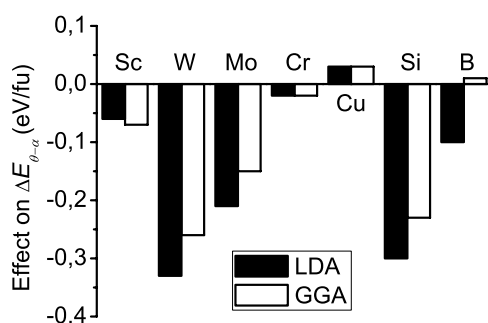


Figure 2. The effect of different additives on the relative stability between the α and θ phases of alumina, i.e., $(\Delta E_{\theta-\alpha})_{\text{doped alumina}} - (\Delta E_{\theta-\alpha})_{\text{pure alumina}}$. Values above the zero level indicate an increased relative stability of the α phase, whereas values below it indicate an increased relative stability of the θ phase (fu = chemical formula unit).

to α transformation goes via the θ phase, this should give an upper limit for $\Delta E_{\theta-\alpha}$. Given that the α phase is the thermodynamically stable form, this energy difference is also expected to be larger than zero. Thus, the true value for pure alumina is probably between the two values obtained with the different approximations in our calculations.

In figure 2, the change in the relative stabilities as compared to pure alumina is plotted for the different additives. We emphasize the trend showing that the larger additives make the θ phase more favourable. This may be explained by the earlier discussed differences in formation energies caused by the disturbances of large ions, since these differences were shown to be smaller in the less dense θ phase. Also the smaller Si and B ions increase the relative stability of the θ phase, partly due to their preference for the tetrahedral positions available in this structure. For W, Mo, and Si doping the θ -stabilizing effect is even predicted to be so large that the θ phase becomes more stable than the α phase according to both the LDA and GGA, as shown in table 5. Thus, these dopants could be suitable for increasing the thermal stability of metastable phases. Our results suggest that doping with W, Mo, or Si could even completely stop the transformation to the α phase. This might, however, be the case only if the added atoms remain in their predicted positions at elevated temperatures. Moreover, at higher temperatures entropy contributions need to be considered. Such effects have been studied previously for pure alumina and shown to increase the relative stability of the θ phase at elevated temperatures [26]. Hence, this raises the question of whether phase separations will occur or not at higher temperatures, a question that clearly needs further study. Furthermore, considering the large effects of additives on alumina phase stability described herein, we suggest that the changes induced in the relative bulk stability of different phases should be considered as a part of the explanation for the previously observed changes in transformation temperatures of doped aluminas. This suggestion is based on the fact that, according to our results, a phase separation is necessary for the θ to α transformation to occur, i.e., the transformation would be controlled by dopant diffusion. If the barrier for diffusion is higher than that of pure alumina, the transformation is likely to be shifted to higher temperatures, as observed in the experiments mentioned in section 1.

The only dopant causing a slight increase in the relative stability in favour of the α phase is Cu. Thus, even though the effect described here is rather small, Cu doping might be a feasible approach in order to facilitate low-temperature α -alumina growth. This is also in agreement with experiments showing that Cu accelerates the θ to α transformation [10].

In this context it is also worth noting that it might be of interest to study the influence of the dopants on surface energies, since α -alumina growth has been found to be highly surface

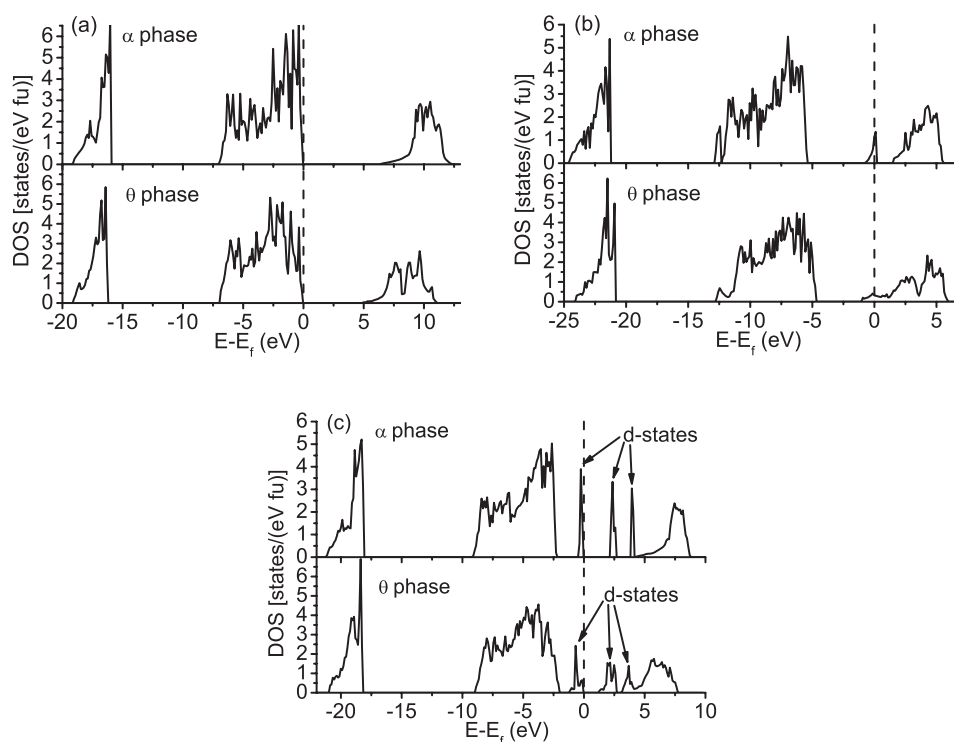


Figure 3. Calculated (LDA) densities of states for (a) Al_2O_3 , (b) $\text{Al}_{1.75}\text{Si}_{0.25}\text{O}_3$, and (c) $\text{Al}_{1.75}\text{Cr}_{0.25}\text{O}_3$, showing the raised Fermi level of Si-doped alumina and the Cr d states occurring in the alumina bandgaps. Note that the Fermi levels are aligned with 0 eV (fu = chemical formula unit).

energy controlled and the formation of metastable phases at the nucleation stage of growth is probably caused by their lower surface energy [32, 33].

3.4. Effects of additives on the electronic structure

The DOSs for pure alumina, displayed in figure 3(a), show, as expected, insulating behaviour for both phases. The calculated bandgaps for the α phase are 6.6 eV (LDA) and 6.2 eV (GGA), respectively, and the corresponding values for θ -alumina are 5.6 and 5.0 eV. These values are underestimations of the measured bandgaps of 8.8 and 7.4 eV for the α and θ phase, respectively [34, 35]. This is a shortcoming of DFT in general and our results agree well with previous calculations [36].

For the B-doping case, only minor changes in the DOS compared to pure alumina occurred, as expected due to the similarities in electronic structure of B and Al. However, as Si was added (DOS shown in figure 3(b)) some changes in the conduction band appeared and the Fermi level was raised to this region. These effects can be attributed to the extra valence electron that Si has compared to Al. Due to the apparent metallic nature of the Si-doped θ phase a test was performed with an increased number of k points, but no significant changes were observed. For the transition-metal-doped aluminas additional states also occurred in, or above, the alumina bandgaps, due to the d electrons of these atoms, as shown for Cr doping in figure 3(c). The positions of these states differ slightly for different additives. So does also

the occupancy of the additional states (and the position of the Fermi level), depending on the number of d electrons localized to the 3+ ions. For example, the Fermi level of Sc-doped alumina is located at the same position as in pure alumina, since Sc only has one 3d electron (and two 4s electrons) and the Sc^{3+} ion consequently has none left.

Further, a general distinction can be made between the DOS of the α and θ phases for the transition-metal-doped aluminas in that the peaks occurring for θ -alumina are more smeared out. This is probably because the added atoms are located closer to each other in this phase than in the corundum structure, due to the short b distance and the periodic boundary conditions, which might result in a slight overlap of the wavefunctions and, consequently, broader peaks. Hence, this effect is probably due to our structural model and does not necessarily reflect practical conditions.

4. Conclusions

DFT calculations have been used to predict the behaviour of α - and θ -alumina as one eighth of the Al atoms are substituted for different additives. The effects on bulk moduli were found to be small, while some changes in the DOS were observed; e.g., additional d states occurred as transition metals were added. Concerning the relative stability of the two phases, only one dopant, Cu, gave a slight increase in the relative bulk stability of the α phase as compared to the θ phase. Most other additives were predicted to have the opposite effect. Smaller atoms, preferring the tetrahedral positions available in the θ phase, were found to increase the relative stability of this phase. So also were the larger additives, plausibly due to the fact that the less dense θ phase adjusts more easily to the disturbance of a large ion. The dopants found to give the largest effects in favour of the θ phase were W, Mo, and Si, for which the energy of the θ phase was predicted to be even lower than that of the α phase. This means that the expected phase transformation to the α phase at elevated temperatures is predicted not to occur, as long as the dopants do not diffuse out of the alumina lattice. In applications, addition of the above-mentioned atoms might provide ways of facilitating low-temperature α -alumina growth or increasing the thermal stability of transition aluminas.

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