

The Site Symmetry of Eu^{3+} in $\text{ZnS}:\text{Eu}$ Nanoparticle

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Abstract: Nanosized ZnS doped with different concentrations of Eu^{3+} were prepared and analyzed by x-ray diffraction technique. The experimental results show that ZnS belongs to the cubic structure. From the photoluminescence (PL) emission spectra, it can be seen that the ratio of the emission intensity of Eu^{3+} at 616 nm to that at 590 nm increases as the increasing of Eu^{3+} . This phenomenon reveals that the site symmetry of Eu^{3+} reduces as the increasing of Eu^{3+} .

Keywords: ZnS:Eu nanoparticle, photoluminescence emission spectra, site symmetry.

Introduction

Nanosized ZnS materials doped or not doped with impurities have been prepared and studied¹⁻³. Chen and his coworkers⁴ studied and reported the thermoluminescence (TL) of ZnS nanoparticles. They found that both the TL and the surface fluorescence increase as the particle size is decreased, and the TL is related to the surface states. Mn-doped ZnS nanoparticles yield the best external photoluminescent quantum efficiency of about 18% at room temperature and luminescent decay time is at least five orders of magnitude faster than that of the corresponding Mn^{2+} radiative transition in the bulk crystals⁵. In the present letter, the site symmetry of Eu^{3+} in $\text{ZnS}:\text{Eu}^{3+}$ nanoparticles is studied. Since the rare-earth ions are excellent luminescence centers, nanosized ZnS doped with rare-earth ions may become a new kind of very useful material.

Experimental

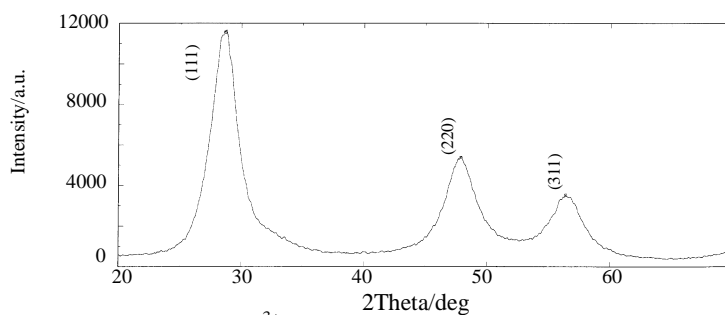
Zn $(\text{CH}_3\text{COO})_2$ solution (0.13 M) 150 ml and Eu $(\text{CH}_3\text{COO})_3$ solution (0.002 M~0.012 M) 150 ml were mixed and stirred, then Na_2S solution (0.4 M) 50 ml was added. The mixture was kept stirring for 30 minutes. The precipitate was filtered, washed by water and alcohol, respectively, dried at 50~60°C for 24 hours, and fired at 450°C for 2 hours. Before firing, a little S (about 50 mg) was added. The average size of the particles was about 20 nm measured by TEM. The samples were also analyzed by

x-ray diffraction technique with a Rigaku x-ray diffractometer (model D/max-B). The PL emission spectra were measured by MPF-4 fluorescence spectrophotometer.

Results and Discussion

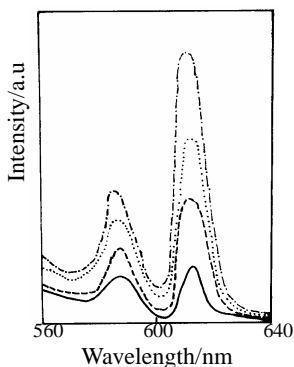
The x-ray diffraction pattern of ZnS:Eu³⁺ is shown in **Figure 1**. It can be seen clearly that the sample exhibits a zinc-blende crystal structure, and the peaks are broader, characteristic of the nanoparticles. Estimating from the Debey-Scherrer formula, the average size of the particles is about 15.7 nm. The result agrees with that of TEM.

Figure 1. The x-ray diffraction pattern of ZnS:Eu³⁺ (Eu/Zn is 1.5%).



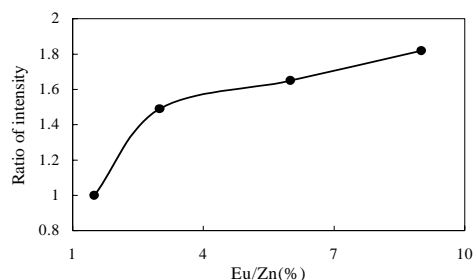
The emission peaks of Eu³⁺ at 590 nm and 616 nm are sensitive to the site symmetry⁶. If the site symmetry of Eu³⁺ belongs to O_h group, the emission at 590 nm originated from magnetic-dipole allowed ⁵D₀-⁷F₁ transition is dominant. When the site symmetry of Eu³⁺ is reduced, the intensity of the emission at 616 nm increases, which is the electric-dipole allowed ⁵D₀-⁷F₂ transition. So the emission spectra can be used to study the site symmetry of Eu³⁺ ions, *i.e.* to study the microstructure around the Eu³⁺ ions, and the defects in the lattice of ZnS caused by doping of Eu³⁺. **Figure 2** shows the emission spectra of the ZnS:Eu nanomaterials doped by the different dopant concentration of Eu³⁺, which are excited at 396 nm. In **Figure 2** it can be seen that the intensity of the emission at 616 nm increases more quickly than that at 590 nm. The relationship between the ratio and the concentration of Eu³⁺ is shown in **Figure 3**.

Figure 2. The emission spectra of ZnS:Eu nanoparticles (excited at 396 nm).



Eu/Zn(%) is (—): 1.5, (---): 3, (···): 6, (-·-·): 9.

Figure. 3. The relationship between the ratio of the intensity of the emission at 616 nm to that at 590 nm (excited at 396 nm) and the concentration of Eu^{3+} .



From **Figure. 3**, It can be seen clearly that the ratio of the intensity of the emission at 616 nm to that at 590 nm increases as the concentration of Eu^{3+} increases, which indicates that the concentration of Eu^{3+} ions in the asymmetric site increases more rapidly than that in the symmetric site. The ion size of Eu^{3+} and Zn^{2+} are 0.95 Å and 0.77 Å, respectively. As the ion size of Eu^{3+} is much larger than that of Zn^{2+} , the defects appear when Eu^{3+} gets into the lattice of ZnS . Eu ions are trivalent, and Zn ions are bivalent. When Zn^{2+} ions are substituted by Eu^{3+} ions, charge unbalance can not be avoided in the lattice, which causes vacancies of Zn^{2+} and substituted ions $\text{Eu}^{3+}\text{Zn}^{2+}$. The effect of these defects in $\text{CaS}:\text{La}$ are discussed in great detail by Choi⁷. Both ZnS and CaS belong to cubic structure, and the lattice constants are 5.4060 Å and 5.6948 Å, respectively. It is similar. As the ion sizes of La^{3+} and Eu^{3+} are similar since both of them are lanthanide elements, the defects caused by doping rare-earth ions in CaS would be similar with that caused by doping Eu^{3+} in ZnS . The more Eu^{3+} ions get into the lattice, the more defects exist. The site symmetry of Eu^{3+} is reduced further. Therefore the emission intensity at 616 nm increases more quickly than that at 590 nm.

Conclusion

The results mentioned above reveal that the site symmetry of Eu^{3+} depends on the concentration of Eu^{3+} . As the concentration increases, more Eu^{3+} ions get into the asymmetric site than that get into the symmetric site. It is also shown in the photoluminescence emission spectra. The emission intensity at 616 nm increases more quickly than that at 590 nm. The site symmetry of Eu^{3+} is influenced by the defects caused by doping of Eu^{3+} in ZnS lattice.

Acknowledgments

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References

1. J. Ma, X. Huang, J. Cheng and Z. Zhao, *J. Mater. Sci. Lett.*, **1996**, *15*, 1247.
2. T. Gacion, L. Malier and J. P. Boilot, *Chem. Mater.*, **1997**, *9*, 1502.
3. R. Rossetti, R. Hull, J. M. Gibson and L. E. Brus, *J. Chem. Phys.*, **1985**, *82*, 552.
4. W. Chen, Z. Wang, Z. Lin and L. Lin, *Appl. Phys. Lett.*, **1997**, *79*, 1465.
5. R. N. Bhargava, D. Gallagher and T. Wolker, *J. Lumin.*, **1994**, *60-61*, 275.
6. Q. Su, "Chemistry of Rare Earth", Science and Technology Publishing House of Henan, **1993**, p.310.
7. H. Choi, C. Kim, C. Pyun *et. al.*, *J. Solid State Chem.*, **1997**, *131*, 101.

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