Effects of yttria concentration on the EPR signal in x-ray-irradiated yttria-stabilized zirconia

C. B. Azzoni and A. Paleari

Dipartimento di Fisica A. Volta, dell' Universita di Pavia, via Bassi 6, 27100, Pavia, Italy

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The anisotropic EPR signal already observed in x-ray-irradiated yttria-stabilized zirconia is analyzed between 140 and 300 K in samples containing 12% and 24% Y_2O_3. A temperature-dependent broadening is detected and attributed to spin-lattice interactions whose mechanisms are discussed. The analysis of the data as a function of the concentration of stabilizing oxide contributes to the explanation of the stability properties of the center, also studied by means of isochronal and isothermal pulsed annealings. The results confirm the already proposed model and the intrinsic nature of the defect.

INTRODUCTION

The purpose of this work is the investigation of some features of the anisotropic electron-paramagnetic-resonance (EPR) signal[1] observed in x-ray-irradiated zirconia[2] and in hydrogen-reduced zirconia.[3,4] The model we already proposed[2] for this EPR center (from now on named $[ZrO_7/e^-]$) consists of an electron localized at a cation site near an oxygen vacancy, substantially representable as a Zr^{3+} ion in a $4d^1$ configuration. In this way it is possible to account for many features of the EPR signal: The rearrangements of the oxygen atomic positions around the vacancies give rise to a structural disorder of the anionic sublattice that causes a spread in the value of the component of the g tensor orthogonal to the defect axis, and small deviations of the local directions of the defect axis with respect to the $\langle 111 \rangle$ crystal directions. This can explain the inhomogeneous and anisotropic broadening of the signal and its asymmetry at low temperatures.

In this Rapid Communication we present preliminary results which agree with the proposed broadening mechanism and with the discussed intrinsic nature of the $[ZrO_7/e^-]$ center. We have also observed a good stability of the center concentration at room temperature, in contrast with that reported by other authors for samples exposed to x rays.[4] Then we have studied the stability properties of the $[ZrO_7/e^-]$ center by means of isochronal and isothermal pulsed annealings above the room temperature. A complete reversibility exists between the x-ray activation of the centers and their thermal quenching, confirming the electronic trapping nature of these processes at the intrinsic defect sites.

Samples of differently stabilized zirconia (12% and 24% of Y_2O_3) are considered to verify the influence of the center concentration on these processes. Then the competitive role of the impurities in the electronic trappings activating the $[ZrO_7/e^-]$ centers is discussed together with the role of the hydrogen.

EXPERIMENT

Single crystals (in the form of bars of $\simeq 1 \times 1 \times 10$ mm^3) of yttria-stabilized zirconia (12% and 24% of Y_2O_3) from Ceres Corporation were measured after x-ray exposure at

room temperature up to a dose of $\simeq 10^4$ Gy and a mean energy of the beam of 15 keV. Using, for ZrO_2, a mass attenuation factor of 40 cm^2/g it is possible to calculate[5] the effective irradiated volume of the samples finding out that the paramagnetic centers were created mainly at the surface, the attenuation length being about 0.05 mm.

The EPR spectra (X-band) were detected at temperatures between 140 K and room temperature, both in the configuration $B \| \langle 111 \rangle$ and $B \perp \langle 111 \rangle$ (where the $\langle 111 \rangle$ crystal directions coincide, except for small deviations[2] with the defect axis) in order to study the thermal dependence of the line shape of the signal. The effects of the modulation field were taken into account in the evaluation of the linewidths. The microwave power was kept at suitably low values to avoid saturation effects.

The samples were then annealed for 5 min at temperatures between 50 and 300°C (isochronal pulsed annealing) and, after a reirradiation at the same dose, they were subjected to repeated annealings of 3 min at 200°C (isothermal pulsed annealing). After every treatment the samples were measured at 150 K in the configuration $B \| \langle 111 \rangle$.

RESULTS

The EPR signal has the same spectroscopic features in the two types of samples, therefore the same type of paramagnetic center $[ZrO_7/e^-]$ seems to be induced in both of the samples. The amplitude of the first derivative of the EPR signal decreases more than an order of magnitude between 140 K and the room temperature with a law that depends on the crystal orientation in the magnetic field. The decrease of the intensity is followed by an increase of the linewidth ΔB. The broadening of the signals corresponding to $g_\|$ and $g_\perp$ (see Fig. 1) is comparable, but the change of $\Delta B_\|$ normalized to the low-temperature value is higher than that of $\Delta B_\perp$. Increasing the temperature, the signal of $g_\|$ becomes more symmetric and Lorentzian in line shape.

The analysis of the data of Fig. 1, together with the amplitudes of the signals, shows that for both the samples the signal area, and hence the number of EPR centers, does not change, except for the Boltzmann factor, in the temperature range of the measurements. Comparing the two samples, for equal irradiation doses and taking into ac-
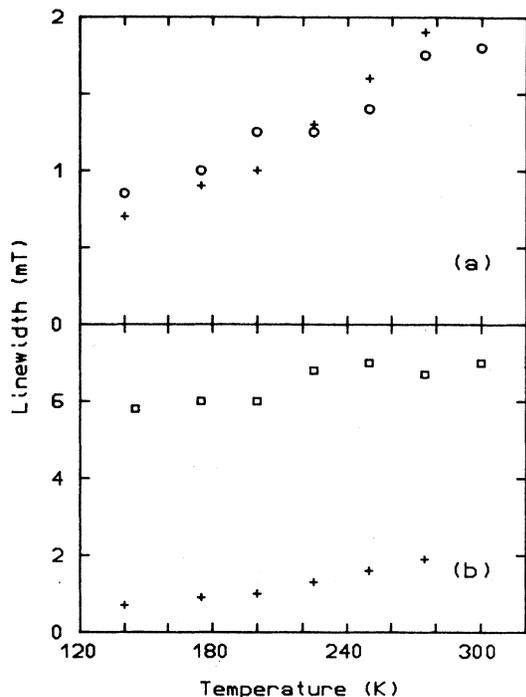
FIG. 1. (a) Comparison between the temperature dependences of linewidths of the EPR derivative signal $\Delta B_\parallel$ of the $[ZrO_7/e^-]$ center in the samples with 12% (+) and 24%K (o) Y_2O_3. (b) Temperature dependence of the linewidths for B parallel to the defect axis (+) and orthogonal to it (□).

reduced by less than 10% after more than three months at room temperature. It quenches after 5 min at 300 °C (see Fig. 2) in both the samples. Reirradiating at the same x-ray dose, the EPR signal reappears with the same features it had before the thermal treatment, showing the reversibility of the processes. The time decay of the defect concentration is observed for the reirradiated samples by means of pulsed annealings at 200 °C, finding a half-life of about 20 min.

DISCUSSION

A noteworthy result is the proportionality between the paramagnetic defect population, as calculated from the EPR signal area, and the concentration of trivalent cations related to the oxygen vacancies: This result confirms the hypothesis about the intrinsic nature of the $[ZrO_7/e^-]$ center.

The data of Fig. 1 show that $\Delta B_\parallel(T)$ and $\Delta B_\perp(T)$ differ for a constant contribution of about 5 mT to $\Delta B_\perp$, which constitutes an inhomogeneous and T-independent broadening of the orthogonal component of the EPR signal, accordingly to the model,[2] while the T-dependent contribution to ΔB has about the same magnitude in the two cases. Different concentrations of stabilizing oxide do not correspond to relevant differences of ΔB, expected from T-independent contributions of dipolar interactions. Then defect cluster formation can be excluded even if the defect number changes by a factor of 2. The temperature

count their different volumes, the density of paramagnetic defects results proportional to the concentration of stabilizing oxide and then to the oxygen vacancy density.

The data of Fig. 1 also show that the slope of $\Delta B_\parallel(T)$ is slightly greater for the sample with 12% Y_2O_3 than for the sample with 24% Y_2O_3.

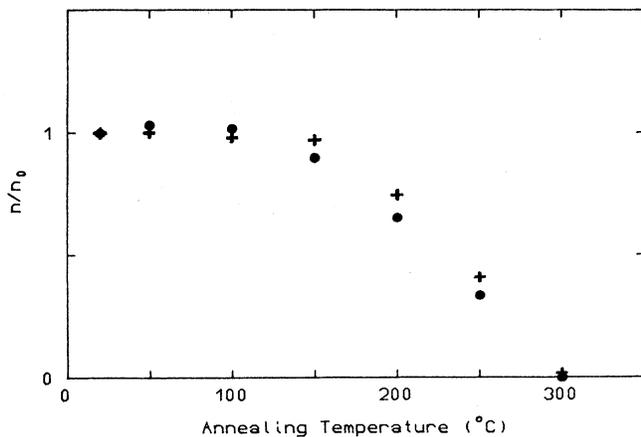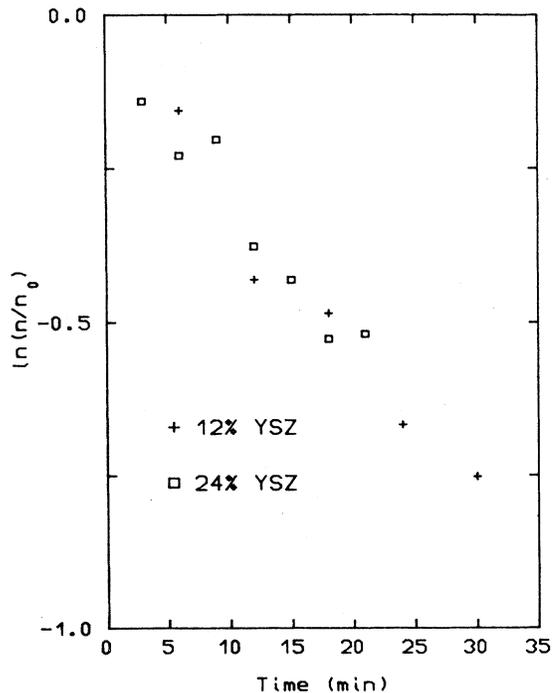The signal of the x-ray-induced $[ZrO_7/e^-]$ center is

FIG. 2. 5 min isochronal pulsed annealing results on the relative density n/n_0 of $[ZrO_7/e^-]$ centers created by x ray in yttria-stabilized zirconia with 12% (●) or 24% (+) of Y_2O_3.

FIG. 3. Change of the relative population n/n_0 of x-ray-activated $[ZrO_7/e^-]$ centers in ZrO_2-Y_2O_3 (12%) (+) and in ZrO_2-Y_2O_3 (24%) (□) during isothermal pulsed annealings at 200 °C.

dependence of the signal broadening may then be attributed to spin-lattice interactions, accordingly with the strong electron-phonon interactions observed by others[6,7] by means of optical measurements.

The small difference in the slope of $\Delta B(T)$ detected in the samples with 12% and 24% Y_2O_3, arises probably from the particular spin-lattice relaxation process. In order to study the exact dependence of ΔB vs T, the temperature range of the measurements needs to be extended and measurements down to the liquid-helium temperature are planned. Actually, in the considered temperature range, the nearly linear experimental dependence of ΔB (see Fig. 1) is also reproducible by means of an exponential law or a power of T. While a direct relaxation process (for which $\Delta B \propto T$) is not probable in the considered temperature range, the phononic density being low at the energies comparable with that of the EPR transition, indirect relaxation mechanisms, such as Raman and Orbach processes, could be relevant.[8] A spin-lattice relaxation process due to Raman scattering, dominant at high temperature, predicts a T^9 law. An Orbach process also has to be taken into account because of the existence of an excited level of the $[ZrO_7/e^-]$ center at a suitable distance from the ground state. In fact the two levels constituting the t_{2g} ground doublet of the Zr^{3+} ion are split by the axial component of the crystal field[2] and their energy separation δ can amount to some 10^2 cm^{-1}. In this case $\Delta B(T)$ should have a $e^{-\delta/kT}$ exponential dependence. Different defect concentrations could induce, in such a model, small changes of the axial component of the crystal field at cation sites, giving rise to slightly different behavior of $\Delta B(T)$. The spectroscopic parameters of the EPR spectrum would remain unchanged, depending mainly on the cubic component of the crystal field.

The stability properties of the $[ZrO_7/e^-]$ center are not different in the two types of samples (see Figs. 2 and 3) probably because the change of the number of centers is not large enough to modify the defect kinetics; also in this case, the $[ZrO_7/e^-]$ center does not show clustering properties as evidenced by the discussion of the concentration dependence of ΔB. Supposing electronic detrapping mechanisms are the basis of the quenching process of the $[ZrO_7/e^-]$ centers, as suggested by the reversibility of the annealing and irradiation treatments, it is possible to analyze the data of the isochronal and isothermal pulsed annealings by means of the simple relation, characteristic of a first-order kinetic process, of the type n/n_0 $=\exp[-vt\exp(-E/kT)]$, where n/n_0 is the relative center concentration, while v and E are the frequency and the energy of detrapping. E is estimated to be about 0.4 eV, which may be interpreted as the depth of the energy level of the defect with respect to the conduction band.

The lower stability of the $[ZrO_7/e^-]$ center reported by other authors, with respect to that which we observed, may arise from a higher density of impurities that could be responsible for competitive electronic trapping during the activation of the $[ZrO_7/e^-]$ centers. On the contrary, the high stability typical of hydrogen-reduced samples[3,4] may be evidence of the compensative role of hydrogen at the impurity sites that could be inhibited in the competitive process of electronic trapping.

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[8]See, for example, A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Ions (Clarendon, Oxford, 1970).