Synthesis and Characterizations of Organic based Mechanoluminescent Materials

（課程博士・様式７）（Doctoral qualification by coursework,Form 7）

学 位 論 文 要 旨

Abstract of Doctoral Thesis

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Abstract :

This research devoted to study synthesis and characterization of an organic based mechanoluminescent (ML) materials. The organic europium-doped dibenzoylmethide triethylammonium (EuD_4TEA) is a well-known ML material and is used as a basis for this study. In this thesis, the enhancement of the ML properties and crystalline structure was investigated.ML is a light-emission event that results from a mechanical action on a solid. Fracto-, plastico- and elastico-ML are various forms of ML. Among the various ML forms, fracto-ML is well known because most of the inorganic materials emit light when they are fractured. For example, mechanical stress relaxation during and prior the earthquake results in fractoluminescence. Additionally, plastico-ML can be observed by peeling an adhesive tape in a vacuum. When the crystal bonds are broken along oppositely charged planes and then reconnect, light is emitted as the charges pass through the gaps that were created from the fracture. Once the material is fractured, the electrons are excited to higher energy levels and then transition to the lower energy levels. The energy difference between the corresponding levels is emitted as a light with different wavelengths. The third type of ML mechanism, elastico-ML, results from a mechanical stress that produces a piezoelectric field on the surface of crystals. This electric field that is near the color center is high because of changes in the local structure. These changes may reduce the carrier trap depth or effect band bending. After decreasing the carrier trap depth, the thermal de-trapping of the carriers may occur. Trapped charge carriers can tunnel to the conduction band because of the band bending. The electrons from the conduction band may be captured by the excited state of the activator ions. This may cause a de-excitation of the color center and produce the emission. When plastico-mechanoluminescent materials are plastically deformed, a movement of dislocation occurs. Similarly, an electric field generated by the charge dislocation causes a bending of the valance, conduction and dislocation bands. Trapped electrons tunnel to the conduction band and the recombination of electrons and holes enables the light emission characteristic of the color center. However, the conduction band electrons are trapped by the color center, and a potential energy transfer occurs as a result of the de-excitation of the rare-earth cation. Both functions occur, and electron-hole recombination is greater than that caused by the impact excitation. To date, many inorganic mechanoluminescent materials have been synthesized with various dopants.Our group has synthesized a novel ML material with the addition of 1-ethenylpyrrolidin-2-one

[(polyvinylpyrrolidone) (PVP)], which changed the ligand EuI_2, $EuBr_2$ and $EuCl_2$ of the mechanoluminescent material. This study investigated the ML substance structure, molecular orbital electron distributions of the ligands, ML mechanism and enhancement in the photoluminescence (PL) intensity with PVP. For the first time, the ML material structure was characterized using nuclear magnetic resonance spectroscopy (NMR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and Gaussian DFT/B3LYP/6-31G(d,p) software. The ML properties were characterized using a multichannel spectroscope (Hamamatsu Photonics, PMA).We have investigated the low-temperature effect on the form mechanoluminescent material with different ligands. The study revealed that ML intensity can be controlled by the addition of ligands with different oxidation state of Eu. The highest enhancement of the ML intensity is obtained by adding Eu^{+2} containing ligands. The higher ML intensity in case of Eu^{+2}, can be explained by higher flexibility of the coordinated structure, because Eu^{+2} has only two bonds with benzoyl groups. Therefore, higher flexibility of the coordinated structure, allows higher orbital overlapping and reduce the distance between cation, and ligand. Moreover, ML intensity is affected by different chalcogenide anions from Eu compounds – EuI_2, $EuBr_2$ and $EuCl_2$. The highest enhancement of the ML intensity is obtained by adding EuI_2, followed by EuBr2 and the lowest ML intensity was observed in case of $EuCl_2$. The low ML intensity in case of $EuCl_2$, can be explained by the high electron affinity of Cl^- anions, which is disrupting EuD_4TEA band structure and reducing radiative recombination of electrons.Since changing the valence of the ML, material occurs to varying the ML and PL intensity of the materials. However, DSC characterization depicted that glass transition of the ML material changes after treated with liquid nitrogen and occur to increase the crystallinity of the synthesized ML materials. Integrated materials were distinguished by using Differential scanning calorimetry (DSC), X-ray photon spectroscopy (XPS) and X-Ray diffractometer (XRD).

The material can be applied to the real-time visualization of the stress field near the tip of a crack, an ML light source, determination of laser and ultrasonic powers, secret message writing and earthquake-detection sensors. The further study concerned to fabricate the ML thin film without using any binder or resin. The first time we have achieved to form a thin film of the PVP-added EuD_4TEA. The thin films with different quantities of the PVP addition are developed on an Al_2O_3 buffer layer fabricated on Ni substrate. The present study has examined a relationship among both the ML and the photoluminescence characteristics of thin films and the counting amount. For the first time, we have fabricated the ML thin film without any use of binder or resin. The results infer that the properties are entirely related to a crystallinity of the thin films. Also, we have succeeded to form a thin film with using synthesized ML nanoparticles. Research carried out about synthesis and fabricated the Mechanoluminescent thin film by using mechanoluminescent nanoparticles. Novel organic based mechanoluminescent material is incorporated by using polyvinylpyrrolidone with higher intensity.