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Radiation damage produced in $BaHfO_3$ irradiated with thermal and fast neutrons

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Samples of $BaHfO_3$ were irradiated with fast and thermal neutrons to produce ^{181}Hf. Attenuations of the γ-γ perturbed angular correlations in ^{181}Ta were observed, and they may have been caused by the interaction between defects (produced during or after neutron irradiation) and oxygen vacancies. Several defect structures were detected. For one of the structures, an excitation energy of 12 meV was measured, which was attributed to an electron state below the conduction band. The values of the dielectric constant and of the effective electron mass were also deduced.

INTRODUCTION

In a recent publication we have reported time-differential perturbed-angular-correlation (TDPAC) results for ^{181}Ta in $BaHfO_3$.[1] This perovskite with cubic structure showed attenuations that could have been caused by defects. The same kind of perturbations were observed previously in $SrTiO_3$, $BaHfO_3$, and $BaTiO_3$ when samples were prepared with ^{181}Hf.[2] In these cases a unique interaction was detected and, for $BaHfO_3$ samples, the relaxation parameter $\lambda=0.031$ ns^{-1} was found.[2] In $BaHfO_3$ samples, irradiated with thermal neutrons to produce ^{181}Hf, two interactions appeared.[1] One very strong interaction that could not be characterized was annealed out at 1273 K, and a second one was characterized by a relaxation mechanism with $\lambda=0.0644$ ns^{-1} that changed abruptly at 1273 K to a lower value, $\lambda=0.0442$ ns^{-1}. This value almost coincides with the one reported in nonirradiated samples.[2] At 1273 K, the population of the second site is 100%. The thermal behavior of λ led us to conclude that the process observed was associated with defects. As oxygen vacancies are the most common defects in these materials, the relaxation observed after the high-temperature annealing was proposed to be caused by oxygen hopping from an occupied lattice site to a vacant one. This differs from a mechanism proposed elsewhere involving anharmonic effects produced at the 4^+ site.[2]

Using the Abragam and Pound theory[3] and a point-charge model for calculating the electric-field gradient tensor (EFG) at probes, the hopping time τ_c was deduced. Although this model is very crude for calculating the EFG, it can be used to estimate of the value of τ_c.

Another characteristic observed in ABO_3 compounds[2] is that the relaxation parameter λ is not very different from one perovskite to the other. As the lattice constants are very similar, of the order of 4 Å, this would indicate that all these materials have the same defect which probably is related to oxygen vacancies and impurities that produce electron states below the conduction band, as will be explained below.

The unresolved strong interaction was assigned to ^{181}Ta probes in radiation-damaged sites, probably composed of either vacancies or interstitial-vacancy configurations.

In most other samples irradiated with thermal neutrons to produce ^{181}Hf, metals, metallic alloys, and compounds, no signals caused by radiation damage appear. Probably the damage is annealed out at irradiation temperatures (approximately 60 °C) in most samples. However, damage produced in $BaHfO_3$ survives up to 1100 K and should be connected to the preexistence of lattice defects. When ^{181}Hf is produced by thermal neutrons, recoil is produced by emission of γ rays. The maximum energy of the γ-ray spectrum is 5695.6 keV (Ref. 4) and many other lower-energy γ's are emitted. If a mean γ energy is considered, the mean recoil energy would be of the order of 30 eV. For the maximum energy γ ray emitted, the recoil is 95 eV. Both energies are enough to produce at least single point defects.

Another way to produce defects is by irradiating the sample with fast neutrons. Thus, 1 MeV neutrons will produce a ^{181}Hf recoil with an initial kinetic energy approximately 60 times the one produced by the thermal-neutron γ-emission process. The defects produced in this way would be different from those observed and reported previously.[1]

In this work, we present TDPAC results obtained from a fast-neutron-irradiated $BaHfO_3$ sample, and we compare them with those obtained previously for a thermal-neutron-irradiated $BaHfO_3$ sample. This comparison should allow us to observe whether or not the same annealing process occurs in both types of samples, and to confirm that the attenuations are correlated with defects, i.e., radiation damage, oxygen vacancies, and impurity states in the band gap. Then, we can deduce the excitation energy of an electronic state in the band gap. From this energy and using hydrogenic Bohr model the dielectric constant and an "effective" electron mass are also deduced.

EXPERIMENT

The $BaHfO_3$ samples were fabricated from a stoichiometric ground mixture of commercially available high-purity $BaCO_3$ and HfO_2. Pellets of approximately 5 mm diameter and less than 1 mm thick were obtained by pressing. These pellets were then fired at 1400 K in open air for 48 h. Part of each pellet was analyzed by x-ray-diffraction technique and gave the pattern of a cubic lattice with a lattice constant of 4.17 Å.[5] Another part of each sample was irradiated in a flux of approximately 10^{13} fast neutrons/cm^{2}s for 24 h near the core of São Paulo reactor and TDPAC-analyzed by two spectrometers, one with four BaF_2 detectors and a resolution time of 1 ns and the other with four NaI(Tl) detectors with a resolution time of 3 ns. The first two TDPAC spectra were obtained with the BaF_2 spectrometer and the rest with the NaI(Tl) spectrometer.

The TDPAC technique measures the perturbation in the angular distributions of the nuclear-radiation cascade caused by the interaction between excited probe nuclei and extranuclear fields.[6] The probability $W(\theta,t)$ that nuclei emit radiations γ_2 in a θ direction with respect to and at a time t later than the emissions of γ_1 is given by

$$W(\theta,t)=1+A_2G_2(t)P_2(\cos\theta)+A_4G_4(t)P_4(\cos\theta)\ ,$$

where A_2 and A_4 are coefficients that depend on the spins of the involved nuclear states and on the radiation multipolarities. $P_2(\cos\theta)$ and $P_4(\cos\theta)$ are the Legendre polynomials and $G_2(t)$ and $G_4(t)$ are the perturbation factors that describe the hyperfine interaction. For a fast relaxation process, $G_k(t)=e^{-\lambda_k t}$ and $\lambda_k \propto \tau_c\langle\omega_Q^2\rangle$ is the mean squared average of the electric quadrupole frequency at time $t=0$ and τ_c the correlation time.[3] For static high-frequency (hf)-perturbation, $G_k(t)=\Sigma\sigma_{kn}e^{-\delta}\omega^{t}_{kn}\cos\omega_{kn}t$, where σ_{kn} and ω_{kn} depend on hyperfine field characteristics and δ is a Lorentzian frequency width related to the existence of lattice imperfections.[6]

After irradiation with fast neutrons the $BaHfO_3$ samples were annealed two times, one for 48 h and the other for 96 h in open air at maximum temperature of 1300 K.

RESULTS AND DISCUSSION

From the time coincidence spectra, the corresponding attenuation factors $A_2(t)$ were deduced, and, in Figs. 1(c) and 1(d), measurements at room temperature are shown. A two-component perturbation-factor function was fitted to the data. It included a fraction f_1 of a static quadrupole interaction and a fraction $(1-f_1)$ of a time-dependent interaction of the Abragam and Pound type. The periodic perturbation represents interactions of the 481 keV excited level of ^{181}Ta in HfO_2, having nuclear spin precession of $5/2^+$, with the following hyperfine parameters: $\omega_Q=125_5$ MHz, $\eta=0.30_3$, $\delta=0.05_1$, and $f_1=20\%$. The presence of HfO_2 reveals that the reaction was not completed and small grains ($\delta\simeq0.05$) are still present. Neither the abundance nor the hf parameters of HfO_2 changed with the thermal treatments performed. Thus the changes observed in the rest of the material cannot be attributed to the presence of HfO_2.

For comparison with the thermal-neutron-irradiated sample two room-temperature (RT) measurements are included in Figs. 1(b) and 1(a) representing the as-irradiated and the annealed sample analyses, respectively.

After the first annealing, at 1300 K, the fast-neutron-irradiated (FNI) sample was characterized with a relaxation parameter $\lambda=0.110$ ns^{-1} at RT [see Fig. 1(d)]. For the FNI sample measured at liquid-helium temperature LHeT, $\lambda=0.160$ ns^{-1}. This value is almost 50% larger than the one at RT, and it shows that this defect structure, contrary to what was observed in other cases, is temperature dependent. The next thermal treatment, in which the sample was annealed at 1300 K, produced changes in the nuclear-spin relaxation. The relaxation parameter at RT was lowered to $\lambda=0.075$ ns^{-1} which almost coincides with the value obtained for the "*as*"-thermal-neutron-irradiated (TNI) sample. When the FNI sample was measured at 20 K, the corresponding $\lambda=0.077$ ns^{-1}. This value coincides well with the value

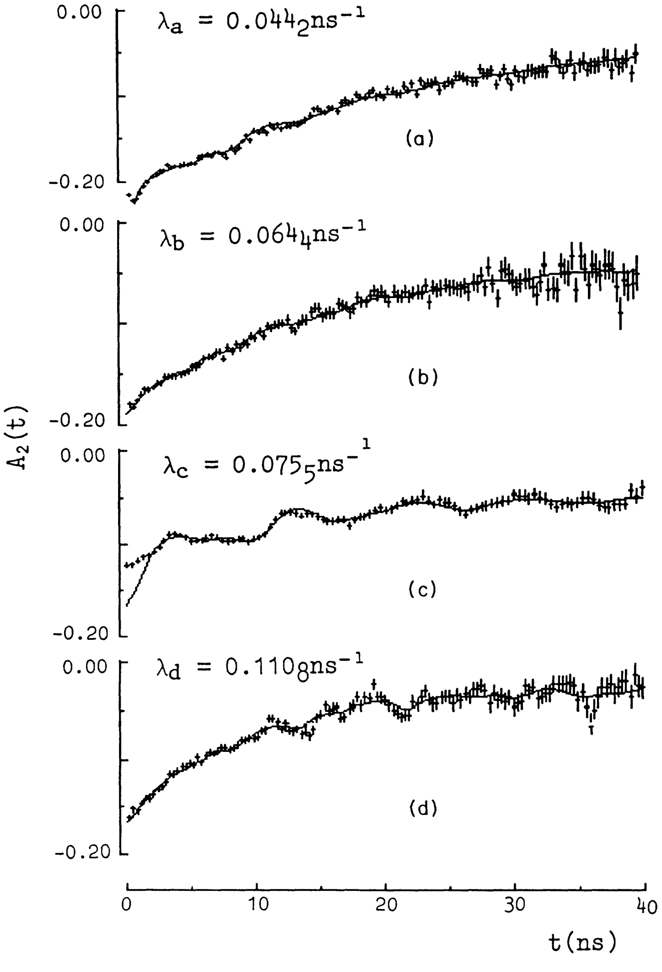

FIG. 1. Attenuation factors vs delay time, measured at RT. For $BaHfO_3$ irradiated with thermal neutrons: (a) corresponds to the annealed sample and (b) the "as-" irradiated sample. The other two correspond to the fast-neutron-irradiated $BaHfO_3$ sample: (c) annealing at 1300 K for 96 h and (d) annealed at the same temperature for 48 h, respectively.

$\lambda=0.076$ ns^{-1} measured in the TNI sample at liquid-nitrogen temperature (LNT). From these results, we conclude that after the second annealing the defect structure that produced relaxation in the fast-neutron-irradiated sample is similar to that produced by thermal-neutron irradiation. Thus curves *a*, *b* and *c*, and *d* represent relaxation rates corresponding to three different defect structures.

The thermal-neutron irradiation of ^{180}Hf, yielding ^{181}Hf excited levels, does not produce defects. But when ^{181}Hf excited levels decay to ground state by γ-rays emission, defects can be produced. From the tabulated γ energies and comparing the intensities of ^{181}Hf decay with the fractions of nuclei perturbed by the λ_b relaxation and the unresolved interaction, respectively, measured in the thermal-neutron-irradiated sample, it could be inferred that the recoil energies produce both defects. When the recoil ϵ_r is less than 49 eV the "*b*" defect structure could be produced. The other structure, the unresolved one, should be caused by hafnium ions recoiling with energies approximately between 52 and 96 eV.

In the thermal-neutron-irradiated sample another effect is observed, namely the increase of the anisotropy $A_2(T)$, at zero delay times, with temperature. This effect could represent the annealing out of a very fast process, relaxing in very short times compared to the spectrometer resolution time of 0.7 ns^1. $A_2(T)$ increases monotonically with temperature until the maximum value is reached at about 1273 K. Further measurements at 1350 K and RT do not show any further changes, indicating that the transformation was irreversible. It was also observed that λ jumps to a lower value above 1273 K, indicating that both defect structures are correlated. Thus, at temperatures below 1273 K, two correlated defects were observed; and by heating up the sample, one of the defect structures is annealed out causing also a modification in the other defect structure.

The thermal evolution from the so-called defect structures "*b*" to "*a*" can be also studied. This process can be seen in Fig. 2 where the logarithmic ratio $A_2(T)/A_2(\mathrm{RT})$ is plotted as a function of the reciprocal absolute temperature. $A_2(\mathrm{RT})$ is the maximum value of anisotropy measured at RT. The data seem to obey an Arrhenius law with an "excitation energy" of 0.012 (2) eV.

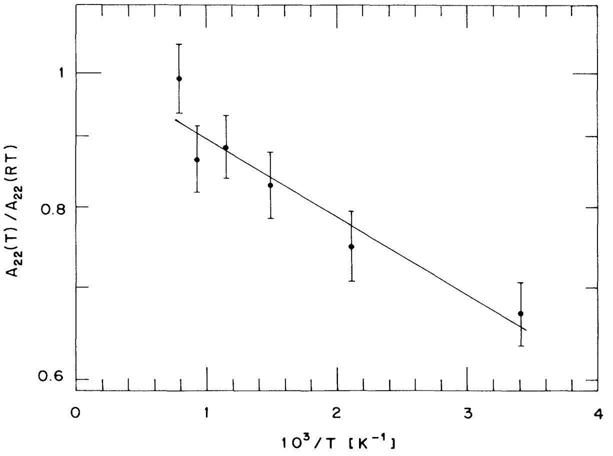

FIG. 2. Relative anisotropy $A_2(T)/A_2(\mathrm{RT})$ as a function of $1/T$.

Perovskites are materials with defects, O vacancies being the most common. The β decay of ^{181}Hf to ^{181}Ta produces still another defect, an *n*-type impurity at the center of the oxygen octahedron. The initial activity indicates that the ratio of Ta impurities to host Hf atoms is of the order of $1{:}10^7$. Thus a donor state could have been produced below the conduction band, by β decay, and, from the experimental data we infer that this state had probably been trapped by an oxygen octahedron.[7] This coupling between an O vacancy and this impurity state could originate the relaxation observed in nonirradiated samples and it should not be very distinct for different cubic ABO_3 compounds because of structural similarities. When other defects are produced, by fast-neutron-irradiation or gamma emission after thermal-neutron irradiation, they seem to play a role also, by interacting with the O-vacancy–impurity-state substructure. Now a more complex defect structure appeared, formed by the coupling of defects produced by radiation damage (or the defects produced by the annealings of radiation damage) with the O-vacancy–impurity-state substructure. Thus, the relaxations shown in Figs. 1(d), 1(c), and 1(b) would correspond to two different complex structures, and that in Fig. 1(a) would show that all radiation damage was annealed out leaving only the presence of the simple substructure of an impurity state trapped by the oxygen octahedron. Then different defects that interact with that substructure would also interact with "trapped" electrons, producing different trapped states. In this scenario, the excitation energy of 12 meV measured would be the energy difference between two distinct electron trapped states. This mechanism could also explain qualitatively why the TDPAC perturbation observed at ^{181}Ta in cubic $BaTiO_3$ samples with Ca impurities is a factor of 2 greater with respect to those measured in pure $BaTiO_3$.[8]

If these electronic states in the material are considered as hydrogenic, then the excitation energy deduced can be used for estimating the dielectric constant *k* of the material and the effective electron mass m^* if the Bohr radius is known. Consistent with our previous assumption that the electron is "captured" by the oxygen octahedron, we assume that the ground state has a Bohr radius of approximately 2.5 Å. This simple model allows us to obtain $k\approx180$ and $m^*\approx40m$. To the best of our knowledge, the dielectric constant for $BaHfO_3$ has not been measured before, but our value is consistent with the values obtained for other hafnium perovskites.[9]

CONCLUSIONS

In neutron-irradiated $BaHfO_3$ samples, different defect structures are produced by fast- and thermal-neutron irradiation. Thermal annealing changes these structures, producing in the end two common defects. The interaction between these defect structures, O vacancies and *n* impurities produced by the β decay of hafnium, would produce different electron states below the conduction band. The present data indicate that the energy difference between these electron states is 0.012 eV. A simple hydrogenic model gives the dielectric constant $k \approx 180$ and the electron effective mass $m^* \approx 40m$.

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