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論　文　内　容　要　旨

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学位論文題目	Control of Optical Properties of Oxynitride Pigments and Phosphors 酸窒化物顔料および蛍光体の光学特性の制御に関する研究		

内容要旨

Oxynitrides have received great attention because of their fascinating chemical and physical properties in the past two decades. Oxides are usually colourless, but the substitution of oxygen by nitrogen with lower electronegativity, enhances the absorption edge in many materials. Thus, oxynitrides may show bright colours. Due to excellent chemical and thermal stability as well as bright colour without containing toxic elements; oxynitride materials are a good candidate for ecofriendly inorganic pigments, phosphor materials, visible-light-driven photocatalysis and dielectric materials. This research work is basically focused on bandgap tuning in oxynitride compound through proper adjustment of the O/N ratio for the application of non-toxic pigments and oxynitride phosphors for white LEDs.

In this research study, a number of oxynitrides for different applications such as; $(Ba_{1-(x+y)}Sr_xEu_y)_2Si_6O_{12}N_2$ phosphors for white LED, $LaTiO_2N$ co-nitridation with urea or thiourea and W^{6+} doped $La_{1.1}Ti_{1-xWx}(O,N)_3$ (X=0-0.05) for non-toxic pigment applications; were synthesized and their structural as well as optical properties have been investigated. Further, synthesis mechanism of Sr_2TaO_3N also briefly discussed. Oxynitrides have been synthesized by solid state reaction under diluted hydrogen flow or by thermal ammonolysis of oxide precursors. The structural study of $Ba_3Si_6O_{12}N_2$ and perovskite-types oxynitrides has been carried out by powder X-ray diffraction, and optical properties have been explored.

$(Ba_{1-(x+y)}Sr_xEu_y)_2Si_6O_{12}N_2$ oxynitride phosphors were successfully synthesized via solid-state reaction method. Substitution of barium by strontium caused a redshift of emission due to decrease in the lattice volume of the $(Ba_{1-(x+y)}Sr_xEu_y)_2Si_6O_{12}N_2$ phosphors. Shrinkage of the oxynitride lattice and enhancement of discrepancy between 5d levels in Eu^{2+} attributed redshifts, so that the emission maximum ranged from green (520nm) to yellow-green (548 nm). The optical properties of silicon rich $(Ba_{1-(x+y)}Sr_xEu_y)_2Si_6O_{12}N_2$ phosphors, illustrate their potential for white LED applications.

$La_2Ti_2O_7$ precursors were prepared by the sol-gel method. Mixtures of oxide precursor ($La_2Ti_2O_7$) and urea or thiourea were prepared, and then subjected to thermal ammonolysis at 950℃ for 5 h. The products formed at different $La_2Ti_2O_7$:urea or $La_2Ti_2O_7$:thiourea mass ratioswere systematically characterized by SEM, XRD, particle size distribution analysis, BET, UV-Vis, XPS and O/N analysis. In particular, the addition of urea was highly beneficial for $LaTiO_2N$ synthesis, yielding pure phase products with higher nitrogen content than $LaTiO_2N$ powders prepared in the absence of urea was observed. This result illustrates more quick method and development in synthesis of oxynitrides powders.

A series of new $La_{1.1}(Ti_{1-x}, W_x)(O, N)_3$ perovskite with different compositions (X=0.01, 0.02, 0.03, 0.04, 0.05) were synthesized by a thermal ammonolysis of oxide precursors prepared via a sol-gel method. Crystal structure and morphological changes of the microstructure with increasing tungsten content has been studied. The decent W^{6+} doping and excess of La relative to Ti in the oxynitride showed positive effect on red-shifting of the absorption edge of $LaTiO_2N$ perovskite oxynitride. Among all $La_{1.1}(Ti_{1-x}, W_x)(O, N)_3$ compositions (X = 0.03) showed the highest redshift with decreasing bandgap.

Formation process of the new layered perovskite Sr_2TaO_3N oxynitride having a K_2NiF_4-type structure from oxide precursor with $Sr_6Ta_2O_{10.188}$ - type phase was examined under an ammonia flow. Excess amount of strontium deviated from the stoichiometric composition of Sr/Ta=2 also seemed to promote the formation of Sr_2TaO_3N under the ammonia flow. The synthesized Sr_2TaO_3N after two cycles of 24h-nitridation of the oxide precursors showed brighter reddish-orange colour than $SrTaO_2N$. The usage of oxide precursor $Sr_6Ta_2O_{10.188}$ was beneficial in fast formation of Sr_2TaO_3N in 48h nitridation, compared with several 15h heating cycles in flowing ammonia which has been reported by Marchand et al. in 1999.

In conclusion, this research studies shows several creative work in the oxynitride perovskite field. The investigations gave a better understanding of the Synthesis, Optical and Structural properties of oxynitride. Synthesis techniques/experimental set-up were developed to obtain homogeneous nitridation in short period of time. It was demonstrated that $LaTiO_{2+x}N_{1-x}$ and $(Ba_{1-(x+y)}Sr_xEu_y)_2Si_6O_{12}N_2$ oxynitride have a diversity of potential applications as non-toxic pigments and phosphor for white LED application. Comparative study on

the oxideand oxynitride complex perovskites, the effect of mixed O/N anions on the cation ordering and bandgap have been examined. This research work thus opens a number of different opportunities for future investigations in the synthesis and study of optical properties of the oxynitride powders.