

## Photoluminescence in yttria-stabilized zirconia of aging effects

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Photoluminescence properties are studied on yttria-stabilized zirconia (YSZ) samples aged up to 1000 h at the temperature of 1073 K where the aging-induced decrease in conductivity is reported. Multiple peaks are observed under irradiation of sub-band-gap light of 3.81 eV by a He-Cd laser. Their intensities depend on aging time, and the aging-time developments of the intensities are characterized by two regions. One of these time regions exhibits large deviation and deformation of the aging-time behavior. The deformation is observed at the region of the first few hundred hours of aging for 8 and 10YSZ. The time region with deformation coincides with that of the main decrease in conductivity. The other time region without deformation contains two types of mutually complementary behavior for 8YSZ or exhibits slow and smaller change in the intensities for 10YSZ.

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### I. INTRODUCTION

The solid oxide fuel cell (SOFC) has been a subject of active research because of its advantages over other fuel cells: it is free from electrolyte-management problems as it utilizes a true solid electrolyte; it can take advantage of the internal conversion of hydrocarbon fuels; and it has a high overall thermal efficiency owing to the high operating temperature.<sup>1</sup> Yttria ( $Y_2O_3$ ) stabilized zirconia ( $ZrO_2$ ) (YSZ) is the most frequently used electrolyte in the SOFC because of its physical properties, availability, and cost.<sup>2</sup> Among all, YSZ has high ionic conductivity at the operating temperature of 800–1000 °C (1073–1273 K). Nevertheless, it suffers a conductivity decrease with aging at this temperature. For example, in 8YSZ (8 mol. % yttria-doped zirconia;  $x$  mol. % yttria-doped zirconia is abbreviated as  $x$ YSZ hereafter) and 10YSZ, the dopant concentration of which is close to that of the highest conductivity, up to 20% of the decrease in conductivity is observed within the first few hundred hours of aging at the temperature of 1073 K.<sup>3</sup> As an oxide-ion conductor, the ionic conduction in YSZ is determined by migration of oxygen ion vacancies<sup>4</sup> which are introduced with yttria doping. One of the present authors made an investigation into the aging-induced change in the local structures of the oxide vacancies through structural studies by means of x-ray diffraction (XRD), high-resolution transmission electron microscopy (TEM), extended x-ray absorption fine structure (EXAFS), and internal friction measurements.<sup>3,5–7</sup>

On the other hand, studies on the electronic states in the band gap (band-gap states) of the vacancies through photoluminescence (PL) measurement have been made,<sup>8</sup> which are based on the accumulated knowledge on the color centers of anion vacancies including those of oxides.<sup>9</sup> Unfortunately, these studies do not concern change in the local structures of the oxide vacancies induced by aging in YSZ,<sup>10</sup> which brings

about change in the localized band-gap electronic states. A recent study by Petrik *et al.*<sup>8</sup> made a detailed investigation on the PL bands of the band-gap states which were assigned to those from  $F^-$ ,  $F_A^-$ , and  $F_{AA}$ -type centers,<sup>9,11</sup> although it is limited to the 9.5YSZ samples without aging and the measurements over 120 K. These assignments were based on the structure models for the oxide ion vacancies in YSZ proposed in a series of EXAFS studies.<sup>12</sup> The models were fourfold-coordinated oxide ion vacancies whose nearest neighbors were  $Zr^{4+}$  ions only ( $F$ -type), substituted by an  $Y^{3+}$  ion ( $F_A$ -type) and substituted by two  $Y^{3+}$  ions ( $F_{AA}$ -type). *Ab initio* electronic-structure calculations should give insight into these defect structures and their localized electronic structures, but even the precise prediction of the band-gap energy is still difficult at present.<sup>13</sup> It is also difficult for the *ab initio* calculations to predict the defect structures because of the strong dependence on the sample shape and size in YSZ.<sup>14</sup>

There are also studies by more advanced spectroscopy on the samples without aging.<sup>15–17</sup> A small amount of an additional rare-earth ion is doped in many of these studies as a probe. Such an ion, which is expected to substitute for the  $Y^{3+}$  ion without any effect, modifies the ionic conduction, however it is similar to the  $Y^{3+}$  ion in size and valence state. The most dramatic case is YSZ with scandia ( $Sc_2O_3$ ) doping, where the aging effect can be suppressed with its high conductivity retained.<sup>18</sup> The suppression is also observed for  $In_2O_3$ -doped YSZ, even though the conductivity is partially dropped.<sup>19</sup>

As summarized in Ref. 5, several explanations have been proposed for the aging-induced decrease in conductivity. One of those explanations is the trapping of oxide ion vacancies toward dopant  $Y^{3+}$  cations as the aging progresses. The decrease in conductivity through vacancy trapping by cations has also been proposed to be a model to explain the conductivity drop in the higher dopant cation concentration. Never-

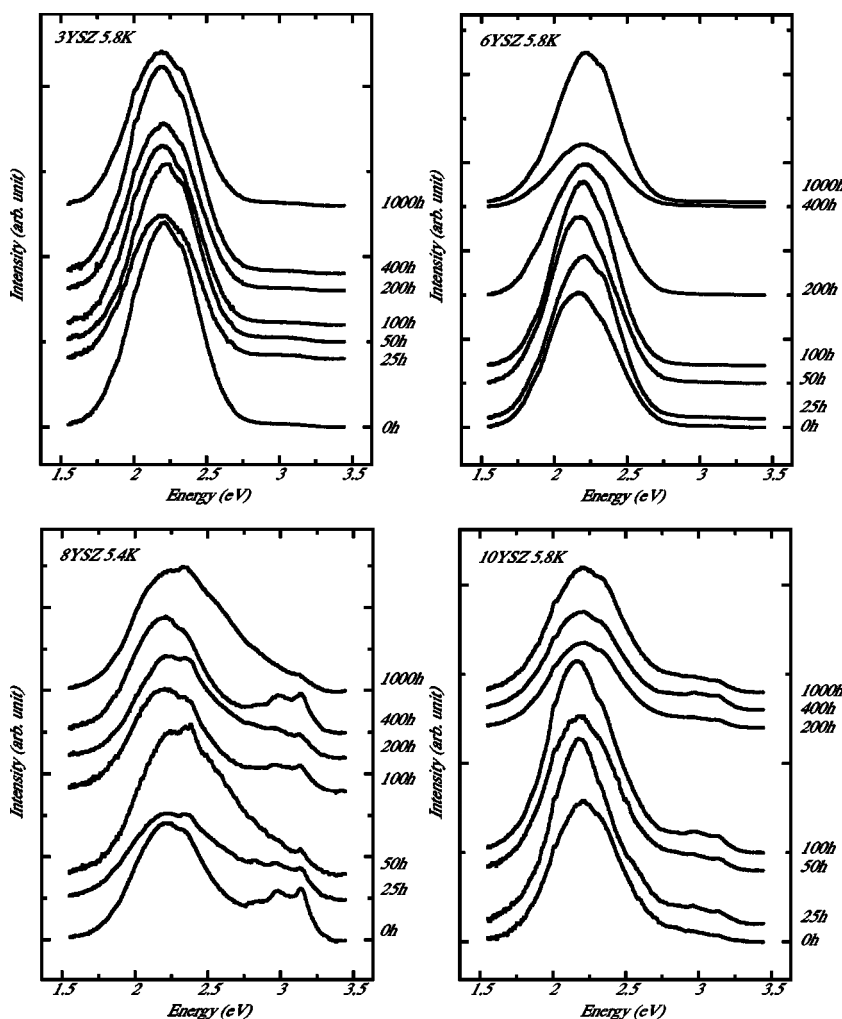


FIG. 1. The PL spectra observed at low temperatures for the samples aged up to 1000 h. The excitation energy was 3.81 eV of the He-Cd laser. Artificial shifts in base line were introduced to improve readability of the spectra.

theless, favorable distribution of the vacancies in equilibrium, which must be crucial in the “trapping” process within the model, has not been determined to be close to  $Zr^{4+}$  or  $Y^{3+}$ , both in experimental and calculational approaches.<sup>20,21</sup> Not only EXAFS and quasielastic light scattering (QELS) experiments, but also molecular-dynamics (MD) simulations cannot determine wherein lies the equilibrium favorable location of the oxide ion vacancies: the nearest neighbor of  $Zr^{4+}$ ,  $Y^{3+}$ , or  $Y^{3+}-Y^{3+}$  pair.<sup>22–26</sup> Moreover, it was revealed in a previous study that it is rather the relaxation of the anisotropy of the lattice distortion by redistribution of the vacancies, not simple “trapping” of the vacancies, that is responsible for the aging- and cation-concentration-induced decrease in conductivity.<sup>6</sup>

In the present study, we investigate the PL properties of the YSZ samples aged up to 1000 h at the temperature where the aging-induced decrease in conductivity is reported. Measurements at the temperature which is lower than the reported study by Petrik *et al.*<sup>8</sup> reveal a multiple-peak structure of the spectra. We also report the results for the samples of lower dopant concentration, 3 and 6YSZ, than those of the conductivity maximum at around 8–9 mol. %. A possible model is proposed to explain the aging-time development of the spectra, which strongly depends on the progress of aging and the dopant concentration. We discuss the effects of the

aging-time progress of the lattice distortion on the spectra based on the model.

## II. EXPERIMENTAL DETAILS

Polycrystalline samples were commercially obtained from Nikkato for 3YSZ, 6YSZ, and 8YSZ, and from Daiichi Kigenso for 10YSZ. Chemical analysis results and sintering conditions were given in a previous study.<sup>3</sup> The sample surfaces were mechanically polished and a rectangular surface of  $4 \times 22$  mm<sup>2</sup> area was used. Thickness of the samples was 3 mm. The aging process under 1073 K up to 1000 h was also described in a previous paper.<sup>3</sup>

The samples were mounted on the cold head of a closed-cycle He-gas refrigerator equipped with optical quartz windows and cooled down to  $5.6 \pm 0.2$  K. For the PL study, a He-Cd laser [wavelength 325.0 nm (3.81 eV)] was used for excitation. Intensity of the excitation light was 4 mW ( $0.51$  W cm<sup>-2</sup>). The incident beam was chopped at 0.3 kHz for lock-in amplification. The emission light was dispersed by a monochromator and detected by a photomultiplier. Photoluminescence excitation (PLE) spectra were obtained through excitation by the dispersed light of a 50 Hz pulsed Xe-flash lamp with a monochromator. The obtained spectra was divided by the lamp spectra.

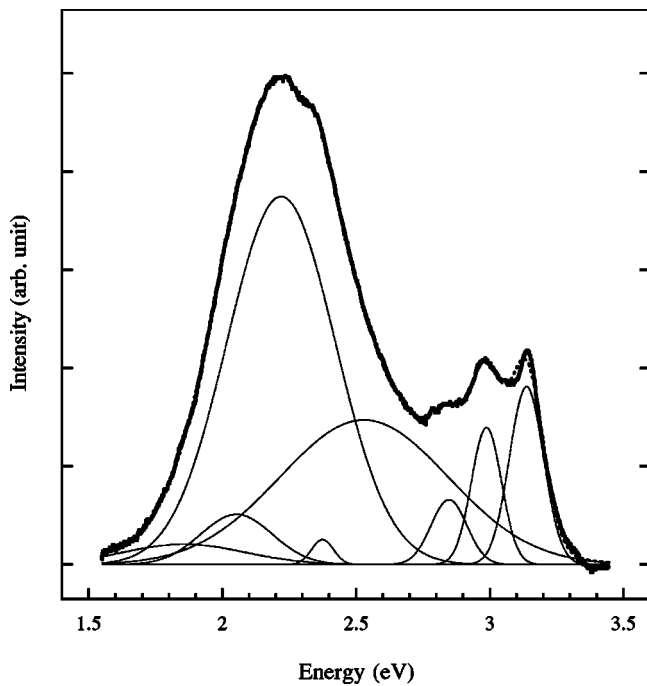


FIG. 2. The PL spectrum for 8 YSZ aged for 0 h and fit by Gaussian line-shape functions. The experimental data are shown by a solid line and the fit is shown by a broken line. Each Gaussian is also shown by a thin solid line.

III. RESULTS

The PL spectra for the aged samples are given in Fig. 1. The shapes of the spectra have multiple emission bands as typically shown in the 8YSZ data. We need eight Gaussians in order to successfully fit the experimental spectra as demonstrated in Fig. 2. The peak positions of the eight Gaussians are 3.14 eV, 2.98 eV, 2.85 eV, 2.53 eV, 2.37 eV, 2.22 eV, 2.05

eV, and 1.86 eV, with errors of 0.01 eV. Evaluated intensities against the aging time are plotted in Fig. 3. The most intense peak is 2.22 eV for all samples. The aging-time dependence of the full width at half maximum (FWHM) for the band at 2.22 eV fluctuated about 0.1 eV. Absolute emission intensity strongly depends on dopant concentration, as seen in Fig. 4.

Examples of the PLE spectra for the samples before aging are shown in Fig. 5. All of the presented spectra seem to have strong absorption at above 5 eV. This value corresponds with the reported band-gap energy due to interband transition between valence and conduction bands<sup>27</sup>. This suggests that radiative centers for all of these emission bands are those connected with the localized electronic states in the band gap and trap photoexcited carriers in the extended electronic states of the conduction band when photoexcited at more than 5 eV. The excitation at 3.81 eV by a He-Cd laser should result in a direct photoexcitation to the localized states. Although the He-Cd laser does not seem to excite at the center of the PLE band for the main peak at 2.22 eV, the actual excitation process by the He-Cd laser occurs not as far from the absorption-band center as it seems in the PLE spectra. This will also be discussed later. On the other hand, the position of the band itself fluctuates between the samples of different dopant concentrations. The change in the recombination probability because of the fluctuation as well as the change in the number of recombination centers which results from the increase in the dopant determine the change in the emission intensity, as will be discussed in the next section. Therefore, the PL intensity does not increase monotonically relative to the dopant concentration, as we have seen in Fig. 4.

IV. DISCUSSION

The reported aging-time dependence of conductivity is given in Fig. 1(b) in Ref. 3. It is noticeable from a compari-

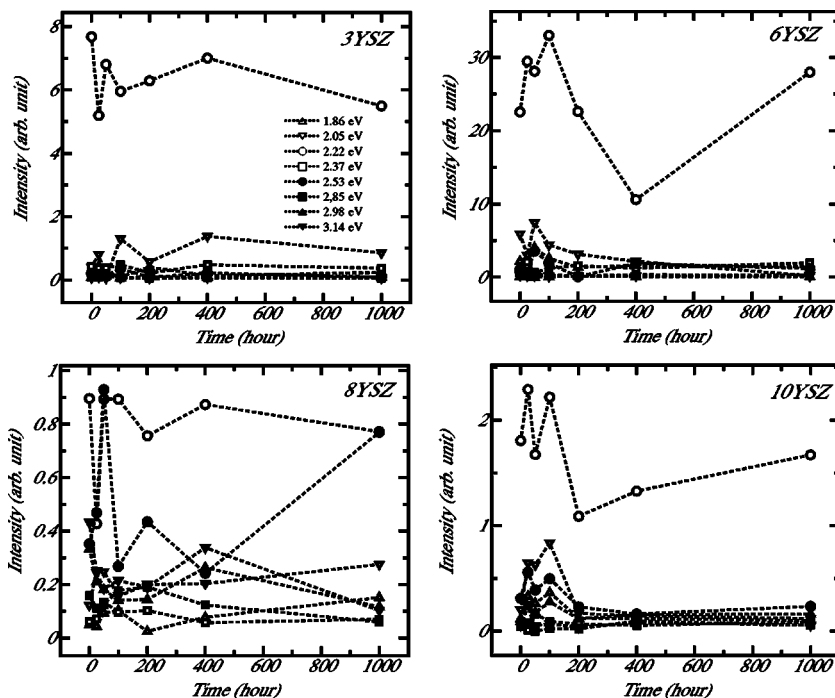


FIG. 3. The aging-time dependence of the PL intensities for each emission band presented in Fig. 2.

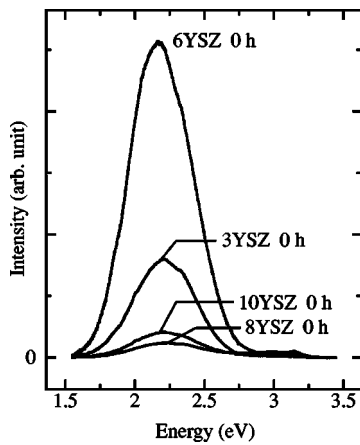


FIG. 4. The dopant-concentration dependence of the PL spectra for 3, 6, 8, and 10 YSZ aged for 0 h.

son between the aging-time-dependent PL intensity in Fig. 3 and conductivity that their aging-time behaviors have a correlation. For example, 3YSZ, which has a small deviation of the PL intensity for the main peak at 2.22 eV except its early stage of aging, shows little decrease in conductivity without its very beginning of aging, while those which have large and continuous deviation of the intensity, such as 6YSZ, show a considerable and constant decrease in conductivity, which is also demonstrated as a continuous and constant progress of the rate of resistivity increase versus square root of time in Fig. 2(b) in Ref. 3. More interesting cases are those for 10YSZ and 8YSZ in Fig. 6. In each of the rate of resistivity increases, the initial significant and constant increase in the rate versus square root of time diminishes at the square root of 100 and 200 h, respectively, for 8 and 10YSZ. The aging-time dependence of the PL intensity plotted against the square root of the aging time for 10YSZ in Fig. 6(b) demonstrates that the deviation of the intensity, not only for the peak at 2.22 eV, concentrates at the first 200 h, which is shaded in the figure. As for the 8YSZ, it should be noted that some other peaks show similar aging-time dependence of the PL intensity to that of the main peak at 2.22 eV (type I: 2.98 eV, 3.14 eV), and another peak shows complementary behavior (type II: 2.53 eV), after the increase rate of resistivity has partially settled at 100 h. Before 100 h, where the rate increases constantly and considerably, such complementary behavior is distorted with the deviation.

The complementary behaviors explained above can be understood if we follow the assignment of the PL emission bands in the reported study by Petrik *et al.*<sup>8</sup> They assigned the PL at 2.5 eV (Ref. 28) and another PL at 2.25 eV in their measurement to the emission from  $F$ -type ( $F^0, F^+, \dots$ ) and  $F_A$ -type oxygen vacancies ( $F_A^0, F_A^+, \dots$ ),<sup>9,11</sup> respectively, when photoexcited at less than 5 eV. The former type was observed at 2.69 eV in their measurement when excited by a 5.82 eV laser. The assignment of 2.5 eV PL to  $F$ -type, which is an electron-trap anion (oxygen ion) vacancy coordinated only by normal cations, is based on the study which demonstrates that the direct excitation to the band-gap state yields the PL.<sup>28</sup> When we follow their other attribution of the 2.25 eV PL to the  $F_A$ -type centers, which is with an adjacent

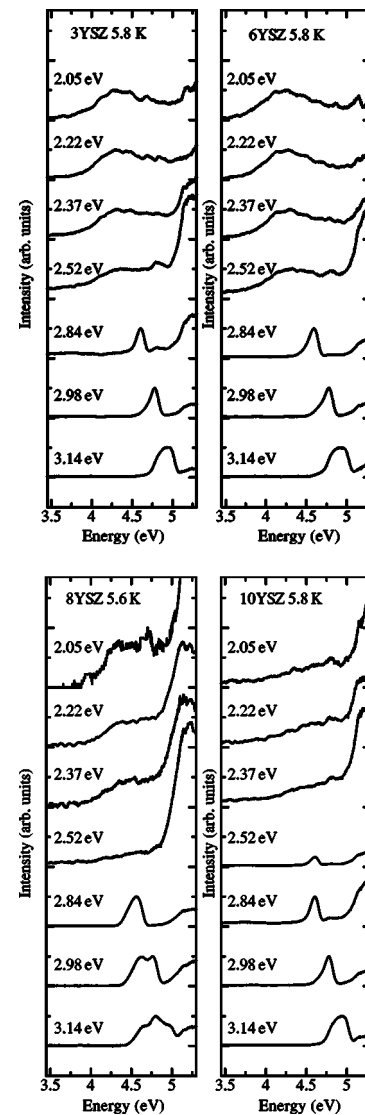


FIG. 5. The PLE spectra at low temperatures for the emission bands in (a) 3 and 6 YSZ and (b) 8 and 10 YSZ aged for 0 h and excited by a Xe-flash lamp.

cation impurity ( $Y^{3+}$ ), the complementary behaviors for intensity increase and decrease after 100 h correspond to the process of trapping the anion vacancy from  $Zr^{4+}$ -ion neighbors to the  $Y^{3+}$  ion and vice versa. It does not conflict with the EXAFS results before and after aging obtained by one of the present authors.<sup>6</sup>

The similar time behaviors within type I peaks, also described above, can then be understood if we follow the conventional assignment of the PL emission bands for color centers.<sup>9,11</sup> It typically takes a  $1s$ -orbital-type state as a ground state and a  $2p, 3p, \dots$ , or  $sp^3$  hybrid of  $2s$  and  $2p$  states for the fourfold  $F$ -type oxygen ion vacancy in this case, as excited states. When the time dependence of the electron transition probability between the ground and excited states is small, emission intensity only depends on the number of radiative centers, and multiple emissions which originate from the same type of centers should exhibit similar time behaviors as far as localized states of lower-level excitations are concerned.

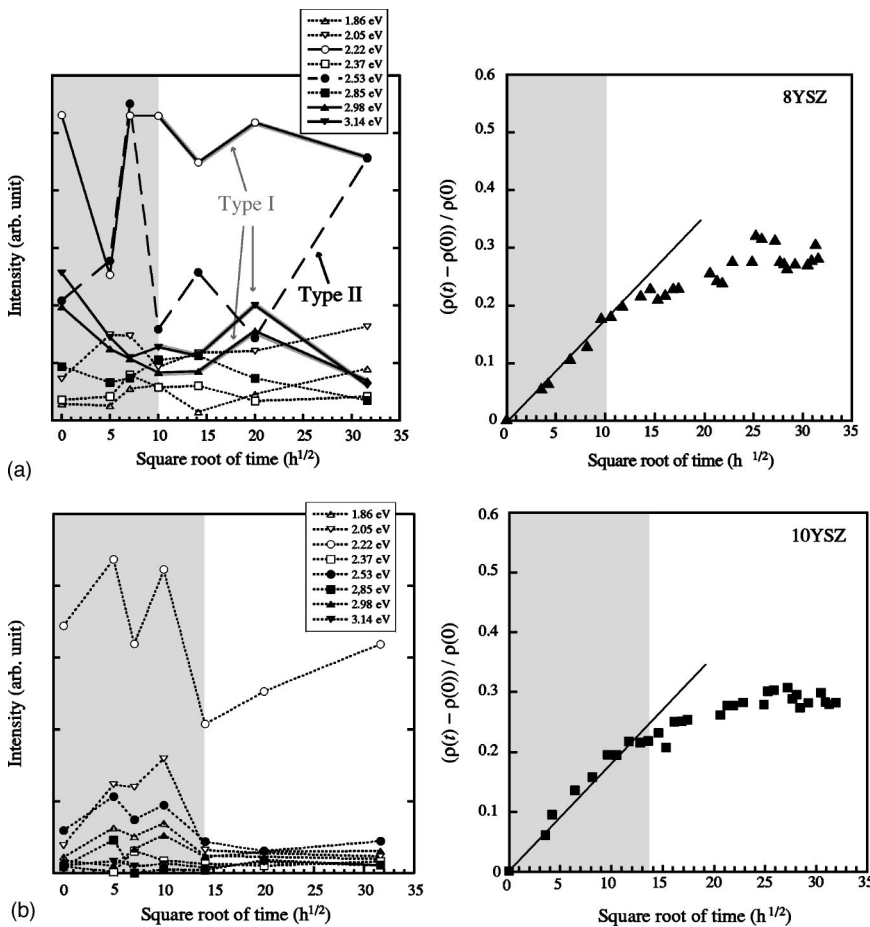


FIG. 6. The aging-time dependence of the PL intensity and the rate of resistivity increase (Ref. 3) vs square root of time for (a) 8 YSZ and (b) 10 YSZ.

The above interpretation of the complementarity and similarity in the aging-time behavior holds as long as the PL intensity is determined by the number of the radiative center. Change in the radiative recombination probability because of strong perturbation on the electronic states should violate not only the complementary time behavior between two types, but also the similar time behavior in the same type. The difference in size and anisotropy between the excited electron states wave functions breaks the uniform time development of the PL intensities of the same type under such perturbation. This is the case for the first 100 h in 8YSZ, where neither the complementarity nor the similarity is present. As for the 10YSZ in its first 200 h, they are relatively uniformly deformed. This suggests that the perturbation is large compared with the small unperturbed intensity fluctuations after 200 h, but not large enough to be affected by the difference between the excited states.

Following the conventional assignment of the ground and excited states for the PL emission, the effect of the lattice deformation at the time region, where a large decrease in conductivity is observed, is interpreted through the time dependence of the PLE spectra. Presented in Fig. 7 are the examples of change in the first 25 h of aging in 8YSZ. Fits with Gaussians for the main peak at 2.22 eV are also given in Fig. 8. These PLE peaks are observed at non-negligibly higher energy than the excitation energy by the He-Cd laser (3.81 eV). This is probably because strong excitations occur from the valence band, where the carriers are more popu-

lated, to the states in the band gap with a Xe-flash lamp at more than 4.0 eV, while the excitations are limited between the band-gap states when excited with a He-Cd laser as we schematically illustrated in Fig. 9. Here, we assume that the main peak  $\alpha$  in PLE at  $\sim 4.4$  eV for the emission peak at 2.22 eV is located close to the energy position which is 3.81 eV above the ground state  $G$  within an error of half the bandwidth, and we also assume that peaks  $a$  and  $b$  (and possibly  $c$  also) for the emission peak at 2.98 and 3.14 eV are not distanced from the position. Then, the peaks for type I in the PL emissions are a recombination between  $G$  and  $\alpha, a$ , or  $b$  located as shown in Fig. 9, passing through the

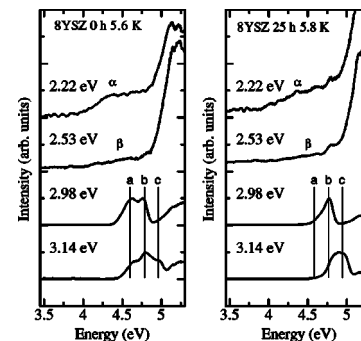


FIG. 7. The PLE spectra for the emission bands at 2.22 eV, 2.53 eV, 2.98 eV, and 3.14 eV for the samples aged for 0 h and 25 h. The labels  $\alpha, \beta$ , and  $a-c$  correspond to those in Fig. 9.

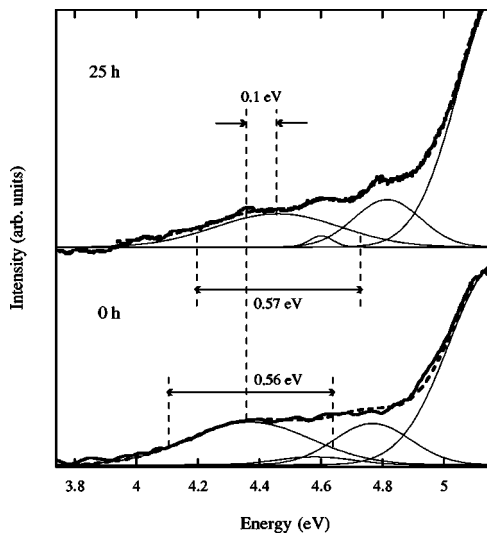


FIG. 8. The PLE spectra and fits by Gaussian line-shape functions for 8 YSZ aged for 0 h and 25 h.

large Stokes shift for the emission.<sup>8</sup> A similar process is expected for the type II peak at 2.53 K, which is also illustrated in Fig. 9. Deformation of the time development of the PL intensity at the early stage of aging, other than the fluctuation due to the recombination-center population, can be understood as the deformation of the absorption band of these excited states as typically shown for the band  $\alpha$  in Fig. 8. After the first 25 h of aging, the band  $\alpha$  shifts its position by 0.1 eV while its bandwidth does not fluctuate more than 0.01 eV. This shift changes the radiative recombination probability through the change in nonradiative recombination probability results from the change in  $\Delta E$  at C as illustrated in Fig. 10. This schematic is a simplification, of course, and not only the relative position between the ground and the excited states, but also the ground state itself, is modified. The present result that the bandwidth fluctuation for the PLE band (fluctuation of energy difference between  $A'$  and  $B'$ ) is small while the PLE band shift (at  $A'$ ) is substantial and the

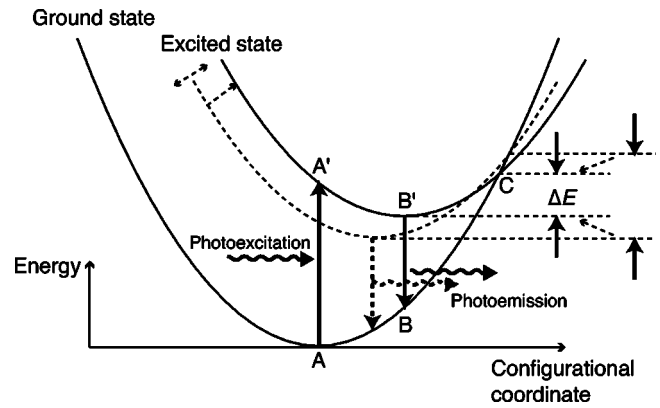


FIG. 10. A schematic for the photoexcitation and photoemission processes illustrated in a configuration-coordinate diagram.

same order as the bandwidth fluctuation of 0.1 eV for the PL emission band (fluctuation of energy difference between A and B) corresponds with the fact that the PL peak positions (energy difference between  $B'$  and B) do not fluctuate much.

Previous studies on the aging effect through the structural method, such as high-resolution transmission electron microscopy, x-ray diffractometry, and internal friction measurement,<sup>5,6</sup> have revealed that the lattice distortion, which should deform the electronic structures responsible for the excitation-emission process, do exist and relaxation of its anisotropy plays a central role in the conductivity decrease. The samples of these dopant concentrations with high ionic conductivity, especially 8YSZ, do have particularly high internal friction, or large lattice distortion, as already demonstrated and discussed in Refs. 5 and 6. The distortion, which causes the aging-time-dependent change in the conductivity and is proved to exist within 1000 h, reasonably explains the presence of the deformation of the time development of the PL intensity at the earlier time region for 8 and 10YSZ when it is concentrated on the first few hundred hours. With this explanation, no contradiction exists between the time range of the deformed aging-time development of PL intensity and

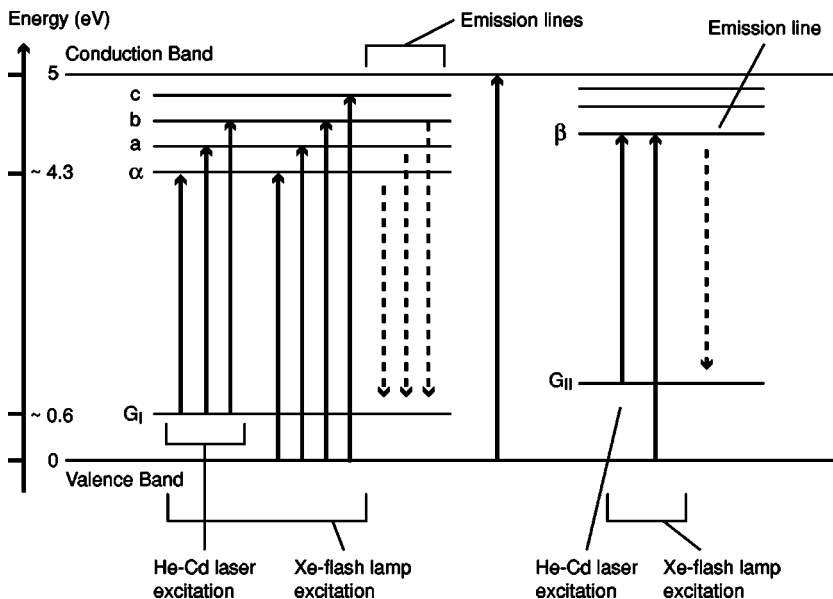


FIG. 9. A schematic for the photoexcitation (solid line) and photoemission (broken line) processes.

that of the main decrease in conductivity as presented in Fig. 6. This means at the same time that the rest of the aging time, where the trapping of the anion vacancy is dominant, which is evident in 8YSZ, is of secondary importance to the aging-induced conductivity decrease regardless of whether the trapping cation is the host  $Zr^{4+}$  or the dopant  $Y^{3+}$ , as the conductivity decrease itself is reduced at that time region.

## V. CONCLUSION

Photoluminescence properties of yttria-stabilized zirconia were studied for the samples aged up to 1000 h at 1073 K under irradiation of sub-band-gap light of 3.81 eV by a He-Cd laser. Multiple emission bands were observed especially in 8 and 10YSZ, and their intensities were dependent

on aging time. The developments of their intensities against aging time were characterized by two regions. One region contains two types of mutually complementary behavior of PL intensities against aging time in 8YSZ, and slow and smaller variation of intensities in 10YSZ. Both of the behaviors were deformed in the other time region of 8YSZ and 10YSZ and the deformation was observed at the first few hundred hours of aging. The latter time region coincided with that of the main decrease in conductivity.

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