The Mechanism of Ionic Conductivity in Stabilized Cubic Zirconia

V. G. Zavodinsky

Institute of Materials Science, Far East Division, Russian Academy of Sciences, Khabarovsk, 680042 Russia
e-mail: vzavod@mail.ru
Received July 18, 2003

Abstract—The electron-density functional method (in the gradient approximation) and the pseudopotential method are used to study the mechanism of ionic conductivity in the cubic phase of zirconia stabilized with magnesium or yttrium. The oxygen-ion migration in the stabilized zirconia is shown to be a two-stage process, which consists in the formation of active oxygen vacancies and in oxygen-ion jumps from one active vacancy to another. The total activation energy of these processes is calculated to be 1.0–1.5 eV, which agrees with experimental data. © 2004 MAIK "Nauka/Interperiodica".

1. INTRODUCTION

Zirconium dioxide (ZrO_2) is of interest as a ceramic material with useful optical, electrical, thermal, strength, and other properties. Phase transitions in it and impurity-induced stabilization have been the subject of many experimental and theoretical studies. At temperatures below 1170°C, the monoclinic phase (*m*) of undoped ZrO_2 is thermodynamically stable. Undoped ZrO_2 is tetragonal (*t* phase) from 1170 to 2370°C and cubic (*c* phase) from 2370°C to the melting point (2706°C) [1, 2]. The cubic phase can be stabilized (i.e., the $c \longrightarrow t$ phase transition temperature can be reduced) by introducing additions such as MgO, CaO, Y_2O_3, etc. Zirconium dioxide is dielectric; its band-gap width was experimentally determined to be 6 eV and is virtually independent of phase type [3].

Pure zirconium dioxide is a good insulator; there is virtually no ionic conductivity in it, since the formation of oxygen vacancies requires a high energy. The stabilization of ZrO_2 with impurities whose degree of ionization is lower than that of Zr results in a certain amount of oxygen vacancies, and stabilized zirconium dioxide conducts an electric current at temperatures above 1000°C [4]. The temperature dependence of the conductivity has a complex two-exponential character, and the conductivity is not a linear function of the number of oxygen vacancies [5–7].

Solier *et al.* [8] proposed a model to explain the conductivity of stabilized zirconium dioxide. According to this model, oxygen vacancies form immobile associates (clusters) at low temperatures and their decomposition requires a certain energy. Thus, the ionic-conductivity activation energy is the sum of two components, the energy E_a of vacancy removal from a cluster and the vacancy migration energy E_m. Analysis of the temperature dependence of the Gibbs energy and the entropy

[9] showed that, for stabilized zirconium dioxide with 12 mol % Y_2O_3, $E_a = 0.52$ eV and $E_m = 0.73$ eV. Another approach taking into account relaxation effects [10] gives $E_a = 0.5$ eV and $E_m = 0.66$ eV.

Recently, Bogicevic *et al.* [11] attempted to theoretically study (from first principles) the mechanism of ionic conductivity in stabilized zirconium dioxide. The authors used the electron-density functional to study the binding of individual oxygen vacancies with impurity atoms and proposed that this binding (rather than clusterization) could be the cause of the complex ionic conductivity. However, they used small cells (from 11 to 23 atoms) for simulation; therefore, the results obtained in [11] have to be refined.

In [12], the electronic structure of zirconium dioxide stabilized with CaO and Y_2O additions was studied using nonempirical calculations. It was shown (by studying the Zr_8O_{16} cell without taking relaxation into account) that the additions change the electronic spectrum only insignificantly. By analyzing the interaction between impurity atoms and oxygen vacancies, it was qualitatively concluded in [12] that this interaction is responsible for a decrease in the ionic conductivity at high concentrations of the additions.

The goal of this work is to study the energy characteristics of individual oxygen vacancies near impurity and Zr ions (by using supercells consisting of up to 96 atoms) and to attempt to describe the ionic conductivity of ZrO_2 without the vacancy-clusterization hypothesis. Moreover, we present the results of calculating the electronic structure of stabilized zirconium dioxide (with allowance for lattice relaxation) and consider the effect of oxygen-ion diffusion on the density of states.
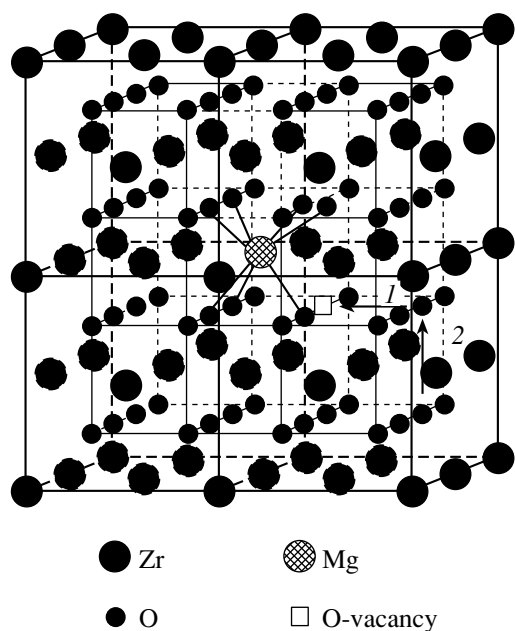
Fig. 1. Schematic atomic arrangement in cubic zirconium dioxide stabilized with 3.125 mol % MgO. Arrows show the motion of oxygen ions during (*1*) the formation of an active vacancy and (*2*) the migration responsible for the electric conduction.

2. CALCULATION PROCEDURE

Calculations were performed using the FHI96MD program [13] based on the electron-density functional theory [14, 15], the pseudopotential method, and a plane-wave basis. To calculate the exchange and correlation energies, we applied the gradient approximation proposed in [16]. Pseudopotentials were constructed using the technique developed in [17] and the FHI98PP program [18] and were checked for the absence of ghost states and the ability to represent the basic lattice characteristics of bulk materials (lattice parameter, modulus of elasticity).

The cut-off energy for a set of plane waves was taken to be 44 Ry, and the main cell of cubic zirconium dioxide was taken to be a $Zr_{32}O_{64}$ supercell. This supercell is shown schematically in Fig. 1 for the case of addition of 3.125 mol % MgO. Because of such a large supercell and the high cut-off energy, we had to consider only one k point in the Brillouin zone when calculating the total energy, namely, the Γ point. To construct

the density of states, the calculated energy levels were broadened using 0.2-eV-wide Gaussian curves.

Using the equation of state from [19], we found the equilibrium lattice parameter a and bulk modulus of elasticity B for the cubic phases ZrO_2, MgO, and Y_2O_3. The results and the corresponding experimental data from [20–25] are listed in Table 1. It is seen from the table that the calculated values agree satisfactorily with the experimental values; that is, the constructed pseudopotentials adequately describe the energetics of interaction between Zr, Mg, and Y atoms and oxygen atoms and can be applied for studying the ZrO_2–MgO and ZrO_2–Y_2O_3 systems.

3. RESULTS AND DISCUSSION

Before studying the mechanism of oxygen-ion migration in the stabilized zirconium dioxide, let us consider the behavior of oxygen vacancies in the pure material. The oxygen vacancy migration energy in pure (undoped) c-ZrO_2 was calculated to be 1.5 eV. However, the formation of an oxygen vacancy requires a higher energy (according to our calculation, the energy required to remove an oxygen atom from the crystal is about 7 eV, which is an extremely high value for thermally activated processes). That is why pure zirconium dioxide is not a conductor.

To study the behavior of oxygen vacancies in stabilized zirconium dioxide, we chose the ZrO_2–MgO system, and, to compare the calculated activation energies with the experimental data, we performed additional calculations for the ZrO_2–Y_2O_3 system. This approach simplifies the simulation, since one oxygen vacancy is associated with one Mg^{+2} ion, whereas in the case of yttrium oxide one oxygen vacancy corresponds to two Y^{+3} ions. Therefore, to describe the ZrO_2–Y_2O_3 system having the same concentration of oxygen vacancies as the ZrO_2–MgO system, we would have to use the double supercell. Moreover, detailed analysis of the ZrO_2–Y_2O_3 system requires study of the effect of the mutual arrangement of an oxygen vacancy and impurity ions, which is beyond the scope of the task set in this work.

To study the effect of the concentration of a stabilizing impurity on the behavior of oxygen vacancies, we considered the $Zr_{31}Mg_1O_{63}$, $Zr_{30}Mg_2O_{62}$, and $Zr_{28}Mg_4O_{60}$ configurations, which correspond to 3.125, 6.25, and 12.5 mol % MgO, respectively. Mg atoms were distributed almost uniformly and randomly in the

Table 1. Calculated and experimental values of the lattice parameter and modulus of elasticity for Zr, Mg, and Y oxides

Parameter	ZrO_2		MgO		Y_2O_3	
	calculation	experiment	calculation	experiment	calculation	experiment
a, nm	0.522	0.513 [20]	0.424	0.421 [21]	1.11	1.06 [24]
B, GPa	215	194 [22]	160	162 [23]	150	137 [25]

superlattice; one oxygen atom was removed from the nearest environment of each Mg atom so that the neighboring impurity atoms had no common bonding oxygen atoms. Moreover, an impurity atom could not substitute for a zirconium atom located at the supercell boundary, since boundary atoms were fixed while optimizing the geometry (the fixation of impurity atoms during simulation was not warranted physically). Such a distribution of impurity atoms and oxygen vacancies cannot be realized unambiguously, since there are several tens of almost equivalent configurations. The long time required for the calculation did not allow us to study all configurations; therefore, we analyzed only three variants of each configuration and found that the scatter of the energy parameters did not exceed 0.1 eV. We give their average values below.

The calculations showed that an oxygen vacancy located near an impurity atom can move around this atom by overcoming a certain migration barrier E_{bar}, whose height depends on the impurity concentration and varies in the range 0.5–0.7 eV (Table 2).

The total energy for a vacancy in any equilibrium position is, of course, the same. However, this type of motion of oxygen vacancies cannot be responsible for through ionic conduction, since oxygen ions do not move from one part of the crystal to another. This motion can only contribute to displacement currents, which are characteristic of high-frequency electric circuits. To provide through conduction, oxygen vacancies must be located near zirconium atoms. Such vacancies can be called active, since they are responsible for a directed transfer of oxygen ions. For an oxygen vacancy to form near a zirconium atom, one oxygen atom must be transferred from the zirconium surrounding to the magnesium surrounding (process *1* in Figs. 1, 2). In this case, the total energy is calculated to be 0.5–0.8 eV higher (Table 3). This increment is the formation energy of active oxygen vacancies E_a. It is an order of magnitude smaller than the oxygen vacancy formation energy in the pure material. The vacancy migration energy E_m, i.e., the barrier between two equivalent positions of an oxygen atom near neighboring zirconium atoms (Fig. 2, process *2*), is equal to 0.5–1.0 eV. Hence, the total activation energy for ionic conductivity E_{tot} is 1.0–1.5 eV. Note that the height E_b of the energy barrier that an oxygen atom must overcome to form an active vacancy is also small. Its value is almost independent of the impurity concentration and is about 1.0 eV; that is, active vacancies can form at the temperatures of ionic conductivity.

Unfortunately, we failed to find experimental data for the conductivity activation energy of magnesium-stabilized zirconium dioxide. Therefore, to check the results obtained in this work, we performed analogous calculations for zirconium dioxide stabilized with 12.5 mol % yttrium. The formation energy E_a of an active vacancy is calculated to be 0.6 eV, and the vacancy migration energy E_m was found to be 0.7 eV;

Table 2. Height of an energy barrier for an oxygen atom moving around a magnesium atom

Concentration MgO, mol %	E_{bar}, eV
3.125	0.73
6.25	0.60
12.5	0.46

Table 3. Energy parameters describing the ionic conduction of stabilized zirconium dioxide

Impurity concentration	E_a, eV	E_m, eV	$E_{tot} = E_a + E_m$, eV
ZrO$_2$–MgO system			
3.125	0.6	1.0	1.6
6.25	0.5	0.5	1.0
12.5	0.8	0.5	1.3
ZrO$_2$–Y$_2$O$_3$ system			
12.5	0.6	0.7	1.2

Note: E_a is the formation energy of an active oxygen vacancy, E_m is the migration energy of an active vacancy, and E_{tot} is the total activation energy for ionic conductivity.

these energies agree well with the experimental data [4, 26]. A comparison of these values with the corresponding values obtained for the ZrO$_2$–MgO system indicates that the energetics of the oxygen-ion migration in stabilized zirconium dioxide depends only weakly on the type of stabilizing impurity.

4. ELECTRONIC STRUCTURE OF STABILIZED ZIRCONIUM DIOXIDE

Magnesium-stabilized zirconium dioxide is known to be a dielectric; however, its electronic structure is poorly understood. There is not even any information on the band-gap width of this material. It is of special interest to study the contribution from oxygen vacan-
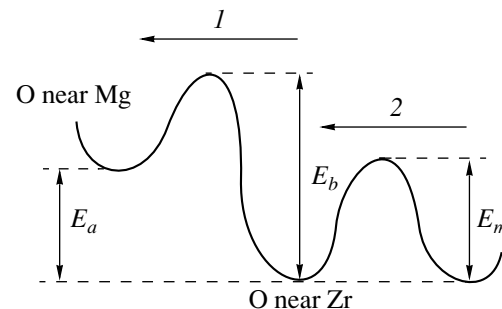

Fig. 2. Schematic diagram for the formation of an active oxygen vacancy (process *1*) and an oxygen-ion jump from one active vacancy to another (process *2*).
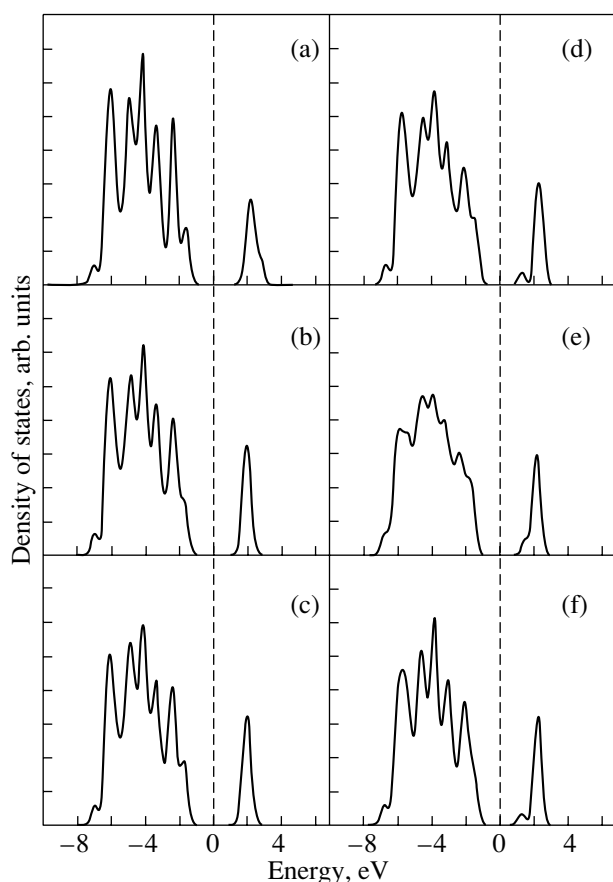
Fig. 3. Density of states for pure and stabilized zirconium dioxide: (a) pure ideal ZrO_2; (b) the same but with an addition of 3.125 mol % MgO, equilibrium configuration; (c) the MgO content is 3.125 mol % and an oxygen ion is located between two active vacancies; (d, e) the MgO contents are 6.25 and 12.5 mol %, respectively; and (f) ZrO_2 with an addition of 12.5 mol % Y_2O_3. Vertical dashed lines show the Fermi level.

cies (especially during their migration) to the electronic structure.

Figure 3a shows the density of states of pure cubic zirconium dioxide, and Figs. 3b–3f shows the density of states for stabilized c-ZrO_2.

The band-gap width for pure cubic zirconium dioxide is calculated to be 3.5 eV, which is significantly lower than the experimental value (6 eV) but agrees well with the values (3.3–4.1 eV) obtained by other authors [27–31] in the context of the electron-density functional theory, which always gives underestimated values of the band-gap width. The density-of-states curve in Fig. 3a is similar to the corresponding curve constructed in [31], where a 96-atom supercell with one point (Γ) in the Brillouin zone was also studied.

An addition of 3.125 mol % MgO (Fig. 3b) changes neither the shape of the density of states nor the band-gap width. As the MgO concentration increases to 6.25 mol % (Fig. 3d), the valence-state distribution

changes slightly and a peak related mainly to oxygen vacancies appears near the conduction-band bottom (1 eV below). A similar peak was detected in [12] for the 0.875 ZrO_2–0.125 CaO system. A further increase in the MgO content to 12.5 mol % (Fig. 3e) leads to broadening of this peak and its mergence with the conduction-band bottom. The valence-state band becomes smoother, and its maxima and minima level off. The density of states of the zirconium dioxide stabilized with 12.5 mol % Y_2O_3 (Fig. 3f) is virtually identical to the density of states corresponding to an addition of 6.25 mol % MgO, which suggests that the electronic structure is mainly affected by oxygen vacancies, which are in the same amount in the ZrO_2–12.5 mol % Y_2O_3 and ZrO_2–6.25 mol % MgO systems.

We also calculated the density of states corresponding to a migrating oxygen ion (when it is directly between two active oxygen vacancies). Figure 3c shows the calculation result for zirconium dioxide stabilized with 3.125 mol % MgO. Comparison with Fig. 3b indicates that, in this case, the electronic structure is identical to that at equilibrium. In particular, it remains a dielectric with the same band-gap width, although the ionic motion is a through charge transfer, i.e., an electric current.

5. CONCLUSIONS

First-principles calculations have shown that oxygen vacancies forming near impurity ions during doping of cubic zirconium dioxide are inactive for oxygen diffusion, since the transfer of oxygen ions bound to neighboring zirconium ions to the vacancies is accompanied by an increase in the total energy of the crystal. However, this transfer generates active oxygen vacancies surrounded by zirconium ions. The migration of these active vacancies does specify the ionic conductivity. Thus, oxygen-ion diffusion in stabilized zirconium dioxide is a two-stage process with a total activation energy of 1.0–1.5 eV.

The band-gap width of cubic zirconium dioxide stabilized with magnesium or yttrium is calculated to be 3.3 eV. The electronic structure of the stabilized ZrO_2 remains virtually unchanged during the motion of oxygen ions from one active vacancy to another.

REFERENCES

1. R. Aldebert and J. P. Traverse, J. Am. Ceram. Soc. **68**, 34 (1985).

2. R. J. Ackermann, S. P. Garg, and E. G. Rauth, J. Am. Ceram. Soc. **60**, 341 (1977).

3. R. H. French, S. J. Glass, F. S. Ohuchi, *et al.*, Phys. Rev. B **49**, 5133 (1994).

4. T. H. Etsel and S. N. Flengas, Chem. Rev. **70**, 339 (1970).

5. Y. Suzuki, T. Takahashi, and N. Nagae, Solid State Ionics **3–4**, 483 (1981).

6. P. Aberland and J. F. Baumard, Phys. Rev. B **26**, 1005 (1982).

7. J. Bauerle and J. Hrizo, J. Phys. Chem. Solids **30**, 565 (1969).

8. J. D. Solier, I. Cachadiña, and A. Dominquez-Rodriguez, Phys. Rev. B **48**, 3704 (1993).

9. I. Cachadiña, J. D. Solier, and A. Dominquez-Rodriguez, Phys. Rev. B **52**, 10872 (1995).

10. C. León, M. L. Licia, and J. Santamaria, Phys. Rev. B **55**, 882 (1997).

11. A. Bogicevic, C. Wolverton, G. M. Crosbie, and E. B. Stechel, Phys. Rev. B **64**, 014106 (2001).

12. V. M. Zaĭnullina and V. P. Zhukov, Fiz. Tverd. Tela (St. Petersburg) **43** (9), 1619 (2001) [Phys. Solid State **43**, 1686 (2001)].

13. M. Bockstedte, A. Kley, J. Neugebauer, and M. Scheffler, Comput. Phys. Commun. **107**, 187 (1997).

14. P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

15. W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

16. J. P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986).

17. N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

18. M. Fuchs and M. Scheffler, Comput. Phys. Commun. **119**, 67 (1999).

19. F. D. Murnagham, Proc. Natl. Acad. Sci. USA **30**, 244 (1944).

20. C. J. Howard, R. J. Hill, and B. E. Reichert, Acta Crystallogr. B **44**, 116 (1988).

21. K. J. Chang and M. L. Cohen, Phys. Rev. B **30**, 4774 (1984).

22. J. Haines, J. M. Leger, S. Hull, *et al.*, J. Am. Ceram. Soc. **80**, 1910 (1997).

23. O. L. Anderson and P. Andreatch, J. Am. Ceram. Soc. **49**, 404 (1966).

24. C. Proust, Y. Vaills, Y. Luspin, and E. Husson, Solid State Commun. **93**, 729 (1995).

25. W. R. Manning, O. Hunter, Jr., and B. R. Powell, Jr., J. Am. Ceram. Soc. **52**, 436 (1969).

26. V. V. Kharton, E. N. Namovich, and A. A. Vecher, J. Solid Electrochem. **3**, 61 (1999).

27. S. E. Kul'kova and O. N. Muryzhnikova, Physica B (Amsterdam) **192**, 284 (1993).

28. H. Jansen, Phys. Rev. B **43**, 7267 (1991).

29. F. Zandiehnadem, R. A. Murray, and W. Y. Ching, Physica B (Amsterdam) **150**, 19 (1988).

30. L. Soriano, M. Abbate, J. Faber, *et al.*, Solid State Commun. **93**, 659 (1995).

31. G. Stapper, B. Bernasconi, N. Nicoloso, and M. Parinello, Phys. Rev. B **59**, 797 (1999).

Translated by K. Shakhlevich