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Change of photoluminescence property of ferroelectric compounds with the gamma-ray irradiation

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ABSTRACT

We investigated the emission properties of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ polycrystals and $(K_{0.5}Na_{0.5})(Mn_{0.005}Nb_{0.995})O_3$ thin films with strong gamma (γ)-ray irradiation by using temperature dependent photoluminescence spectroscopy. At the lowest temperatures, sizable visible emissions were identified for the γ-ray irradiated samples as well as un-irradiated ones. In both kinds of compounds, the visible emission intensity tended to be increased without changing the spectral shape, as the γ-ray dose increased. This indicates that the γ-ray irradiation should increase all kinds of already-existing defects evenly, without preferring the formation of some particular type of defect.

1. Introduction

Ferroelectric/piezoelectric materials have been widely used in commercial fields including transducers, sensors, and non-volatile memory devices [1,2]. In addition to their uses in an ordinary life, the electric properties of the ferroelectric materials in some extreme conditions have been attracting more attention. In particular, the radiation effect with high energy photons, e.g., gamma-ray, has been studied for use in devices operating in irradiation environments such as space applications, military system, and nuclear-reactors. There have been several reports on the γ-ray irradiation effect on some ferroelectric compounds in films and polycrystalline forms [3,4]. In most cases, the degradation of the physical property in the ferroelectric compounds has been observed because of defects induced by the γ-ray irradiation, whereas there have been few reports on direct observation of the defect formation by the γ-ray irradiation.

Optical spectroscopy is known to be a powerful tool for investigating defects and structural disorder in a wide bandgap of compounds. The defects and the related local lattice distortion/structural disorder should be involved in forming the intermediate energy state within the bandgap, which can be probed by spectroscopic techniques such as absorption and emission spectroscopies. It is valid for the case of defects formed by the gamma-ray irradiation. The newly formed F-bands have been detected in the absorption spectra of the gamma-ray irradiated potassium halide single crystals [5]. Strong thermoluminescence signals have been observed in the irradiated oxides with rare-earth ion activators [6–8]. Some oxide phosphors have been observed to lose some photoluminescence (PL) intensity [9]. In relation to the study on the ferroelectric compound, we recently have investigated the visible emission property of $Pb(Zr,Ti)O_3$ (PZT) thin films irradiated with γ-ray [10]. The visible emission was found to emerge near 550 nm upon the γ-ray irradiation, and the intensity of the emission increased with the increasing dose of γ-ray (D_G). The spectrum of the γ-ray-induced emission was quite narrow, which was quite distinguished from that caused by normal defects such as oxygen vacancies. It has been suggested that the γ-ray irradiation should generate a specific type of defect inside the PZT films that can be detected by using low-temperature photoluminescence spectroscopy.

Extending the previous work to other ferroelectric materials, we investigated the effect of γ-ray irradiation on two well-known ferroelectric compounds, $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) and $(K_{0.5}Na_{0.5})(Mn_{0.005}Nb_{0.995})O_3$ (KNMN). The BLT compound has a fast switching speed, long retention, superior fatigue resistance, and no pollution to the environment. For these advantages, it has been considered an ideal candidate material for use in ferroelectric memory device [11,12]. The KNMN has been intensively studied as a lead-free ferroelectric material [13]. While pure $(K_{0.5}Na_{0.5})NbO_3$ is a highly promising candidate for replacing lead-based ferroelectric materials because of several advantages, such as, its high Curie temperature, relatively high piezoelectric properties, and low coercive fields, it has been recently revealed that

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small amounts of Mn substitution for Nb, i.e., KNMN, could reduce the leakage current and improve ferroelectric/piezoelectric properties.

In this paper, we investigated the emission properties of the BLT polycrystals and the KNMN thin films using strong γ-ray irradiation. The visible emissions, which were detected even for $D_G = 0$ kGy, were found to increase in both samples with the increasing D_G. Our results were compared with the emission property of the irradiated PZT films.

2. Experiment

KNMN thin films were synthesized on a Pt/Ti/SiO_2/Si (Pt/Si) substrate by using the chemical solution deposition technique with spin-coating [14]. To compensate for the volatilization of alkaline metals during the high-temperature annealing process, 10% K and Na excess was added to the precursor solution, and the molarity was adjusted to 0.4 M. The KNMN precursor solutions were dropped onto a Pt/Si substrate using a micropipette and spin-coated at 3000 rpm for 30 s. After a sequence of drying, calcination, and heat-treating, the final annealing process for the crystallization of the films was performed in a preheated tube-type furnace at 750 °C. BLT polycrystalline samples were fabricated in the conventional solid state reaction method. A mixture of raw material powders (Bi_2O_3, La_2O_3 and TiO_2) with a molar ratio of Bi_2O_3:La_2O_3:TiO_2 = 13:3:24 was used [11].

For the γ-ray irradiation on the samples studied here, we used a ^{60}Co source at room temperature in air with different total doses at the Jeonju branch of the Korean Atomic Energy Research Institute (KAERI). ^{60}Co decays to the stable isotope ^{60}Ni by β-decay [10,12,14,15]. The activated nickel nucleus emits two γ-rays with energies of 1.17 and 1.33 MeV. The D_G used in this work was increased up to 1000 kGy (Gy ≡ J/kg, the absorption of one joule of radiation energy per kilogram of matter). The PL spectra of the irradiated KNMN films and BLT polycrystals were measured using photo-excitation by a He-Cd laser (λ = 325 nm) [16,17]. For temperature dependent measurement, the sample was positioned in a closed-circulated refrigerator with optical windows, and the measurement temperature was controlled from 10 K to 300 K.

3. Results and discussion

3.1. Structural and electric properties of KNMN films and BLT bulks

We briefly reviewed the structural and electrical properties of KNMN thin films [14] and BLT polycrystalline bulks [18] with the γ-ray irradiation. In both samples, we found that their crystalline quality did not vary significantly with an increase in the total dose. As for the electrical property, it was also observed that the remnant polarization value of our samples decreased by ~10%, and the dielectric constant of our samples films decreased with increasing D_G. The change of the electric property of our irradiated BLT bulk was quite comparable to those in the BLT films [12]. The observed variation of the electrical properties on D_G might be mainly associated with the mobile defects in the compounds such oxygen vacancy and the stored energy gained from the γ-rays. The effect of the γ-ray irradiation on the electric property of ferroelectric material may be closely related to the high energy transfer and creation of electron-hole pairs. High-energy γ-ray irradiation can displace many atoms from their sites to other sites, which produces defects such as interstitials, impurities, and vacancies. These defects can easily accumulate along the domain walls and grain boundaries, which may lead to the pinning of the domain walls. As for the ionizing effect, many electron–hole pairs can be generated by ionizing effects, and these charges can be trapped by radiation-induced defects. These trapped charges can produce a local field in a direction opposite to that of the external field, which degrades the polarization switching.

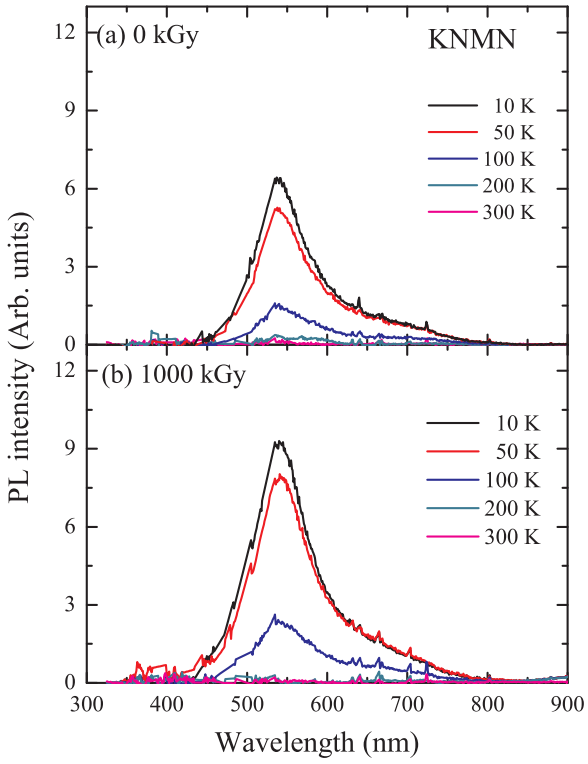

Fig. 1. Temperature dependent PL spectra of KNMN films irradiated at (a) $D_G = 0$ kGy and (b) $D_G = 1000$ kGy.

3.2. Temperature dependence of PL with different doses

To understand the effect of the γ-ray irradiation on the physical properties of our samples in more details, we performed temperature-dependent photoluminescence spectroscopy using 325 nm photo-excitation with the He-Cd laser. Fig. 1(a) and (b) show the temperature-dependent PL spectra of KNMN films for $D_G = 0$ and 1000 kGy, respectively. The PL spectra of the two films showed common temperature-dependent evolution. At room temperature no distinct emission signals were identified. However, with decreasing temperatures a broad structure ranging from 450 nm to 800 nm emerged below 200 K and developed at lower temperatures down to 10 K. For clarity, we estimated the integrated PL intensity (I_{int}) from the peak area calculated by integrating the PL intensity in the peak region. As shown in Fig. 2(a), the I_{int} increased distinctly below 200 K in both $D_G = 0$ and 1000 kGy films. The increase of the emission at lower temperatures may originate from the suppression of the non-radiative decay of the excited electrons, which is caused by the reduction of the thermally excited phonons [19]. It is interesting to see that the visible emission in KNMN was rather asymmetric with a long tail in the longer wavelength side. This implies that a satellite emission might exist near 650 nm in addition to a main peak near 550 nm. We note that the Mn^{4+} plays a role as an activator of the red emission [20]. Small inclusion of Mn^{4+} in our films is likely to be responsible for the satellite emission near 650 nm. On the other hand, the peak position (E_{peak}) of the main emission, estimated with the center of the emission, did not change with temperature in either film, as shown in Fig. 2(c). From these results, we found that the temperature dependence in the PL intensity does not depend significantly on the γ-ray irradiation in the KNMN films, apart from the absolute values of I_{int} and E_{peak}.

We turn to the emission spectra of BLT polycrystalline bulks. Fig. 3(a) and (b) show the temperature-dependent PL spectra of the BLT bulks for $D_G = 0$ and 1000 kGy, respectively. As in the case of the KNMN films, both samples show quite similar temperature dependence of the PL spectra. At room temperature, no sizable emission signal was