

## Examination of the mechanism of phase stability of zirconia, alloyed with magnesium and calcium

V.G. Zavodinskii

The effect of the atoms of magnesium and calcium on the stability of the cubic phase of zirconia was investigated by the method of the functional of electronic density (taking into account the gradient correction) and the method of the pseudo-potential. It has been confirmed that the main reason for the instability of the real cubic zirconia is the instability of its oxygen sub-lattice in relation to distortion. The substitution of the zirconium atoms by the atoms of magnesium or calcium, with the simultaneous removal of the appropriate amount of oxygen, results in the distortion of the oxygen lattice exceeding the value corresponding to the distortion. This stabilises the cubic phase of zirconia.

### Introduction

The zirconium dioxide ( $ZrO_2$ ) is interesting as a ceramic material, having valuable optical, electrical, thermal, strength and other characteristics, and the phase transition in this material and impurity stabilisation are the subject of many experimental and theoretical investigations. At temperatures below  $1170^\circ C$ , the monoclinic phase (*m*) of the unalloyed  $ZrO_2$  is thermodynamically stable. From the temperatures of  $1172$  to  $2370^\circ C$ , unalloyed zirconia is tetragonal (*t*), and at temperatures above  $2370^\circ C$  up to the melting point ( $2706^\circ C$ ) the unalloyed zirconia is cubic (*c*) [1, 2]. The cubic phase may be stabilised, i.e. the  $c \rightarrow t$  transition temperature maybe reduced by introducing various additions, such as MgO, CaO,  $Y_2O_3$ , etc.

The analysis of the phase diagrams [3-5] shows that at high temperatures, the transition of tetragonal zirconia alloyed with different additions, to the cubic phase, takes place at approximately the same concentration of the impurity. However, only the addition of  $Y_2O_3$  makes it possible to produce the cubic zirconia, stable at room

temperature. The cubic phase  $ZrO_2$ -CaO is stable only up to  $850^\circ C$ , and the cubic zirconia with the addition of MgO dissociates with the precipitation of tetragonal  $ZrO_2$  and MgO at temperatures below  $1100^\circ C$ .

In fact, both the tetragonal and monoclinic phases may be represented as derivatives of the cubic phase which has the structure of fluorite. The tetragonal phase forms from the cubic phase by specific rearrangement of the oxygen cubic sub-lattice (in the sub-lattice, one half of the oxygen atoms is displaced in relation to the other half) and the elongation of the elementary cell in the direction of displacement of the oxygen atoms. The monoclinic phase forms from the tetragonal phase by shear deformation of the entire elementary cell with some change of the length of the sides of the cell.

Although the cubic phase is the phase with the highest temperature, it has the highest density, and as regards energy it is only slightly inferior to the tetragonal phase: by  $0.052$  eV per unit  $ZrO_2$  [6].

According to the experiments [7] and calculations [8], the instability of the cubic

phase is associated with a tendency of the oxygen sub-lattice for distortion of the cubic symmetry along the direction  $\langle 100 \rangle$ . The positions of the oxygen atoms  $z_o$  along this direction may be expressed by means of the distortion parameter  $d$ :

$$z_o = (0,25 + d) \cdot c,$$

Here  $c$  is the lattice constant along the direction of distortion, and the value  $d$  may have both positive and negative.

The total energy of the crystal has two minima as a function of  $d$  (one minimum at the positive value of  $d$ , the other one at the negative value). The central position of the oxygen atoms (at  $d = 0$ ) corresponds to the ideal cubic structure and is not stable. The experimental value of the equilibrium value of  $d$  is 0.065, the theoretical value 0.052. As shown in [1], the distortion of the oxygen sublattice is characteristic not only of the tetragonal phase of the zirconia but also of the cubic phase. The cubic structure becomes stable only at high temperatures when the oxygen atoms jump from one minimum to the other one, and the cubic symmetry is realised in the mean.

There has been a number of investigations [9–14] in which attention has been given to the reasons for the stability of the cubic zirconia, alloyed with the impurities such as Y, Mg, Ca. The majority of the authors assume that the main reason for the stabilisation is the local increase of the strength of the Zr–O chemical bond as a result of the re-distribution of the electronic density in the vicinity of the ion of the impurity atom. The authors of [14] also discussed the role of oxygen vacancies, the interaction of defects, and the electronic structure of the impurity atom. However, no direct relationship was investigated between the presence of impurities and the tendency for phase rearrangement.

In this work, investigations were carried out into only the stabilisation of the cubic zirconia by magnesium and calcium because the case of yttrium is far more complicated.

In the introduction of trivalent yttrium, one oxygen atom for every two yttrium atoms is removed from the zirconia. This is accompanied by the difficulties associated with the consideration of the correlation between the distribution of the atoms of yttrium and oxygen vacancies which require separate examination.

### The method and details of calculations

Calculations were carried out using FHI96MD program [15] based on the theory of the functional of electronic density [16, 17], the method of the pseudo-potential and the basis of flat waves. To calculate the volume and correlation energy we use the gradient approximation in the form proposed by the authors of [18] (PW 91). The pseudo-potentials were constructed using the Truller-Martins method [19] using the FHI98PP program [20]; they were calculated for the absence of ghost states and verified for the capacity to reproduce the main lattice characteristics of bulk materials (lattice constant and elasticity modulus).

The energy of truncation of the set of the flat waves was assumed to be equal to 44 rydberg, the minimum cell of the cubic zirconia was the cell  $Zr_4O_8$ , whose form is indicated in the figures, and the supercell was represented by the minimum cell taken from three measurements containing a to-

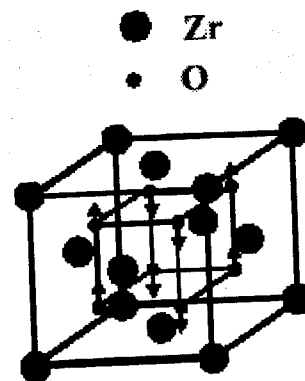


Fig. 1. The distribution of the zirconium and oxygen atoms in the cell of cubic zirconia. The arrows indicate the direction of displacement of the oxygen atoms from the ideal cubic positions in distortion.

tal of 32 zirconium atoms and 64 oxygen atoms ( $Zr_{32}O_{64}$ ). The very large supercell combined with the high truncation energy required restriction for the single  $k$ -point (in particular, the gamma point) in the Brillouin zone for the determination of the total energy. This is fully acceptable for non-metallic materials. In operation with the minimum cell, containing 4 zirconium atoms and 8 oxygen atoms, two special points were used: (0.25; 0.25; 0.25) and (0.25; 0.25; 0.75) with the weight of 0.25 and 0.75, respectively. The accuracy of calculating the total energy was 0.0001 eV for the unit of  $ZrO_2$ , i.e. the error was considerably smaller than the difference of the energies of the cubic and tetragonal phases (0.05 eV).

Using the Murnagham equation of state [21]:

$$E_{tot}(V) = E(V_0) + \frac{BV}{B'(B'-1)} \times \left[ B' \left( 1 - \frac{V_0}{V} \right) + \left( \frac{V_0}{V} \right)^{B'} - 1 \right],$$

where  $E_{tot}$  is the total energy,  $V$  is the volume of the cell,  $V_0$  is the equilibrium value of the volume of the cell,  $E(V_0/a)$ — is the equilibrium value of energy,  $B'$  is the derivative of  $B$  in respect of pressure, we determine the equilibrium constants of the lattice ( $a$ ) and the volume moduli of elasticity ( $B$ ) for the cubic phases  $ZrO_2$ ,  $MgO$  and  $CaO$ . The results are presented in Table 1 in comparison with the experimental data.

As indicated by the data in Table 1, the

calculated values are in fully satisfactory agreement with the experimental data, i.e. the pseudo-potential determined in this work described quite adequately of the energetics of interaction of the atoms of Zr, Mg and Ca with the oxygen atoms and may be used for examining the system  $ZrO_2$ - $MgO$  and  $ZrO_2$ - $CaO$ .

## The experimental results and discussion

### The distortion of oxygen atoms in pure cubic zirconia

The stability of the lattice of cubic zirconia in relation to the displacement of the oxygen atoms from the ideal cubic positions was investigated on the  $Zr_4O_8$  cell. Initially, all the atoms of the cell were placed in the ideal cubic positions with the theoretical equilibrium lattice constant  $a = 0.522$  nm and, subsequently, the total energy and the forces, acting on the atoms were calculated. In this case, only the boundary atoms of the cell (zirconium) were fixed, and the oxygen atoms were regarded as free. It appears that the oxygen atoms do not move spontaneously from the ideal cubic positions, the forces on the atoms are equal to zero, and the lattice is quasi-stable. The attempt to vary the geometry of the lattice from cubic tetragonal (elongation in one direction and compression into other directions) increased the total energy.

In this work, it was the required to examine in detail the distortion of the oxygen sublattices. The pure zirconium because the

**Table 1** The calculated and experimental values of the lattice constant and elasticity parameters for the size of Zr, Mg and Ca

Parameter	$ZrO_2$		$MgO$		$CaO$	
	Calculated	Experiment	Calculated	Experiment	Calculated	Experiment
$a$ , nm	0.522	0.509 [14]	0.424	0.421 [23]	0.488	0.480 [27]
$B$ , GPa	215±20	194 [24]	160±10	162 [25]	115±10	111 [26]
$B'$	3.9		4.1		4.5	

The experimental value  $a = 0.509$  nm for the cubic zirconia was obtained in [14] by measurements at high temperatures and interpolation to 0 K. The value  $B = 194$  GPa in [24] was obtained in examination of the cubic zirconia stabilised by yttrium and by interpolation to the zero content of yttrium.

main task was examination of the mechanism of stabilisation of cubic zirconia by impurities. We were interested only in the final state in which the oxygen sublattice is after deviation from the cubic symmetry. Therefore, we specified small displacements of one (arbitrary) oxygen atom (by 0.0001 nm) and it was shown that this results in the increased displacement of half of the oxygen atoms in one direction and of the other half in the opposite direction resulting in the distortion of the oxygen lattice in the direction  $\langle 100 \rangle$  and in the formation of non-zero forces on the atoms of the zirconium sub-lattice. The calculated value of the equilibrium distortion  $d$  for the cubic zirconia was 0.045 which is close to the value of 0.04 obtained in [22] for the cubic phase. The mean displacement of the oxygen atoms was 0.012 nm.

In order to confirm that the approach used in this work describes efficiently the transition from the cubic tetragonal phases, we changed the form of the cell stretching it in one direction (in the direction of oxygen distortion) and compressing in other two directions, fixing every time its boundaries (i.e. fixing the zirconium atoms). It appears that the cell becomes equilibrium at the calculation ratio of  $c/a = 1.02$  which is very close to the value of 1.026, characteristic of the tetragonal phase, i.e. the transition from the cubic to tetragonal symmetry takes place without any barriers and, for this purpose, any smaller initial disordering of the oxygen sublattice is suitable. However, the stability of the cubic phase at high temperatures is determined by the presence of vibrations of the oxygen sub-lattices (from one distortion minimum to another) which take place in relation to the mean, cubic positions. The zirconium atoms which are heavier do not manage to track fast collective oscillations of the oxygen atoms and carry out thermal oscillations in relation to the cubic positions. With a decrease of temperature, the oxygen sublattice stops in one of the distortion minima, and the zirco-

nium atoms react to this distortion, and the cubic lattice is rearranged into tetragonal. It was shown in [22] that the energy of activation of the collective vibrations of the oxygen sublattices is in good agreement with the temperature of transition from the tetragonal to cubic phase.

The instability of the oxygen sublattices of cubic zirconia in relation to the small displacement of the oxygen atoms was verified on the  $Zr_{32}O_{64}$  supercell (with one  $k$ -point). The effect was the same as in the lattice of  $Zr_4O_8$  (with two  $k$ -points): the displacement of one oxygen atom results in the collective effect of the paired shift of the oxygen atoms with the value of distortion  $d$  approximately 0.05 with the simultaneous formation of non-zero forces on the zirconium atoms.

#### The atomic structure of stabilised zirconia

The  $Zr_{32}O_{64}$  supercell was used for the examination of the effect of the impurities Mg, Ca and Y on the atomic structure of the cubic phase  $ZrO_2$ . The zirconium ions in zirconia have the charge +4, the magnesium and calcium atoms the charge +2 and, therefore, to examine the charge equilibrium, together with the introduction of one atom of Mg and Ca we removed one oxygen atom from the nearest neighbourhood of the impurity atom. In this case, the atoms of the impurity were distributed in such a manner that they were located approximately uniformly in the supercell, but without any ordering. Special attention was given to the fact that the adjacent atoms of Mg and Ca do not have common binding oxygen atoms. Of course, one atom cannot be distributed uniformly or without ordering. Therefore, the atom was placed in the centre of the supercell. The concept 'approximately uniformly but without ordering' relates to the cases in which the number of the impurity atoms in the supercell is greater than 1. In this case,

when taking into account the translation of the supercell, the atoms of the impurities are distributed at approximately the same distance in all three measurements, but in this case there was no artificial symmetry of the distribution of the atoms inside the supercell. Thus, we examine the configurations  $Zr_{31}M_1O_{63}$ ,  $Zr_{30}M_2O_{62}$  and  $Zr_{28}M_4O_{60}$  (M is Mg or Ca), corresponding to the molar concentrations of MgO and CaO equal to 3.125, 6.25 and 12.5%, respectively. Examination of the high concentrations of the impurity is complicated by the closed distribution of the period the atoms and oxygen vacancies in relation to each other resulting in the need for special examination of the effect of interaction of these atoms and is outside the framework of the present work.

The effect of the impurity on the atomic structure of the cubic zirconia is manifested in the relaxation of the lattice in the vicinity of the impurity atoms and oxygen vacancies with the cubic symmetry retained. Calculations show that the impurity atoms more from the ideal sites of the lattice, and are repulsed from the closest oxygen vacancies. The zirconium atoms, in the immediate vicinity of the oxygen vacancy, are also repulsed from the vacancy. The displacement is maximum for Mg and minimum for Y and depends only slightly on the concentration of the impurity. The values of the displacement of the impurity atoms from the ideal positions are presented in Table 2. The displacement of the zirconium atoms is approximately the same in all cases, and equals 0.015 nm.

Table 3 gives the data on the displacement of the oxygen atoms. The oxygen atoms, close to the oxygen vacancies, are

**Table 2** The mean displacement of the impurity atoms (nm) in stabilised cubic zirconia

Molar content of addition, %	Displacement of impurity atoms, nm	
	Mg	Ca
3.125	0.025	0.022
6.25	0.026	0.023
12.5	0.028	0.024

**Table 3** The displacement of the atoms of oxygen (nm) in the stabilised cubic  $ZrO_2$

Molar content of addition, %	$ZrO_2$ -MgO		$ZrO_2$ -CaO	
	Mean displacement, nm	Percent of displaced atoms	Mean displacement, nm	Percent of displaced atoms
3.125	0.020	3	0.020	3
6.25	0.022	8	0.022	8
12.5	0.024	17	0.024	17

attracted to the vacancy. The number of the oxygen atoms, whose displacement is greater than 0.012 nm, corresponding to the value of the distortion of the oxygen sublattices, required for the transformation of the cubic phase the tetragonal, is approximately proportional to the impurity concentration. The mean value of the displacement depends only slightly on the concentration and type of the impurity.

These results are in correlation with the fact according to which the transition of tetragonal zirconia, alloyed with different and additions, at high temperatures to the cubic phase takes place approximately of the same impurity concentration [3-5]. We believe that the mechanism of stabilisation of the cubic zirconia, determined by the suppression of the tendency of the oxygen sublattices were distortion, could also be formally retained in the case of low temperatures: at list, at high concentrations of the stabilising additions. The instability of the cubic phases  $ZrO_2$ -MgO and  $ZrO_2$ -CaO is associated, in our view, with a different reason, namely: with the large discrepancy of the lattice constant of  $ZrO_2$ , MgO and CaO. In the case of MgO, the mismatch with the cubic lattice is 18.1%, in the case of CaO it is 6.4%, showing the high mechanical stresses in the eutectoid separation of the phases, resulting in the cracking of the crystal. In addition to this, are the cells of MgO and CaO are characterised by a completely different constitution (type NaCl) in comparison with the cell of the cubic zirconia (type  $CaF_2$ ) which complicates their contact with the main crystal.

## Conclusions

Calculations carried out on the basis of the first principles show that the small displacement of even a single oxygen atom from its position in the ideal cubic lattice of the zirconium dioxide results in the increase of the displacement of the atom and of all other atoms of oxygen along the given direction. This results in the formation of non-zero forces applied to the atoms of the zirconium sublattices, leading to the elongation of the cell and the transition to the tetragonal phase. If the part of the ions of  $Zr^{4+}$  is substituted by the ions with a smaller charge, the excess atoms of oxygen leave the crystal and of the remaining ionised atoms of oxygen are displaced from their cubic positions. The resultant disordered cubic sublattices is stable and does not interfere with the lattice of the anions characterised in the mean by cubic symmetry. However, for the complete the realisation of the stabilising effect of a specific addition it is necessary to ensure that the geometrical parameters of the lattices of the oxide of the given impurity and cubic zirconia are similar.

## References

- Aldebert R., Traverse J. P. J. Am. Ceram. Soc., 1985, v.68, p.34.
- Ackermann R. J., Garg S. P., Rauth E. G., J. Am. Ceram. Soc., 1977. v.60,p.341.
- Viechnicki D., Stubican V. S. J. Amer. Ceram. Soc., 1965. v.48, p.292.
- Stubican V. S., Ray S. P. J. Amer. Ceram. Soc., 1977, v.60, p.534.
- Ruh R., Garret H. I., Domogala R. F. J. Amer. Ceram. Soc., 1977, v.60, p.399.
- Finnis M. W., Paxton A. T., Methfessel M., van Schilfgaarde M. Phys. Rev. Lett., 1998, v.81, p.5149.
- Teufer G., Acta Crystallogr., 1962, v.15, p.1187.
- Jansen H. J. F., Gardner J. A. Physica B+C, 1988, v.150, p.10.
- Orlando R., Pisani C., Roetti C., Stefanovich E. Phys. Rev. B, 1992, v.45, p.592.
- Bogicevic A., Wolverton C., Crosbie G. M., Stechel E. B. Phys. Rev. B, 2001, v.64, p.014106.
- Stapper G., Bergnasconi M., Nicoloso N., Parinello M. Phys. Rev. B, 1999, v.59, p.797.
- McCullough D., Trueblood K. N. Acta Crystallogr., 1959, v.12, p.507.
- Zainullina V.M., Zhukov V.P., FTT, 2001, vl. 43, No. 9, p. 1619.
- Stefanovich E. V., Shluger A. L., Catlow C. R. Phys. Rev. B, 1994, v.49, p.11560.
- Bockstedte M., Kley A., Neugebauer J., Scheffler M. Comp. Phys. Commun., 1997, v.107, p. 187.
- Hohenberg P., Kohn W. Phys. Rev. B, 1964, v. 136, p.864.
- Kohn W., Sham L.J. Phys. Rev. A, 1965, v.140, p.1133.
- Perdew J. P., Wang Y. Phys. Rev. B, 1986, v.33, p.8800.
- Troullier N., Martins J.L. Phys. Rev. B, 1991, v.43, p.1993.
- Fuchs M., Scheffler M. Comp. Phys. Commun., 1999, v.119, p.67.
- Mumagham F. D. Proc. Natl. Acad. Sci. USA, 1944, v.30, p.244.
- Jomard G., Petit T., Pasturel A., Magaud L., Kresse G., Hafner J. Phys. Rev. B, 1999, v.59, p.4044.
- Wyckoff R. W. G. Crystal Structures. Wiley, New York, 1963.
- Haines J., Leger J. M., Hull S., Petit J. P., Pereira A. S., Perotoni C. A., da Jornada J. A. H. J. Am. Ceram. Soc., 1997, v.80, p.1910.
- Anderson O. L., Andreatch P. J. Am. Ceram. Soc., 1966, v.49, p.404.
- Chang P., Grahm E. K. J. Phys. Chem. Solids, 1977, v.38, p.1355.
- Pearson W. B. A Handbook of Lattice Spacings and Structures of Metals and Alloys. Pergamon, New York, 1958.

**Viktor Grigor'evich Zavodinskii** – Institute of Materials Science of the Khabarovsk Scientific Centre of the Far Eastern Division of Russian Academy of Sciences, Doctor of Physico-Mathematical Sciences, Deputy Director for Science, head of a laboratory. Specializes in compute modelling of the atomic and electronic structure of solids and molecules.