

Effect of trivalent-ion impurities on luminescence of $\text{SrIn}_2\text{O}_4:\text{Pr}^{3+}$

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Introduction

A red-emitting phosphor, $\text{SrIn}_2\text{O}_4:\text{Pr}^{3+}$, can be excited by a low-energy electron-beam of about $10\text{V}^{(1)}$. It is, therefore, a potential candidate of Cd-free phosphors for vacuum fluorescent tubes or field emission displays. An interesting point of this phosphor is that addition of Al^{3+} , Y^{3+} or Gd^{3+} increases luminescence efficiency considerably^{1,2)}. The present authors found that other trivalent ions, such as B^{3+} or Sc^{3+} , increase efficiency also. This work intends to make clear how these codopant ions improve efficiency.

Experimental

Powder samples of $\text{SrIn}_2\text{O}_4:\text{Pr}^{3+}$ were prepared by a conventional solid-state reaction by firing of an intimate mixture of SrCO_3 , In_2O_3 , $\text{Pr}(\text{NO}_3)_3$ and an oxide of impurity ion. The concentration of Pr was fixed at 0.2 atom.% per Sr^{2+} site. Firing was made at 1200°C for 3hrs. in platinum crucibles.

Samples settled on ITO-glass were irradiated by low-energy electrons by using a Kimball Physics e-gun, model EFG-7, and luminance was measured from the backside of the glass substrate.

Results and Discussion

As shown in Fig. 1, luminance under low-energy electron excitation is improved by codoping of B^{3+} , Lu^{3+} or Gd^{3+} and quenched by La^{3+} .

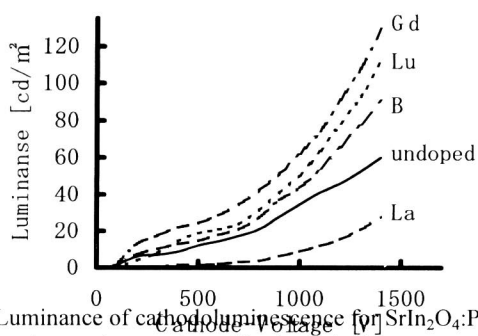


Fig.1 Luminance of cathodoluminescence for $\text{SrIn}_2\text{O}_4:\text{Pr}^{3+}$ samples at room temperature. The impurity ions were added at a nominal concentration of 5 atom.% per In^{3+} ions.

Addition of these codopants increases X-ray diffraction line width; for example, FWHM of a diffraction line at $2\theta = 63.5^\circ$ by Cu $\text{K}\alpha 1$ radiation is 0.19 degree for Gd-codoped sample, while it is 0.14 degree for a sample without any codopants. Obviously these codopants do not improve crystallinity of the phosphor.

At 12K, photoluminescence (PL) spectra excited at 245nm, or in the fundamental absorption region, show a strong and broad band peaked at around 450nm (for B or Sc addition) or at 500nm (for Y or Gd addition) in addition to the emission lines of Pr^{3+} . With an increase in temperature, the intensity of the broad band is decreased and quenched completely above 200K. Meanwhile, Pr^{3+} luminescence is enhanced and exceeds that of the sample without codopants in intensity at 300K. It was also found that new thermoluminescence glow peaks appear at 150-250K by doping of Al, B or Gd. These results indicate that excitation energy is partly emitted at defects created by the codopants at low temperature, while it is transferred efficiently to Pr^{3+} at higher temperature, because carriers trapped at the defects are thermally released.

Comparison of ionic radii suggests that B^{3+} and Lu^{3+} will substitute for In^{3+} and that most probably La^{3+} does for Sr^{2+} . Then a question is raised on the site Gd^{3+} occupies, since it has an ionic size just in the middle of Sr^{2+} and In^{3+} . It was found that

X-ray diffraction lines of In_2O_3 remained in as-fired samples increase in intensity when B_2O_3 is added. This result proves that B^{3+} ions are accommodated at In^{3+} site. On the contrary, the intensity of the X-ray diffraction lines by residual In_2O_3 is decreased when Gd_2O_3 is added. One can, therefore, assume that Gd^{3+} ions mostly substitute for Sr^{2+} site. Rietveld analysis of X-ray diffraction patterns also supports an assumption that more than 90% of Gd^{3+} ions occupy Sr^{2+} site.

However, PL spectra of $\text{SrIn}_2\text{O}_4:\text{Eu}^{3+}$ can be interpreted to arise from two types of Eu^{3+} , one at Sr^{2+} site and the other at In^{3+} site, when compared with analysis of PL spectra of $\text{SrY}_2\text{O}_4:\text{Eu}^{3+}$ ^{3,4)}, which is isostructural to $\text{SrIn}_2\text{O}_4:\text{Eu}^{3+}$. Consequently it is concluded that a part of Gd^{3+} ions can replace In^{3+} ions also.

As shown in the difference in peak wavelength of the broad PL band, the defects created by Gd^{3+} and Y^{3+} may be different from the defects by B^{3+} and Lu^{3+} , as a result of the difference in occupied site. However, these defects work in trapping free carriers and feeding Pr^{3+} ions even if their atomic structure may be different.

Summary

Luminescence efficiency of $\text{SrIn}_2\text{O}_4:\text{Pr}^{3+}$ is increased by codoping of trivalent ions, such as B^{3+} , Lu^{3+} or Gd^{3+} . Defects created by these ions show broad-band luminescence at low temperature, but supply thermally released free carriers at higher temperature, leading to efficient energy transport to Pr^{3+} ions.

Acknowledgment

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