

Thesis Summary

Photoluminescence Properties of Distorted Titanates Investigated

by X-ray Absorption Spectroscopy

(X線吸収分光法による歪んだチタン酸化物のフォトルミネセンスの研究)

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The titanium oxygen polyhedral, TiO_4 with tetrahedron structure, TiO_5 with square pyramidal structure, and TiO_6 with octahedron structure, commonly exist in titanate materials from the microscopic scale point of view. The physical properties of titanates are highly dependent on the local structure of these titanium oxygen polyhedra. For example, Ba_2TiO_4 , which contains a series of isolated TiO_4 tetrahedra, has excellent CO_2 sorption properties. Fresnoite structure materials containing TiO_5 polyhedron exhibit strong second harmonic generation response and have been widely used for second-order nonlinear optical materials. A TiO_6 octahedron is more famous than TiO_4 and TiO_5 and contained in the titanates with perovskite structure, which is a hot research topic nowadays. The typical example is the ferroelectricity in BaTiO_3 and PbTiO_3 , which is produced by displacement of a titanium ion in an octahedron cage. In terms of structural similarity, TiO_5 can be considered to result from the TiO_6 octahedron with Ti ion displacement along the z-axis. The local structural nature of these polyhedra in materials is essential for the physical property.

The self-activated titanate phosphors with TiO_5 polyhedra show excellent photon emission property under UV irradiation, i.e., photoluminescence (PL). This phenomenon was also seen in the BaTiO_3 with distorted TiO_6 octahedron. It is interesting to see the PL and ferroelectric properties result from the distortion of TiO_6 octahedron. The “self-activated phosphors” term is from no ion-doped existed in the phosphors, while the conventional phosphors are created by doping ions in a matrix as the color center. The function of the doped ions is to form in-gap states. To figure out the role of the TiO_5 polyhedron in self-activated titanate phosphors, the investigation of local electronic states in the TiO_5 polyhedron is required. In addition, the incipient ferroelectric materials SrTiO_3 , which is known as centrosymmetric for the whole temperature range, also show PL property with faint blue light emission below 37 K. This motivates us the investigation of the local structure of TiO_6 with the influence of temperature and UV irradiation. Beyond that, to explain the reports about the appearance of the dipole moment and the the increase of dielectric constant in SrTiO_3 under UV irradiation also requires the local structure information. Due to the sensitivity of the atomic species and high resolution of spatial distribution, XAFS is an ideal approach for the investigation of electronic states of self-activated phosphors and the local structure of SrTiO_3

with UV influence.

The Ti K-edge XANES of self-activated titanate phosphors ($\text{Ba}_2\text{TiSi}_2\text{O}_8$, $\text{Sr}_2\text{TiSi}_2\text{O}_8$, and $\text{Na}_2\text{TiSiO}_5$) were measured with UV irradiation, two features in the pre-edge region were observed: A giant pre-edge feature and hump. The electronic states of features are determined by the theoretical calculation. The electronic state of pre-edge originated from the hybridization from Ti $3d$, Ti $4p$, and O $2p$ acts as in-gap states to produce visible light emission in the PL process. The electronic state of hump originated from the sub-band of Ti $4p$ acts as electron traps, which receive the excited electrons by UV. These results confirm the color center nature of TiO_5 polyhedron. The energy diagram of self-activated titanate phosphors was proposed to explain the PL property.

To explore the local structure that benefits to produce PL property, Ti K -edge EXAFS of SrTiO_3 was conducted with temperature from 22 K to 300 K and UV irradiation. By using the tetragonal structure model of SrTiO_3 to fit the data, the dynamic Ti ion displacement along the z -axis is confirmed, which illustrates the instantaneous existence of TiO_5 polyhedron. With UV irradiation, the Ti ion vibration along the z -axis is significantly enhanced, which can explain the appearance of dipole moment and the increase of dielectric constant in SrTiO_3 .

The in-gap states are necessary to produce PL property in non-ion-doped titanates, the TiO_5 polyhedron can create the in-gap states. The distortion of TiO_6 octahedron in SrTiO_3 results in the TiO_5 polyhedron. As a result, the PL property can be a effective characterization method to investigate the information about in-gap electronic states and determine the local structure distortion in no ion-doped titanates. The simultaneous existence of PL and ferroelectric property caused by the local structure distortion point out a new direction for exploring new multifunctional materials.