Green Emission Band Site of Ce^{3+} in $YAlO_3:Ce^{3+}$ Phosphor

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It is well known that $YAlO_3$ is a good laser host material[1] and $YAlO_3$ activated with rare-earth and transition metal ions is used for scintillators and screens in optical devices.[2,3] The fluorescence excitation spectra of $YAlO_3:Ce^{3+}$ phosphor reveal that the UV and visible emission spectra are arising from 4f-5d transitions of Ce^{3+} ion in $YAlO_3$.[4,5] In this communication, we are going to report the cerium site in $YAlO_3:Ce^{3+}$ which have been debated over the years.[5] Especially, the site of Ce^{3+} green emission band is not known exactly.

Experimental

The $YAlO_3:Ce^{3+}$ phosphor was prepared from starting compositions consisting of $Y(NO_3)_3\cdot 5H_2O$, $Al(NO_3)_3\cdot 9H_2O$, and CeO_2. The concentration of cerium was varied from 0.001 to 0.05 mole%. The constituents were well mixed and reacted at 1000 °C for 5hrs. The phases of products were checked through the conventional XRD technique. For emission measurements, an Oriel 1000W Hg (Xe) lamp and a 250 nm band pass filter (Oriel 53340) combination were used for an excitation source. The emission spectra were obtained using a 75 cm Spex monochromator equipped with an RCA31034 photomultiplier tube. The signals from the photomultiplier tube were electronically amplified and displayed on an X-Y recorder.

Results and Discussion

The emission spectra of cerium doped $YAlO_3:Ce^{3+}$ along with undoped $YAlO_3$ are shown in Figure 1. We observed one broad emission band peaking around 370 nm in undoped $YAlO_3$ and two broad emission bands, *i.e.*, around 370 nm and 500 nm, in cerium doped $YAlO_3$. The origin of 370 nm emission band has been interpreted as a self-activating center, *i.e.*, optical transition between conduction band of $YAlO_3$ to oxygen 2p band.[6] The emission band around 370 nm exhibits red shift and a new emission band around 500 nm is appearing when we doped Ce^{3+} ions in $YAlO_3$. Also the red shift of 370 nm emission band and the emission intensity of 500 nm band are enhanced when the Ce^{3+} ion concentration is increased in $YAlO_3$. The apparent red shift of 370 nm emission band is attributed to the Ce^{3+} 5d absorption located near 350 nm.[4] This absorption band of Ce^{3+} is located at high energy side of $YAlO_3$ emission band. Thus, the increment of Ce^{3+} concentration in $YAlO_3$ enhances the absorption and the apparent red shift in $YAlO_3:Ce^{3+}$ can be observed accordingly. The Ce^{3+} absorption in

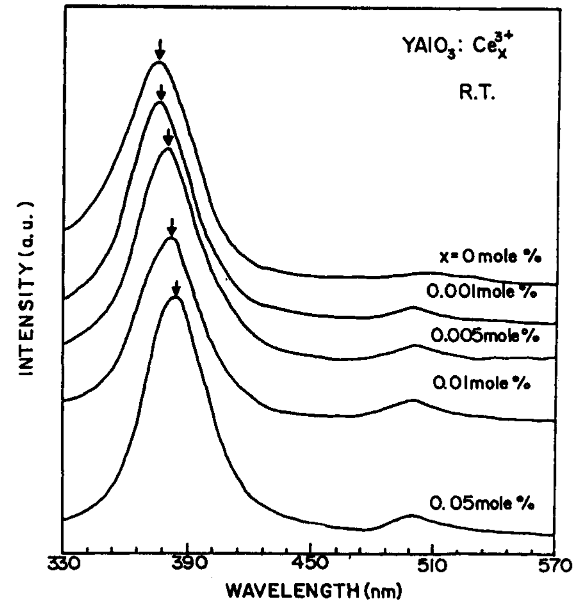

Figure 1. Emission spectra of $YAlO_3:Ce^{3+}$.

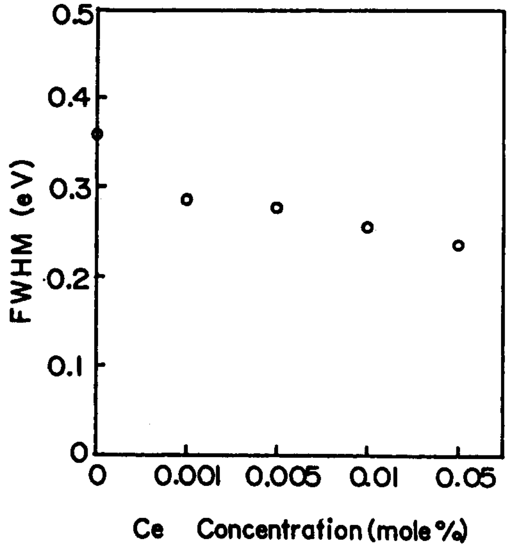

Figure 2. Cerium concentration dependent FWHM of 370 nm emission band of $YAlO_3:Ce^{3+}$. The energy of 1 eV corresponds to 8066 cm^{-1}.

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$YAlO_3:Ce^{3+}$ also exhibits the apparent narrowing of emission band. The Figure 2 depicts Ce^{3+} concentration dependent FWHM (Full Width at Half Maximum) of 370 nm emission band. As can be seen in Figure 2, the band narrowing is more pronounced as the concentration of Ce^{3+} in $YAlO_3$ is increased. The foregoing observations positively support that two emission bands in $YAlO_3:Ce^{3+}$ is closely related to Ce^{3+} ions in $YAlO_3$ host.

The Ce^{3+} sites in $YAlO_3$ have been proposed[7] and conjectured[8], but the supporting arguments are less convincing. The $YAlO_3$ has perovskite structure same as $SrTiO_3$ and the existing polyhedra are YO_{12}, YAl_8 and AlO_6 in this structure. The ionic radii of Ce^{3+}, Y^{3+} and Al^{3+} are 0.94 Å, 0.92 Å and 0.51 Å respectively. Thus the more probable Ce^{3+} sites in $YAlO_3$ are YO_{12} and YAl_8 polyhedra where Ce^{3+} is substituted for Y^{3+} from the ionic radii argument. It is generally accepted that the UV emission band in $YAlO_3:Ce^{3+}$ is originated from the occupied site of Ce^{3+} in YO_{12} polyhedron. The green emission center in $YAlO_3:Ce^{3+}$ has not been established to date. Mares *et al.*[8] reported the green emission band in $YAlO_3:Ce^{3+}$. They also suggested that the possible occupied site of green emission of Ce^{3+} in $YAlO_3$ is YAl_8 polyhedra without any positively convincing arguments. The Ce^{3+} related green emission band was disappeared when $YAlO_3$ was codoped with Nd^{3+}, Cr^{3+} and Ce^{3+}.[8] This observation suggested that many types of polyhedra, *i.e.*, YAl_8, $CeAl_8$, and $NdAl_8$, could be formed when Nd^{3+}, Cr^{3+} and Ce^{3+} ions were codoped in $YAlO_3$. Thus energy transfer between ions, $Ce^{3+} \rightarrow Nd^{3+}$ and $Ce^{3+} \rightarrow Cr^{3+}$, could be possible and the energy transfer between ions was manifested with disappearing of green emission band. The above rationale supports that the origin of green emission band site of Ce^{3+} in $YAlO_3$ is YAl_8 polyhedron where Ce^{3+} is substituted for Y^{3+}.

In summary, we investigated the emission characteristics of $YAlO_3:Ce^{3+}$ and the origin of Ce^{3+} related green emission band site in $YAlO_3:Ce^{3+}$ has been established as YAl_8 polyhedron. In other words, the cerium is substituted for yttrium such that $CeAl_8$ polyhedron can be formed and cerium in this site is the origin of green emission band in $YAlO_3:Ce^{3+}$.

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Superfast Transfer *via* Crossover of F Electronic Energy to OH^- Vibration in RbCl

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Since Dexter, Klick, and Russell reported a crossover mechanism which provides a criterion for the nonradiative quenching of simple impurity centers,[1] the fate of an electronically excited F center in alkali halides has been studied as one of the typical cases.[1-3] The relaxed excited F (F*) centers in rubidium and potassium halides have a strong luminescence with a microsecond-long lifetime at cryogenic temperatures, while those in lithium and sodium halides have a poor luminescence.[4,5] This remarkable difference in the two types of hosts can be explained by the difference in crossover energy barriers from the relaxed excited state to the crossing point of the excited and ground state potential curves.[1] However, the luminescence in KCl, in which the barrier is too high for effective crossover, is reported[6,7] to decrease by the concentration increase of doped molecular defects such as OH^- and CN^-. F_H formation, association of F center with a molecular defect, makes F absorption broader and lower in energy and quenches F luminescence drastically.[8] Vibrational emission and anti-Stokes Raman scattering from molecular defects observed after F center excitation indicate that the electronic excitation energy of an F center transfers into the stretching vibrational mode of a molecular defect.[9-11]

The energy transfer rate in randomly distributed crystals is varied very much, depending on transfer distance, temperature and host.[8-12] However, the superfast transfer component in aggregated crystals is much the same, regardless of concentration, isotope, and host.[13] This superfast recovery, resulting from the deactivation of an excited F-molecular defect pair, is achieved by the lattice relaxation[14] of the ex-