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Photoluminescence excitation bands corresponding to defect states due to oxygen vacancies in yttria-stabilized zirconia

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Abstract

We have investigated the relationship between the structure of the photoluminescence (PL) excitation bands from yttria-stabilized zirconia (YSZ) and the defect states caused by oxygen vacancies in YSZ. The PL excitation spectra of YSZ samples with 2–8 mol% Y_2O_3 concentrations were measured at room temperature, and PL excitation bands from the YSZ samples were observed around 240 and 280 nm. We found a linear relationship between the intensity of the PL excitation band at 241 nm and the concentration of oxygen vacancies in the YSZ samples. The concentration of the oxygen vacancies could be estimated from this linear relationship. Moreover, we found that the PL excitation bands around 240 and 280 nm can be attributed to the bulk and local states of oxygen vacancies in the YSZ samples, respectively.

Keywords: Luminescence; Point defects; Grain boundaries

1. Introduction

Currently, one of the most popular electrolytes for use in fuel cells is yttria-stabilized zirconia (YSZ), which operates efficiently as an oxide ion conductor around 1×10^3 K [1–3]. The ion conductivity originates from the presence of oxygen vacancies in YSZ, and hence it is important to characterize these oxygen vacancies for applications of the ion conductor.

Photoluminescence (PL) spectroscopy is a useful method for studying the electric band structure of YSZ [4–12]. However, few studies have reported PL bands corresponding to oxygen vacancies in YSZ [7,10–12]. An understanding of the quantitative relationship between the PL of YSZ and oxygen vacancies in the YSZ is still lacking. Moreover, little is known about the PL excitation bands of YSZ. Excitation spectra are expected to provide more accurate information about defect states due to oxygen vacancies than absorption spectra because the measurement sensitivity for PL excitation spectra is, in principle, higher than that for absorption spectra.

In this study, PL and PL excitation spectra of YSZ samples with different Y_2O_3 concentrations (2–8 mol%) were measured at room temperature, and two PL excitation bands appeared around 240 and 280 nm from all of the YSZ samples. We found that the intensity of the PL excitation band that appeared around 240 nm increased linearly as the Y_2O_3 concentration increased. On the basis of these results, we considered the relationship between the PL excitation bands and the oxygen vacancies in the YSZ samples.

2. Experimental

The 2–8 mol% Y_2O_3–ZrO_2 powder samples (2Y–8Y samples) and the 10 mol% CeO_2–ZrO_2 powder sample (10Ce sample) that we used were commercially-available material (Tosoh Co., Japan). The powder samples were pressed into pellets by a cold isostatic pressing method. The pellets were sintered at 1773 K for 4 h and then polished. A 9.5 mol% Y_2O_3–ZrO_2 single-crystal sample (9.5Y sample) that we used was also available commercially (Crystal GmbH, Germany).

The PL and PL excitation spectra of the samples were measured at room temperature using a Spex Fluorolog 3-

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22 spectrophotometer. The spectrophotometer consisted of a 450-W xenon lamp as the excitation light source, two double monochromators (one in the excitation side and another in the emission side), a Peltier-cooled photomultiplier, and a photodiode reference detector. The PL excitation spectra were corrected by dividing the raw luminescence signals from the samples by the reference signals of the excitation light. Optical filters (UV-33 and L-42) were used to eliminate secondary light during measurements of the PL and PL excitation spectra, respectively.

3. Results and discussion

3.1. PL excitation band around 240 nm

Two PL bands, corresponding to two excitation wavelengths, were observed from all of the YSZ samples except the 2Y sample. Fig. 1 shows the PL spectra of the 8Y sample. One PL band appeared around 450 nm under 240 nm excitation, whereas another PL band appeared around 570 nm under 280 nm excitation. Two PL bands also appeared for the 3Y–6Y samples, which depended on the excitation wavelength (240 or 280 nm). We consider the PL band that was observed under 240 nm excitation in this section and the PL band observed under 280 nm excitation in the next section. The PL band observed under 240 nm excitation agrees with that reported previously, and the PL band can be attributed to intrinsic defect states due to oxygen vacancies [10,12]. The 2Y sample has the lowest Y_2O_3 concentration of the YSZ samples that we tested, and hence has the least extrinsic defect states due to the presence of Y ions in the YSZ samples. Consequently, no PL band corresponding to extrinsic defect states could be observed from the 2Y sample under the present conditions, and therefore just one PL band corresponding to the intrinsic defect states could be observed from the 2Y sample.

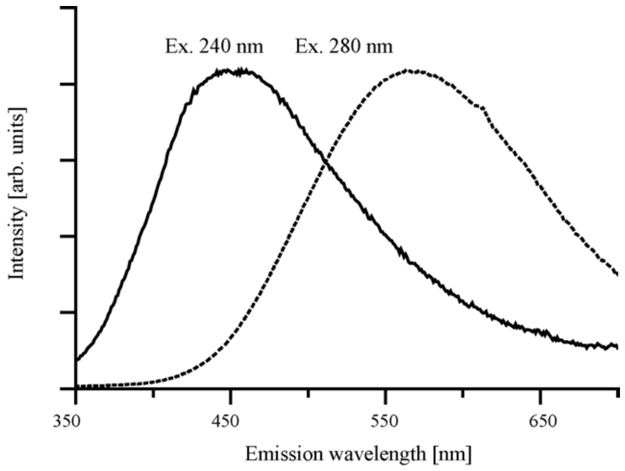

Fig. 1. PL spectra of the 8Y sample under 240 and 280 nm excitation.

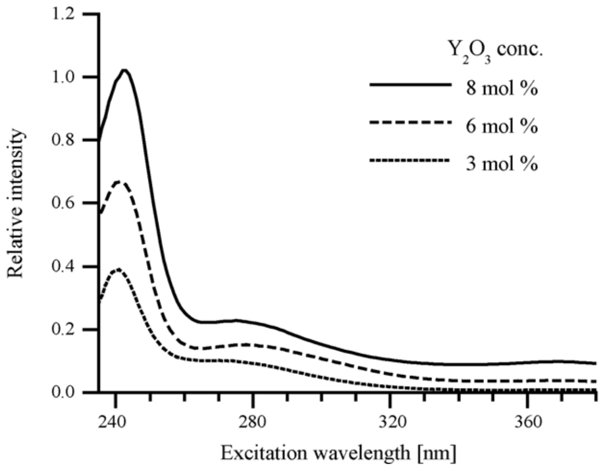

Fig. 2. PL excitation spectra of the 3Y, 6Y, and 8Y samples for emission at 450 nm. The intensity of the PL excitation band from the 8Y sample at 241 nm is taken to be unity.

To investigate the excitation band structure of the PL band under 240 nm excitation, the PL excitation spectra of the YSZ samples were measured for emission at 450 nm. One PL excitation band was observed around 240 nm (Fig. 2), and we found that the intensity of the PL excitation band at 241 nm increases linearly as the Y_2O_3 concentration increases (Fig. 3); there is a quantitative relationship between the PL intensity and the concentration of oxygen vacancies, because the concentration of oxygen vacancies increases as the concentration of Y_2O_3 increases. The concentration of oxygen vacancies could be estimated from this quantitative relationship. The value of the regression coefficient of the linear fit in Fig. 3 (0.984) is very close to unity. Moreover, the intersection of the fitted line with the y-axis (0.033) is very close to zero. These results mean that the PL excitation band around 240 nm for the emission at 450 nm can be attributed to defect states of

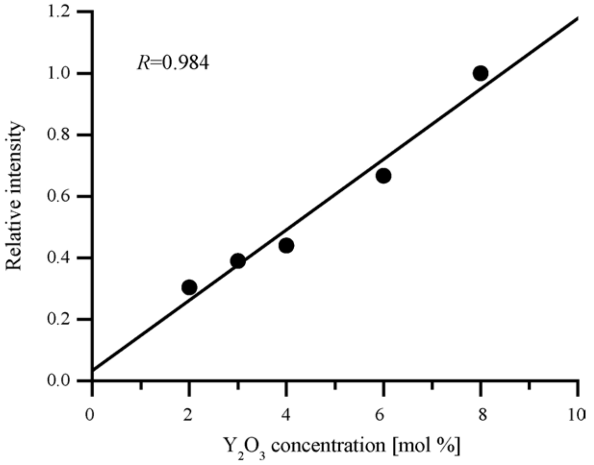

Fig. 3. Plot of the intensity of the PL excitation band from the YSZ samples at 241 nm for emission at 450 nm against Y_2O_3 concentration. The intensity of the PL excitation band from the 8Y sample at 241 nm is taken to be unity.

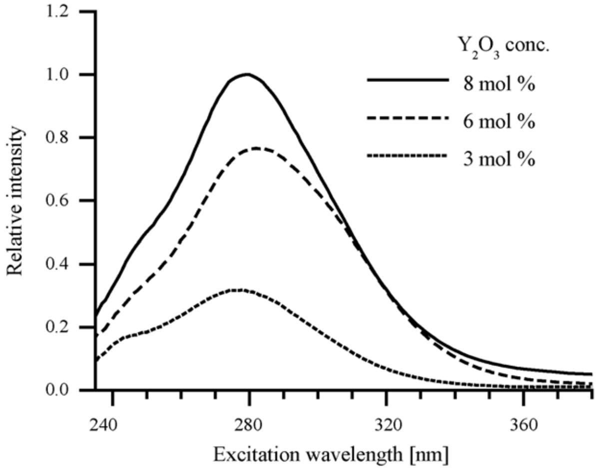

Fig. 4. PL excitation spectra of the 3Y, 6Y, and 8Y samples for emission at 574 nm. The intensity of the PL excitation band from the 8Y sample at 280 nm is taken to be unity.

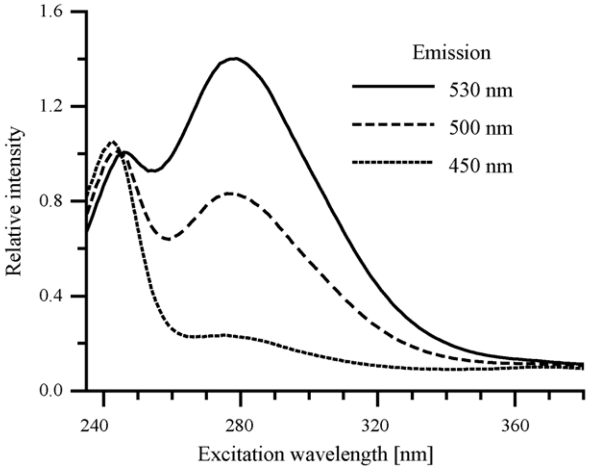

Fig. 6. PL excitation spectra of the 8Y sample for emissions at 450, 500, and 530 nm. The intensities of the PL excitation bands at 245 nm are taken to be unity.

oxygen vacancies due to the presence of Y ions. This is supported by the result that the intensity of the PL excitation band from the 10Ce sample (<0.01) was very close to zero; the 10Ce sample has no Y ions and no oxygen vacancies to maintain charge neutrality.

3.2. *PL excitation band around 280 nm*

To investigate the excitation band structure of the PL band under 280 nm excitation (Fig. 1), the PL excitation spectra of the YSZ samples were measured for emission at 574 nm. One PL excitation band was observed around 280 nm (Fig. 4). The intensity of the PL excitation band at 280 nm increased as the Y_2O_3 concentration increased (Fig. 5). On the contrary to the case of the PL excitation band around 240 nm (Fig. 3), the intersection of the fitted line with the y-axis (-0.258) is far from zero (Fig. 5). Furthermore, the deviation from a linear relationship illustrated in Fig. 5 is larger than that in Fig. 3. These results suggest that the relationship between the intensity of the PL excitation band at 280 nm and the concentration of Y_2O_3 does not have a simple linear correlation.

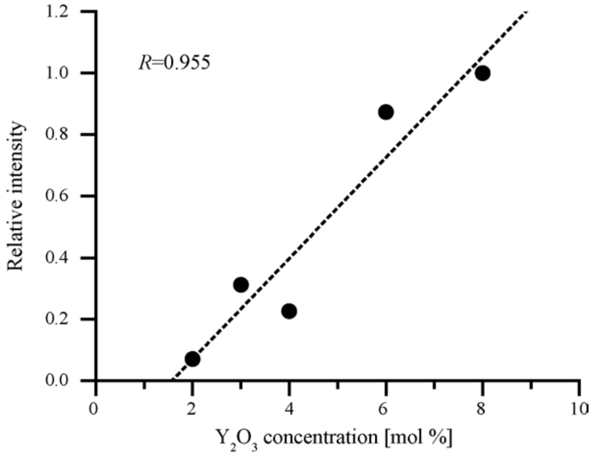

Fig. 5. Plot of the intensity of the PL excitation band from the YSZ samples at 280 nm for emission at 574 nm against Y_2O_3 concentration. The intensity of the PL excitation band from the 8Y sample at 280 nm is taken to be unity.

To understand the difference between the two PL excitation bands around 240 and 280 nm, the PL excitation spectra of different samples were compared for different emissions. We found that the PL excitation band around 280 nm can be attributed to defect states that occur at the grain boundaries in the YSZ samples, at their surfaces, or at both, whereas the PL excitation band around 240 nm can be attributed to bulk defect states. Fig. 6 shows the PL excitation spectra of the 8Y sample for emissions at 450, 500, and 530 nm. The intensity of the PL excitation band around 280 nm increased compared to that around 240 nm as the emission energy decreased. This is reasonable, because the PL excitation band around 280 nm corresponds to the PL band around 570 nm (Fig. 1). The same trend was observed for the 2Y–6Y samples. In contrast, the PL excitation spectra of the 9.5Y sample (single crystal) for emissions at 450, 500, and 530 nm were almost identical (Fig. 7). The 9.5Y sample has no grain boundaries, and therefore the PL excitation band around 280 nm can be attributed to defect states due to oxygen vacancies that exist at the grain boundaries in the YSZ samples, at their surfaces, or at both. At these sites, Y ions are distributed heterogeneously and are likely to cause the defect states. On the other hand, the PL excitation band around 240 nm can be attributed to bulk defect states of oxygen vacancies in the YSZ samples. These results are consistent with a proposed model [10] that oxygen vacancies with one Y^{3+} ion and one Zr^{4+} ion as nearest neighbors to the vacancy lead to one PL excitation band at 266 nm (280 nm in our study), whereas those with two Zr^{4+} ions as nearest neighbors to the vacancy lead to the excitation band at 213 nm (240 nm in our study).

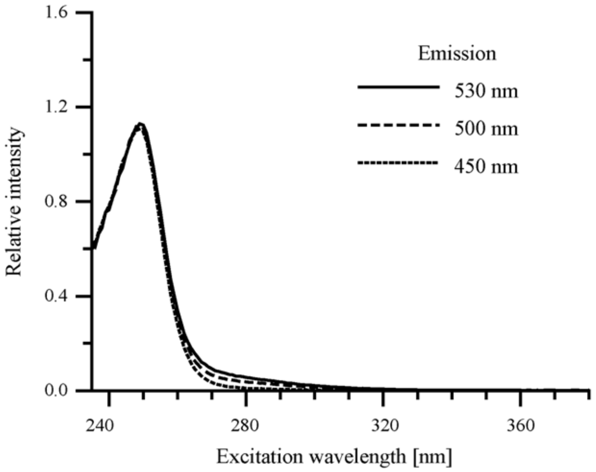

Fig. 7. PL excitation spectra of the 9.5Y sample (single crystal) for emissions at 450, 500, and 530 nm. The intensities of the PL excitation bands at 245 nm are taken to be unity.

4. Conclusions

The PL excitation spectra of YSZ samples with 2–8 mol% Y_2O_3 concentrations were measured, and PL excitation bands were observed around 240 and 280 nm. We found a linear relationship between the intensity of the PL excitation band at 241 nm and the concentration of oxygen vacancies in the YSZ samples. The concentration of oxygen vacancies could be estimated from the linear relationship. On the other hand, the relationship between the intensity of the PL excitation band at 280 nm and the concentration of oxygen vacancies did not exhibit a simple linear correlation. By comparing the PL excitation spectra for some emissions from the 8Y sample with those from the 9.5Y sample, we found that the PL excitation bands around 240 and 280 nm can be attributed to bulk and localized states of oxygen vacancies in the YSZ samples, localized states which exist at grain boundaries in the YSZ samples, at their surface, or at both.

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References

[1] M. de Ridder, R.G. van Welzenis, A.W. Denier van der Gon, H.H. Brongersma, S. Wulff, W.F. Chu, W. Weppner, J. Appl. Phys. 92 (2002) 3056.
[2] E. Wanzenberg, F. Tietz, D. Kek, P. Panjan, D. Stöver, Solid State Ionics 164 (2003) 121.
[3] M. Hattori, Y. Takeda, Y. Sakaki, A. Nakanishi, S. Ohara, K. Mukai, J.H. Lee, T. Fukui, J. Power Sources 126 (2004) 23.
[4] S.Kh. Batygov, V.I. Vashchenko, S.V. Kudryavtsev, I.M. Klimkovich, E.E. Lomonova, Sov. Phys. Solid State 30 (1988) 378.
[5] C. Bonola, P. Camagni, N. Omenetto, G. Samoggia, J. Lumin. 48–49 (1991) 797.
[6] P. Camagni, P. Galinetto, G. Samoggia, N. Zema, Solid State Commun. 83 (1992) 943.
[7] E.D. Wachsman, G.R. Ball, N. Jiang, D.A. Stevenson, Solid State Ionics 52 (1992) 213.
[8] S.E. Paje, J. Llopis, J. Phys. Chem. Solids 55 (1994) 671.
[9] M.Kh. Ashurov, M.Z. Amonov, A.F. Rakov, Inorg. Mater. 33 (1997) 394.
[10] N.G. Petrik, D.P. Taylor, T.M. Orlando, J. Appl. Phys. 85 (1999) 6770.
[11] H. Nakajima, T. Mori, S. Itoh, M. Watanabe, Solid State Commun. 129 (2004) 421.
[12] H. Nakajima, T. Mori, S. Itoh, J. Mater. Res. 19 (2004) 2457.