An Approach to Develop New Ternary Oxide Phosphors;
Reduction of Defects by Impurity Addition

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Abstract

Luminescence efficiency of phosphors, $SrTiO_3:Pr^{3+}$ and $SrIn_2O_4:Pr^{3+}$, is increased remarkably by III-group impurities. This effect is explained by a picture that carriers thermally released from impurity-induced traps supply energy to Pr^{3+} ions. The impurities also improve carrier transport efficiency by reducing lattice defects. This picture indicates a possibility to develop new ternary oxide phosphors.

1. Introduction

One may sometimes find it difficult to develop new phosphors, since phosphors have a long history of research and development. This talk is intended to show that we still have a good hope by looking at old materials from a new point of view.

This work was stimulated by a discovery of a new red phosphor, $SrTiO_3:Pr^{3+}$, Al, by Futaba group[1] in 1996. Luminescence of rare earth ions doped in $SrTiO_3$ or $BaTiO_3$ has been investigated since 1950's as a probe to analyze ferroelectricity[2,3], but luminescence efficiency high enough to be commercially applicable had never been reported before. Later in 1999, another example of the efficiency improvement by Al-addition, i.e. $SrIn_2O_4:Pr^{3+},Al$[4], was reported. The magic which turns an inefficient material to a bright phosphor can be apparently found by understanding of the effect of Al addition.

It was observed that these two groups of materials show some similar luminescence properties in common, which have led the present authors to a picture comprising of (a) a decrease in lattice-defect concentration by impurity addition, (b) trap formation by impurity which thermally feed free carriers to activator ions and (c) a good energetic coupling between the host and activator absorption. In the following sections, experimental results, which support this picture, will be presented and the picture will be discussed in more detail.

2. Efficiency improvement of $SrTiO_3:Pr^{3+}$ by impurity addition

Under any excitation source, $SrTiO_3:Pr^{3+}$ shows only feeble luminescence. Meanwhile, when oxide or hydroxide of Al or Ga is added to starting materials, a fired product shows bright red luminescence by cathode-ray and UV excitation. The increase in the efficiency amounts to 200 times at the optimum Al concentration, about 20mol.% against one mole of the phosphor[1]. This phosphor is suitable for low-energy electron excitation, since its luminescence can be observed at an accelerating voltage as low as $10V$[1].

Luminescence properties characterizing this impurity effect can be summarized as follows.

(a) Excitation of Pr^{3+} ions takes place through free carriers created by excitation energy. This is evidenced by quite similar excitation spectra of self-trapped exciton luminescence of undoped $SrTiO_3$ and Pr^{3+} luminescence of $SrTiO_3:Pr^{3+},Al$[5], as shown in Fig.1
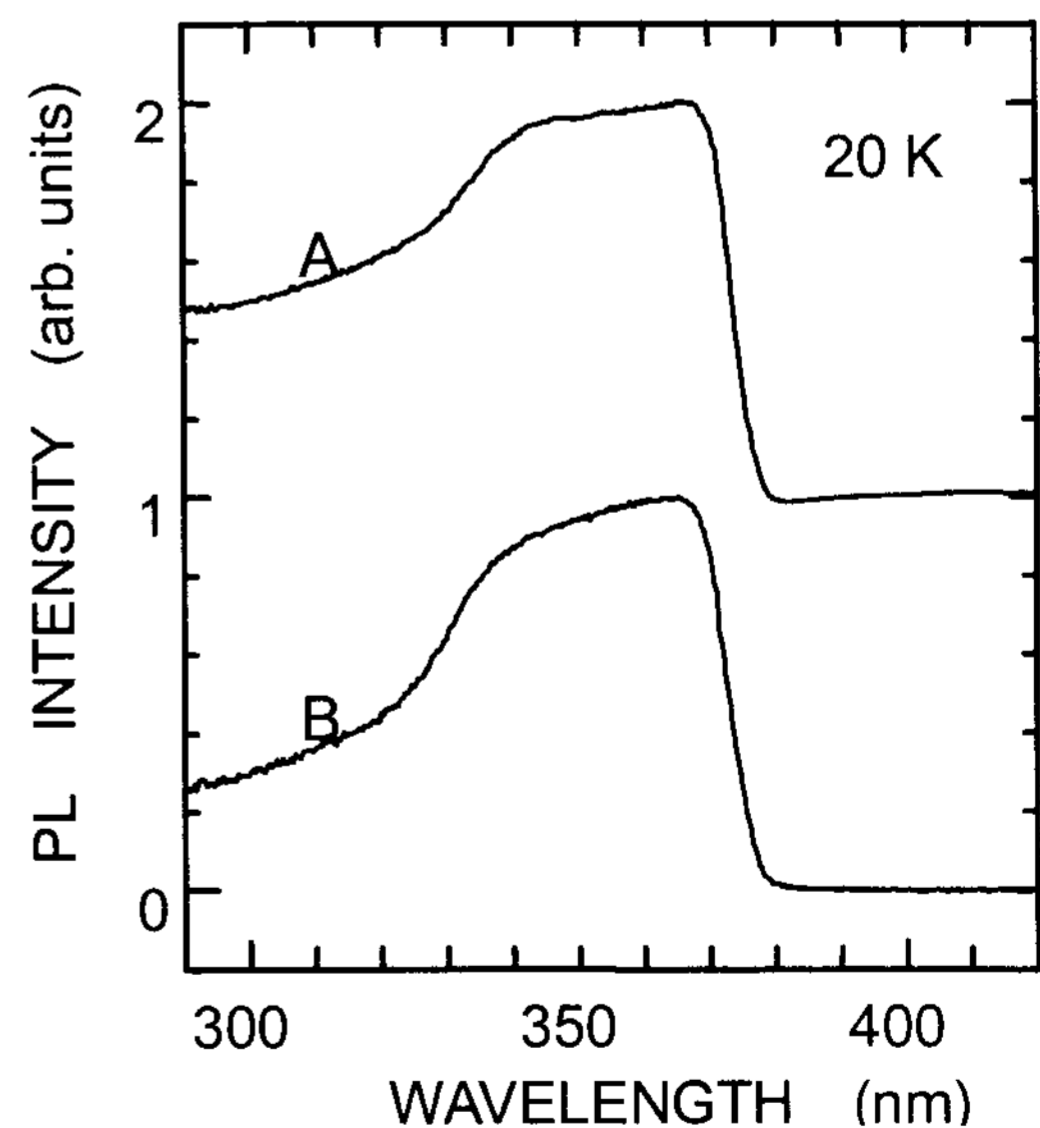

Fig.1 Excitation spectra of self-trapped exciton luminescence of undoped $SrTiO_3$ (A) and Pr^{3+} luminescence at 617nm of $SrTiO_3:Pr^{3+},Al$[5] (B). The nominal Al concentration of $SrTiO_3:Pr^{3+},A$ is 23mol.%.

(b) It can be considered that spectral overlap of the host absorption and the allowed transition of an activator ion is required to increase efficiency by the Al addition. This assumption is supported by a fact that the Al-addition does not increase the efficiency of Eu^{3+} luminescence, which has the charge transfer band located near the fundamental absorption edge.

Figure 2 compares an excitation spectrum of $SrTiO_3:Pr^{3+}$ (A) and that of $SrTiO_3:Eu^{3+}$ (B) at 20K. The on-set of the luminescence intensity observed for A corresponds to the fundamental absorption edge, because it is found also in the excitation spectrum of the self-trapped exciton luminescence shown in Fig.1. The 4f-5d absorption band of Pr^{3+} cannot be identified in the excitation spectra of $SrTiO_3:Pr^{3+}$ or $SrTiO_3:Pr^{3+}$,Al. It is presumably located in the fundamental absorption region. In contrast the charge-transfer band of Eu^{3+} can be clearly found just around the absorption edge, as shown by the curve B of Fig.2. The low luminescence intensity at wavelengths shorter than 370nm observed for the curve B indicates low energy-transfer efficiency from $SrTiO_3$ to Eu^{3+}.
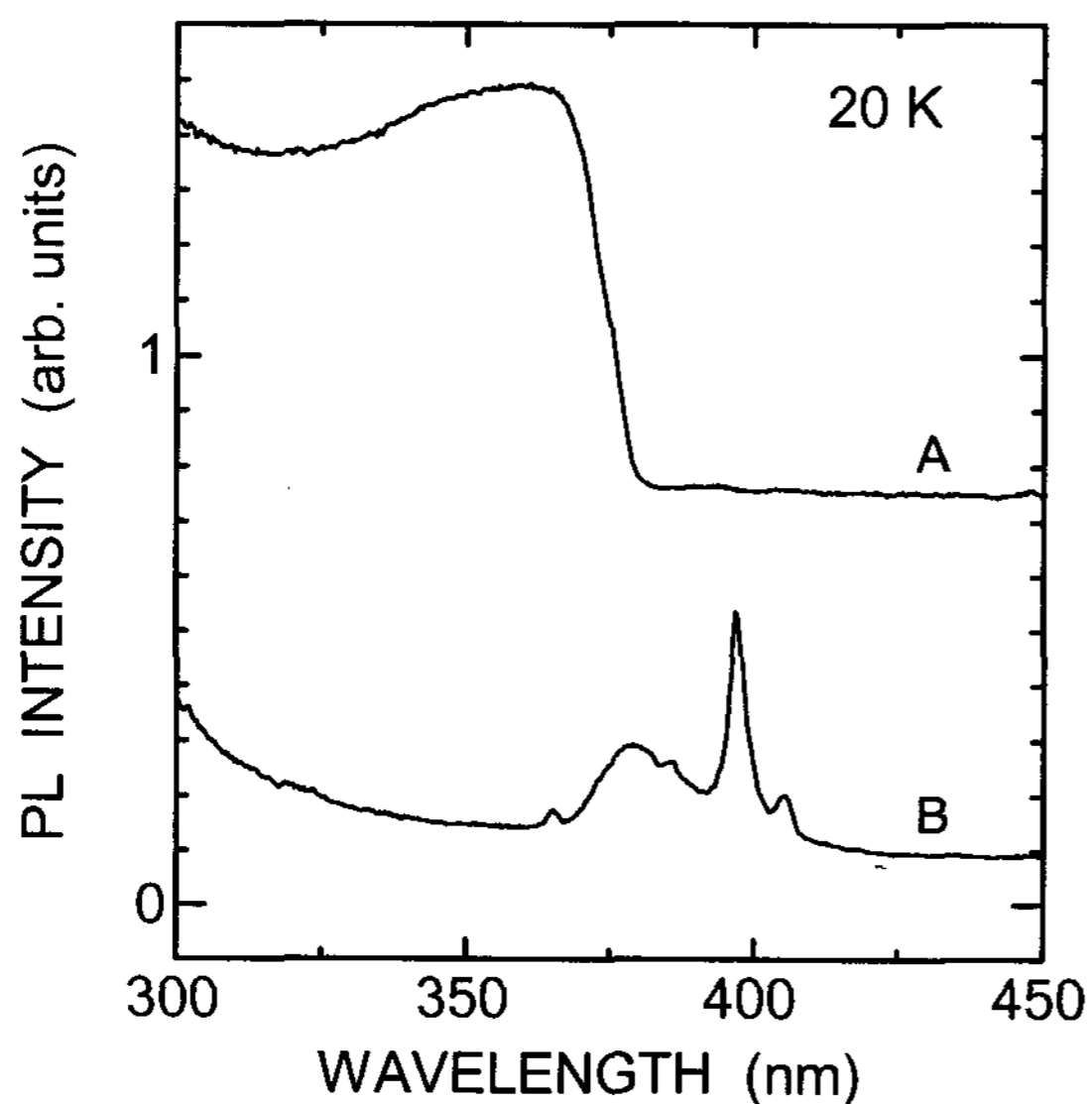

Fig.2 An excitation spectrum of $SrTiO_3:Pr^{3+}$ (0.2mol.%) (A) and that of $SrTiO_3:Eu^{3+}$ (5mol.%) (B) at 20K. On the lower curve B, the band with a peak at 380nm results from the charge-transfer band and peaks with narrow widths around 400nm arise from 4f-4f transitions of Eu^{3+}.

(c) In a chemical composition deviated from the stoichiometry to the Sr-excess side, the efficiency is decreased and X-ray diffraction line width is increased. Possible reasons of the X-ray diffraction line broadening are point defects generated to compensate extra charges by excess Sr^{2+} and SrO layer defects previously reported[6]. In the Ti-excess side, segregated TiO_2 phase is detected by X-ray diffraction measurements. Doped Al^{3+} ions are considered to work in two ways; one as a charge compensator by being introduced at Ti^{4+} site against Pr^{3+} at Sr^{2+} site and the other as a scavenger of the SrO layer defects by forming $SrAl_2O_4$[5].

(d) With an increase in temperature from 10K, photoluminescence intensity excited in the host absorption (at 325nm) increases up to about 100K as a result of energy conversion from the self-trapped exciton luminescence. Above 100K, an Al-free sample shows strong thermal quenching in the region up to 260K, while samples added with Al show much less quenching above 150-160K. As a result, a difference in the luminescence intensity between the two kinds of samples is expanded at room temperature. The suppression of the thermal quenching is presumably caused by thermal release of carriers trapped at Al^{3+} ions or Al^{3+}-induced defects, because a strong thermoluminescence glow appears by the Al-addition with a peak at 160K.

Based on these results, we propose the following luminescence mechanism of $SrTiO_3:Pr^{3+}$,Al. First we consider that carriers generated by cathode-ray or UV light are supplied to Pr^{3+} either directly through the conduction band or indirectly through the trapping states induced by Al-doping. The latter path of the carriers contributes to the excitation of Pr^{3+} more at a higher temperature. In addition, doped Al^{3+} ions reduce defects in $SrTiO_3:Pr^{3+}$, leading to a decreased nonradiative transition probability.

3. Efficiency improvement of $SrIn_2O_4:Pr^{3+}$ by impurity addition

Since the first report[4] on the effect of Al-addition on $SrIn_2O_4:Pr^{3+}$, other additives, mostly III-group ions with relatively small sizes, e.g. Lu^{3+}, Y^{3+}, B^{3+}, Sc^{3+} and Gd^{3+}, were found to increase the efficiency[7,8]. In contrast to these ions, La^{3+} with a larger ionic size was found to quench the luminescence of Pr^{3+}. Among these impurities, Gd^{3+} with a nominal concentration of 5mol.% gives the highest luminance, which is about 77% as high as that of $SrTiO_3:Pr^{3+}$,Al under 1.4kV

cathode-ray excitation[8].

Obviously the III-group ions do not work as charge compensators, but can work as traps as indicated by thermoluminescence glow peaks they induce(Fig.3).
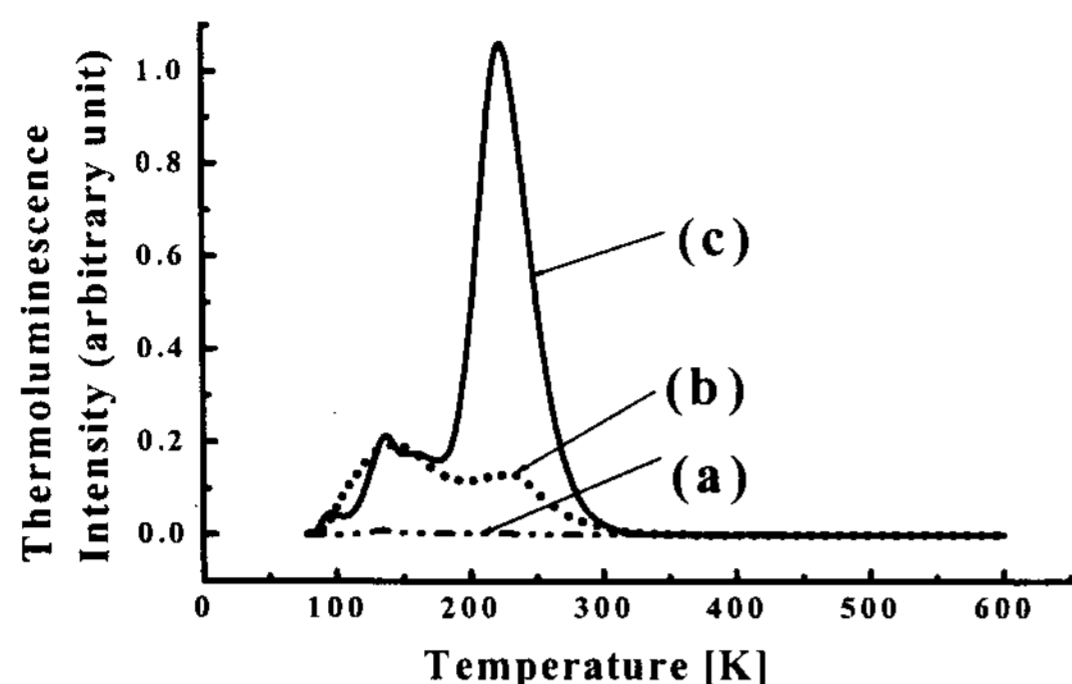

Fig.3 Thermoluminescence glow curves of $SrIn_2O_4:Pr^{3+}$ codoped with B(c) or Gd(b) and with no intentional codoping (a). The nominal concentration of B and Gd is 2.5 and 5.0mol.%, respectively.

The temperature dependence of the luminescence intensity is small for $SrIn_2O_4:Pr^{3+}$ without codoping. Meanwhile the luminescence intensity, specifically that of transitions from $^1D_2$ state, is increased greatly when the III-group ions are doped. One can, therefore, assume that thermal release of carriers from the impurity-induced traps contribute to the increased luminescence efficiency. This is a situation quite similar to the temperature dependence of luminescence from $SrTiO_3:Pr^{3+}$,Al.
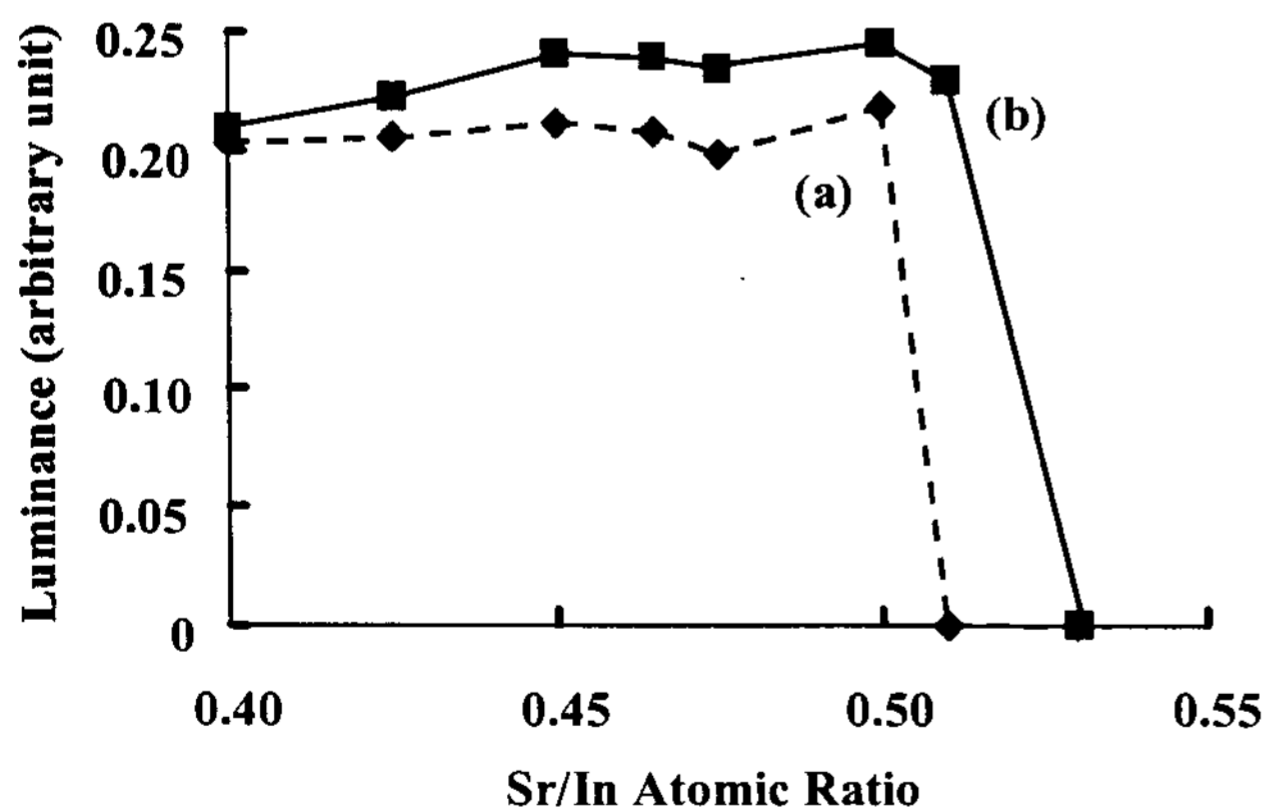

Fig.4 Luminance as a function of Sr/In atomic ratio at room temperature. Curve (a) shows luminance of $SrIn_2O_4:Pr^{3+}$ with no codoping and curve (b) luminance of $SrIn_2O_4:Pr^{3+}$ with 2.1mol.%B. Excitation was made by 254nm light.

There is a marked difference in the efficiency

depending on the Sr/In atomic ratio; the efficiency of $SrIn_2O_4:Pr^{3+}$ without any additives keeps a fairly high level at the stoichiometry and in the In-excess side, but shows a sharp drop nearly to zero in the Sr-excess side. The efficiency, therefore, depends critically on the chemical composition near the Sr/In atomic ratio of 0.50. The composition where the efficiency drops shifts to the Sr-excess side when B is doped, and to the In-excess side when Gd is doped. These results, shown by Figs.4 and 5 , can be understood if B^{3+} ions are introduced to the In^{3+} site and Gd^{3+} ions to the Sr^{2+} site.
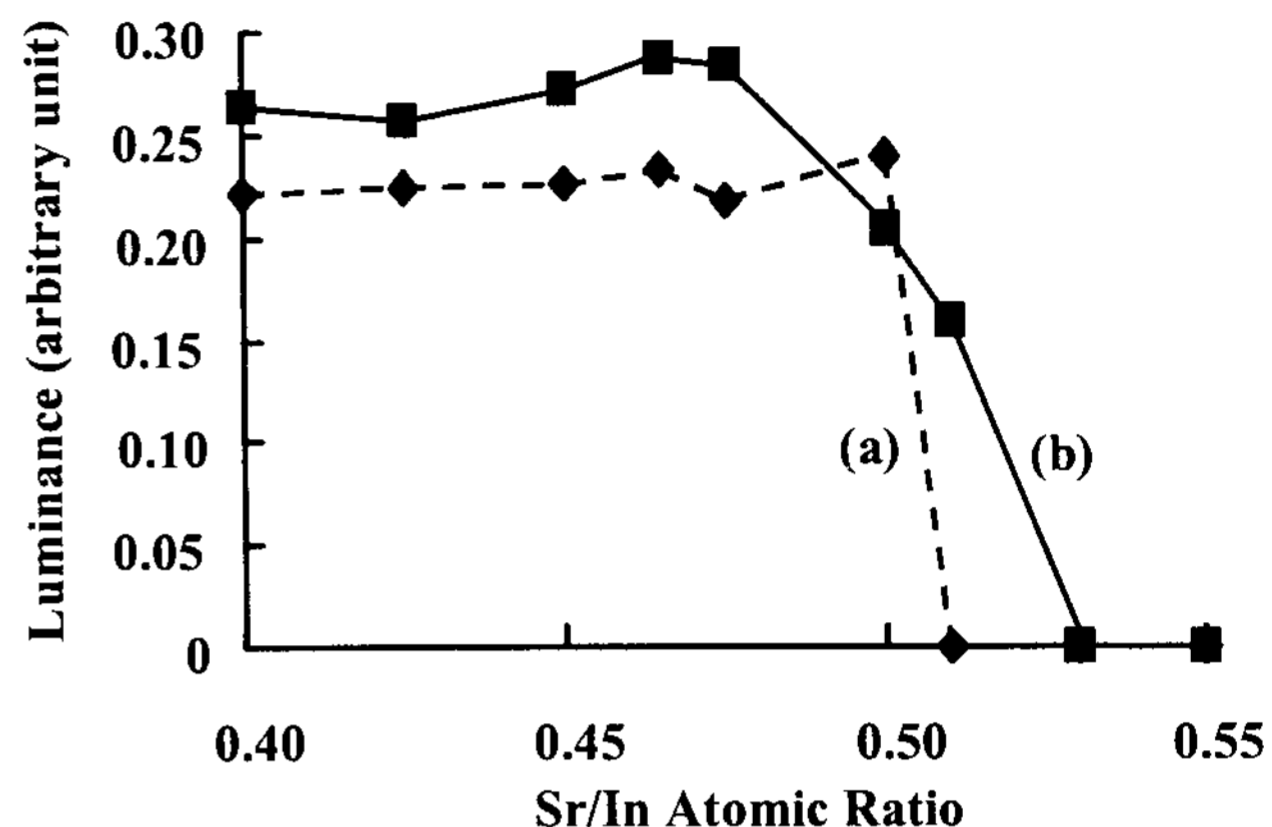

Fig.5 Luminance as a function of Sr/In atomic ratio at room temperature. Curve (a) shows luminance of $SrIn_2O_4:Pr^{3+}$ with no codoping and curve (b) luminance of $SrIn_2O_4:Pr^{3+}$ with 5.0mol.%B. Excitation was made by 254nm light.

In fact X-ray diffraction lines ascribed to In_2O_3 increases in the intensity with an increase in the concentration of added B_2O_3 and decreases with an increase in the concentration of added Gd_2O_3 (Fig.6). This result supports the above assumption on the lattice sites which B^{3+} or Gd^{3+} ions substitute for.

Fig.6 Relative intensity of a powder X-ray
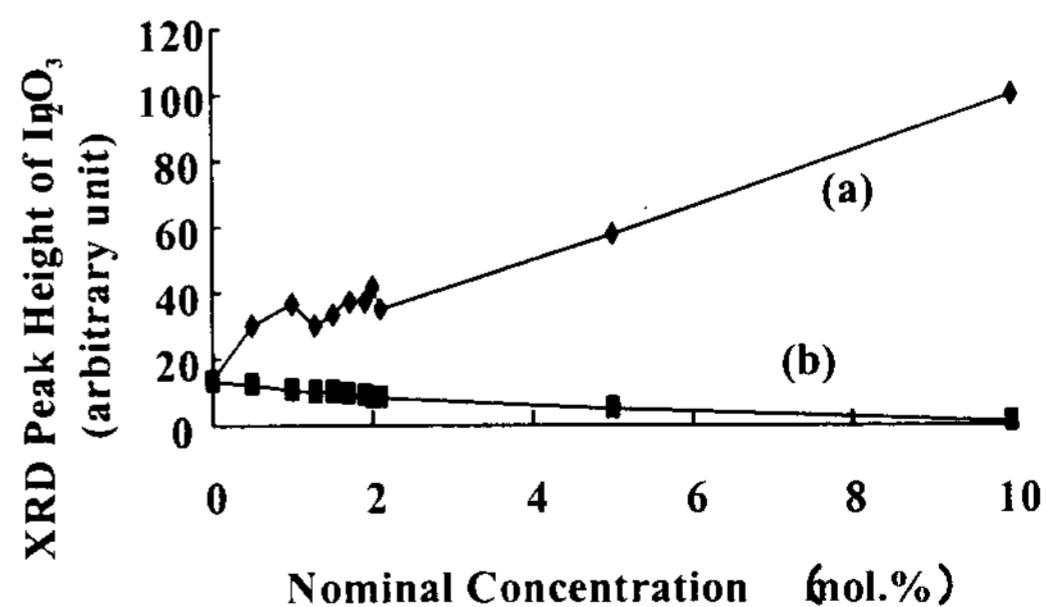
diffraction line by In_2O_3 in $SrIn_2O_4:Pr^{3+}$ doped with B (a) or Gd (b).

Samples of $SrIn_2O_4:Pr^{3+}$ show white body color

at the stoichiometric composition and yellowish hue in the Sr-excess side. This difference can be clearly seen in diffuse reflectance spectra (Fig.7) as a broad absorption band below the fundamental absorption edge of Sr-excess samples. The low efficiency in the Sr-excess side can be ascribed to defects inducing the above absorption band.
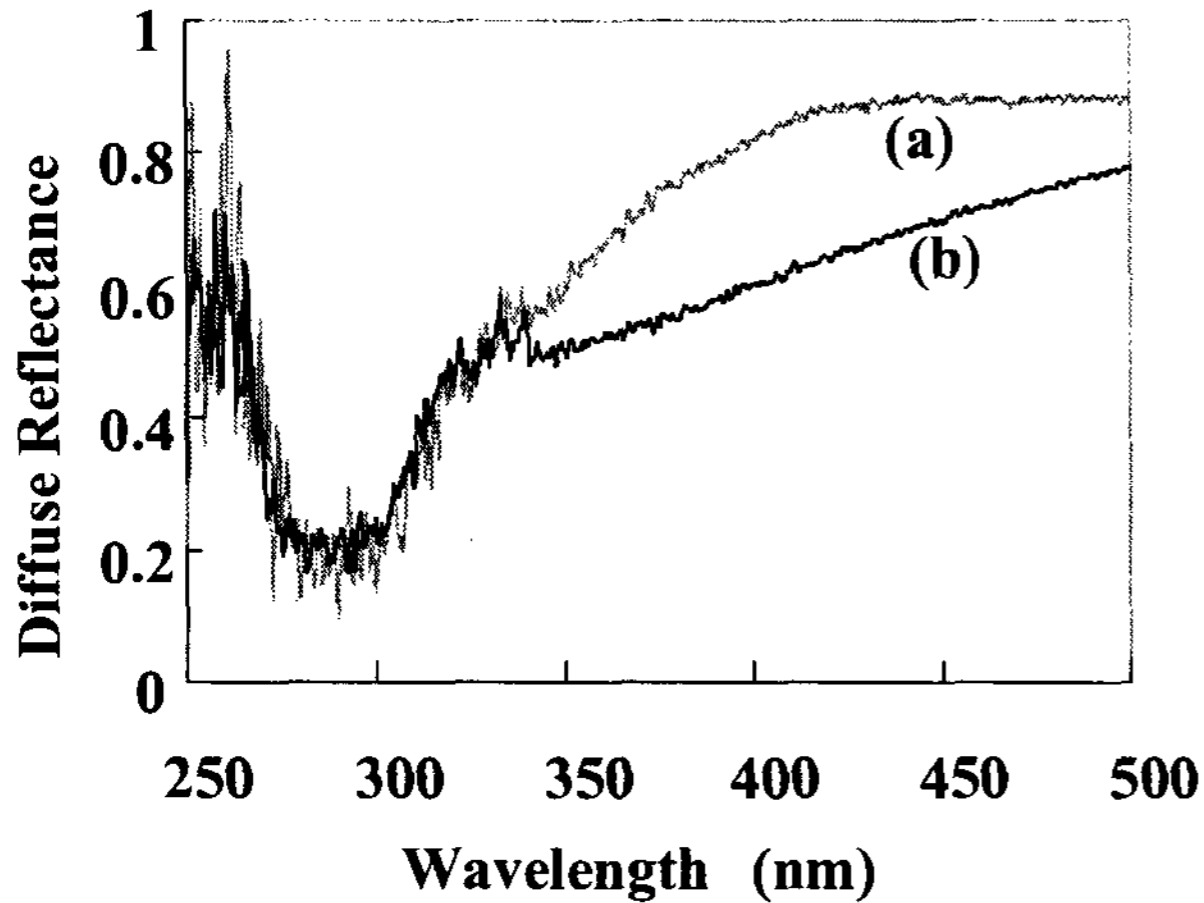

Fig.7 Diffuse reflectance spectra of $SrIn_2O_4{:}Pr^{3+}$ with Sr/In atomic ratio of 0.50 (a) and with Sr/In atomic ratio of 0.55 (b).
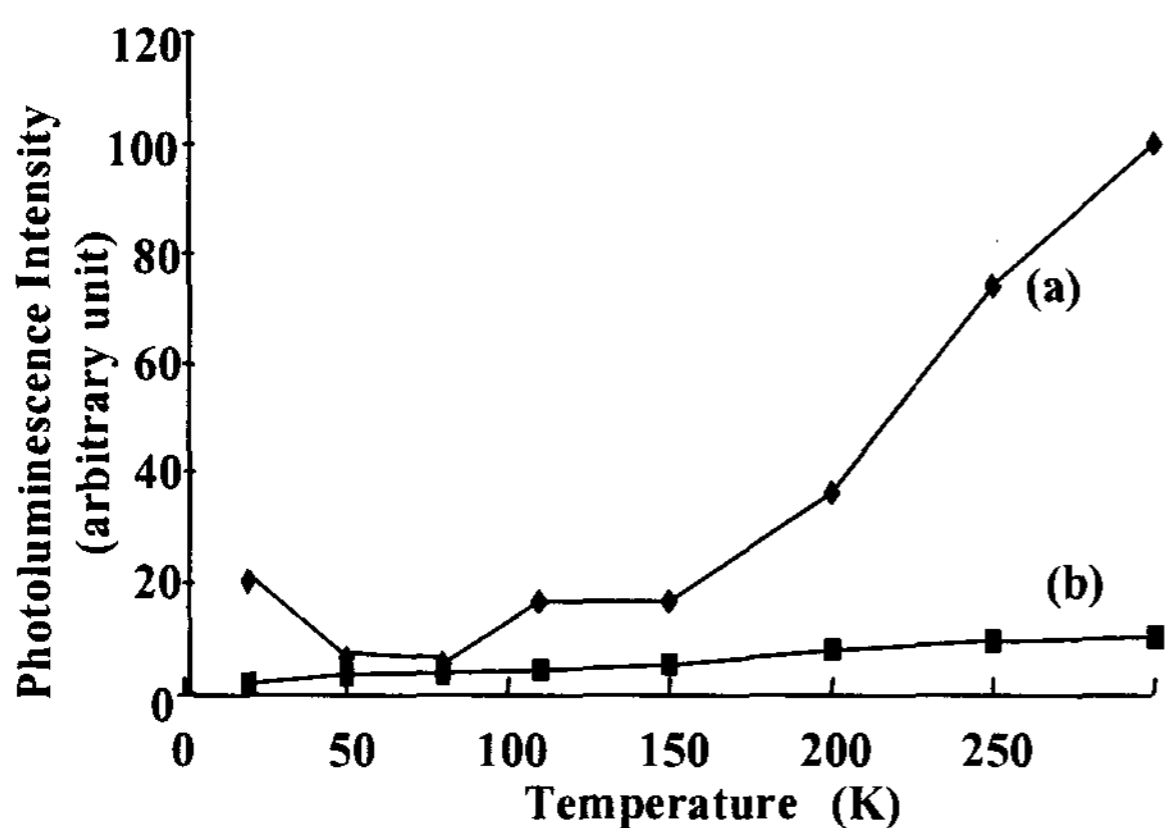

Fig.8 The photoluminescence intensity from $^1D_2$ state of Pr^{3+} doped in $SrIn_2O_4$ with Sr/In atomic ratio of 0.465 (a) and of 0.51 (b) as a function of temperature. Excitation was made by 325nm light of a He-Cd laser.

The low efficiency of a Sr-excess composition can be seen in temperature dependence of the efficiency as well. Figure 8 compares photoluminescence intensity from $^1D_2$ state of Pr^{3+} for two samples, one with an In-excess composition (curve a) and the other with a Sr-excess composition (curve b), in a temperature range from 20 to 300K. With an increase in temperature, the luminescence intensity of the In-excess sample increases remarkably, while that of the Sr-excess sample remains at a low level. As

a result, the difference between the two is enlarged at room temperature. An increase in the luminescence intensity with an increased temperature is observed for $SrIn_2O_4{:}Pr^{3+}$ and $SrTiO_3{:}Pr^{3+}$ both codoped with other III-group ions, as described above. It can be speculated, therefore, that an excess amount of In^{3+} ions may form traps, which provide carriers at room temperature, just as the other codopants.

4. Conclusion

The luminescence properties of $SrTiO_3{:}Pr^{3+}$ and $SrIn_2O_4{:}Pr^{3+}$ doped with III-group ions show quite similar features. They can be interpreted essentially by the same picture described in section 2. A luminescence efficiency, which varies with a deviation from the stoichiometry is known also for other ternary oxides. Investigation of the relation between the composition and the efficiency may lead to development of new phosphors or improvement of conventional phosphors.

5. Acknowledgment

6. References

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