

論文内容要旨

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学位論文題目	Development of New Red Phosphors and Effects of Coordination Environment around Activator on Luminescence Properties (新規赤色蛍光体の開発と賦活剤周りの配位環境に由来する発光特性への影響)		
内容要旨 <p>White light LEDs are widely used in social life. However, due to the lack of the red component, the white light LED has a poor color rendering index. To solve this program, some red phosphors, which have the absorption band in the near-UV to blue light, have been synthesized.</p> <p>Some nitride phosphors have been commercialized because of their good photoluminescence (PL) properties and high stability. However, higher temperature (1800-2000 °C) and the reductive atmosphere are needed to synthesize nitrides. New oxide phosphors have been developed, taking advantage of low fabrication costs. The achievement of this study is the development of new red phosphors with lower fabrication costs. In addition, the relationship between PL properties and the coordination environment is revealed. The PL properties depend on the coordination environment around the activator, which is derived from the crystal structure of the host material. Therefore, the oxide host materials were carefully selected in this study.</p> <p>Firstly, the relationship between PL properties and the coordination environment around Eu^{3+} in the garnet-type $\text{Ca}_2\text{EuZr}_{2-x}\text{Sn}_x\text{Ga}_3\text{O}_{12}$ ($x = 0, 0.5, 1, 1.5, \text{ and } 2$) phosphors are discussed. The distortion of the eight-coordinated dodecahedron affects the intensity derived from ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ (~610 nm) and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ (~710 nm) transitions of Eu^{3+}. The degree of this distortion was revealed by Rietveld analysis. The Rietveld analysis is an effective way to elucidate the distortion of the eight-coordinated dodecahedron of these phosphors, where Eu^{3+} constitutes the host material of the garnet, because of a diffraction method that describes the average structure of the materials. A method to describe the rotation angles of the top and bottom faces of the eight-coordinated dodecahedron in a garnet-type structure is proposed by simple geometric calculations utilizing the ratios of the edges of the dodecahedron. This method reveals the relationship between the emission intensity of Eu^{3+} at 610 nm and 710 nm and the coordination environment in the garnet-type structure. Controlling the emission wavelengths is useful for further applications. Phosphors emitting red light near 600 nm have good visibility and are suitable for application in high-color-rendering white LEDs. The infrared wavelength</p>			

near 700 nm is suitable for plant growth.

Secondly, Mn-activated perovskite-type $\text{La}_{5/3}\text{MgTaO}_6$ red phosphor and pyrochlore-type $\text{Mg}_2\text{LaTaO}_6$ green phosphor are discussed. The Mn-activated perovskite-type $\text{La}_{5/3}\text{MgTaO}_6$ red phosphors are cost-effective compared with Eu^{3+} -activated phosphors because Mn is cheaper than Eu. X-ray absorption fine structure (XAFS) spectroscopy methods were utilized to reveal the distortion of the Mn^{4+} -occupied octahedron. It appears that the Rietveld analysis reveals the distortion of the polyhedron in the previous section. However, it is difficult to investigate the coordination environment around only Mn by the Rietveld analysis due to the two points: the analytical methods for describing long-range-order structure (average structure) and low concentration of Mn^{4+} in the host material. It should be noted that the XAFS method provides important information of the local structure around a specific element. Therefore, the XAFS method was utilized to investigate the relationship between the distortion of the Mn-occupied octahedron and luminescence property. A-site deficiency in the perovskite-type structure plays a crucial role in the red emission of Mn^{4+} in the host material of $\text{La}_{5/3}\text{MgTaO}_6$ because of the displacement of Mn^{4+} from the center of inversion.

Finally, Mn-activated pyrochlore-type $\text{Mg}_2\text{LaTaO}_6$ phosphor exhibited green emission under UV excitation at 254 nm owing to the oxide ion deficiency of $\text{Mg}_2\text{LaTaO}_6$, indicating that the defects affect the coordination environment around Mn^{2+} as an activator. In general, the green emission is derived from Mn^{2+} . However, Mn^{2+} is achieved by the calcination in the reductive atmosphere due to lower valence state than Mn^{4+} . The green emission from Mn^{2+} was realized in the crystal structure of the pyrochlore-type $\text{Mg}_2\text{LaTaO}_6$ even by the calcination in air atmosphere, resulting in the cost-effective fabrication.