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Cathodoluminescence of $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ thin films doped with Tm^{3+} , Tb^{3+} and Mn^{2+}

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Abstract

Thin-film phosphors of $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ doped separately with Tm^{3+} , Tb^{3+} and Mn^{2+} were deposited by spray pyrolysis of aqueous solutions. Because these phosphor films were activated at 600°C , they are suitable for use on glass substrates. The films containing Tm^{3+} , Tb^{3+} and Mn^{2+} exhibited blue, green and yellow cathodoluminescence (CL), respectively. The chromaticity coordinates, dominant wavelength and purity were determined for each phosphor. Films deposited on aluminosilicate ceramic plates exhibited enhanced CL intensity compared to those on glass plates. The CL luminance and efficiency of each phosphor depended on the electron beam voltage and current density. Saturation effects were observed as the current density increased.

1. Introduction

Oxide-based phosphors have attracted much interest over the years, because they are more stable chemically and thermally than sulphide phosphors [1–3]. Borates, such as SrB_4O_7 and $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$, which contain the tetrahedral borate group BO_4 , were found to be very suitable hosts for luminescent ions, such as Eu^{2+} , Sm^{2+} , Ce^{3+} . The photoluminescence (PL) and cathodoluminescence (CL) properties have been characterized for SrB_4O_7 and $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ powders doped with various ions [4–6].

There are advantages to using thin-film phosphors compared to powder phosphor layers. The thin-film structure makes it possible to use smaller pixel spot sizes to achieve higher resolution [7, 8]. Another significant advantage is the lower outgassing from thin oxide films in field-emission displays (FEDs) [9]. For industry, the preparation of thin films by the spray pyrolysis method is attractive for large-scale and large-area production [10]. In a recent paper we reported the preparation of thin films of $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}:\text{Eu}$ for the first time by spray pyrolysis [11]. As-grown films exhibited mainly red emission associated with the transitions between electronic levels of Eu^{3+} ions. After annealing at 600°C in various atmospheres including air, the PL and CL spectra of the films each consisted of a sharp line at 425 nm (due to $d \rightarrow f$ transitions of Eu^{2+}) with good chromaticity coordinates for a blue phosphor. Thus,

the specific crystal structure of $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ was effective in reducing Eu^{3+} to its corresponding divalent state Eu^{2+} at elevated temperature even without the introduction of reducing agents. Similar to europium ions, other lanthanide ions, such as thulium (Tm) and terbium (Tb), and some transition ions such as manganese (Mn) also have more than one oxidation state. It would be interesting to determine whether this effect occurs for these elements. In this paper, we report the use of spray pyrolysis to grow thin films of $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ doped separately with Tm^{3+} , Tb^{3+} and Mn^{2+} . The CL properties of these films were characterized.

2. Experimental procedure

Thin films of $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ doped with thulium, terbium and manganese ions were deposited by spray pyrolysis on Corning 7059 glass and aluminosilicate ceramic plates. The spray pyrolysis method was reported previously [11]. In brief, stock precursor solutions of SrCl_2 and H_3BO_3 were mixed separately with $\text{Tm}(\text{NO}_3)_3$, $\text{Tb}(\text{NO}_3)_3$ and $\text{Mn}(\text{NO}_3)_2$ in appropriate ratios to provide solutions of various dopant concentrations relative to Sr in $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$. The spray was developed by an ultrasonic nebulizer and was directed towards the substrate by a carrier gas of humid air at a flow rate of 1.2 l min^{-1} , and the consumption rate of the solution was around 3.5 ml h^{-1} . The spray chamber was mounted on an x - y translation table to raster the aerosol to cover an area of $2.5 \times 5.0 \text{ cm}^2$. The deposition temperature was 300°C . After deposition, the films were annealed at 600°C for 1 h in air, nitrogen or hydrogen.

The morphology was determined using a scanning electron microscope (SEM). The CL was obtained using a CL luminoscope (Relion Industries ELM-2B). Luminescence spectra were measured using an Ocean Optics S2000 CCD spectrometer with a $400 \mu\text{m}$ diameter single-strand UV/VIS optical fibre. A Minolta T-1M illuminance meter was used to determine the luminance of the films.

3. Results and discussion

Both composition analysis and x-ray diffraction (XRD) spectra in our previous work showed that $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ films were formed by spray pyrolysis [11]. The as-grown film deposited at 300°C was amorphous or consisted of very small crystallites. After annealing at 600°C , the film had an XRD that is consistent with the orthorhombic structure of polycrystalline $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$.

Figure 1 shows the SEM of the as-grown film at 300°C (figure 1(a)) and a film annealed in air at 600°C (figure 1(b)) on a glass substrate. The as-grown film, which was dense and pinhole-free, was covered with some small particles. These particles were probably due to intermediate products of the pyrolysis because they disappeared after annealing at 600°C as shown in figure 1(b). This behaviour was also evident in the XRD pattern reported previously [11].

Figure 2 shows the CL spectra resulting from 5 kV beam excitation at room temperature for $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ films doped separately with 2% Tm, Tb and Mn. These films were annealed in air at 600°C . 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 excited states of Tm^{3+} ions may take place via a large number of relaxation paths and result in UV, visible and infrared (IR) emission [12]. Figure 2(a) shows that major blue-emission peaks of the Tm-doped film occurred at 455 and 476 nm, which correspond to the transitions $^1\text{D}_2 \rightarrow ^3\text{F}_4$ and $^1\text{G}_4 \rightarrow ^3\text{H}_6$, respectively. The transition $^1\text{G}_4 \rightarrow ^3\text{F}_4$ is related to the minor emission peak at 650 nm. The CL emission of $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ films doped with Tm exhibited features similar to those obtained for other host films [13, 14],

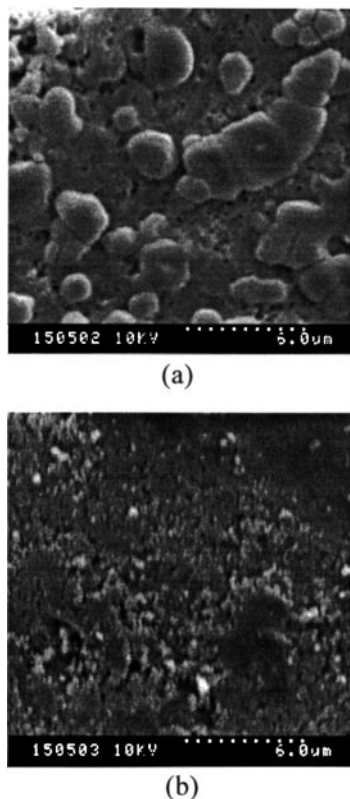


Figure 1. SEM images of $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ thin film deposited by spray pyrolysis: (a) as grown at 300°C ; (b) annealed in air at 600°C .

and single crystal $\text{Y}_2\text{O}_3:\text{Tm}$ [15]. For Tb^{3+} , figure 2(b) shows the major green-emission peak at 546 nm and a few minor peaks at 489, 587 and 623 nm. These peaks are characteristic of transitions between electronic energy levels of Tb^{3+} ions. The major peak centred at 546 nm corresponds to the transition $^5\text{D}_4 \rightarrow ^7\text{F}_5$, while the transitions $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$ and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ of the Tb ion are related to the emission peaks at 489, 587 and 623 nm, respectively. These emissions are similar to those observed for $\text{Y}_{3-x}\text{Al}_5\text{O}_{12}:\text{Tb}_x^{3+}$ powders [16]. For the Mn-doped sample, a relatively broad yellow emission centred around 582 nm associated with electronic energy levels of Mn^{2+} ions is illustrated in figure 2(c).

Several groups reported that Eu^{3+} , Tm^{3+} and Sm^{3+} could be reduced to the corresponding divalent rare-earth ions in borates, such as SrB_4O_7 and $\text{SrB}_6\text{O}_{10}$, which contain the tetrahedral BO_4 group [4, 5]. The reduction could even be done in air at high temperature without the introduction of reducing agents. It was suggested that the rigid three-dimensional network of BO_4 tetrahedra is necessary to stabilize the divalent rare-earth ions at high temperature in an oxidizing atmosphere. Furthermore, Mn^{2+} and Pb^{2+} were found to retain the divalent state in $\text{SrB}_6\text{O}_{10}$ when fired in air [17, 18]. The structure of $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ consists of a 3D $(\text{B}_5\text{O}_9)_\infty$ network, in which three BO_4 tetrahedra and two BO_3 triangles are linked together with one another [4]. Thus, the abnormal reduction of Eu^{3+} to Eu^{2+} was attributed to: (a) the presence of BO_4 tetrahedra in a 3D $(\text{B}_5\text{O}_9)_\infty$ network; and (b) the replacement of three Sr^{2+} ions by only two Eu^{3+} ions. According to this model, a negative Sr^{2+} vacancy was formed, and an electron was transferred from this defect to Eu^{3+} by thermal stimulation. However,

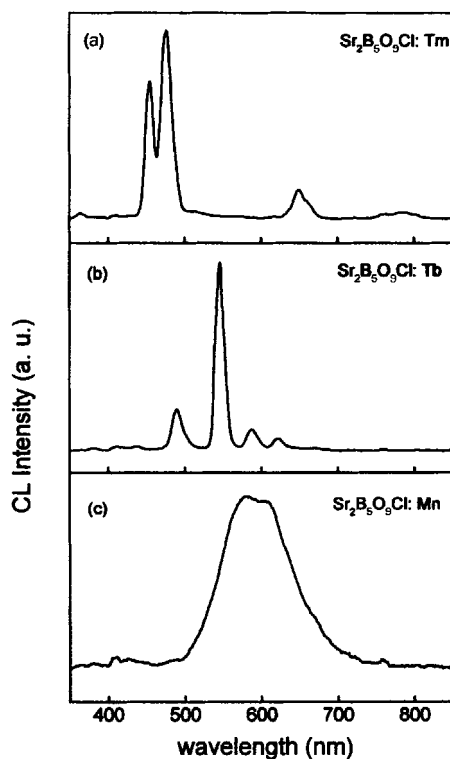


Figure 2. CL spectra for Tm-, Tb- and Mn-doped $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ films with a 2% concentration of the dopant in the spray solutions. These films were deposited at 300°C and annealed in air at 600°C .

the reduction to the divalent state is not general for all rare-earth dopants. Terbium can occur in the trivalent and tetravalent states but not in the divalent state in oxide hosts. Compared to that of europium, reduction of thulium to the divalent state is much more difficult and has been observed only in a few borates. The present work supports this conclusion. Thus, the corresponding reduction was minimal for Tm^{3+} and Tb^{3+} in $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ as shown in figure 2. Moreover, all characteristic peaks of Tm^{3+} and Tb^{3+} shown in figure 2 were unchanged when a reducing atmosphere was used in the heat treatment, further indicating that these ions were difficult to reduce in $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$. For Mn, figure 2(c) shows that the emission was due to the Mn^{2+} even when $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ was annealed in air. Obviously, Mn was not oxidized to any of its higher valences such as +3, +4, and +5. Perhaps the 3D $(\text{B}_5\text{O}_9)_\infty$ network in $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ stabilizes Mn^{2+} even under oxidizing conditions during heat treatment.

Most lighting specifications refer to colour in terms of the 1931 CIE (Commission Internationale de L'Eclairage) chromaticity colour coordinates. In general, the colour of any light source can be represented as an (x, y) coordinate in this colour space. The colour coordinate (x, y) can be calculated by integrating the spectrum of the light source with three different functions called the 1931 CIE colour-matching functions. The location of the colour coordinates of each film on the CIE chromaticity diagram is presented in figure 3. Table 1 lists the chromaticity coordinates, dominant wavelength and colour purity. In comparison with the blue phosphor $\text{Y}_2\text{O}_3:\text{Tm}$ in our previous study [14], the Tm-doped $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ film had better CIE properties. On the other hand, the coordinates of $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}:\text{Tb}$ were not as good as that obtained for the $\text{Y}_2\text{O}_3:\text{Tb}$ film for use as a green phosphor [14].

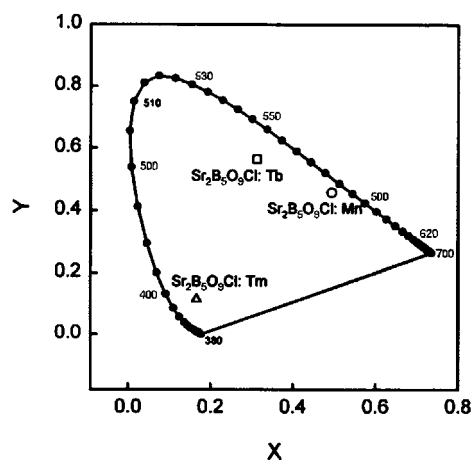


Figure 3. A CIE chromaticity diagram showing the chromaticity points of Tm-, Tb- and Mn-doped Sr₂B₅O₉Cl films.

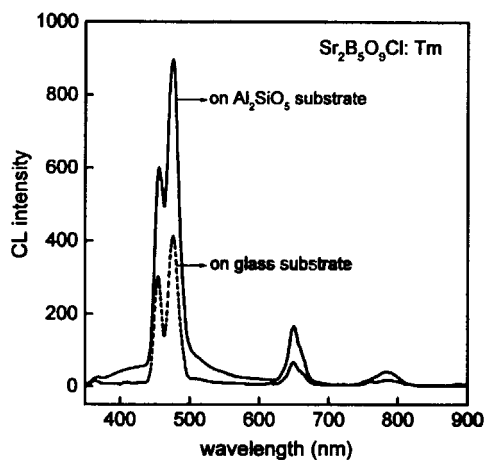


Figure 4. Comparison of CL spectra of thin films of Sr₂B₅O₉Cl:Tm grown on glass and aluminosilicate substrates. The film thickness was about 1.0 and 2.8 μm on glass and aluminosilicate, respectively.

Table 1. Chromaticity coordinates, dominant wavelength and purity for blue, green and yellow phosphor films.

Sample	CIE (x, y)	Dominant wavelength (nm)	Purity (%)
Sr ₂ B ₅ O ₉ Cl:Tm	(0.166, 0.115)	472	81
Sr ₂ B ₅ O ₉ Cl:Tb	(0.313, 0.564)	546	62
Sr ₂ B ₅ O ₉ Cl:Mn	(0.495, 0.458)	582	87

It is interesting that changing the substrate from glass to aluminosilicate caused a substantial increase in the CL intensity of films prepared and annealed under the same conditions, as shown in figure 4. In addition, the line positions and linewidth did not change as the substrate changed. A similar improvement in the CL intensity was observed for other

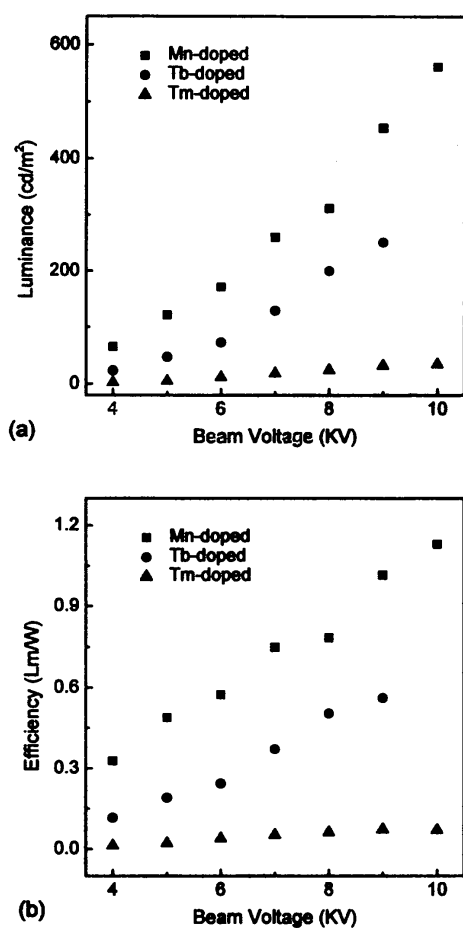


Figure 5. CL luminance (a) and efficiency (b) of Tm-, Tb- and Mn-doped $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ films at a constant current density of $62 \mu\text{A cm}^{-2}$ as a function of electron beam voltage. The film thickness was about $1.0 \mu\text{m}$.

thin film phosphors in our recent reports [11, 14]. Previous study indicated that there is little difference between the XRD linewidths for $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ films on aluminosilicate and glass [11]. But the film thickness was larger on aluminosilicate than on glass. ($2.8 \mu\text{m}$ versus $1.0 \mu\text{m}$). Moreover, it is believed that one problem with thin-film phosphors for display application has been internal reflection [9, 19]. Internal reflection causes a substantial amount of the light generated in the phosphor layer to be 'piped' along the horizontal direction and essentially lost. Consequently, only a fraction of the light from thin-film phosphors escapes through the surface for detection by the observer. This explanation has been used to account for the observation that $\text{Y}_2\text{O}_3:\text{Eu}$ thin films have a larger PL intensity on diamond-coated silicon substrates than on bare silicon because the diamond layer is rougher than the silicon surface [20]. Since the aluminosilicate substrate has a rougher surface morphology than glass, a similar explanation may apply.

Figure 5 shows the luminance and efficiency as a function of electron beam voltage for $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ films doped separately with Mn, Tb and Tm. Between 4 and 10 kV both luminance and efficiency increased continually as the acceleration voltage increased at a constant current

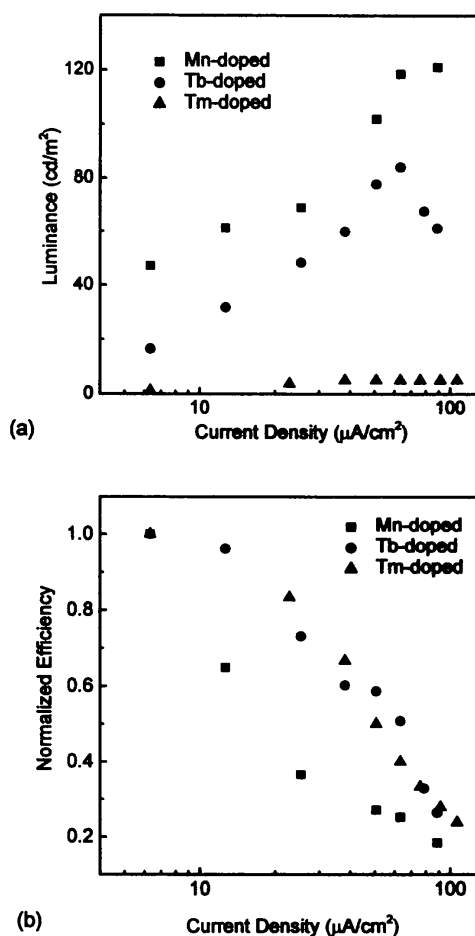


Figure 6. CL luminance (a) and normalized efficiency (b) of Tm-, Tb- and Mn-doped Sr₂B₅O₉Cl films at 5 kV as a function of current density.

density of $62 \mu\text{A cm}^{-2}$, and saturation was not evident. Since the luminescence was measured on the side irradiated by the electron beam, the lower efficiency at low voltage indicates that the transfer of the recombination energy of the electron-hole pair to a luminescent ion occurred with lower probability near the surface than deeper in the film. In addition, this increase occurred probably because the penetration depth and excited volume increased as the voltage increased. Similar behaviour occurred for sulphide phosphors such as SrGa₂S₄:Ce and ZnS:Ag, Cl [21], and for other oxide phosphors such as Ta₂Zn₃O₈ and Y₂O₃:Tm [14, 19].

Figure 6 shows the luminance and normalized efficiency as a function of beam current density at a constant voltage of 5 kV for the three phosphors. At low current density ($j \leq 62 \mu\text{A cm}^{-2}$), the luminance of these phosphors increased rapidly with increasing current density. At high current density ($j > 62 \mu\text{A cm}^{-2}$), the luminance saturated and/or decreased with any additional increase in current density (figure 6(a)). Figure 6(b) illustrates that the efficiency decreased as current density increased for all phosphors. Compared to those of the Tm and Tb phosphors, the efficiency of Mn-doped Sr₂B₅O₉Cl film decreased more severely. The decreases are related to the saturation illustrated in figure 6(a). The physical processes

responsible for saturation can be complex, with several mechanisms contributing, including ground-state depletion and thermal quenching [22]. The thermal quenching contribution to saturation is due to a heating of the phosphor material and, as a consequence, to an increase in the nonradiative rate of decay. It has been shown that ground-state depletion is directly proportional to the luminescence decay time, and phosphors with shorter decay times are more resistant to current saturation because of activator recycling [9, 19]. The sharper decrease in efficiency observed for the Mn-doped $\text{Sr}_2\text{B}_5\text{O}_7\text{Cl}$ film in figure 6(b) may be due to ground-state depletion of Mn luminescent centres as a result of longer decay rates, because the transition is both spin and parity forbidden. In fact, Mn^{2+} in ZnGa_2O_4 was reported to have a long decay constant ranging from 4 to 10 ms [23]. To elucidate the nature of saturation effects in $\text{Sr}_2\text{B}_5\text{O}_7\text{Cl}$ films doped with Mn, Tb and Tm, measurements of the luminescent decay are planned.

4. Conclusions

Spray pyrolysis was used to prepare thin films of $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ doped with Tm^{3+} , Tb^{3+} and Mn^{2+} that exhibited blue, green and yellow CL emission, respectively. The peaks of the CL spectra at room temperature were characteristic of transitions between electronic energy levels of Tm^{3+} , Tb^{3+} and Mn^{2+} ions. The CL features of these phosphors showed little dependence on the annealing atmosphere (air, N_2 and H_2). Unlike Eu in this host, annealing even in a reducing atmosphere did not reduce the dopants, Tm and Tb. The chromaticity coordinates, dominant wavelength and purity for each phosphor were near the values required for FEDs. Both the luminance and the efficiency of these phosphors continued to increase with increasing beam voltage. On the other hand, saturation effects were observed at high current density for the three $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ films. The more severe current saturation of Mn-doped $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ film may be due to ground-state depletion of Mn luminescent centres.

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References

- [1] Lee R Y, Zhang F L, Penczek J, Wagner B K, Yocom P N and Summers C J 1998 *J. Vac. Sci. Technol. B* **16** 855
- [2] Park J C, Moon H K, Kim D K, Byeon S H, Kim B C and Suh K S 2000 *Appl. Phys. Lett.* **77** 2162
- [3] Kumar D, Sankar J, Cho K G, Craciun V and Singh R K 2000 *Appl. Phys. Lett.* **77** 2518
- [4] Pei Z, Zeng Q and Su Q 2000 *J. Phys. Chem. Solids* **61** 9
Pei Z, Zeng Q and Su Q 1999 *J. Solid State Chem.* **145** 212
Pei Z, Zeng Q, Su Q and Wang S 1999 *Spectrosc. Lett.* **32** 895
- [5] Peterson J R, Xu W and Dai S 1995 *Chem. Mater.* **7** 1686
- [6] Dotsenko V P, Berezovskaya I V, Efryushina N P, Voloshinovskii A S, Dorenbos P and van Eijk C W E 2001 *J. Lumin.* **93** 137
- [7] Feldman C and O'Hara M 1957 *J. Opt. Soc. Am.* **47** 300
- [8] Choe J Y, Ravichandran D, Blomquist S M, Morton D C, Kirchner K W, Ervin M H and Lee U 2001 *Appl. Phys. Lett.* **78** 3800
- [9] Holloway P H, Trottier T A, Abrams B, Kondoleon C, Jones S L, Sebastian J S and Thomes W J 1999 *J. Vac. Sci. Technol. B* **17** 758
- [10] Esparza A, Garcia M and Falcony C 1998 *Thin Solid Films* **325** 14
- [11] Hao J and Cocivera M 2001 *Appl. Phys. Lett.* **79** 740
- [12] Sun X D and Xiang X-D 1998 *Appl. Phys. Lett.* **72** 525

- [13] Nakanishi Y, Wada H, Kominami H, Kottaisamy M, Aoki T and Hatanaka Y 1999 *J. Electrochem. Soc.* **146** 4320
- [14] Hao J, Studenikin S A and Cocivera M 2001 *J. Lumin.* **93** 313
- [15] Guyot Y, Moncorge R, Merkle L D, Pinto A, McIntosh B and Verdun H 1996 *Opt. Mater.* **5** 127
- [16] Choe J Y, Ravichandran D, Blomquist S M, Kirchner K W, Forsythe E W and Morton D C 2001 *J. Lumin.* **93** 119
- [17] Koskentalo T, Leskela M and Niinisto L 1985 *Mater. Res. Bull.* **20** 265
- [18] Leskela M, Koskentalo T and Blasse G 1985 *J. Solid State Chem.* **59** 272
- [19] Rack P D, Potter M D, Kurinec S, Park W, Penczek J, Wagner B K and Summers C J 1998 *J. Appl. Phys.* **84** 4466
- [20] Cho K G, Kumar D, Lee D G, Jones S L, Holloway P H and Singh R K 1997 *Appl. Phys. Lett.* **71** 3335
- [21] Zhang F-L, Yang S, Stoffers C, Penczek J, Yocom P N, Zaremba D, Wagner B K and Summers C J 1998 *Appl. Phys. Lett.* **72** 2226
- [22] Stoffers C, Lee R Y, Penczek J, Wagner B K and Summers C J 2000 *Appl. Phys. Lett.* **76** 949
- [23] Poort S H M, Cetin D, Meijerink A and Blasse G 1997 *J. Electrochem. Soc.* **144** 2179