Effect of point defects on heat capacity of yttria-stabilized zirconia

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First-principles calculation and anharmonic dynamical theory were used in sequence to explain a large excess heat capacity observed in yttria-stabilized zirconia in comparison with the additive rule value. It is found that the excessive shape of heat capacity decays gradually with the Y2O3 doping when the number of environmentally different O sites falls to its zero value at 33 mol % Y2O3-ZrO2 due to the Y atoms adjacent. The model and results presented in this work provide a new insight into the complex behaviour and characterisation of fast-ion conductors.

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Point lattice defects both native and artificial, such as vacancies, self-interstitials, solute and substitute atoms, strongly affect the most fundamental properties of materials. In yttria-stabilized zirconia (YSZ), the material with numerous commercial applications, formed by the addition of Y2O3 to ZrO2, the trivalent dopant Y3+ substitute for some of the host cations and, in order to maintain charge neutrality, one O vacancy (Vox) must be created for each pair of dopant cations. Y2O3 is used to stabilize the tetragonal (t) phase of (ZrO2)100-x(Y2O3)x over the composition range 2 < x < 9 mol % and the cubic (c) fluorite phase with 4 < x < 40 mol %. The presence of relaxed V0 and Y substitute atoms makes the local atomic environments of YSZ rather different from the stoichiometric high-temperature t- and c-polymorphs of pure ZrO2 whose 8-fold cations are distorted and perfectly coordinated, respectively. In YSZ, the average cation coordination number, ranged between 7 and 8, is reduced gradually with increasing Y2O3. If the V0 associates with Zr ions, as the X-ray absorption findings suggest, it may support a coordination-driven ordering model of stabilization. Placing Y in the next nearest neighbour (NNN) cation positions allows the coordination of Zr in the nearest neighbours (NN) sites to the V0 to be similar to the monoclinic ZrO2 arrangement, with Zr located in 7-fold coordination environments, while Y remains 8-fold coordinated.

The electron energy-loss near-edge structure (ELNES) of YSZ demonstrates the features of the experimental O K-edge shapes which depend on the crystal structures and the Y2O3 composition. In modelling the most important and widely used properties of YSZ the relaxation mechanism is essential. The effects of relaxation were treated within the plane-wave, pseudopotential based free energy molecular dynamics (FEMD) technique. Using the relaxed configurations (RC) of point defects, the ELNES calculations were carried out. Since the results of calculation show very good agreement with the experimental O K-edge signal, it seems that theory reflects the realities of relaxation. There is much yet to be learned about the fundamental nature of transport processes in YSZ. Thus, our motivation is to make a contribution to the microscopic modelling and tailoring the heat capacity of YSZ.

A large excess heat capacity (EHC) has been observed in YSZ at low and room temperatures for 7.8, 9.7 and 11.4 mol % Y2O3 compared to the heat capacity calculated from those of pure ZrO2 and Y2O3 by the additivity rule: \[ \Delta C_p = C_p^{Y2O3} - [(1-x) \ C_p^{ZrO2} + x \ C_p^{Y2O3}] \]. The shape of \( \Delta C_p(T) \) is very similar to that of the Schottky disorder. The same behaviour of heat capacity may yield the two-level system (TLS), quite a simple model, used to simulate the low-temperature properties of amorphous insulators: \[ C^{TLS}_p = k_B (\Delta / T)^2 e^{-\Delta / T} \left( e^{-\Delta / T} + 1 \right)^2, \] where \( \Delta \) is the energy difference between the levels.

It appears that for an anharmonic oscillator (AO), which dynamics is defined by the double-well potential \( U(x) = -x^2 + ax^3 + bx^4 \), \( a, b > 0 \) with a maximum at \( x_0 = 0 \) and two minima at \( x_1 \) and \( x_2 \), separated by the energy \( \Delta = U(x_2) - U(x_1) > 0 \), the temperature dependence of heat capacity is similar to that of TLS. The partition function \( Z_{AO} = k_B \sum_{i} \int dx dv \exp \left\{ -k_B T \left[ -x^2 / 2 + U(x) \right] \right\} \) is calculated assuming \( |U_0| \gg |U_i| \). If \( U \) is approximated near its minima by the second-degree polynomials, \( U_1 \sim (x-x_1)^2 \omega_1^2 / 2 \) and \( U_2 \sim (x-x_2)^2 \omega_2^2 / 2 + \Delta \) where \( \omega_i \) are the frequencies of small vibrations at \( x_i \), then, using the general thermodynamic relations, one can obtain \( C^{AO}_p = k_B \left\{ \omega_1^2 / \left[ \exp(\Delta / T + \omega_1 / T) - 1 \right] \right\} + k_B \). In the latter, the temperature dependence of the first term, \( \Delta C(T) \), which defines the difference in heat capacity between anharmonic and harmonic oscillators, is close to \( C^{TLS}_p \) and finally, at \( \omega_1 / \omega_2 = 1 \), \( \Delta C \equiv C^{TLS}_p \). Hence, the EHC effect may appear as the result of strong anharmonic vibration modes either localized or delocalized ones.

The fact that at \( x > 8 \) mol % Y2O3 \( \Delta C_p \) decreases with increasing the dopant concentration may suggest that the delocalized anharmonic vibrations cause the EHC effect. It is known that the main contribution to the structural transformations comes from particular vibrational modes. In pure ZrO2, a zone-boundary soft phonon, \( X_2 \), which breaks the \( c \)-symmetry of the O sub-
lattice, displacing the O atoms toward their positions in the t-phase, may be responsible for the c–t phase transformation. In YSZ, the experimental data are not fully clarified for this soft mode because of the static disorder in the O sublattice. Using the RC of YSZ, the \( X_2^- \)-like phonon was calculated by means of the frozen-phonon method for each composition of \((ZrO_2)_{100-x}(Y_2O_3)_x\) between 3 and 10 mol % \( Y_2O_3 \). For 10 mol % \( Y_2O_3 \), the effective potential has a single minimum and, with decreasing \( Y_2O_3 \) content, the potential develops two minima. The temperature dependence of the phonon frequency, calculated within the modified pseudoharmonic approximation, quantifies accurately the transition temperature above which the c-phase is stabilized. In the 3 mol % \( Y_2O_3 \) case, it may start around room temperature. The upper boundary of the single t-phase field in the experimental phase diagram shows a similar rapid drop of temperature with \( Y_2O_3 \) concentration. However, the \( X_2^- \)-like soft phonon of YSZ, in another words, the delocalized vibrations can not be responsible for the EHC effect because of the potential symmetry.

Regarding anharmonic effects, the atomic vibrations localized near the \( V_0 \) should be considered as well. YSZ is a solid electrolyte in which ionic transport takes place by anions moving among their positions by the vacancy diffusion mechanism. If any two \( V_0 \) sites, which an O atom occupies before and after a diffusive jump, are non-equivalent then theory enables the double-well asymmetric potential profile. In such a study of diffusion, the molecular dynamics technique can fruitfully be used. The principal output of the dynamic computation is the set of atomic trajectories from which all other properties are calculated. Molecular dynamics has been used in the past by many authors to calculate the potential energy dependant on the position of diffusion atom. Even if one could calculate the induced trajectories through the saddle-point the results were strongly affected by the reaction coordinates of all other atoms. The benefits and limitations of this molecular dynamics approach have been discussed and it is generally accepted now that using the large unit cells this scheme is very complicated for precise calculation whereas the results, obtained in such a way, are not always satisfactory.

The features of the computed \( U \) profile were demonstrated using the single-\( V_0 \) 11-atom \( Zr_2Y_2O_7 \) cell, which contains two formula units of \( ZrO_2 \) and one formula unit of \( Y_2O_3 \), that corresponds to a composition of 33 mol % \( Y_2O_3 \). The RC, shown in the (a) panel of Fig. 1, was used in a further static optimization using the displacements of O-2 along the z-direction while all other atoms are fixed at their relaxed positions. In this case, labeled in the panel (b) of Fig. 1 as a “solid pass” trajectory, the O-2 position in the \( z=0 \) plane corresponds to the saddle point with the potential barrier \( E_b \) of ~0.2 eV/cell. If Zr in the \( z=0 \) plane were allowed to relax when the O-2 is moved, as shown in Fig. 1 as the “soft pass” trajectory, then the equilibrium position of O-2 is much closer to the saddle point while \( E_b \) becomes significantly less. In \( Zr_2Y_2O_7 \), where all O sites are equivalent to each other, the Zr/Y environment enables the symmetric form of \( U(x) \) and therefore can not result in the EHC effect. The saddle-point neighborhood plays a key role on the instability-barrier formation, which is very sensitive to the model parameters. Thus, the dynamics theory of ion transport is still very much a semiempirical science and further simplification, based on the realities for the activation energy, should be made.

Atomistic RC of the (96-\( y \))-atom supercells \((y=1,2,...)\) allow to model \((ZrO_2)_{100-x}(Y_2O_3)_x\). In the 95-atom cell, which corresponds to ~3 mol % \( Y_2O_3 \), the RC with both Y atoms in the NNN shell was obtained. Fig. 2 shows the RC energies, expressed as an equivalent temperature per 12-atom cell, to give an idea of the relative stability and temperature required. In the 94-atom cell, the RC with two \( V_0 \)s along the (111) fluorite direction results in a 6-fold coordinated and six 7-fold coordinated NN Zr atoms. This result supports the interpretation of the neutron data by Goff et al. Electrostatic considerations suggest that \( V_0 \)s should repel. From this point of
of coordination lowering model. Since the shortest distance
vacancies consistent with both electrostatics and the Zr-
is rather reasonable. The repulsion tendencies between
dc conductivity $[13]$ YSZ, obtained from the Arrhenius relation for the ionic
2 in YSZ at low $Y$ $V_{\text{O}}$% $Y_{2}O_{3}$, is created. The difference $\Delta=210$ K between these
atoms is created. The difference $\Delta=210$ K between these
NN-NNNN configuration is realized. We
take $E_b=E_a \approx 1$ eV using the activation energy $E_a$ of
YSZ, obtained from the Arrhenius relation for the ionic
dc conductivity $[16] \sigma \sim \omega_0 e^{2} e^{\exp(-E_a/k_B T)}$, where $\omega_0$
is the attempt frequency. To form the effective potential,
characterized by $E_b$, $\Delta$ and the distance moved during a
single jump $d=\sqrt{x_1-x_2}$, the three-parameter polynomial
$U(x)=-ax^2+bx^3+cx^4$ was used. Since $E_b \gg \Delta$,
the O vibrations near the $U$ minima may be estimated
as $\omega \approx \sqrt{\frac{32E_b}{md^2}}$, where $m$ is the O mass. As a result,
$\omega \approx 5 \times 10^{14}$Hz is close to that found experimentally $[15]$
showing very reasonable model approximation.

In Fig. 3a the calculated EHC shape $\Delta C_p(T)=\mathcal{N}_{TLS}$.
$C_p^{TLS}$ is plotted, with its dependence on temperature and
dopant concentration. Here $\mathcal{N}_{TLS}$ was obtained in
such a way that each maximum coincides with the experimental EHC amount $[7]$ at 7.76, 9.7 and 11.3 mol % $Y_{2}O_{3}$. The EHC observations of 7.76 mol % $Y_{2}O_{3}$ are shown in Fig. 3a to illustrate the similarity. All theoretical $\Delta C_p$ shapes, with a maximum at 88 K, have been aligned with the experimental peak at $T_m=75$ K using the $T/\Delta$ dimensionless scale. The (b) panel of Fig. 3 shows that the $\mathcal{N}_{TLS}/N_y$ ratio ($N_y$ is the number of $V_{\text{O}}$) falls quickly with increase in $Y_{2}O_{3}$ content and, finally, $\mathcal{N}_{TLS}/N_y \rightarrow 0$ at $x=33$ mol % when the $U$ symmetry for diffusion atom should appear. At low concentrations of $Y_{2}O_{3}$, not all possible diffusion jumps lead to the asymmetric $U$. For example, in 3 mol % $Y_{2}O_{3}$, $N_y=1$ whereas $\mathcal{N}_{TLS}$ falls from six to four since two O NN sites to $V_{\text{O}}$ are energetically equivalent due to the $Y$ atoms adjacent. The number of such environmentally equivalent O sites, which not contribute to the EHC effect, increases with increasing the dopant concentration.

The high-probability $O$ hopping via $V_{\text{O}}$ between the low-energy equivalent sites, localized close up to each other, can be considered as some sort of the vacancy block, which results in the anisotropic absorption peak to the internal frictions measured in 9.5 mol % $Y_{2}O_{3}$. $[15]$ This observation is in agreement with our findings confirming earlier suggestions that some vacancies exist in bound states as di-$V_{\text{O}}$ along the [111] fluorite direction. As the number of $V_{\text{O}}$-blocks increases with $Y_{2}O_{3}$ doping, the peak magnitude for the localized relaxation may not scale simply with the dopant concentration, reaching a maximum at some critical concentration $x_m$ correlated with that of the EHC maximum. At $x > x_m$, the number of sites on the O sublattice with similar local environment increases significantly. This may lead to the long-range transport of $O$ ions via vacancies reducing therefore the local hopping process in $V_{\text{O}}$-blocks. Regarding the con-

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Relaxed energies of the 95-atom YSZ cell are plotted vs positions of the two Y dopant cations on the NN or/and NN cation shells. The diffusion jump of the lower apical NN O allows to construct the double-levels potential $U$ shown in the diagram as a sketch.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Calculated $\Delta C_p$ for the 7.76, 9.7 and 11.35 mol % $Y_{2}O_{3}$-ZrO$_2$ are shown vs $T/\Delta$ in the (a) panel compared with the experimental EHC shape of 7.76 mol % $Y_{2}O_{3}$. In the panel (b), the ratio of $\mathcal{N}_{TLS}$, obtained using $\Delta C_p$, to the number of vacancies $N_y$ are shown as $\square$ for each $Y_{2}O_{3}$ concentration and connected by eye.}
\end{figure}
centration profile of localized relaxation explained, such observations at \( x > x_m \) may be masked by overlap between the isotropic and anisotropic absorption peaks due to diffusion and \( V_0 \)-block relaxation, respectively.

In summary, our study of YSZ being performed using the \textit{ab initio} relaxed configurations and dynamical model of O hopping allows to explain the EHC anomaly observed with the \( \text{Y}_2\text{O}_3 \) doping. In YSZ, as it has been demonstrated, the anisotropic absorption peak of internal frictions and EHC effect have a common vacancy-block nature showing great potential for theory to deal with the realistic model of doped ceramics. Because of the general physics involved we believe that similar excessive behaviour of heat capacity might be observed in a wide class of ionic conductors where anion hopping goes through non-equivalent positions.

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[1] C.P. Flynn, \textit{Point Defects and Diffusion}, (Clarendon Press, Oxford, 1972), p. 423.
[2] E.C. Subbarao, in \textit{Science and Technology of Zirconia}, edited by A.H. Heuer and L.W. Hobbs, \textit{Advances in Ceramics}, Vol. 3 (American Ceramic Society, OH, 1981).
[3] P. Li et al., Phys. Rev. B \textbf{48}, 10063 (1993).
[4] E.V. Stefanovich et al., Phys. Rev. B \textbf{49}, 11560 (1994).
[5] S. Ostanin et al., Phys. Rev. B \textbf{65}, 224109 (2002).
[6] A. Alavi et al., Phys. Rev. Lett. \textbf{73}, 2599 (1994).
[7] T. Tojo et al., J. Thermal Analysis Calorimetry \textbf{57}, 447 (1999).
[8] D.W. Liu et al., Phys. Rev. B \textbf{36}, 9212 (1987); D.N. Argyriou and M.M. Elcombe, J. Phys. Chem. Solids \textbf{57}, 343 (1996).
[9] S. Ostanin et al., Phys. Rev. B \textbf{66}, 132105 (2002).
[10] R.A. Miller et al., in \textit{Science and Technology of Zirconia}, edited by A.H. Heuer and L.W. Hobbs, \textit{Advances in Ceramics}, Vol. 3, (American Ceramic Society, OH, 1981).
[11] C.H. Bennett, in \textit{Diffusion in solids. Recent developments}, edited by A.S. Nowick and J.J. Burton, (Academic Press, NY, 1975).
[12] S. Ostanin et al., Phys. Rev. B \textbf{62}, 14728 (2000).
[13] A. Cheikh et al., J. Europ. Ceram. Soc. \textbf{21}, 1837 (2001).
[14] J.P. Goff et al., Phys. Rev. B \textbf{59}, 14202 (1999).
[15] M. Ohta et al., Physica B \textbf{316-317}, 427 (2002); M. Ohta et al., Phys. Rev. B \textbf{65}, 174108 (2002).