

Defect Structure and Related Properties in Stabilized Zirconia

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Measurements of optical reflectivity and absorption spectra in the UV region are discussed, in order to clarify the influence of stoichiometric defects on the electronic states of cubic stabilized zirconia with different concentrations of substitutional ions. Results show that while the stoichiometric disorder does not affect the properties related to the fundamental electronic structure, it induces marked shifts of the absorption edge, due to the introduction of localized states in the bandgap. It has been observed that the entity of this phenomenon is inversely related to the concentration of the substitutional ions. This result contradicts the notion of stoichiometric vacancies as a reservoir of randomized defects.

1. Introduction

Pure ZrO_2 , or zirconia, is known to possess different structural phases, which are stable in different temperature ranges. At room temperature, the monoclinic structure is the only stable form for the massive compound. The cubic and tetragonal forms do not exist under ordinary conditions; they can be stabilized by adding to ZrO_2 finite amounts of another oxide, such as Y_2O_3 or CaO , whose cation is aliovalent with respect to Zr.

As a result of adding n mol of yttria or calcia to 1 mol of pure zirconia, the stoichiometric formula of the mixed oxide becomes $Zr_{1-x}Y_xO_{2-x/2}$ or $Zr_{1-x}Ca_xO_{2-x/2}$, in order to fulfill charge neutrality. This implies a defect in the occupancy of oxygen sites, i.e. the presence of stoichiometric vacancies, in a ratio of 1:2 or 1:1 to the number of foreign ions. The index x scales in the two cases as $2n/(1 + 2n)$ or $n/(1 + n)$; therefore, for small values of n there are practically equal amounts of structural vacancies for a given concentration of the dopant oxide, irrespective of its type.

Current theory considers stabilization to be the result of competition between steric and energetic mechanisms (*e.g.*, see ref. 1). On the one hand, the accommodation of sizeable numbers of Ca^{2+} or Y^{3+} ions in the monoclinic ZrO_2 tends to induce a closer packing and higher symmetry of the surrounding anions, owing to the large cationic radius of the dopant. On the other hand, the oxygen vacancies accompanying the substitutional ions oppose this increase of cationic coordination, as long as they can associate as nearest neighbors to the excess charge of the aliovalent impurity. As an indication of this, stabilization of the cubic phase begins at about 6 mol% in the case of zirconia-yttria and at 12 mol% in the case of zirconia-calcia, which implies equal concentrations of the substitutional ions but a factor of 2 in the concentration of vacancies. If only steric accommodation were concerned, the larger Ca ions should promote an earlier stabilization effect than Y ions.

The above considerations suggest that the structure requires a preferential arrangement of anionic defects in order to be stabilized. The presence of ordering processes is all the more plausible, as the vacancies are present in very large numbers on the order of $10^{20}/\text{cm}^3$, and can easily interchange with oxygen ions. Experiments by means of diffuse X-ray scattering⁽²⁾ and electron diffraction⁽³⁾ have shown in fact that oxygen relaxations occur around the vacant sites and that they are spatially correlated, giving rise to features of short-range order in the anion sublattice. Vacancies therefore can hardly be viewed as independent, random defects.

Recently, lattice-energy calculations performed on an ideal model system $\text{ZrO}_2:\text{Ca}$ indicated that oxygen vacancies are formed preferentially as nearest neighbours to the Zr ion.⁽¹⁾ Meanwhile, a direct EXAFS analysis of the site structure of cubic and tetragonal zirconias was performed, showing that the oxygen coordination is nearly 7 for the Zr site, but is 8 for the impurity site;^(4,5) this confirms that the vacancies tend to keep away from the stabilizing ions.

For better insight into these problems, one needs systematic tests of bulk properties that are sensitive to structural disorder as a whole, beyond the conventional viewpoint of isolated defects. The following is a review of recent work performed by us in these directions.

2. Defect Structure and Electronic Properties in YSZ

Oxygen vacancies and foreign ions are sources of electric and elastic imbalance on the atomic scale. Their presence in large concentrations results in a diffuse perturbation of crystalline fields. As a consequence, the distribution of valence and conduction states is likely to be modified in the mixed oxide, with respect to that of the pure compound.⁽⁶⁾ This might lead to the alteration of properties associated with the band structure, in particular: i) shape of the fundamental absorption edge, ii) optical energy gap and iii) spectrum of the first interband transitions. These effects should be similar to those observed in highly disordered or amorphous materials;⁽⁷⁾ however, if the defects in stabilized zirconias are not completely randomized, it is reasonable to suppose that certain features of incipient ordering be conveyed in the above-mentioned properties.

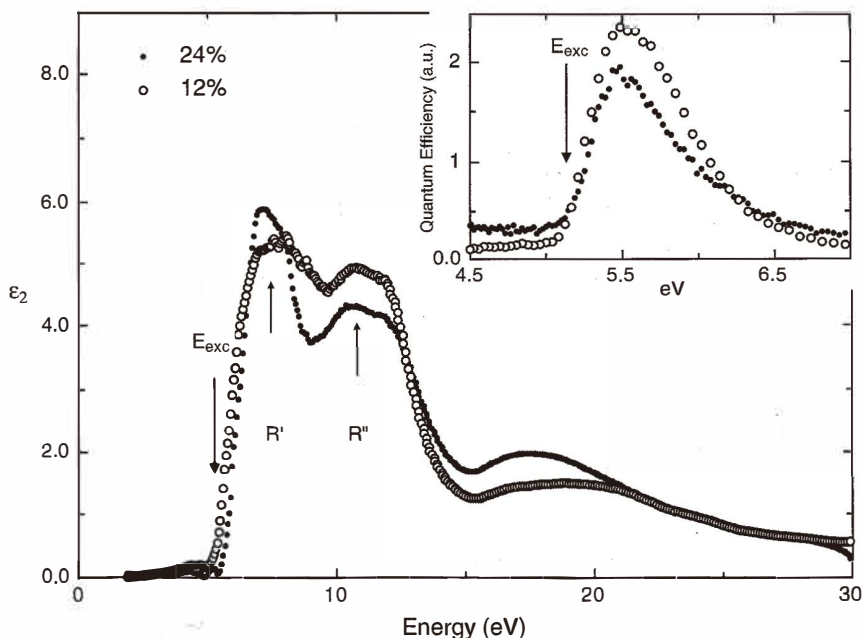


Fig. 1. Spectra of the imaginary part of the dielectric constant, ϵ_2 , for two samples of YSZ of different stoichiometries. Inset shows the excitation spectra of recombination luminescence for the same samples. The arrow indicates the excitonic edge.

Figure 1 illustrates the spectral responses of two samples of YSZ, with yttria concentrations of 12 mol% and 24 mol%, in the vacuum UV region above 5 eV. The respective ϵ_2 spectra, derived from reflectivity measurements, clearly show the presence of the first interband transition, with two distinct overlapping components R'-R''. In spite of the different stoichiometry of the two samples, this transition shows a fixed absorption threshold at about 5.5 eV, the same overall width and the same peak positions of the component lines. The changes in relative heights of the two peaks probably reflect a minor influence of stoichiometry on the shape of the valence band and of the two conduction subbands to which the transition is connected;⁽⁸⁾ however, they do not seem to affect the basic invariance of the phenomena, in particular the existence of a well-defined optical gap, independent of concentration.

Confirmation of this was obtained from parallel observations of recombination luminescence, of which the excitation spectra for the same samples are shown in the inset of Fig. 1: these results clearly prove the existence of an excitonic threshold at about 5.2 eV, also independent of stoichiometry, which agrees with the energy gap measured from the absorption spectra.⁽⁹⁾

The above features clearly suggest an intrinsic stability of the electronic structure, independent of lattice disorder. Conversely, a marked influence of disorder was found in

the absorption tail, i.e., in the spectral region immediately below the gap. To observe this, direct transmission measurements are required, as the accuracy obtained from reflectance observations becomes very poor at low absorption levels. Systematic experiments were performed to this end on a wide series of thin plates of YSZ, with yttria content varying from 9 mol% to 24 mol%, as well as a sample of cubic zirconia with 15 mol% of calcia. The results are given in Fig. 2, showing a characteristic behavior of the absorption edge, which is summarized as follows:

a) Absorption begins to develop well below the intrinsic gap energy E_g , with an exponential tail which is described in a logarithmic plot of the absorption coefficient $\mu(E)$ vs energy by the straight lines:

$$\log \mu(E) = A + B (E_g - E).$$

This extra absorption is very similar to the well-known Urbach tail, which is observed in many insulating solids and is currently associated with the presence of dynamic lattice disorder.⁽⁷⁾ However, the phenomenon in YSZ was found to be nearly independent of

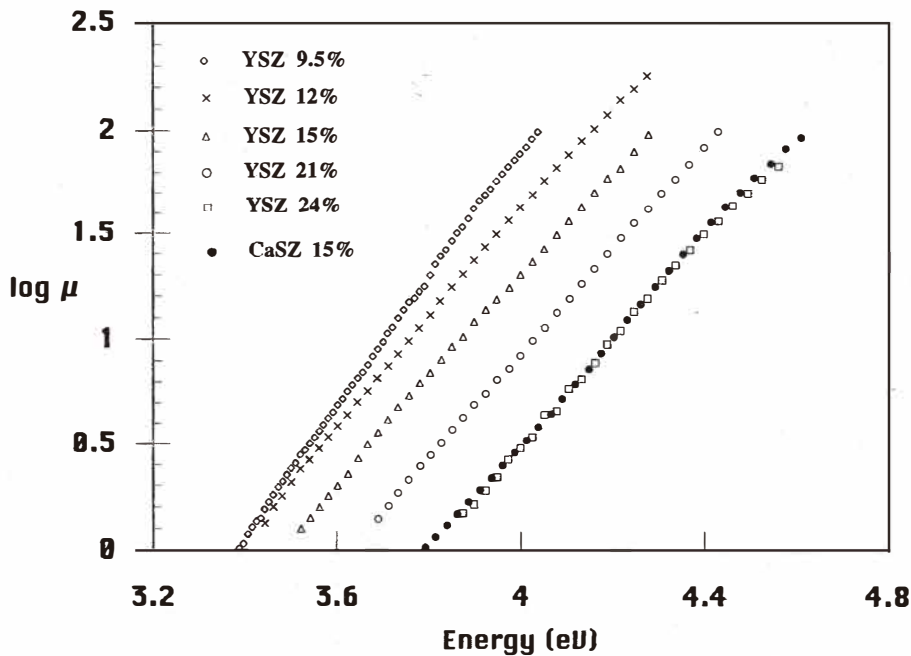


Fig. 2. Semilogarithmic plots of the RT absorption coefficient $\mu(E)$ in the near UV region below the gap. Measurements refer to a series of YSZ samples of different stoichiometries and to a CaSZ sample. Symbols: experimental data. Straight lines: visual guide to linear interpolation (see text).

temperature indicating that the nature of the effect is static, i.e. connected with built-in lattice disorder. It is notable that the slope of $\log \mu(E)$ is nearly the same in all cases irrespective of the type and concentration of the stabilizer (a slight deviation in this respect is present only in the case of the 9.5% sample). This general behavior supports the idea that the dominant mechanism of extra absorption is the perturbation of intrinsic states, owing to the combined presence of the foreign ions and of the corresponding oxygen vacancies.

b) As stoichiometry increases, the observed log plots are rigidly shifted to higher and higher energy; in other words, the energy threshold for extra absorption increases, while the constant A decreases upon increasing the concentration of the stabilizer (e.g., Y). Correspondingly, the integral of extra absorption up to the limit E_g also decreases. We conclude that the strength of the effect, admittedly due to lattice disorder, is inversely related to the total number of imperfections (vacancies plus impurities) which are the source of structural disorder.

This contradiction is lifted only if we assume that a progressive ordering develops as the number of vacancies increases. Such a conclusion is in good agreement with the results from electron diffraction,⁽³⁾ according to which short-range order appears in the anion sublattice at high vacancy concentrations.

The optical gap and the first direct transition are governed in principle by the shape of the occupied valence band (based on O-2p orbitals) and of the empty conduction band (based on Zr-4d levels).⁽⁶⁾ The presence of a large number of imperfections ensures that the fundamental transition O-2p \rightarrow Zr-4d will be perturbed on a large fraction of sites. The effect however, can also depend on the configuration of the defect system. This may be understood qualitatively by comparing two extreme situations of the crystalline potential, namely, a few isolated vacancies distributed at random or a multitude of vacancies, correlating with the rest of the structure in an ordered way. The argument is that in the first case, we must deal with proper singularities, which tend to promote the formation of localized levels well inside the gap. In the second case, the perturbation of the crystalline field should be smooth and regular, so as to contribute as an additive component of a periodic potential. This is likely to give a limited *smearing* of perturbed valence and conduction states around their ideal band edges. This arguments are supported by recent results of computer modelling, according to which the structure of cubic YSZ is described in terms of alternating blocks of Zr-O and Y-O coordination, where the structural vacancies are embedded so as to ensure local charge neutrality.⁽¹⁰⁾

3. Point Imperfections vs Structural Disorder

Independent of ordering phenomena, there are a variety of aspects which are related to the presence of individual vacancies. One of these is the formation of electronic centers, of which the study by suitable combinations of optical and EPR techniques can provide insight into the structure and the concentration of the underlying defects.

A variety of centers are known to be formed in YSZ, as the result of electron and hole trapping, following specific treatments of irradiation, or thermo- and electrochemical reduction.⁽¹¹⁾ The best known among them is a so-called T center, which has axial

symmetry and consists of an excess 4d electron on a Zr^{3+} ion, midway between two oxygen vacancies at the opposite ends of a cube diagonal. Structural characterization has been accomplished by means of EPR measurements,⁽¹²⁾ optical observation has shown that the center is also connected to an absorption band in the near UV region.⁽¹³⁾ This center can be formed in sizeable quantities, which are monitored by optical and paramagnetic experiments. Another representative center is the so-called F^+ , which owing to its paramagnetic isotropy has been identified as an electron trapped by an oxygen vacancy, regularly surrounded by four Zr^{4+} ions. Neglecting other centers, the identification of which is less clear, these two entities are particularly important as probes of isolated vacancies and vacancy pairs. Studying their production during ionizing irradiation, which does not introduce atomic displacements, one can quantify the respective amounts of the underlying defect in the as-received material. Some of our results are summarized in Table 1.⁽¹³⁾ Here, the saturated concentrations of T and F^+ centers measured after RT X-ray irradiation, are compared with estimated densities of the precursor defect (single or double vacancy) derived from the knowledge of stoichiometry, under the assumption of a purely random distribution. The data are reported for two samples of different yttrium content, so as to evidence the corresponding trends.

From the data of Table 1, the points of interest can be summarized as follows: i) for the two samples, F^+ -center concentrations are markedly lower than T-center concentration and they contradict the estimated concentration of monovacancies with respect both to absolute numbers and dependence on stoichiometry; ii) T-center concentrations increase with increasing yttrium content, but they remain lower than those predicted by random divacancy precursors.

These observations indicate that the situation deviates from the conventional viewpoint of a free-vacancy reservoir, where aggregation processes would be governed by purely probabilistic laws. In other words, true point defects (mono- or divacancies) are a very small fraction of the total defects, whereas the great majority of vacancies are in a state which apparently prevents an efficient trapping of electrons. This again confirms the existence of ordered configurations among them in the defect system.

Table 1
EPR center densities (spin/cm³), as calculated from the EPR signal area, in X-ray irradiated samples with different contents of stabilizing Y_2O_3 . Precursors densities for the F^+ and T centers have been calculated assuming a random distribution of stoichiometric oxygen vacancies, using the Bernoullian distribution law.

Y_2O_3 mol.%	12%	24%
stoichiometric vacancies	1.0×10^{21}	2.0×10^{21}
F^+ precursor (calc.)	1.3×10^{20}	1.0×10^{20}
F^+ centers (exp.)	2.0×10^{16}	$< 10^{15}$
T precursor (calc.)	2.3×10^{18}	6.6×10^{18}
T centers (exp.)	4.0×10^{17}	5.6×10^{17}

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