Journal of University of Science and Technology Beijing
Vol.7(2000), No.1, p.45

Materials

Conductivity of $(Zr_{1-x}M_x)O_2$ Ceramic

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(Received 1999-04-21)

Abstract: In the ZrO_2-based ceramic systems doped with different oxides (Y_2O_3, MgO and Al_2O_3), the behaviors of electronic and ionic conductivity have been investigated by the quantum chemical SCF-Xα-SW method. The results of the electronic energy spectra and local state density of atoms show that, for the ZrO_2 system doped with Al_2O_3, the energy gap near the Fermi energy level becomes smaller, which implies that the electronic conductivity increases. Since the binding energy between Al and O atoms is increased, the energy for oxygen vacancy migrating is enhanced and the ionic conductivity decreases. In the M_xO_y-doped ZrO_2 systems, due to the doping effect of Al_2O_3, MgO and Y_2O_3, the ionic conductivity increases successively, and the electronic conductivity decreases successively. The calculation results are in agreement with that of references and experience.

Key words: Zirconia; Doping; Conductivity; SCF-Xα-SW method

M_xO_y-doped ZrO_2 is one kind of functional material being required with different conductivity under various conditions. For example, in oxygen sensors of the EMF type, it is basically required as an oxygen ion conductor with a transference number of ion larger than 0.9. It is desired to have a larger electronic conductivity for heating elements. With different oxides doped, the materials would have different electrical conduction [1], however, the lack of the predicting theory for the effect of doping results in the blindness and even a large waste in the development and utilization of M_xO_y-doped ZrO_2 materials. There are many successful examples for metals and supercoducting materials using SCF-Xα-SW method to study electronic structure of multivariate system [2–4]. This paper intends to apply this method to the oxide ceramics, especially doped ZrO_2 system in which the doping is just closely associated with electrical conduction.

1 Calculation Method and Model

For several decades, the SCF-Xα-SW method has been developed into a kind of perfect calculation method and a powerful tool for solving problems of multiple atom systems. Its main idea is as follows: for the investigated system, using the approximation of a Xα potential statistical mean and a Muffin-tin potential, the atomic cluster is divided into three regions, in which, by using the multiple-wave function representation and the continuous condition at each boundary, expectation equations are solved with self-consistent and their energy characteristic values, wave functions, self-consistent potentials and Hellmann-Feynman (HF) forces and so forth, are given [5].

According to the characteristics of SCF-Xα-SW method, a most typical 5Zr8O atomic cluster with thirteen atoms in ZrO_2 structure (as shown in **figure 1**(a)) is taken as the calculation model (as shown in figure 1 (b)). In this model cluster, there are two kinds of atoms, Zr and O. Its central position is occupied by Zr atom, therefore this cluster includes both of the nearest neighbor and the second-nearest neighbor atoms of Zr. Thus it is convenient to discuss the electrical conduction of four systems with the centers occupied by Zr, Mg, Y, Al, *etc.* In the calculation of electronic structure, the configurations of the outer-shell electrons of Zr and O are taken as $4d^25s^2$ and $2s^22p^4$ respectively. The lattice parameter of ZrO_2 is a_0=0.510 nm [6]. When the calculation is self-consistent, the maximum of relative change in potential is smaller than 1.0×10^{-5} eV (threshold value).

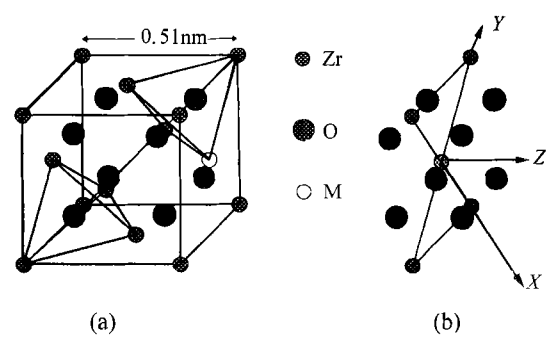

Figure 1 Lattice Structure of $(Zr_{1-x}M_x)O_2$, (a) Lattice Cell of $(Zr_{1-x}M_x)O_2$; (b) Calculation Model.

2 Results and Discussions

The energy spectra of four systems are shown in **figures 2, 3, 4**, and **5**. It is obvious that their energy spectra have similar features. Their Fermi levels are in the range of E_F = 2.910 4–3.318 4 eV (as shown in **table 1**), the energies of the outer-shell electrons are in the range of 0.680–1.224 eV under the Fermi level, and the

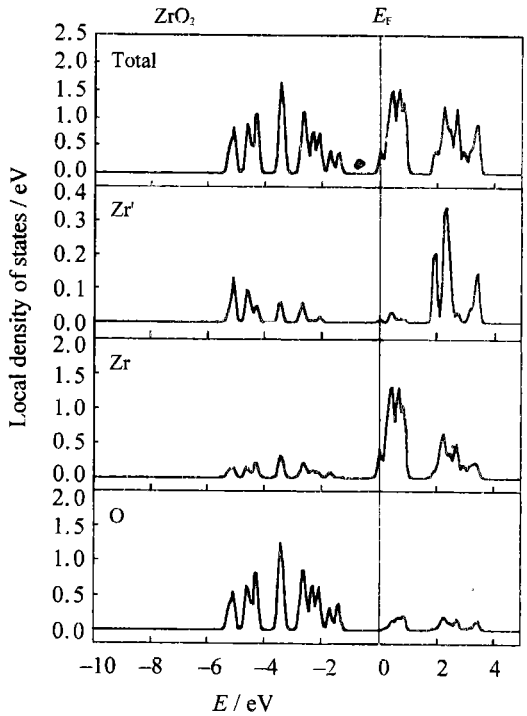

Figure 2 Energy spectrum of Zr_4O_8

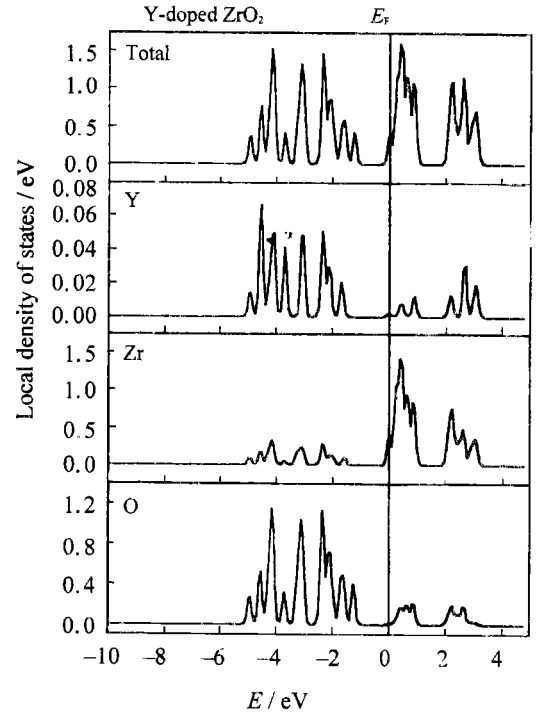

Figure 3 Energy spectrum of YZr_4O_8

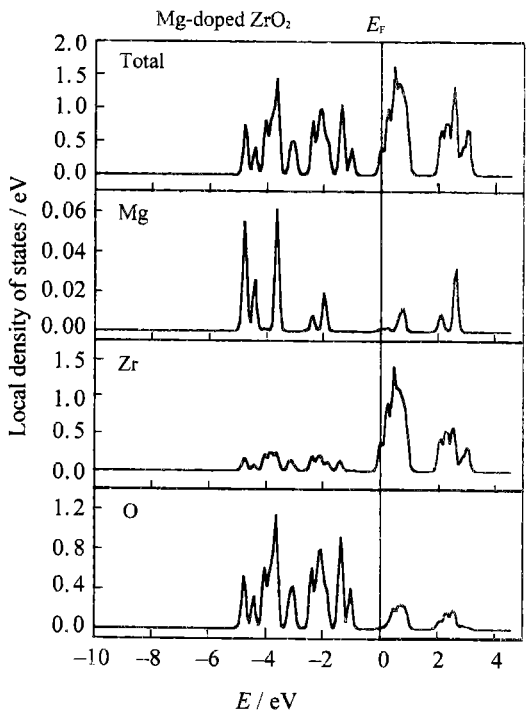

Figure 4 Energy spectrum of $MgZr_4O_8$

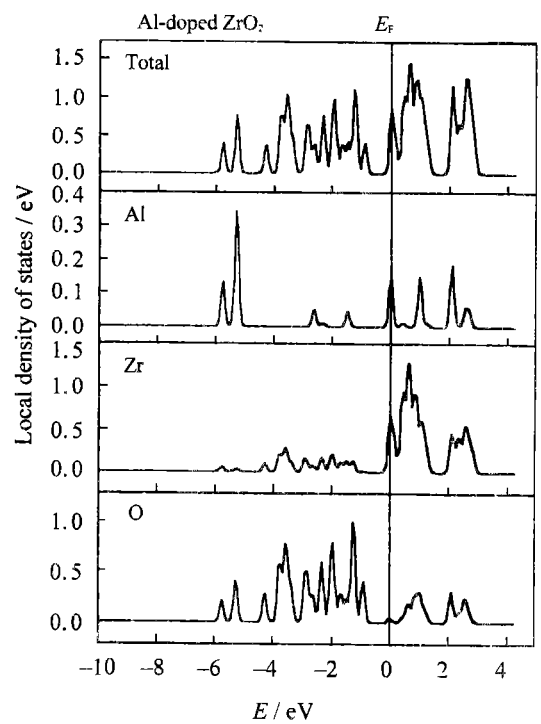

Figure 5 Energy spectrum of $AlZr_4O_8$

density of state on Fermi level and the empty level above the Fermi level is mainly due to the contribution of Zr.

The differences of energy spectra are mainly attributed to the different contributions of the central atom (substitute atom) to the total density of state. There are different widths of energy gaps near the Fermi level for four systems. The values of energy gaps are close to

Table 1 Fermi energy level and the energy gap in the different doped ZrO_2 systems

Atom cluster model	Fermi energy level E_F /eV	Energy gap $\triangle E_g$ /eV
$Zr'Zr_4O_8$	−3.3184	1.224
YZr_4O_8	−3.2232	1.088
$MgZr_4O_8$	−3.2368	0.857
$AlZr_4O_8$	−2.9104	0.680

that of Si, which is a typical characteristic value of semiconductor. The sequence of energy gaps is Zr>Y>Mg>Al. Thus by doping Y, Mg, Al, the electrical conduction of ZrO_2 ceramic can be changed. Because the electronic conductivity increases rapidly with the decreasing of energy gap near the Fermi level, the Al-doped-system with the minimum energy gap shows the maximum electronic conductivity. It is worthy to be noted that the density of state (DOS) of Al-doped-system is different from that of other systems. Al has a big contribution to the DOS of Fermi level. For Al-doped-system, the peak of DOS is higher than that of other systems. Such electronic structure is beneficial to electronic conductivity of Al-doped-system. The calculation results show that the sequence of electronic conductivities of those M_xO_y-doped systems is Al>Mg>Y.

In the M_xO_y-doped ZrO_2 ceramic, the valences of doping atoms are lower than that of Zr atoms. For maintaining electrical neutrality of the crystals, oxygen vacancies emerged in varying degrees. It is known that the oxygen ionic conductivity is attributed to the formation energy and migration energy of the oxygen vacancy.

According to the local density of state of the doping atom and oxygen as shown in figures 2–5, the binding energies between various doping elements and oxygen are different.

By comparing figure 3 with figure 5, it can be clearly seen that the Al–O bond of Al-doped-system is stronger than the Y–O bond of Y-doped-system. Since binding force between Al and O is stronger than that between Y and O, the formation energy of the oxygen vacancy in the Al-doped-system is larger than that in the Y-doped-system. Therefore, ionic conductivity of the Al-doped-system is weak.

Contrary to the Al-doped-system, O in the Y-doped-system is weakly bound to Y, and the formation energy of the oxygen vacancy is smaller, which results in a good ionic conductivity in this system. Ionic conductivity of Mg-doped-system is between the values of Al-doped-system and Y-doped-system.

In addition, the migration energy of the oxygen vacancy is related to the coupling bond between Zr atoms within the penetrated structural layer in the transport direction. For four systems, because the local density of state of Zr atoms only has a little difference, ionic conductivities of different systems are mainly attributed to the formation energy of the oxygen vacancy that is decided by the binding of doping atoms and oxygen. Therefore, Y-doped-system has the largest ionic conductivity.

In order to design a new functional material, especially to obtain peculiar ionic conductivity and to eliminate electronic conductivity effectively, before preparing material, it is an effective method to study electrical structure of different clusters by the quantum chemistry.

3 Conclusions

This study shows that the energy gap near the Fermi energy level of Al-doped-system is smaller, its electronic conductivity is stronger, while the strong combination of Al and O atoms increases the formation energy of oxygen vacancy and leads to the weakness of ionic conductivity. Contrary to Al-doped-system, Y-doping leads to a strong ionic conductivity and a weak electronic conductivity. The conduction of Mg-doped-system is between the above two systems. These results are in agreement with the results of the references [1, 6] and experimental results. The SCF-Xα -SW method can be successfully used to research the conduction of oxide ceramics.

References

[1] Z. Z. Yang, J. B. Tu: [In:] *Proceedings of the 6th Chinese Conference on Solid State Ionics*, China, Fuzhou, 1992. p.7.

[2] S. Y. Liu, R. Z. Hu, C. Y. Wang: *J. Appl. Phys.*, 75 (1993), No. 5. p. 3204.

[3] K. Li, T. Yu, Z. Gao, D. M. Wang, X. Y. Wang: *J. of Beijing University (Nature Science)*, 27 (1991). p. 146.

[4] N. Chen, Q. Lin, W. Ye, Y. Li, S. Y. Liu: *Chinese Science Bulletin*, 41 (1996), No. 4. p. 300.

[5] Y. G. Pan, J. Q. Li, J. K. Zhu, D. Li: *Theory and Its Application on Xα-Method*, Science Publishing House, Beijing, 1987. p. 234.

[6] Z. X. Lin, Z. K. Guo et al.: *Fast Ionic Conductor* (Solid Electrolyte), Science Publishing House, Beijing, 1983. p. 228.