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Site selected excitation of Sm^{2+} in substitutional disordered crystal $KLaF_4$

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Abstract

Substitutional disordered crystals $KLaF_4$ (KLF) have CaF_2-type crystal structure with space group of O_h^5 where K^+ and La^{3+} ions occupy randomly cation sites. Since the nearest environment of Sm^{2+} impurity ions differs from site to site producing different crystal fields of Sm^{2+}, the $4f^6$ and $4f^5 5d^1$ energy levels of Sm^{2+} are distributed. The optical absorption and fluorescence spectra of Sm^{2+} are inhomogeneously broadened. The KLF:Sm^{2+} crystal was irradiated by light emitted from a laser diode at 681.6 nm with 40 mW for 30 min. The fluorescence intensity excited at 681.6 nm after 30 min was reduced with an amount of 30% compared with that before irradiation, whereas those excited at other wavelengths were almost not influenced by the 681.6-nm irradiation.

Keywords: Spectral hole burning; Substitutional disordered crystal; Fluoride crystal; Sm^{2+}; $KLaF_4$

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1. Introduction

The spectral hole burning (SHB) phenomenon is interesting not only as a method for spectroscopy but also as an application to high density optical memories. SHB characteristics of several Sm^{2+}-doped glasses [1–5] and crystals [6,7] have been reported by many authors. It has been understood that the holes are burned in the $^7F_0$–$^5D_0$ transition line of Sm^{2+} by the one photon or two-photon absorption. Recently, persistent SHB (PSHB) has been also observed in the Sm^{2+}-doped glasses at room temperature [3,5]. Room-temperature observation of PSHB and a high ratio of the inhomogeneous line width to the homogeneous line width are required for an application of PSHB to optical memories.

PSHB mechanisms of Sm^{2+}-doped crystals and glasses have been proposed to be caused by the one-photon or two-photon absorption, followed by trapping of an excited electron of Sm^{2+} to Sm^{3+} sites or unknown defects. However, the detailed mechanism has not been made clear.

Substitutional disordered crystals $KLaF_4$ (KLF) with the CaF_2-type crystal structure where K^+ and La^{3+} ions occupy randomly cation sites are a candidate for PSHB materials because the optical spectra of Sm^{2+} in KLF show inhomogeneous broadening. In this paper, we report the temperature dependence of the lifetimes and the intensities of the Sm^{2+} fluorescence obtained by site selected excitation and the PSHB spectra observed in KLF:Sm^{2+}, and propose a PSHB mechanism.

2. Experimental procedure

The KLF crystal structure belongs to space group of O_h^5. Sm^{2+} ions substitute for K^+ or La^{3+} ions. For example, if Sm^{2+} substitutes for La^{3+}, La^{3+} ions are slightly rich in the surrounding of Sm^{2+} because La^{3+} ions play a role as charge compensators of Sm^{2+}. The KLF crystals doped with 1–4 at.% Sm^{2+} were grown in a reducing atmosphere by spontaneous crystallization from slowly cooled melts.

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The fluorescence due to the $^5D_0$–^7F_J transitions of Sm^{2+} in the KLF crystal was detected using a fiber multi-channel spectrometer (Ocean Optics USB2000) in the range of 680–740 nm with a resolution of 5 nm. Site selected excitation was performed using a Micro Laser Systems laser diode (LD) with tuning wavelengths of 679–683 nm obtained by controlling temperature of an LD.

The lifetime of the fluorescence due to the $^7F_0$–$^5D_2$ transition with the site selected excitation was measured using a Hamamatsu Photonics R943-02 photomultiplier tube at the exit slit of a 1/4 m monochromator connected with a Yokogawa DL1700 digital oscilloscope. The lifetime was measured in the temperature range of 12–300 K.

3. Experimental results

3.1. Temperature dependence of lifetime and intensity of $^5D_0$–$^7F_2$ transition of Sm^{2+}

The nearest environment of Sm^{2+} impurity ions differs from site to site. Different crystal fields of Sm^{2+} produce the distribution of the $4f^6$ and $4f^5 5d^1$ energy levels of Sm^{2+}. Then, the fluorescence spectra of Sm^{2+} are inhomogeneously broadened. A site selected excitation method is a useful tool to reveal the electronic state of the disordered system. Before the measurement of PSHB, the temperature dependence of the lifetime and the intensity of the 718-nm fluorescence line (see Fig. 2) due to the $^5D_0$–$^7F_2$ transition of Sm^{2+} in the KLF crystal were measured.

Fig. 1(a and b) show the lifetimes and the normalized intensities of the fluorescence due to the $^5D_0$–$^7F_2$ transition of Sm^{2+} in KLF obtained with site selected excitation of 681.7, 682.4 and 683.0 nm as a function of temperature, respectively. The lifetime, $\tau(T)$, and the intensity, $I(T)$, of the fluorescence as a function of temperature, T, are given by [8]:

$$\frac{1}{\tau(T)} = \frac{1}{\tau_R(T)} + \frac{1}{\tau_{NR}} \exp\left(\frac{-\Delta E}{kT}\right), \tag{1}$$

$$I(T) = I_0 \frac{\tau(T)}{\tau_R(T)}, \tag{2}$$

where $\tau_R(T)$ and τ_{NR} are radiative and nonradiative decay times, respectively, and ΔE is an activation energy. When the temperature is decreased toward 0 K, the nonradiative decay component is negligibly small, giving rise to the relation of $\tau(0) = \tau_R(0)$. Assuming that $\tau(0) = \tau_R(0) \approx \tau(12)$ and $I_0 \approx I(12)$, a ratio of the normalized lifetime to the normalized intensity is given in the form of:

$$R(T) \equiv \frac{\tau(T)/\tau(12)}{I(T)/I(12)} = \frac{\tau_R(T)}{\tau_R(0)}. \tag{3}$$

$R(T)$ represents the temperature dependence of the radiative lifetime.

The three solid curves in Fig. 1(a) fit the observed data points calculated using Eq. (1) with parameters of ($\tau_R(0)$ [ms], τ_{NR} [μs], ΔE [cm^{-1}]) = (4.9, 3.1, 1100), (4.4, 6.8, 850) and (4.2, 23, 590), for the site selected excitation of 681.7, 682.4 and 683.0 nm, respectively, assuming that the radiative decay time, $\tau_R(T)$, is independent of temperature and equal to $\tau_R(0)$. In the case of $\tau_R(T)$ = constant, Eq. (2) shows that $I(T)$ is proportional to $\tau(T)$. However, there is a big difference between the observed curves of $I(T)$ and $\tau(T)$ as shown in Fig. 1(a and b). Ratios of the normalized lifetimes to the normalized intensities are plotted in Fig. 1(c). The large deviation of the ratio from unity with increasing temperature above 70 K suggests that the radiative decay time has also temperature dependence. However, this behavior is reverse to shortening the radiative decay time through electric dipole transitions induced by odd-parity vibrations. These experimental results deduce another optical quenching other than the phonon-assisted nonradiative decay process, which may

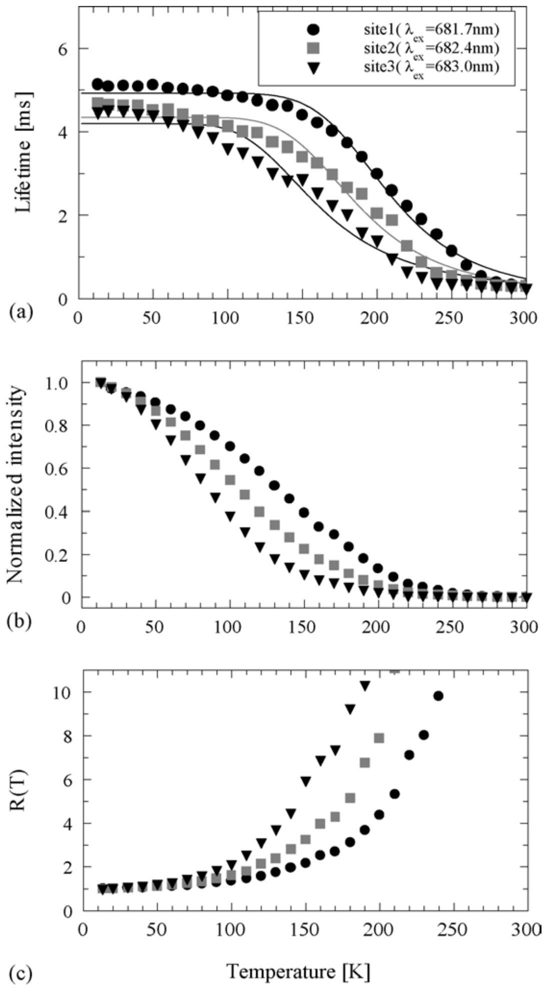

Fig. 1. Temperature dependence of (a) the lifetime and (b) the normalized intensity of the fluorescence due to the $^5D_0$–$^7F_0$ transition with three different excitation wavelengths of 681.7, 682.4 and 683.0 nm. (c) Temperature dependence of a ratio of the normalized lifetime to the normalized intensity represented in Eq. (3). Solid curves are calculated using Eq. (1) and parameters of ($\tau_R(0)$ [ms], τ_{NR} [μs], ΔE [cm^{-1}]) = (4.9, 3.1, 1100), (4.4, 6.8, 850) and (4.2, 23, 590), for site selected excitation of 681.7, 682.4 and 683.0 nm, respectively.

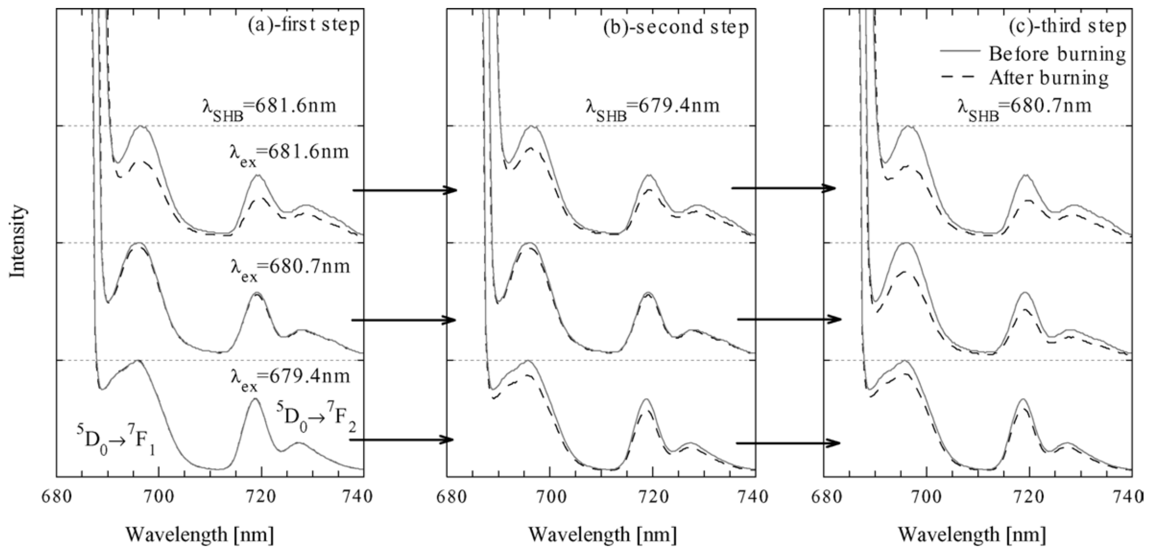

Fig. 2. Fluorescence spectra due to the $^5D_0$–^7F_J ($J = 1, 2$) transition at 12 K by site selected excitation before and after hole burning. Excitation wavelengths of 679.4, 680.7 nm and 681.6 nm are distinguished by λ_{ex} for fluorescence measurements and λ_{SHB} for spectral hole burning. Burning time is 30 min for the three steps.

be strongly associated with a mechanism of PSHB discussed below.

3.2. Fluorescence by site selected excitation

Fig. 2(a–c) show the fluorescence spectra of the $^5D_0$–^7F_J ($J = 1, 2$) transitions with the site selected excitation of $\lambda_{ex} = 679.4$, 680.7, and 681.6 nm before and after the hole burning. Here, λ_{ex} and λ_{SHB} are distinguished by fluorescence measurements and spectral hole burning, respectively. In inhomogeneously broadened spectra, the longer wavelength of excitation leads to the longer wavelength of fluorescence. However, the distinct peak shift of the fluorescence was not clearly observed with an increase of the excitation wavelength because a resolution (∼5 nm) of a fiber multi-channel spectrometer is beyond the line width ($\leqq$1 nm) of the fluorescence.

First, the KLF crystal was irradiated using LD light with $\lambda_{SHB} = 681.6$ nm and power of 40 mW for 30 min. This is called as a burning process. The distribution of various Sm^{2+} sites after burning was measured by monitoring the fluorescence intensities excited at $\lambda_{ex} = 679.4$, 680.7 and 681.6 nm. When the monitoring excitation wavelength was coincident with the burning wavelength, the fluorescence intensity was reduced with an amount of 30% compared with that before burning as shown in the top figure of Fig. 2(a). When the monitoring excitation wavelength (λ_{ex}) was different from the burning wavelength (λ_{SHB}), the fluorescence intensity was the same before and after burning, as shown in lower parts of Fig. 2(a). Fig. 2(b and c) show the difference of the fluorescence spectra before and after the second burning at $\lambda_{SHB} = 679.4$ nm and the third burning at $\lambda_{SHB} = 680.7$ nm for 30 min each, respectively. The fluorescence intensities after the second and third burning were reduced with amounts of 13 and 24%, respectively.

The intensity ratios of the fluorescence at 718 nm due to the $^5D_0$–$^7F_2$ transition of Sm^{2+} before and after burning are plotted in Fig. 3. The first hole at 681.4 nm was burned after one hour. In following second and third steps, the holes at 680.8 and 682.3 nm were burned after one hour each, respectively. The depth of the first hole at 681.4 nm is about 7.5%, whereas the depths of the second and third holes at 680.8 and 682.3 nm is about 10 and 7%, respectively. Although the number of the observed data points in Fig. 3 is not large, Fig. 3

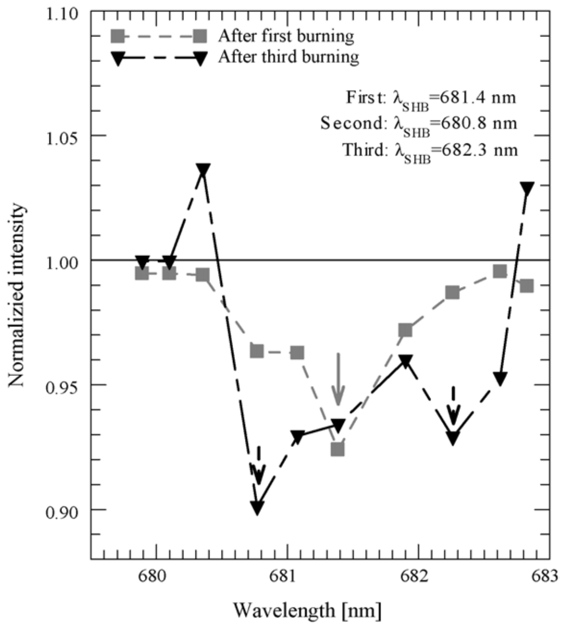

Fig. 3. Ratios of fluorescence intensities between before and after hole-burning at 12 K. A hole at 681.4 nm was burned for 1 h at first step (square), and holes at 680.8 and 682.3 nm were burned for 1 h each at second and third steps (triangle).

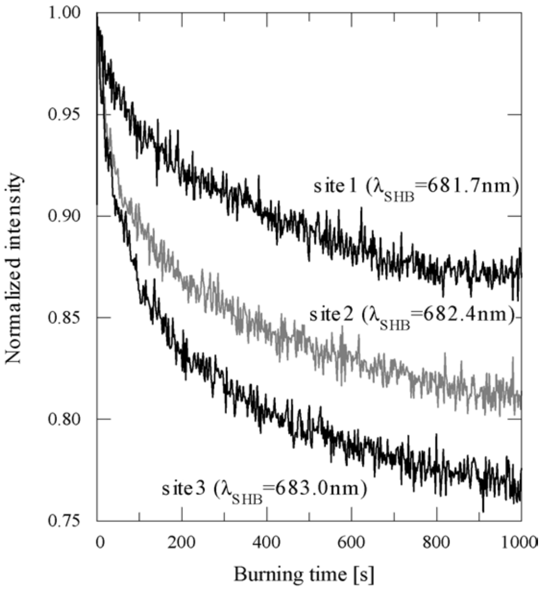

Fig. 4. Normalized intensities of the fluorescence at 696 nm due to the $^5D_0$–$^7F_1$ transition excited at λ_{SHB} = 681.7, 682.4 and 683.0 nm as a function of burning time.

shows that the second and third burning processes hardly affect the first ones.

Fig. 4 shows the normalized intensities of the fluorescence at 696 nm due to the $^5D_0$–$^7F_1$ transition excited at λ_{SHB} = 681.7, 682.4 and 683.0 nm as a function of burning time. The decrease from unity corresponds to the depth of the burning hole. The hole depth and the burning rate strongly depend on the Sm^{2+} sites. The deeper hole and the faster burning rate are achieved by the lower energy excitation. This result seems to be strongly associated with the temperature dependence of the fluorescence intensity with the site selected excitation in Fig. 1 where the intensity excited at the longer wavelength is more rapidly decreased with an increase of temperature.

4. Discussion

The strong absorption bands with peaks at 350 and 500 nm in the range of 220–680 nm are due to the $4f^6$–$4f^55d^1$ parity-allowed transitions. The fluorescence from the $4f^55d^1$ level is expected to appear with short lifetimes and strong intensities with an increase of temperature. In contrast with this expectation, the broadband fluorescence could not be observed at high temperature and the fluorescence due to the $^5D_0$–^7F_J transitions were drastically decreased above 50 K. This behavior is pronounced for the lower energy excitation as shown in Fig. 1.

Fig. 5 shows schematic diagrams of the $4f^6$ and $4f^55d^1$ energy levels for various sites of Sm^{2+} in KLF. In the case of a large crystal field including lower symmetry distortions, the ^7F_J ground state is split widely, while the lowest energy levels of the $^5D_J(4f^6)$ and $4f^55d^1$ excited states are shifted to lower energy. Such a configuration of Sm^{2+} corresponds to site 3 in Fig. 5. The radiative decay time for site 3 is expected to be shortened through mixing of parity-allowed electric dipole transitions induced by odd-parity distortions. According to an increase of the crystal field, the energy level of the lowest $4f^55d^1$ excited state is also shifted to lower energy, resulting in an decrease of ΔE as shown in Fig. 5. This expectation is in agreement with the fitting parameters of Eq. (1) for the site selected excitation in Fig. 1.

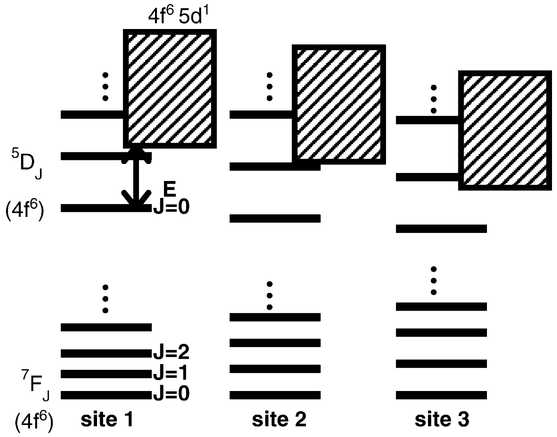

Fig. 5. Schematic diagrams of the $4f^6$ and $4f^55d^1$ energy levels for various sites of Sm^{2+} with different crystal fields.

As shown in Fig. 4, site 3 with the lower energy level of $^5D_0$ is easily burned. We consider a PSHB mechanism, taking into account the above fluorescence experimental results. The 5d wavefunction extends from the central ion toward ligand ions. The 5d wavefunctions of the $4f^55d^1$ excited states are mixed into the wavefunction of the $^5D_0$ excited state by odd-parity distortions or thermal population of the $4f^55d^1$ excited states according to the decrease of ΔE. If electron trapped centers [9], for example, F^- vacancies or Sm^{3+} ions, are located nearby Sm^{2+}, the excited electron of Sm^{2+} moves easily to the electron trapped centers. If the trapped electrons are stable below room temperature, then PSHB can be observed below room temperature. In order to confirm this PSHB model, further ESR experiments are required to identify the structure of the electron trapped center.

5. Conclusions

The SHB spectra in KLF:Sm^{2+} have been observed at 12 K through 1 h irradiation of light emitted from an LD at 681.4 nm with 40 mW. The Sm^{2+} site with the lower energy level of $^5D_0$ is easily burned. An PSHB model that the hole burning occurs through an excited electron of Sm^{2+} transferring via the $4f^55d^1$ excited state to electron trapped centers, for example, F^- vacancies or Sm^{3+} ions is proposed.

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