Hole burning in YSZ:Pr$^{3+}$ and YSZ:Eu$^{3+}$ with various Y$_2$O$_3$ concentration

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Abstract

We have measured the hole spectra in YSZ:Pr$^{3+}$ and YSZ:Eu$^{3+}$ with various Y$_2$O$_3$ concentrations at low temperature. The temperature dependence of the hole width which obtained from the hole spectra in YSZ:Pr$^{3+}$ and YSZ:Eu$^{3+}$ was similar to that for disordered materials. However, the Y$_2$O$_3$ concentration dependence of the hole width in YSZ:Pr$^{3+}$ was contrary to that for YSZ:Eu$^{3+}$ at low temperature. The hole width was the widest in the case of YSZ:Pr$^{3+}$ at 10 mol% Y$_2$O$_3$. On the contrary, it was the narrowest in the case of YSZ:Eu$^{3+}$ at the same concentration of Y$_2$O$_3$. It was found that there are two states in YSZ, in which the degree of ordered differs from each other. Additionally, the Y$_2$O$_3$ concentration dependence of the hole width at low temperature has reflected the ionic conductivity of YSZ at high temperature. It is suggested that the ordering of local structure is responsible for the ionic conduction in YSZ.

Keywords: Yttria stabilized zirconia; Ionic conductor; Hole burning; Homogeneous line-width

1. Introduction

Zirconia (ZrO$_2$) has the cubic fluorite structure above $\sim$2643 K, but only the monoclinic structure is stable at room temperature. The cubic structure is stabilized by addition of heterovalent cations at room temperature. Yttria stabilized zirconia (YSZ) which is stabilized by addition of Y$_2$O$_3$ is a high ionic conductor. This ionic conduction arises from hopping of oxygen ion through anion vacancy created to preserve electrical neutrality when Y$^{3+}$ is added. Because anion vacancy may increase with Y$_2$O$_3$ concentration, the increase of the ionic conductivity of YSZ is expected by the addition of Y$_2$O$_3$. However, the ionic conductivity of YSZ has maximum when the concentration of Y$_2$O$_3$ is about 10 mol%, and it was decreased with increasing Y$_2$O$_3$ concentration higher than 10 mol%. For the origin of that phenomenon, the two models have been suggested. One is that the decrease of ionic conductivity at higher concentration of Y$_2$O$_3$ than 10 mol% is caused by the ordering of oxygen vacancies [1]. The other one is that this phenomenon is due to the clustering of the vacancies [2–5]. Although it has been considered that this phenomenon will be related to the ordered state of ions including oxygen vacancy, the problem has not been resolved yet perfectly.

Hole burning spectroscopy has been established as powerful tool to the dynamical and structural properties of disordered materials. Superionic conductors such as YSZ are one of typical disordered materials. This spectroscopy has been applied to investigate these properties for superionic conductors. Recently, the dynamical property of superionic conductors has been studied by means of Persistent Spectral Hole Burning (PSHB) by several authors [6–8]. They determined the potential energy for the light induced local motion of ions from the analysis of the thermal decay-profile of the persistent hole. On the other hand, the homogeneous line width can be measured using to PSHB in the inhomogeneous broadening of disordered materials [9]. The homogeneous line width is reflected the disordered nature. It is wide in the disordered materials, and is narrow in the crystals [10,11].

PSHB by the local structural change and the $T^{1.2}$ dependence ($T$ : Temperature) of the homogeneous line width was reported in YSZ (Y$_2$O$_3$: only 10 mol%) doped with Pr$^{3+}$ ions by Tanaka et al. [12]. They discussed disordered nature of YSZ compared with the data of a glass and a crystal. On the other hand, PSHB by the optical pumping between hyperfine splitting levels of the ground
state was reported in a fiber YSZ (Y_2O_3; only 9.5 mol%) doped with Eu^{3+} ions by Jang and Weltzer [11]. They reported the homogeneous line width showing linear temperature dependence at low temperature for YSZ:Eu^{3+}. But, both authors have measured for YSZ of nearly 10 mol% Y_2O_3, only.

In this work, a investigation of the hole spectra for YSZ:Pr^{3+} and YSZ:Eu^{3+} with various Y_2O_3 concentration, is reported. We have studied the Y_2O_3 concentration dependence of the homogeneous line width in YSZ:Pr^{3+} and YSZ:Eu^{3+} at low temperature. The relationship between the ordered state of ions including oxygen vacancies and the ionic conduction of YSZ has been investigated.

2. Experimental

Single crystals of YSZ doped with Eu^{3+} ions and Pr^{3+} ions were grown using Xe-arc imaging furnace by a floating-zone method. We have made nine samples with Y_2O_3 (7, 10, 19, 29 and 39 mol%) for YSZ:Pr^{3+} and with Y_2O_3 (7, 10, 19 and 29 mol%) for YSZ:Eu^{3+}. The content of Pr^{3+} ions and Eu^{3+} ions were kept with 2 mol% for all samples. The samples of YSZ:Pr^{3+} were annealed at 700 °C for 1 h. The surfaces of crystals were polished for optical measurements.

Luminescence spectra were obtained by exciting the samples with a XeCl eximer laser (wavelength: 308 nm) and by detecting the luminescence through a double monochromat with a cooled photo multiplier. The sample temperature was kept at 20 K using a helium evaporation cryostat.

The experimental set-up for the measurements and the method of the hole burning experiment is also the same as previous works [6–8]. A CW ring dye laser using Rhodamine 6G with frequency jitter width of 1 MHz was used as a light for the burning of hole and for the detecting of a hole by the scanning of the laser frequency. We made hole burning experiment by using the ^1H_4 \rightarrow ^1D_2 transition of Pr^{3+} for YSZ:Pr^{3+}, and by using the ^7F_0 \rightarrow ^5D_0 transition of Eu^{3+} for YSZ:Eu^{3+}.

3. Result and discussion

Fig. 1(a) shows a luminescence spectrum at 20 K and a excitation spectrum at 10 K in YSZ:Pr^{3+} (Y_2O_3: 10 mol%). The excitation spectra were obtained by detecting a luminescence around 640 nm at 10 K. We assigned the emission band as shown in Fig. 1(a) by a solid curve to a zero phonon band. The hole has been observed between 609.3 and 614.6 nm in the zero phonon band [12]. Fig. 1(b) shows a typical luminescence spectrum in YSZ:Eu^{3+} (Y_2O_3: 10 mol%) at 20 K. The emission band at 580 nm was assigned to the ^5D_0 \rightarrow ^7F_0 transition of Eu^{3+} ions by the analogy with the free ion electronic energy diagram. Because there are the ^7F_0 \rightarrow ^5D_0 emission band is zero phonon band, the absorption band of the ^7F_0 \rightarrow ^5D_0 transition of Eu^{3+} ions is at same wavelength. The holes have been observed at this zero phonon band [11]. The Full Width at Half Maximum (FWHM) of these zero phonon emission bands were estimated by representing the bands by gaussians as shown in Fig. 1(a) and (b) by the solid curves.

The Y_2O_3 concentration dependence of the FWHM of the zero phonon band of the ^1D_2 \rightarrow ^3H_4 transition of Pr^{3+} ions by the analogy with the free ion electronic energy diagram. Because there are the ^7F_0 \rightarrow ^5D_0 emission band is zero phonon band, the absorption band of the ^7F_0 \rightarrow ^5D_0 transition of Eu^{3+} ions is at same wavelength. The holes have been observed at this zero phonon band [11]. The Full Width at Half Maximum (FWHM) of these zero phonon emission bands were estimated by representing the bands by gaussians as shown in Fig. 1(a) and (b) by the solid curves.

The Y_2O_3 concentration dependence of the FWHM of the zero phonon band of the ^1D_2 \rightarrow ^3H_4 transition of Pr^{3+} ions in YSZ:Pr^{3+} and that of the ^3D_0 \rightarrow ^7F_0 transition of Eu^{3+} ions in YSZ:Eu^{3+} are shown in Fig. 2(a) and (b). The FWHM corresponds to the inhomogeneous line width. The inhomogeneous line width was increased linearly with the Y_2O_3 concentration for both YSZ:Pr^{3+} and YSZ:Eu^{3+} in the experimental errors. This result indicates that the degree of ordered was decreased monotonously with increasing of the Y_2O_3 concentration because the inhomogeneous line width was broader for the high disordered materials.
Fig. 3 shows typical hole spectra of YSZ:Pr$^{3+}$ (a) (Y$_2$O$_3$: 29 mol%) and of YSZ:Eu$^{3+}$ (b) (Y$_2$O$_3$: 29 mol%) at low temperature. The holes could be burned in the all region of the zero phonon band for YSZ:Pr$^{3+}$ and in that for YSZ:Eu$^{3+}$. The holes were burned at 613.5 nm for YSZ:Pr$^{3+}$, and at 579.6 nm for YSZ:Eu$^{3+}$.

In YSZ:Pr$^{3+}$, the hole have a single Lorentzian shape as shown in Fig. 3(a) by solid curve. The hole could be observed three hours after that the burning procedure was finished. Neither antiholes nor side holes were observed in all samples of YSZ:Pr$^{3+}$. The hole could be burned YSZ:Pr$^{3+}$ (Y$_2$O$_3$: 7 mol%), and below 22 K in YSZ:Pr$^{3+}$ (Y$_2$O$_3$: 10 mol%), and below 37 K in YSZ:Pr$^{3+}$ (Y$_2$O$_3$: 19 mol%). The hole was hardly observed above 50 K in YSZ:Pr$^{3+}$ (Y$_2$O$_3$: 29 and 39 mol%). These characters of holes indicate the origin of holes is optically induced rearrangement of local structure around Pr$^{3+}$ ions.

In YSZ:Eu$^{3+}$ (Fig. 3(b)), the hole has antiholes and vanished after a few minutes at 4.3 K. The hole could be burned below 10 K in YSZ:Eu$^{3+}$ (Y$_2$O$_3$: 7 mol%), and below 7 K in YSZ:Eu$^{3+}$ (Y$_2$O$_3$: 10 mol%), and below 11 K in YSZ:Eu$^{3+}$ (Y$_2$O$_3$: 19 mol%), and below 15 K in YSZ:Eu$^{3+}$ (Y$_2$O$_3$: 29 mol%). We have concluded that this hole burning is caused by the optical pumping of the hyperfine levels of ground state of the Eu$^{3+}$ ions.

To obtain the hole width from the hole spectrum, (1) in the case of YSZ:Pr$^{3+}$, the hole width was determined from the calculated Lorentzian curve as shown in Fig. 3(a) and (2) in the case of YSZ:Eu$^{3+}$, we represented the hole which have antiholes by two convex Lorentzians and one concave Lorentzian as shown in Fig. 3(b) by solid curve. Hole width was determined from calculated concave Lorentzian curve.

Fig. 3. A typical hole spectrum of (a) YSZ:Pr$^{3+}$ (Y$_2$O$_3$: 29 mol%) at 6 K, and (b) YSZ:Eu$^{3+}$ (Y$_2$O$_3$: 29 mol%) at 4.3 K. Laser power density for burning was of 20 mW/mm$^2$ for YSZ:Pr$^{3+}$, and of 1 mW/mm$^2$ for YSZ:Eu$^{3+}$. Burning time was 300 s.

Fig. 4. The typical temperature dependence of the hole width ($I_h$) in (a) YSZ:Pr$^{3+}$ (Y$_2$O$_3$: 19 mol%) and in (b) YSZ:Eu$^{3+}$ (Y$_2$O$_3$: 19 mol%). Dashed lines are calculation lines. In figure, two solid lines represent the line which proportionate to $T^4$ and the line which proportionate to $T^2$. 

Fig. 2. The inhomogeneous line width calculated from the luminescence spectra for various Y$_2$O$_3$ concentration YSZ:Pr$^{3+}$ (a) and YSZ:Eu$^{3+}$ (b) at 20 K.
YSZ:Eu$^{3+}$ ($Y_2O_3$: 19 mol%) at low temperature. The temperature dependence of $\Gamma_h$ was fitted with a function of $\Gamma_h = aT^b$ by least squares method, as shown in Fig. 4(a) and (b) by dashed line. The temperature dependence of $\Gamma_h$ shows as $\Gamma_h \propto T^{1.2}$ in YSZ:Pr$^{3+}$ ($Y_2O_3$: 19 mol%). For other samples of YSZ:Pr$^{3+}$, $\Gamma_h$ varies as $\Gamma_h \propto T^{1.3}$ in YSZ:Pr$^{3+}$ ($Y_2O_3$: 7 mol%), $\Gamma_h \propto T^{1.1}$ in YSZ:Pr$^{3+}$ ($Y_2O_3$: 10 mol%), $\Gamma_h \propto T^{1.1}$ in YSZ:Pr$^{3+}$ ($Y_2O_3$: 29 mol%), $\Gamma_h \propto T^{1.2}$ in YSZ:Pr$^{3+}$ ($Y_2O_3$: 19 mol%), and YSZ:Eu$^{3+}$ ($Y_2O_3$: 9.5 mol%). In YSZ:Eu$^{3+}$ ($Y_2O_3$: 19 mol%) and YSZ:Eu$^{3+}$ ($Y_2O_3$: 29 mol%), $\Gamma_h$ shows similar temperature dependence ($\Gamma_h \propto T^{1.1}$). In YSZ:Eu$^{3+}$ ($Y_2O_3$: 7 and 10 mol%), the temperature dependence of $\Gamma_h$ could not be obtained because the decay of the hole was fast except near liquid helium temperature.

The homogeneous line width ($\Gamma_{homo}$) depends on the temperature as $\Gamma_{homo} = T^\alpha (\alpha = 1-2)$ in disordered materials such as glasses. In YSZ, the similar temperature dependence of the homogeneous line width was observed at low temperature for YSZ:Pr$^{3+}$ ($Y_2O_3$: 10 mol%) [12] and YSZ:Eu$^{3+}$ ($Y_2O_3$: 9.5 mol%) [11]. The temperature dependence of $\Gamma_h$ shows a disordered nature of YSZ. Then, the hole width obtained in this work reflects the homogeneous line width.

Fig. 5 shows the FWHM of the holes at 6 K for YSZ:Pr$^{3+}$ and at 4.3 K for YSZ:Eu$^{3+}$ with various concentration of $Y_2O_3$. The ionic conductivities which were reported by several authors [13–15] are also shown in this figure. When the ionic conductivity is maximum at 10 mol% $Y_2O_3$, the hole width is the widest in the case of YSZ:Pr$^{3+}$. On the contrary, it is the narrowest in the case of YSZ:Eu$^{3+}$ at the same concentration of $Y_2O_3$. Namely, it seems that the hole width has reflected the ionic conductivity although the dependence in Pr$^{3+}$ doped samples differ from that in Eu$^{3+}$ doped samples. This result will indicate that the ordered state at low temperature have been kept at high temperature when the conductivity was measured. Tojo et al., reported an excess heat capacity at low temperature which is attributed to low-energy modes caused by the defect in YSZ from the measurement of heat capacities for YSZ and pure zirconia [2–5]. The amount of the excess heat capacity at low temperature decreased with the addition of $Y_2O_3$ concentration. They concluded that the decrease of the excess heat capacity is caused by clustering of the oxygen vacancy surrounding Zr$^{4+}$ ion.

In YSZ:Pr$^{3+}$, the hole width is broadest at 10 mol% $Y_2O_3$ and becomes narrower at both concentration regions lower and higher than 10 mol% $Y_2O_3$. On the other hand, in YSZ:Eu$^{3+}$, the hole width is narrowest at 10 mol% $Y_2O_3$ and becomes broader at both concentration regions lower and higher than 10 mol% $Y_2O_3$. For the hole burning experiment, the rare earth ions in the specific crystal field can be chosen when we selected the burning wavelength. The Pr$^{3+}$ ions which excited by a light for the burning are in the same order of crystal field in YSZ:Pr$^{3+}$. Similarly, the Eu$^{3+}$ ions which excited by a light for the burning are in the same order of crystal field in YSZ:Eu$^{3+}$. Therefore, the Pr$^{3+}$ ions will be located in an ordered state at 10 mol% of $Y_2O_3$ and a disordered state appears near the Pr$^{3+}$ ions at higher and lower $Y_2O_3$ concentration than 10 mol%. In the Eu$^{3+}$ ions case, there is opposite situation. These results show that, in YSZ, there are two states with different degree of order. It will be concluded that degree of mixing of ordered and disordered states in YSZ will determine the $Y_2O_3$ concentration dependence of ionic conductivity.

4. Summary

We have observed the hole spectra in YSZ:Pr$^{3+}$ ($Y_2O_3$: 7, 10, 19, 29 and 39 mol%) and YSZ:Eu$^{3+}$ ($Y_2O_3$: 7, 10, 19 and 29 mol%). The temperature dependence of the hole width shows as $\Gamma_h \propto T^{1.1-1.3}$ in both YSZ:Pr$^{3+}$ and YSZ:Eu$^{3+}$. This is similar to that for disordered materials such as glass. This result indicates a disordered nature of YSZ. However, the $Y_2O_3$ concentration dependence of the hole width for YSZ:Pr$^{3+}$ was contrary to that for YSZ:Eu$^{3+}$ at low temperature. In YSZ:Pr$^{3+}$, the hole width is narrower at both concentration regions lower and higher than 10 mol% $Y_2O_3$. On the other hand, in YSZ:Eu$^{3+}$, the hole width is wider at both concentration regions lower and higher than 10 mol% $Y_2O_3$. It was found that there are two states in which the degree of ordered differs from each other. On the other hand, the $Y_2O_3$ concentration dependence of the hole width at low temperature has reflected the ionic conductivity at high temperature in both YSZ:Pr$^{3+}$ and YSZ:Eu$^{3+}$. Our results indicate that the ordered state at low temperature...
temperature has been kept at high temperature and the ordering of local structure is responsible for the ionic conduction in YSZ.

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