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学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Composition Engineering of Lead-free Double Perovskite Nanocrystals for Self-powered Photodiodes
（セルフパワーフォトダイオード創製を指向した非鉛系ダブルペロブスカイトナノ粒子の化学組成工学）

Lead-free double perovskite nanocrystals (LDP NCs) are promising materials as an alternative to lead-based perovskite nanocrystals to solve the problem of toxicity and instability. Specifically, replacing two Pb2+ ions with a combination of monovalent and trivalent cations could be a solution for forming three-dimensional (3D) perovskite structures, whose chemical formula is A2B(I)B(III)X6, which is called double-perovskite structure. LDP NCs have excellent properties such as good stability, long carrier lifetime, long photoluminescence lifetimes, high photoluminescence quantum yield and solution-processability. Therefore, LDP NCs are considered to be promising materials for optoelectronic applications including photodetector, photocatalysts, light-emitting diodes and solar cells.
Cs2AgB’X6 (B’ = In or Bi, X = Cl or Br) has the potential to be applied in optoelectronic devices. While it owns a high absorption coefficient, good stability and low toxicity, there is still a challenge in improving its performance to reach or exceed that of lead-based perovskites. For example, the defects introduced by indium can create trap states in the bandgap of Cs2AgInCl6 thus affecting the material properties. Therefore, the thesis focuses on the composition tuning of LDP NCs for photodiode application by B-site doping strategies as well as the bandgap engineering by X-site anion composition tuning in LDP NCs to realize efficient wavelength-selective photodiodes.
In Chapter 1, a general background about lead-free double perovskites and a simple overview of ultraviolet photodiodes are introduced. In particular, the process and purpose of the research which lead to the conception of the research topic were clarified.
In Chapter 2, Na-alloyment and Bi-doping were employed in improving the optical properties of Cs2AgInCl6 NCs. We synthesized Cs2Ag0.65Na0.35InCl6 NCs doped with bismuth (Bi3+) ions and investigated their photophysical properties to reveal the role of the dopant on the enhanced photoemission properties. Specifically, it was found that the photoluminescence quantum yield (PL QY) increased up to 33.2% by 2% Bi-doping. The optical bandgap of the NCs decreased from 3.47 eV to 3.41 eV as the amount of the dopant increased from 2% to 15%. To find out the effect of Bi-doping, the temperature-dependent PL properties of the undoped and doped NCs were investigated by utilizing steady-state and time-resolved PL spectroscopy. With increasing the temperature from 20 K to 300 K, the PL intensities of the doped NCs decreased slower than the undoped ones. The correlated average PL lifetimes of both the bismuth-doped and undoped NCs decreased with increasing temperature. The experimental results revealed that all the NC samples showed thermal quenching with the temperature increasing, and the PL quenching was suppressed in bismuth-doped NCs.
In Chapter 3, we first demonstrated the highly responsive lead-free perovskite photodiode

based on Cs2Ag0.35Na0.65InCl6 nanocrystals. The composition tuning strategy is introduced to enhance the device performance of photodiodes. Employed with a device structure composed of ZnO: Al electron-transport layer and Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4' -(N-(4-sec-butylphenyl)diphenylamine)] (TFB) hole transport layer, lead-free perovskite nanocrystal photodiodes exhibit a high responsivity of 3.03 A/W and specific detectivity of 1.29 X 1011 Jones under the illumination of a 340 nm light source. Moreover, the ultraviolet (UV) photodiodes show good performance under the self-powered mode, which exhibits a responsivity of 0.07 A/W and specific detectivity of 5.04 x 1010 Jones. Our work verifies the great potential of the Cs2Ag0.35Na0.65InCl6 nanocrystals in the application of environmentally friendly and high-performance UV photodiodes.
In Chapter 4, we studied on Cs2AgBiX6 (X = Cl or Br) NCs, which replaces In3+ by Bi3+ to avoid the generation of indium-caused defects and obtain strong absorption for the photodiode application. The band gap engineering was conducted through the composition tuning from Cs2AgBiCl6 to Cs2AgBiBr6. We fabricated lead-free double perovskite photodiodes with wavelength-selective properties response to UV-Visible range. Specifically, the Cs2AgBiBr6-based photodiode exhibits a characteristic detection peak at 340 nm with a responsivity of 3.21 mA/W, a specific detectivity up to 8.91 X 1010 Jones and a fast response speed with rise/fall time of 30/35 ms. The excellent performance of self-driven photodiodes lights up the prospect of lead-free double perovskite nanocrystals in highly efficient optoelectronic devices without external power sources.
In Chapter 5, we clarify the conclusions and propose the outlook on the efficacy and future potential of the lead-free double perovskite nanocrystals.