Blue-Light Emission from Undoped and Rare Earth-Doped Wide Bandgap Oxides

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Received 10 June 2006; revised 10 September 2006

Abstract: Rare earth-doped oxide thin-film phosphors may emerge as an alternate choice for the blue phosphor, due to their chemical and thermal stability in high vacuum and absence of corrosive gas emission under electron bombardment. The blue phosphors in this study were activated in air at temperatures suitable for glass substrates, which have been used in a number of applications. The effects of rare earth ions and oxide hosts on the blue-light-emitting properties of phosphors are discussed. In addition, novel blue-light emission was observed in certain typical undoped wide bandgap oxides. The luminescence of the oxides depends on the growth and annealing conditions under different atmospheres, suggesting that it is associated with the presence of oxygen vacancies. Radiative processes related to oxygen vacancies were also presented.

Key words: wide bandgap; luminescence; rare earths; oxide; blue light; rare earths


Blue-light emitting materials have been receiving considerable attention due to their applications for a variety of optoelectronic devices and display technologies. Rare earth-doped compounds have long found uses as blue phosphors in a variety of devices due to their intensely luminescent f-d and f-f electronic transitions. Metal sulfides, such as ZnS have been utilized as conventional phosphors due to their excellent brightness. However, the life span of the display devices is limited due to their chemical and thermal instability. One of the solutions to the problem on the basis of sulfides is to search and develop rare earth-doped oxide phosphors with efficient luminescence. Oxide phosphors are more chemically and thermally stable and absence of corrosive gas emission under electron bombardment in comparison with sulfide compounds. Unfortunately, the use of stable oxide compounds is limited by their quite high crystallization temperature. For example, commonly used rare earth-doped oxide blue phosphors, such as Ce-doped Y$_2$SiO$_5$, are generally required to activate at relatively high temperatures for hours, therefore, it is not suitable for the use of glass substrates in certain types of flat panel displays like thin-film electroluminescent (TFEL) devices, and field emission displays (FEDs). For this reason, the recent study has been directed to the development of a low-temperature technology of rare earth-doped oxide phosphors for TFEL and FED. The goal of the study is the preparation of phosphors which may be compatible with display industry technologies.

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- Foundation item: Project supported by the National Natural Science Foundation of China (50472079)
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On the other hand, many oxide materials are usually wide bandgap compounds. The conductivity of oxides can vary from insulator to conductor, depending on the preparation conditions. Undoped wideband gap semiconductors, such as Ga₂O₃ and ZnO have recently attracted much attention because of their abundant electronic, optoelectronic, and luminescent properties. Moreover, renewed attention has been paid to the luminescence properties of perovskite titanates, such as SrTiO₃. The perovskite titanates are already very well-studied compounds because of their useful properties in terms of ferroelectrics and high dielectric constant. Recent reports indicate that old SrTiO₃ can shine with its blue light. Creating oxygen vacancies with certain techniques causes the dielectric insulator to evolve to a metallic-like compound. To date, most of the reported optical and electronic properties of wide bandgap oxides are on the basis of a single crystal or other bulk structures. Comprehensive studies for thin films and nanoscale materials are still in progress. In this study, the studies on the blue-light luminescence in both undoped and rare earth (Tm and Eu)-doped wide bandgap oxides such as Y₂O₃, Ga₂O₃, and borates were studied.

1 Experimental

The chemical method, such as spray pyrolysis deposition, and physical method, such as pulsed laser deposition (PLD) were both used in the experiment. The Corning 7059 glass substrates were used in the deposition. Annealing and softening point of thin sheet glass are 639 and 844 °C, respectively. After deposition, certain thin films were annealed in air at temperatures suitable for the use of glass substrates. The cathod luminescence (CL) spectra were recorded under controlled excitation voltages below 5 kV. In addition, a mercury arc lamp along with a monochromator was used as the excitation source for photoluminescence (PL) measurement. Consequently, both PL and CL spectra were recorded using an Ocean Optics S2000 CCD spectrometer (350 - 900 nm). The spectrometer provides a resolution of 1.5 nm of FWHM. A Minolta T-1M illuminance meter was used to determine the luminance of the films.

2 Results

Fig. 1 shows the CL spectra measured at room temperature on Tm-doped Y₂O₃, Ba₂B₅O₉Cl, and Sr₂B₅O₉Cl films grown on glass substrates. These films were activated in air at temperatures suitable for glass. From Fig. 1, it can be seen that the intense peaks emit sharply around 457 and 476 nm. Besides the major blue-emission peaks, there were a few minor peaks at 650 and 813 nm.

The emission of Eu²⁺ due to 4f⁷→4f⁵5d¹ transition is usually shown as several bands in the broad wavelength, which is very sensitive to the nature of host materials. Fig. 2 shows the CL spectra of Eu-doped Ba₂B₅O₉Cl, Sr₂B₅O₉Cl, and Ca₂B₅O₉Cl films grown on glass substrates. These spectra had an intense peak due to Eu²⁺ in the blue region along with weak peaks due to Eu³⁺ for every compound. Obviously, the emission band shifts to longer wavelength with decreasing ionic radius of the cations, that is, in the order Ba > Sr > Ca.

Fig. 3 shows the CL of Tm-doped Ga₂O₃ (Fig. 3(a)) and undoped Ga₂O₃ thin films (Fig. 3(b)).
It is interesting that the spectrum is shown in Fig. 3(a). There is no obvious blue-emitting peak present which corresponds to the transitions between electronic energy levels of Tm$^{3+}$ as shown in Fig. 1, while only a minor peak appears around 813 nm relating to the transition from $^1G_4 \rightarrow ^1H_6$ of the Tm$^{3+}$ ion. Instead, a broad blue-green emission occurs over the range from 350 to 650 nm. For comparison, the undoped Ga$_2$O$_3$ films were deposited and annealed under the same conditions as those for Tm-doped Ga$_2$O$_3$ films. It is interesting that the Tm-doped film exhibits a spectrum very similar to that for the undoped film except for the peak around 813 nm. As a result, the intensity of the CL emission band was affected strongly by the annealing ambient for the undoped film in Fig. 3(b). The annealing ambient changed from air to forming gas, corresponding to a change from oxygen-rich to oxygen-deficient Ga$_2$O$_3$ films. As forming gas created more oxygen vacancies, this behavior is consistent with the proposed oxygen vacancy model presented in the discussion section.

3 Discussion

3.1 Blue-light emission from Tm-doped oxides

Luminescence from solids is usually associated with impurities, excited states of isolated atoms and ions as well as defects. It is well known that Tm-activated phosphors have complicated energy level schemes due to the strong deviation from Russell-Saunders coupling in the (4f) configuration. As a consequence, the relaxation of the excited states of Tm$^{3+}$ ions may take place via a large number of relaxation paths and result in UV, visible, and infrared (IR) emissions. The peaks shown in Fig. 1 are characteristic of transitions between the electronic energy levels of Tm$^{3+}$ ions. For example, the blue emission peaks centered at 457 and 476 nm correspond to the transition from $^1D_2 \rightarrow ^3F_4$ and $^1G_4 \rightarrow ^1H_6$ of the Tm ion, respectively.

3.2 Blue-light emission from Eu$^{2+}$-doped oxides

Eu$^{2+}$ is unstable in an oxidizing atmosphere, and it can be oxidized to Eu$^{3+}$ easily via Eu$^{2+} \rightarrow$ Eu$^{3+}$. Since Eu$^{2+}$-doped phosphor is a promising blue phosphor; the search for appropriate hosts to stabilize Eu$^{2+}$ is one of the central issues. Annealing the phosphors at relative high temperatures for hours in a reducing atmosphere is required for both crystallization of compounds and reduction of Eu$^{3+}$ to Eu$^{2+}$. Unfortunately, the processes are not suitable for the use of glass substrates in flat panel applications. Moreover, it is not a convenient method to use reducing atmosphere in large-scale production because of the added safety requirements.

Borates, which consist of a rigid three-dimensional network of tetrahedral BO$_4$ groups, are believed to play an important role in preventing the oxidation of the divalent metal ions. Su’s group$^{22}$ found that the abnormal reduction of Eu$^{3+}$ in borate bulks can be activated in nonreducing atmospheres. The abnormal reduction of Eu$^{3+}$ to Eu$^{2+}$ could be related to the rigid three-dimensional network of BO$_4$ tetrahedra, which is necessary to stabilize the divalent rare earth ions in an oxidizing atmosphere. As shown in Fig. 2, the abnormal reduction of Eu$^{3+}$ to Eu$^{2+}$ in thin films may be done at much lower annealing temperatures compared with bulk samples. Furthermore, a change in type and/or composition of alkaline cation in compounds may alter the emitting wavelength.

3.3 Blue-light emission from undoped oxides

The emission band shown in Fig. 3(b) can be separated into three Gaussian bands.$^8$ Two major emissions are centered at 497 and 526 nm, while one minor emission is centered at 424 nm. The result in Fig. 3 is associated with the recombination of an electron on a donor formed by oxygen vacancies with a hole on an acceptor made up of either gallium vacancies or gallium-oxygen vacancy pairs (V$_{Ga}$, V$_{GaO}$).

Another research direction linked to the result of Fig. 3 is the study of titanates which have long been studied and used for dielectric and ferroelectric properties. There is limited number of luminescence studies related to perovskite oxides, such as SrTiO$_3$ (STO). Recently, certain researchers$^{9,10}$ investigated the luminescent spectra of STO perovskites at different tem-
peratures. There are several possible blue-emission peaks in the observed PL spectra of STO thin films. Ken et al.\cite{5} found that the oxygen-deficient surface on the films show a broad blue-emitting peak centered at 430 nm. It is known that STO has an energy gap in an energy range of 3.2 - 3.5 eV. The origin of the blue-emission peaks may be associated to the transitions involving titanate octahedron and oxygen vacancies. Considering the band gap value of Ga$_2$O$_3$ (4.2 - 4.9 eV) and STO, certain possible processes in thin films of Ga$_2$O$_3$ and STO occur shown in the energy diagram of Fig.4. Further studies such as luminescence in undoped wide bandgap oxides at low temperatures are now in progress.

![Energy Diagram](image)

Fig. 4 Certain possible radiative processes in thin films of undoped wide bandgap oxides

(1) Excited electrons with holes in traps; (2) Electrons in traps with holes in traps; (3) Electrons in traps with excited holes; (4) Excited electrons with holes

4 Conclusion

Blue-light emitting thin films of rare earth (Tm and Eu)-doped oxides were activated in air at temperatures suitable for the use of glass substrates, which may be useful to display industry technologies. As blue lines depend on the crystal property of the host matrix, it is possible to tune the material for specific emitting spectra. The luminescent spectra of undoped wide bandgap oxides mainly showing a broad band are likely due to a process that is involved in a recombination of oxygen vacancies.

References:


