



Study of the emission of visible light from perovskite zirconate nanocrystals with Cu-ion implantation



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ABSTRACT

We investigated the emission of visible light from perovskite zirconate CaZrO_3 and BaZrO_3 nanocrystals (NCs) implanted with Cu ions. The CaZrO_3 and BaZrO_3 NCs were synthesized by using the combustion method, and were post-annealed at various temperatures for the purpose of changing their structural properties. The annealed NCs were subjected to Cu-ion implantation with ion doses from 0 up to 1×10^{16} particles/cm². The XRD patterns of the NCs indicated that the Cu-ion implantation did not affect the structural properties of the NCs. In their photoluminescence spectra, we identified sizable yellow and green/blue emissions, which were caused by the Cu-ion implantation, in addition to a violet emission which was due to structural defects of the host compound. As the Cu-ion dose and annealing temperature were increased, the implantation-induced emission became stronger from both the CaZrO_3 and BaZrO_3 NCs. In comparison with the case of the previously studied implanted SrZrO_3 NCs, the intensity and the spectral shape of the Cu-ion emission were found to depend strongly on the identity of the divalent cation (A in AZrO_3) in close relation to the structural properties of the host zirconate. Analysis of absorption coefficient spectra of the NC samples showed that their band gaps were not affected by Cu-ion implantation. From the measured PL spectra, we calculated the CIE color coordinates, and found that colors of the light emitted from the NCs changed from violet-blue to white (close to yellow).

1. Introduction

Ion implantation is known to be a useful technique for modifying the structural, electrical and optical properties of target (matrix) materials [1,2]. The implanted ions transfer their high energy and momentum to the target material, inducing physical and chemical changes inside the material. The implanted ions may also function as dopants. The amount of ion doped when using this implantation technique may exceed the normal solubility limits of the ion in some cases. The amount of damage caused by the implanted ions and several of their properties (e.g., their position, doping concentration, and size of their nanoclusters) may be tailored by varying the ion energy, fluence, and current. For these reasons, ion implantation has been widely used in material science research, including semiconductor device fabrication. In particular, transition-metal ion implantation has been actively employed as a way to dope transition metals into semiconductors and oxides to induce novel electric, magnetic, and optical properties [3–6].

The $4d^0$ band insulator perovskite AZrO_3 (A = divalent cation, e.g., Ca^{2+} , Sr^{2+} , and Ba^{2+}) compounds have attracted much attention as novel electronic materials. Because these materials have high melting

points (over 2600 °C) [7], they can be used for high temperature devices. In particular, CaZrO_3 (CZO) and SrZrO_3 (SZO) have been suggested for use in electrochemical devices due to their good proton conductivity at fairly high temperatures [8]. Also, Cr-doped SZO shows a good resistivity switching behavior that may be applicable to resistive-RAM [9]. And, BaZrO_3 (BZO) has been used as an additive for enhancing the current density in superconducting films [10]. In addition, the useful optical properties of the zirconates have been intensively investigated for possible application in new high-performance optoelectronic devices. Bulk perovskite zirconates have been used as possible host materials for LED phosphors including rare earth ions whose localized bands are related to strong and narrow emissions [11–14]. An intense violet-blue PL emission at room temperature has been reported in undoped nanocrystals [15–18].

Recently we suggested that doping a $3d$ transition metal, such as Cu ions, could lead to a new type of emission of visible light from SZO [19]. The visible emission spectrum of Cu-ion-doped SZO, synthesized using solid-state-reaction method, was found to depend strongly on the photo-excitation wavelength (λ_{ex}) applied. When a long-wavelength UV excitation ($\lambda_{\text{ex}} > 310$ nm) was applied to this SZO, one orange/

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yellow-light emission and one green/blue-light emission were observed, while emission of violet light was dominant when a short-wavelength UV excitation ($\lambda_{\text{ex}} < 310$ nm) was used. As another way to dope Cu ions, the implantation technique was found to be quite useful in inducing novel emission of visible light from zirconates [20,21]. In both bulk and nanocrystal forms, the implanted SZO samples showed yellow and green/blue light emissions comparable to those from the chemically doped SZO samples.

Since the status of the implanted ions depends strongly on the local environment inside the host material, it is imperative to carry out a study involving the tuning of the structural properties of the host material in order to determine the effect of the ion-implantation on the visible-light emission. Moreover, the optical properties of 3d transition metal ions, such as Cu ions, are expected to be strongly affected by the structural environment around the metal ions, which determines the crystal fields generated by neighboring anions [22]. Note that structural distortion can be tuned by using chemical substitution with different sizes of ions at A-site of AZrO_3 . And also, the crystallinity degree of a sample can be controlled in a nanocrystalline form by post-annealing treatment. Therefore, we investigated the emission of visible light from CZO and BZO nanocrystals (NCs) subjected to Cu-ion implantation. We synthesized CZO and BZO NCs using the combustion method, and post-annealed them for the purpose of changing their structural properties. We observed that intense emission of yellow-to-green/blue light from NCs were induced by the implantation of Cu ions, in addition to an emission of violet light due to structural disorder within the host compound. We determined the properties of the visible-light emission from the implanted CZO and BZO NCs and compared these properties to those of SZO NCs.

2. Experiment

The CZO and BZO NCs were prepared using the combustion method, where an exothermic oxido-reduction between an oxidizer (generally a nitrate) and a fuel was used [17,23]. In a silica crucible, $\text{NH}_2\text{-CH}_2\text{-COOH}$ (fuel), $\text{ZrO}(\text{NO}_3)_2$, and either $\text{Ca}(\text{NO}_3)_2$ or $\text{Ba}(\text{NO}_3)_2$ were used as starting materials. These starting materials were mixed in water, dried for 12 h at 200 °C and then heated for 6 h at 600 °C. (The as-synthesized NCs had been annealed at $T_{\text{anneal}} = 600$ °C as part of the synthesis.) Then, the synthesized NCs were post-annealed at temperatures of up to 1400 °C to complete the reaction and to enhance the crystallinity of the synthesized NCs.

In order to implant Cu-ions into the annealed NCs, the metal ion beam facility at the Korea Multi-purpose Accelerator Complex (KOMAC) was used to generate Cu^+ ions [20,21,24,25]. The ion dose was estimated by using the current density of a Faraday cup. During implantation, the operation vacuum was maintained at about 5×10^{-6} Torr where the mean free path was about 10 m, indicating that accelerated Cu ions were not interrupted by other particles. By regulating the irradiation time of the beam, we were able to achieve ion dose (D_{Cu}) values of 1×10^{14} to 1×10^{16} particles/cm². Cu ions at an energy of 100 keV were implanted into the CZO and BZO NC target materials to form Cu-ion-implanted CZO (CZO:Cu) and BZO (BZO:Cu) NCs. The annealed samples were not annealed thermally again.

For structural analysis, X-ray diffraction (XRD) patterns were acquired using a Cu target X-ray tube. The photoluminescence (PL) spectra of the implanted NCs were acquired by exciting them with a He-Cd laser ($\lambda_{\text{ex}} = 325$ nm). The wavelengths of the light emitted from the samples were determined using a grating-type monochromator and a photomultiplier-tube detector. To investigate the electronic structures of the CZO:Cu and BZO:Cu NCs, we acquired the diffuse reflectivity spectra of the NCs in the near-infrared-visible-ultraviolet (NIR-Vis-UV) region (0.5–6.7 eV) at room temperature [26].

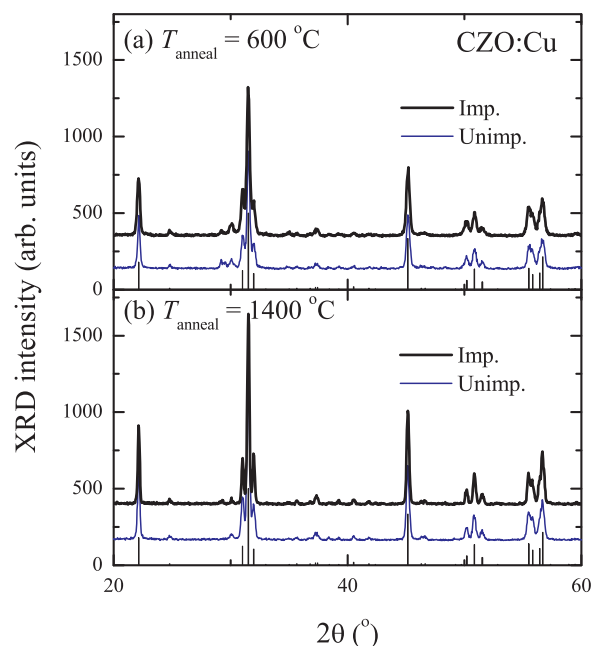


Fig. 1. X-ray diffraction θ - 2θ scans for CZO:Cu NCs annealed at $T_{\text{anneal}} =$ (a) 600 °C, and (b) 1400 °C. The thick and the thin solid lines represent the data for unimplanted (unimp.) and implanted (imp.) NCs, respectively. The bars in the bottom of each panel represent the JCPDS data of CaZrO_3 (35-0645).

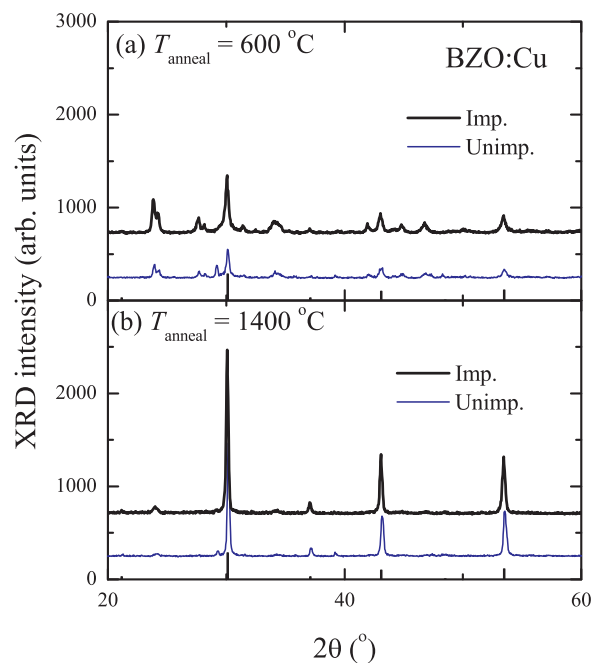


Fig. 2. X-ray diffraction θ - 2θ scans for BZO:Cu NCs annealed at $T_{\text{anneal}} =$ (a) 600 °C, and (b) 1400 °C. The thick and the thin solid lines represent the data for unimplanted (unimp.) and implanted (imp.) NCs, respectively. The bars in the bottom of each panel represent the JCPDS data of BaZrO_3 (24-0102).

3. Results and discussion

3.1. XRD Patterns of the CZO:Cu and BZO:Cu NCs

Figs. 1 and 2 show the XRD patterns of our CZO:Cu and BZO:Cu NCs annealed at different T_{anneal} . First we examine the structural properties of the host materials. The space group of orthorhombic CZO is Pmna , whereas that of cubic BZO is $\text{Pm}3\text{m}$. The ionic radii of Ca^{2+} and Ba^{2+}

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