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Simulation of ionic crystals: calculation of Madelung potentials for stabilized zirconia

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By assuming complete ionicity, a theoretical study of structure and energetics in zirconias stabilized by the addition of Y_2O_3 or MgO, has been reported. The simulation was carried out using the Ewald summation technique. The results indicate that the cubic structures of these ionic crystals are metastable and they transform without an energy barrier to a pseudomonoclinic or tetragonal structure.

Introduction

There is a considerable number of derivatives known as "anion-deficient" fluorite-type structures [1]. Structural determinations have been carried out for many of these compounds by a combination of single-crystal electron and X-ray powder diffractions in order to determine unit cells and space groups [2–5]. They are ordered arrangements of empty $[M_4]$ and anion-centred $[OM_4]$ tetrahedra in a cubic closed packing (ccp) M array, with a pronounced, and only very slightly distorted, fluorite subcell.

The fluorite-type structure of pure zirconia can be stabilized by the addition of suitable oxides, namely yttria (Y_2O_3)-stabilized zirconia (YSZ) and magnesia (MgO)-stabilized zirconia (MgSZ) in which the cation is partially substituted by yttrium or magnesium, respectively [6]. Unfortunately, a great deal of doubt remains about even the nature of the distribution of ions in zirconia. This material has a tendency to adopt different forms of ordering: cubic, tetragonal or monoclinic arrangements. Because some aspects of this ordering may be predicted from an ionic model of zirconia, the aim of this work was to determine and calculate the variation of Madelung potentials according to the displacements of the anions in the YSZ and MgSZ lattices, in order to obtain a theoretical explication of the relative stability of these crystal structures.

2. Method and model

2.1. Method

Coulombic models play a significant role in chemistry and physics. The essence of these simple models is to represent the particles of the system under study by point charges interacting through Coulomb's law [7]. In ionic solids, the Coulombic approach gives rise to the Madelung potential, $V_{\mathrm{Mad}}(x, y, z)$, defined as the potential created at the point of coordinates x, y, z by all the ions in the lattice. This long-range potential can be expressed as an infinite series of Coulombic terms and the sum of these series is difficult to compute accurately because they are conditionally convergent [8].

For ionic crystals, the Madelung potential can be evaluated by combining the contributions within each repeating unit cell. However, the result will not be unambiguously defined unless the methodology of the calculation has physical significance, i.e. the repeating unit has vanishing charge ($\Sigma q = 0$), dipole ($\Sigma\mu = 0$) and quadrupole ($\Sigma Q = 0$) moments, and the sample is specified and the summation over repeating units is carried out over increasing size shells which preserve the specified shape and symmetry [9].

In the literature, various transformations may be found which, applied to long-range forces, produce equivalent absolutely convergent series that converge rapidly [9]. For the calculations given below we have used Ewald's method [10]. This technique has been further improved by different authors; it involves the introduction of a convergence function which must satisfy a mathematical condition [10]. In Ewald's summation technique, Gaussian functions instead of point charges are used to describe the charge distribution about ions in a crystal lattice. The central simulation box is infinitely replicated in all directions, the long-range forces are included by evaluating the interaction of all ions in the central box with all their images in the replicas. Ewald's sum is obtained by rewriting the conditionally convergent sum over Coulomb interactions in terms of two absolutely convergent sums, one in the real space, the other in the reciprocal k space [11].

We have assumed this type of function in our lattice energy calculations, using a program described by Piken and Van Gool [12] and adapted by Pueyo and Richardson [13]. This program has been implemented for a IBM PC computer. To test this program,

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Madelung constants were calculated for structures having c c p or face centred cubic (f c c) lattices. It was found that the program calculated the Madelung constants to these crystals to good accuracy [14].

Calculations were carried out on an IBM 3090/150 computer at Centre d'Informatica, Universitat de Valencia.

2.2. Model

In the calculations, we started with a cubic zirconia structure and used the cell constants and ion coordinates reported by Howard *et al.* [15]. Zirconia has a fluorite type structure (space group *Fm3m*). Essentially, the (Zr^{4+}, Y^{3+} or Mg^{2+}) cations and O^{2-} anions are located at the following positions:

$$\left.\begin{array}{lllll} \text{cations:} & 4(\text{a}) & m3m & 0,\ 0,\ 0 & \\ \text{O anions:} & 8(\text{c}) & \bar{4}3m & 1/4,\ 1/4,\ 1/4 \\ & & & 3/4,\ 3/4.\ 3/4 \end{array}\right\} \begin{array}{l} +\,(000,\ 1/21/20, \\ 1/201/2,\ 01/21/2) \end{array}$$

The cation sites were assumed to be statistically occupied by Zr^{4+} and Y^{3+} (or Mg^{2+}) cations.

Quantitative analysis gives a chemical stoichiometry of $0.84ZrO_2$, $0.16Y_2O_3$ or $Zr(Y)O_{1.862}$, assuming an oxygen-deficient structure [6].

The density of $5.845\ \text{g cm}^{-3}$, measured at room temperature, yields a lattice constant $a = 0.5152$ nm and is in good agreement with the calculated density of $5.824\ \text{g cm}^{-3}$ for the oxygen-deficient structure using a lattice constant of $a = 0.5158$ nm [6].

The simulation has been carried out by considering a total of $116(84 + 32)\ Zr^{4+}$ and substituting $32\ Zr^{4+}$ for $32\ Y^{3+}$; this model implies the elimination of 16 O^{2-} of 232 (116×2) O^{2-} to maintain the electric neutrality. Preliminary calculation renders the same result for the lattice energy if we consider the substitution of $1.1034\ Zr^{4+}$ $((32/116) \times 4)$ and the elimination of $0.5517\ O^{2-}$ $((16/232) \times 8)$ of the $4\ Zr^{4+}$ and $8\ O^{2-}$ which form the repeating fluorite unit.

The most likely displacements of O^{2-} anions are summarized as follows:

$$8(c)\bar{4}3m \left\{ \begin{array}{lll} -\,8(c) & \bar{4}3m & \text{no displacement} \\ -\,32(\text{f}) & 3m & (1/4 + \delta,\ 1/4 + \delta,\ 1/4 + \delta) \\ -\,48(\text{g}) & mm & (1/4 + \delta,\ 1/4,\ 1/4) \end{array} \right.$$

In Fig. 1 the fluorite structure is shown and the directions of the displacements, that have been considered, are depicted by arrows.

3. Results and discussion

3.1. General background

From the point of view of setting up theoretical models of zirconia, structural determinations from X-ray and high-resolution neutron powder diffraction studies [15], and synthetic procedures developed by Monrós *et al.* [16, 17] provide a considerable amount of information on ion distributions. Also, they are proving to be valuable supplementary tools for structural investigations on zirconia.

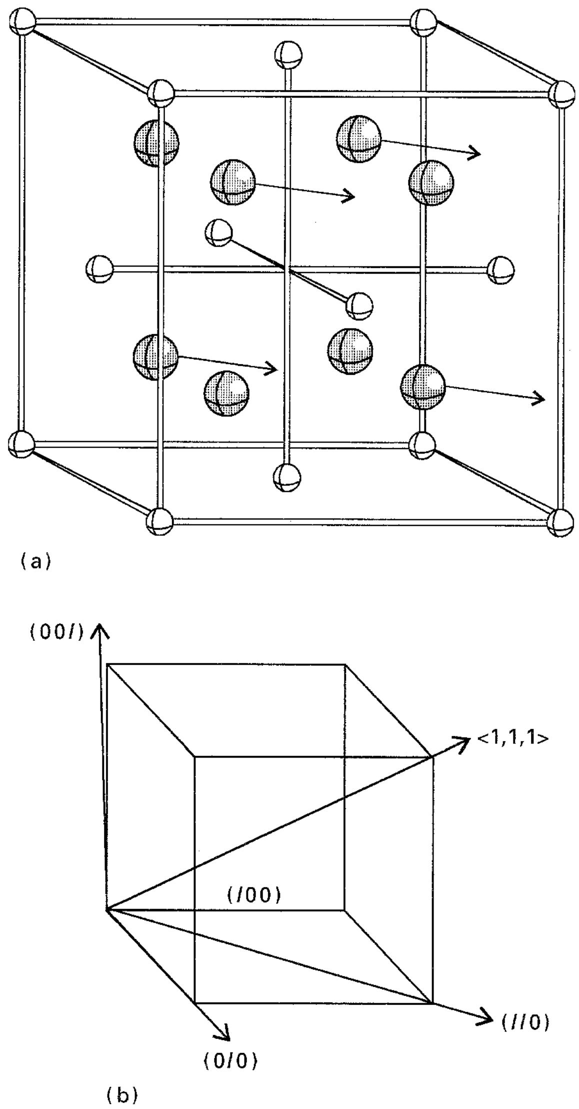


Figure 1 Fluorite-type structure. Considered displacements are pointed out by arrows.

Previous experimental results can be summarized as follows:

(a) Carter and Roth [5] have suggested that O^{2-} anions are slightly displaced from the ideal position of (1/4, 1/4, 1/4), with magnitudes of ≈ 0.02–0.03 nm along the $\langle 1\,1\,1 \rangle$ direction.

(b) Stell and Fender [2] have reported that in the structures $Zr(Y)O_{1.87}$ and $Zr(Yb)O_{1.87}$ a large proportion of the O^{2-} anions are displaced along the $\langle 1\,0\,0 \rangle$ direction by about 0.04 nm, and a small proportion are displaced along $\langle 1\,1\,1 \rangle$ by about 0.05 nm, based on neutron powder diffraction data.

(c) Morinaga *et al.* [4] have studied the structures of $Zr(Y)O_{1.893}$ and $Zr(Ca)O_{1.866}$ using single X-ray diffraction and reported that the O^{2-} anions of $Zr(Y)O_{1.893}$ show displacements similar to those reported by Stell and Fender for $Zr(Y)O_{1.87}$, with amplitudes of 0.026 and 0.013 nm along $\langle 1\,0\,0 \rangle$ and $\langle 1\,1\,1 \rangle$, respectively. However, in $Zr(Ca)O_{1.866}$ the shifts are along the $\langle 1\,0\,0 \rangle$ direction.

From these results Howard *et al.* [15] give the following general interpretation. The main sources of the observed displacements of the O^{2-} anions from their ideal positions are: (i) statistical spatial

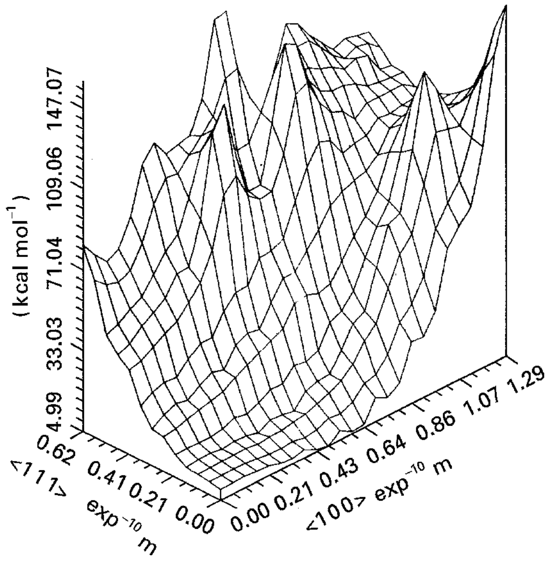


Figure 2 Schematic three-dimensional Madelung potential (kcal mol^{-1}) surface of ⟨1 0 0⟩ and ⟨1 1 1⟩ directions for YSZ. E_{total} = 3055 kcal mol^{-1} (0, 0, 0, point).

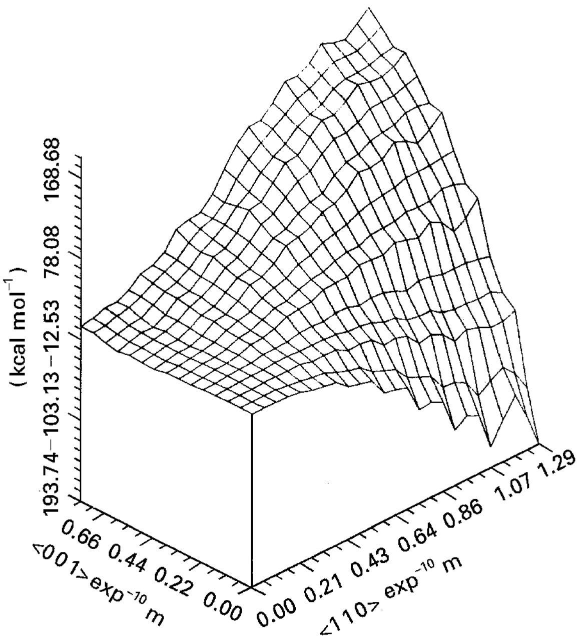


Figure 3 Schematic three-dimensional Madelung potential (kcal mol^{-1}) surface of ⟨1 1 0⟩ and ⟨0 0 1⟩ directions for YSZ.

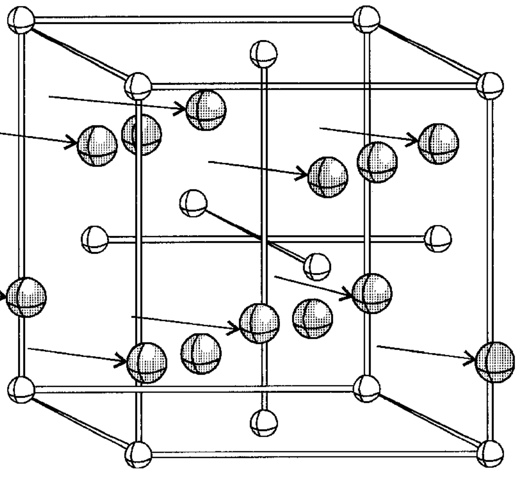


Figure 4 Global minimum; this structure corresponds to a pseudo-monoclinic arrangement.

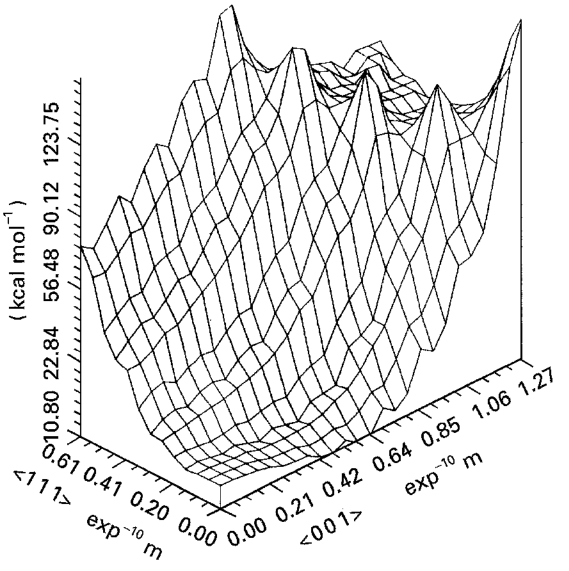


Figure 5 Schematic three-dimensional Madelung potential (kcal mol^{-1}) surface of ⟨0 0 1⟩ and ⟨1 1 1⟩ directions for MgSZ. E_{total} = 3050 kcal mol^{-1} (0, 0, 0, point).

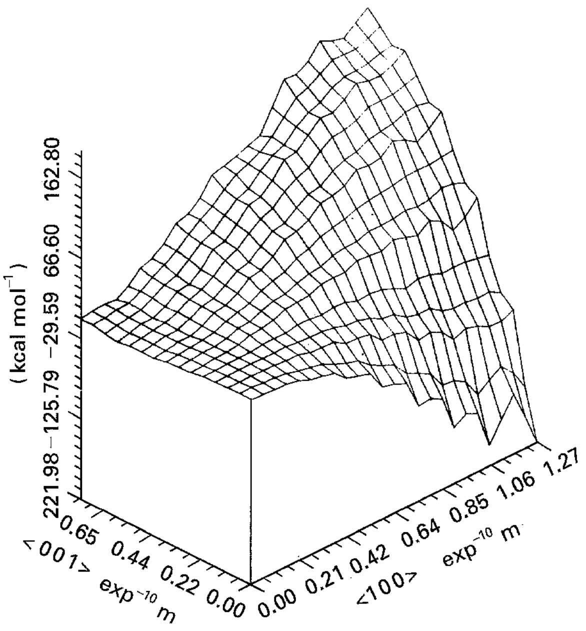
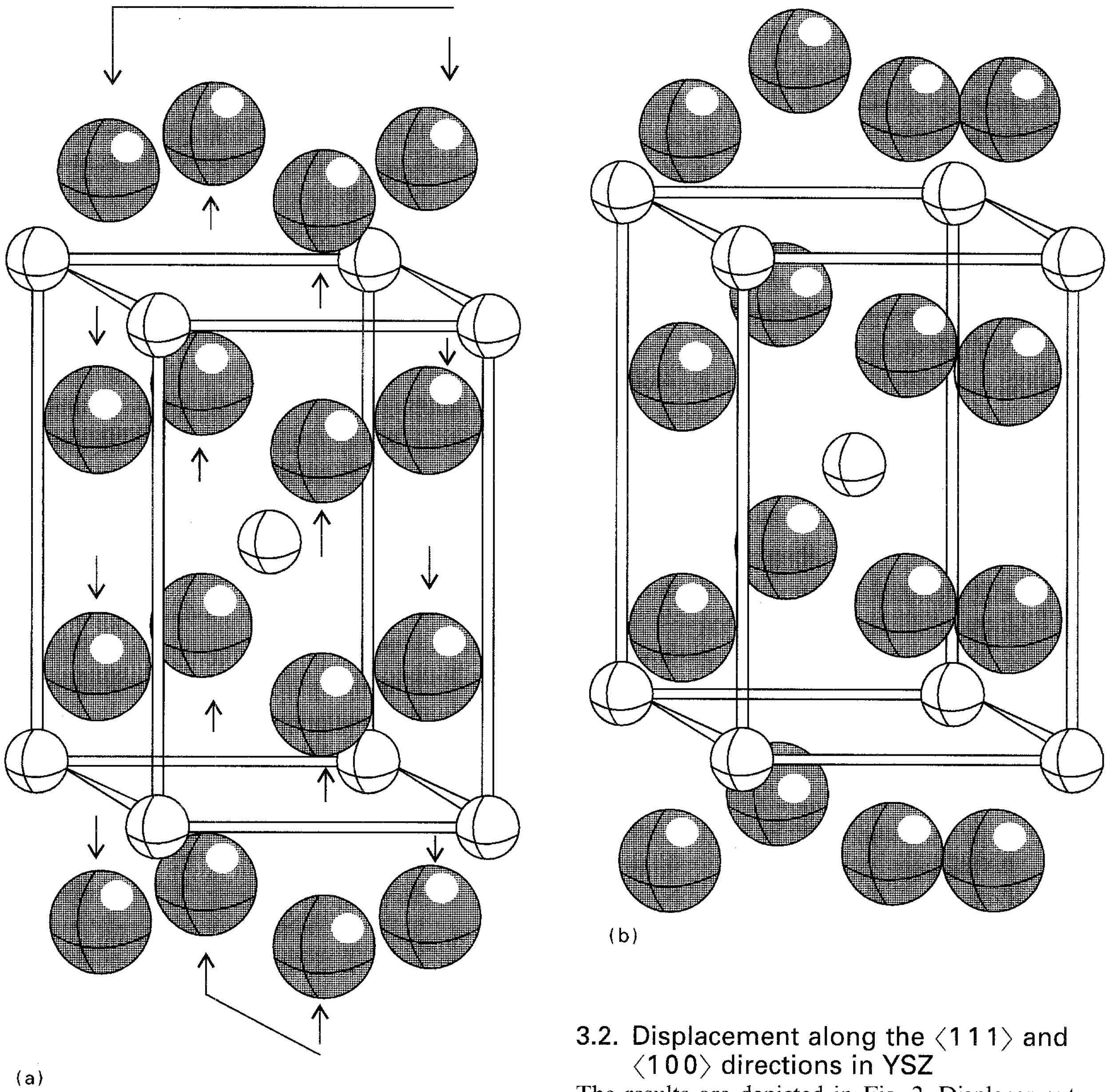


Figure 6 Schematic three-dimensional Madelung potential (kcal mol^{-1}) surface of ⟨0 0 1⟩ and ⟨1 1 0⟩ directions for MgSZ.

distributions of the dopant moieties which are essentially fluorite type but which also include oxygen defects, (ii) anharmonic and/or harmonic thermal vibrations at high temperature, and (iii) mobile and/or hopping O^{2-} ions at high temperature through vacant positions.

These displacements are not only in the (0 0 1) plane but also directed above and below the plane. The magnitude of the deviation is about 0.035 nm from the ideal position. In the ideal fluorite-type structure, vacancies are all filled by O^{2-} anions and there are no displacements. Therefore, the observed displacements along ⟨1 1 1⟩ at room temperature are the average displacements which are mainly attributed to the statistical arrangement of "cluster" in the structure.



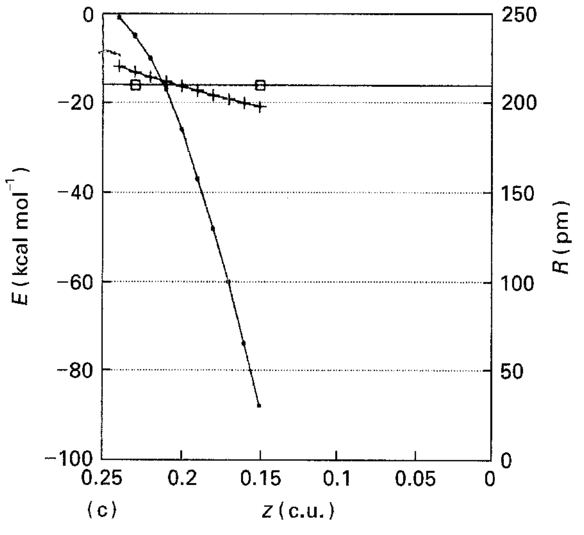


Figure 7 (a) Cubic zirconia structure. The arrows show displacements that lead a tetragonal arrangement. (b) Tetragonal zirconia structure. (c) Variation of Madelung potential (kcal mol^{-1}) with z, crystallographic units (c.u.) for the interconversion from cubic to tetragonal structure. (●) E, (+) R, □ $R_{\min} = 210$ pm.

3.2. Displacement along the ⟨1 1 1⟩ and ⟨1 0 0⟩ directions in YSZ

The results are depicted in Fig. 2. Displacements of O^{2-} anions along the ⟨1 0 0⟩ direction increase the lattice energy slowly, i.e. 0.4 kcal mol^{-1}. For a position of nearly 0.045 nm (0.009 in crystallographic units), the surface presents a minimum, i.e. -5.7 kcal mol^{-1}. The highest increase of Madelung potential corresponds to displacements along the ⟨1 1 1⟩ direction.

When the oxygen anions are moved in both directions: in the zone from 0.0–0.020 nm and from 0.0 to 0.062 nm along the ⟨1 1 1⟩ and ⟨1 0 0⟩ directions, respectively, the surface is plane; this fact shows that the movements around this zone are free, they do not need more than 5 kcal mol^{-1}.

3.3. Displacements along the ⟨1 1 0⟩ direction in YSZ

In Fig. 3 we can see that the movements along the ⟨1 1 0⟩ direction in the interval from 0.0–0.020 nm and along the ⟨1 0 0⟩ direction in the interval from 0.0–0.06 nm have no energy barrier; the displacements are free.

The larger stabilization is along the ⟨1 1 0⟩ direction, the structure which corresponds to global minimum is $\delta = 1/4$ (0.129 nm of the separation from the initial position) and it has a pseudo-monoclinic arrangement (see Fig. 4).

3.4. MgSZ structure

We have also studied the structure of zirconia doped with MgO ($Zr_{0.875}Mg_{0.125}O_{1.875}$). Starting from a fluorite-type structure [15], the results are the same as previously for YSZ. The calculated surfaces are presented in Figs 5 and 6. Analysis and comparison of these figures with Figs 2 and 3 reveal that the topology is very close.

The global minimum is also at (0.127, 0.127, 0) nm position or (1/4, 1/4, 0) in crystallographic units.

3.5. Study of the transformation of cubic YSZ into a tetragonal zirconia

In order to evaluate theoretically the pathway that leads cubic YSZ into a zirconia with tetragonal arrangement, we have carried out an Ewald simulation of this possible transformation.

3.5.1. Model

The tetragonal zirconia [15] (space group $P4_2/nmc$) has the following structure

$$\begin{array}{lll} \text{Cations (Zr or Y)} & 2a\ 4n2 & (0,0,0)\ (1/2,1/2,1/2) \\ \text{Anions (O)} & 4d\ 2mm & (0,1/2,z)(0,1/2,z+1/2) \\ & & (1/2,0,-z+1/2) \\ & & (1/2,0,-z) \\ & & 0 < z < 1/4 \end{array}$$

In Fig. 7a, the cubic fluorite-type structure of zirconia is presented, where Zr^{4+} (or Y^{3+}) occupy the positions of a ccp arrangement, where O^{2-} anions occupy tetrahedral positions. Note that this arrangement is another form of representing this structure.

Fig. 7b shows the tetragonal structure of zirconia; the O^{2-} anions are substantially displaced from ideal fluorite 1/4, 1/4, 1/4 positions ($z = 0$).

A slight increment of the cell parameter c and displacements of O^{2-} anions, as shown in Fig. 7a by arrows, transform the cubic structure (Fig. 7a) into a tetragonal arrangement (Fig. 7b). Fig. 7c shows the variation of Madelung potential as a function of the parameter z, which determines the O^{2-} anions positions, and the minimum cation–anion distance, is depicted. This variation has evinced that the cubic structure can change to a tetragonal structure without an energy barrier.

If we consider the crystalline radii [18], it seems difficult to accept that the neighbour atoms can approach by more than 0.210 nm. This gives a structure in good agreement with the experimental data [14] in which $z = 0.20$.

In the hope of shedding further light on the possibilities for ion distributions in zirconia, calculations of Madelung potentials, in a range of structures and displacements, have been presented. Although we have used idealized models and have neglected important effects (short-range interactions, covalency of bondings, etc.) the theoretical study should be useful as a basis for the discussion of real zirconia.

More sophisticated calculations should be performed in order to obtain more reliable relative energies.

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