

In this thesis, I investigated metal-ion-activated phosphors which show “blue to near infrared quantum cutting” or “red persistent luminescence”.

Quantum cutting phosphor converts an incident photon into two or more photons with lower energy. The rare earth doped materials which show quantum cutting have potential to enhance the conversion efficiency of crystalline Si solar cell up to 38.6 % to reduce the thermalization loss. In the first three chapters,  $\text{Pr}^{3+}$ - $\text{Yb}^{3+}$  codoped systems were investigated with the object of studying blue to near infrared quantum cutting processes.

Persistent phosphors glow in the dark for a given duration after absorption of light. The material is widely used as luminous paints in areas such as dial plates, interior accessories, night lighting after extinction and safety signs. For luminous paint application, red persistent phosphors with long duration and high chemical stability are in high demand because blue and green phosphors are still main materials for the visual signing applications due to the low eye sensitivity in red region and relatively low chemical stability of commercially available red persistent phosphors. In chapter 5 and 6, red persistent phosphor,  $(\text{Ca},\text{Sr})\text{TiO}_3:\text{Pr}^{3+}$  were investigated.

In recent years, red to near infrared persistent phosphors have been promising material for *in vivo* imaging as nonradioactive imaging technique. For the fluorescence *in vivo* imaging, many materials such as organic molecules, quantum dots and rare earth doped metal compounds have been studied. However there are some problems such as low quantum yield, using cancer-causing material in these materials. Above all, the mutual problem is the noise due to the excitation light, which induces auto-fluorescence of biological tissues and scattering of the excitation light itself. On the other hand, by using persistent luminescence for *in vivo* imaging, high signal to

noise ratio can be obtained because persistent phosphor is excited before *in vivo* injection. In chapter 7, enhanced red persistent luminescence of  $\text{MgGeO}_3:\text{Mn}^{2+}$  by Bi codoping was reported.

In chapter 2, the quantum cutting phenomenon of a blue photon into two infrared photons is reported in glasses codoped with  $\text{Pr}^{3+}$ - $\text{Yb}^{3+}$  ions. Oxyfluoride glass with composition of  $32\text{SrF}_2\text{-}0.1\text{PrF}_3\text{-}2.9\text{YbF}_3\text{-}42\text{SiO}_2\text{-}23\text{Al}_2\text{O}_3$  was prepared and photoluminescence properties in the range from visible to near-infrared were investigated. Evidence of several energy transfers, such as  $(\text{Pr}^{3+}: {}^3\text{P}_0 \rightarrow {}^1\text{G}_4) \rightarrow (\text{Yb}^{3+}: {}^2\text{F}_{5/2} \leftarrow {}^2\text{F}_{7/2})$  and  $(\text{Pr}^{3+}: {}^1\text{D}_2 \rightarrow {}^3\text{F}_4, {}^3\text{F}_3) \rightarrow (\text{Yb}^{3+}: {}^2\text{F}_{5/2} \leftarrow {}^2\text{F}_{7/2})$ , were demonstrated in the  $\text{Pr}^{3+}$ - $\text{Yb}^{3+}$  codoped glass. By comparing excitation spectrum of the  $\text{Yb}^{3+}$  emission with absorption spectrum of  $\text{Pr}^{3+}$ , we obtained direct evidence of quantum cutting by the excitation to the  $\text{Pr}^{3+}: {}^3\text{P}_1$  levels at 420~490 nm.

In chapter 3, the loss mechanism in the  $\text{Pr}^{3+}$ - $\text{Yb}^{3+}$  codoped glass that showed quantum cutting(QC) phenomenon was investigated and we found that the multi-phonon relaxation from the  $\text{Pr}^{3+}: {}^1\text{G}_4$  level is the major loss to the quantum cutting process. To reduce the loss,  $\text{Pr}^{3+}$ - $\text{Yb}^{3+}$  codoped glass ceramics containing  $\text{SrF}_2$  crystals were prepared and quantum yields (QY) of  $\text{Yb}^{3+}$  emission by 440 nm excitation were measured. Only glass ceramics with the highest Yb concentration ( $x=2.9$ ) showed higher QY than that of the as-made glass. It is considered that in low Yb concentration  $\text{Pr}^{3+}$  and  $\text{Yb}^{3+}$  ions were divided into different matrix possibly because of different ionic radius between  $\text{Pr}^{3+}$  and  $\text{Yb}^{3+}$  ions.

In chapter 4, quantum cutting of 0.44  $\mu\text{m}$  photon into 1.0  $\mu\text{m}$  and 1.3  $\mu\text{m}$  photons was demonstrated in  $\text{Pr}^{3+}$ - $\text{Yb}^{3+}$  codoped oxyfluoride glass ceramics by spectroscopic investigation from blue to near-infrared region. The  $\text{Pr}^{3+}$ - $\text{Yb}^{3+}$  codoped sample showed

energy transfer ( $\text{Pr}^{3+}:^3\text{P}_0 \rightarrow ^1\text{G}_4$ )  $\rightarrow$  ( $\text{Yb}^{3+}:^2\text{F}_{5/2} \leftarrow ^2\text{F}_{7/2}$ ). Both under 0.44  $\mu\text{m}$  and 0.94  $\mu\text{m}$  excitations, the codoped sample showed  $\text{Pr}^{3+}:^1\text{G}_4 \rightarrow ^3\text{H}_4$  luminescence at 1.3  $\mu\text{m}$ , as well as  $\text{Yb}^{3+}:^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$  luminescence at 1.0  $\mu\text{m}$ . The relative intensity of ( $\text{Pr}^{3+}:1.3 \mu\text{m} / \text{Yb}^{3+}:1.0 \mu\text{m}$ ) by 0.44  $\mu\text{m}$  excitation was much higher than that by 0.94  $\mu\text{m}$  excitation. The mechanism of downconversion was proposed as a quantum cutting process by one-step energy transfer ( $\text{Pr}^{3+}:^3\text{P}_0 \rightarrow ^1\text{G}_4$ )  $\rightarrow$  ( $\text{Yb}^{3+}:^2\text{F}_{5/2} \leftarrow ^2\text{F}_{7/2}$ ), which results in generation of two near-infrared photons via the  $\text{Pr}^{3+}:^1\text{G}_4 \rightarrow ^3\text{H}_5$  and  $\text{Yb}^{3+}:^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$  transitions.

In chapter 5, we have prepared polycrystalline  $\text{CaTiO}_3:\text{Pr}^{3+}$  showing red persistent luminescence by melting method using a solar furnace. Emission, excitation spectra, persistent decay curves and thermoluminescence glow curves were compared with samples prepared by conventional solid-state reaction in conventional electric furnace (EF) at 1200  $^\circ\text{C}$ , 5 h in air. The color of the sample prepared by solar furnace (SF-AM) was dark brownish. After heat treatment at 800 $^\circ\text{C}$ , 5h in air atmosphere, a decolorized sample (SF-HT) was obtained. All samples showed  $\text{Pr}^{3+}:^1\text{D}_2 \rightarrow ^3\text{H}_4$  fluorescence at 613 nm and corresponding persistent luminescence. The SF-AM and SF-HT showed much higher PLE intensity of  $\text{Pr}^{3+}:^3\text{P}_J$  bands in blue region than EF.  $\text{CaTiO}_3:\text{Pr}^{3+}$  made by a solar furnace has a potential to be a red afterglow phosphor even under visible excitation.

In chapter 6, we obtained direct evidence of intervalence charge transfer (IVCT) in  $\text{Ca}_{1-x}\text{Sr}_x\text{TiO}_3:\text{Pr}^{3+}$  ( $x=0, 0.3, 0.5, 0.8, 1$ ) by a photocurrent excitation (PCE) measurement, and propose a mechanism of the persistent luminescence based on the results of the PCE and persistent luminescence measurements. The PCE spectra in all samples showed two bands in UV range due to the band-to-band and IVCT transitions. With increasing Sr content,  $x$ , the host bandgap energy decreased monotonically from 3.59 to 3.23 eV, and the IVCT energy increased from 3.20 to 3.38 eV. PCE bands of the  $\text{Pr}^{3+}:^3\text{H}_4 \rightarrow ^3\text{P}_J$

transitions in blue region were observed only in the samples with  $x=0, 0.3, 0.5$  and the relative intensity decreased with increasing Sr content,  $x$ . Based on temperature dependence of the PCE results in the sample with  $x=0$ , a thermally assisted photoionization process was indicated under the  ${}^3\text{H}_4 \rightarrow {}^3\text{P}_J$  excitation. Red persistent luminescence was observed in the samples with  $x=0, 0.3$  and  $0.5$ , showing trap depth in the range of  $0.48$  to  $0.35$  eV, which was estimated from the thermoluminescence measurement. The afterglow process by the electron moving through the conduction band was evidenced by the similar quenching behavior of the  ${}^3\text{H}_4 \rightarrow {}^3\text{P}_J$  band both in the PCE and afterglow excitation spectra. The difference in the processes of persistent luminescence between the band-to-band, IVCT and  ${}^3\text{H}_4 \rightarrow {}^3\text{P}_J$  excitations was discussed.

In chapter 7, Photoluminescence, persistent luminescence and thermoluminescence properties of  $\text{Mg}_{(0.998-x)}\text{Mn}_{0.002}\text{Bi}_x\text{Ge}_{1.05}\text{O}_3$  ( $x=0, 0.001, 0.005, 0.01, 0.02$ ) were investigated. Mn-Bi co-doped sample with  $x=0.005$  showed strong red persistent luminescence due to  $\text{Mn}^{2+}: {}^4\text{T}_2 \rightarrow {}^6\text{A}_1$ . The persistent luminescence intensity of the sample with  $x=0.005$  was 30 times higher than that of the Mn singly doped sample ( $x=0$ ). Mn-Bi codoped samples showed an additional glow peak at approximately 320 K.  $\text{Bi}_2\text{O}_3$  was proved to be an effective codopant to enhance red persistent luminescence and Bi itself works as an electron trapping center. These results indicate  $\text{MgGeO}_3:\text{Mn-Bi}$  phosphor is a potential candidate for the application of biological imaging.

In chapter 8, The photoluminescence properties of 0.2 %  $\text{Pr}^{3+}$ -doped  $(\text{Y}_{1-0.01x}\text{Zr}_{0.01x})_2\text{O}_3$ , ( $x = 0, 0.1, 1, 3, 4.5, 6$ ) ceramics were investigated. The luminescence intensity due to the transition from the  ${}^3\text{P}_0$  level increased drastically when the Zr content  $x$  increased, which is completely quenched in  $\text{Y}_2\text{O}_3:\text{Pr}^{3+}$  ( $x=0$ ) due to the thermal relaxation through the lowest 5d level of the  $\text{Pr}^{3+}$  ion. By monitoring at 630 nm

( $^1D_2 \rightarrow ^3H_4$ ), we found that the 4f-5d photoluminescence excitation bands for  $Pr^{3+}$  in the two six-fold sites ( $C_2$  and  $S_6$  in the  $Y_2O_3:Pr^{3+}$  ( $x=0$ )) were observed at approximately 300 nm and 340 nm. On the other hand, when monitored at 510 nm ( $^3P_0 \rightarrow ^3H_4$ ), the Zr-doped samples showed an additional 4f-5d band at 280 nm. Based on these results, we concluded that the  $^3P_0$  luminescence is from  $Pr^{3+}$  in a seven-fold site, which is generated by incorporation of an additional oxygen via a defect chemical reaction,  $2ZrO_2$

