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Abstract
We prepared two kinds of Sm-doped strontium borates. When the samples were prepared in air environment, while the Sm^{3+} ions doped in strontium tetraborate (STB) were well reduced, the trivalent Sm ions were partially reduced in strontium hexaborate (SHB). The SHB was successfully reduced by subsequent x-ray irradiation (SHBX) and showed a strong Sm^{2+} emission. The photoluminescence, excitation spectrum and spectral hole burning experiments were conducted for the samples. The crystallographic sites of Sm^{2+} ions were found to be different in the STB and SHBX. Spectral holes were observed at room temperature in both samples STB and SHBX. The measured hole depths were 24% and 63% in STB and SHBX, respectively. As a result, we could obtain effective and novel hole burning material based on the Sm-doped strontium borates with x-ray-induced reduction.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Rare earth (RE) ion doped materials have attracted much attention because of their potential application to optical memory devices and phosphor materials. Of the materials, Sm or Eu doped materials have been studied extensively due to their unique optical properties and high hole burning efficiency. For use of hole burning in real applications, the materials are required to have proper optical properties such as wide inhomogeneous line width as opposed to homogeneous line width, high hole burning efficiency, short burning time, high hole burning temperature etc.

Many studies have concentrated on the development of new hole burning materials and much progress has been made. Glass phase materials are well known host materials in which the inhomogeneous line width is broadened significantly [1–3]. Also, high hole

burning efficiency at high temperature was found in alkaline earth halide host materials [4]. However, there still remain many problems to be solved or improved. For example, though the Sm^{2+}-doped glasses or alkaline earth halide host show very deep hole depth even at room temperature, in many host materials Sm ions are stable in their trivalent state. Thus, one should reduce the Sm^{3+} ions to Sm^{2+} ions. The most widely used and well known reduction method is preparing the samples under a highly reducing atmosphere such as heat treatment in an H_2 stream. Though this method is very effective compared to other reducing methods, it needs a rather complicated gas flow system. The other reduction method is to irradiate samples with high energy radiation such as x-ray [5] or fs laser pulses [6].

Pei and Su showed that the rare earth ions were successfully reduced to RE^{2+} ions in SrB_4O_7 host without any reducing atmosphere or an additional reduction process. Since then, many reports on the development of RE ion doped alkaline earth borates have been published. In this study, we also fabricated Sm-doped SrB_4O_7 and SrB_6O_{10}. The reduction of Sm^{3+} ions in SrB_6O_{10} under x-ray irradiation was observed and its hole burning properties are discussed.

2. Experiment

The preparation of the Sm-doped SrB_4O_7 and SrB_6O_{10} was carried out according to the literature [7, 8]. Stoichiometric amounts of $SrCO_3$ and H_3BO_3 together with a 3 mol% excess of H_3BO_3 to compensate for B_2O_3 evaporation were mixed and ground. The mixtures were heated in an electric furnace in air at 700 °C for 5 h and ground again and reheated at 850 °C for 5 h. The doped amount of Sm (in Sm_2O_3) ions was 2 mol% of Sr^{2+} ions.

The samples were checked with x-ray powder diffraction using the Cu Kα radiation (X'pert MPD, Philips). The resultant XRD patterns were in good agreement with those in JCPDS 15-0801 and 20-1190, respectively. The sample SrB_6O_{10}:Sm, which contained unreduced Sm^{3+} ions, was subsequently irradiated with x-rays for 15 h to reduce the Sm^{3+} ions to Sm^{2+} ions.

Photoluminescence (PL) was measured with a monochromator (Spex 1702) equipped with PMT (Hamamatsu R928) as a detector. 488 nm from an Ar^+ ion laser (Spectra-Physics, BeamLok 2060) was used as the excitation source for PL measurement. For spectral hole burning experiments, an Ar^+ ion laser pumped dye-laser (Coherent, 590) was used as the excitation source and the output power was stabilized with a laser power stabilizer (CRI, LPC) during the excitation and the scanning.

The hole burning experiments were carried out by excitation spectroscopy. The basic principle of excitation spectroscopy is as follows. First, the higher levels of target ions are excited by the site selective excitation method using a tunable light source. After the excitation, the excited electrons decay into the ground state, emitting possible transition lines, which have lower energies than the excitation energy. In this process, if the emission intensity is recorded as a function of the wavelength of an excitation beam, one can get information about the excited bands. Strong emission at a particular excitation wavelength signals that the emitting centre is absorbing strongly at that wavelength. In this way it is possible to determine the shape and position of the absorption bands which excite the emission process.

In this experiment, we excited the $^7F_0 \rightarrow {}^5D_1$ transition bands and monitored the intensity of the $^5D_0 \rightarrow {}^7F_0$ emission for the hole burning experiment. The burning power was 10 W cm^{-2} and the burning time was 10 min.

3. Results and discussion

So far, the structural and optical properties of RE-ion-doped strontium borates have been studied extensively. In much of the literature, it is pointed out that the anion units, BO_3 and
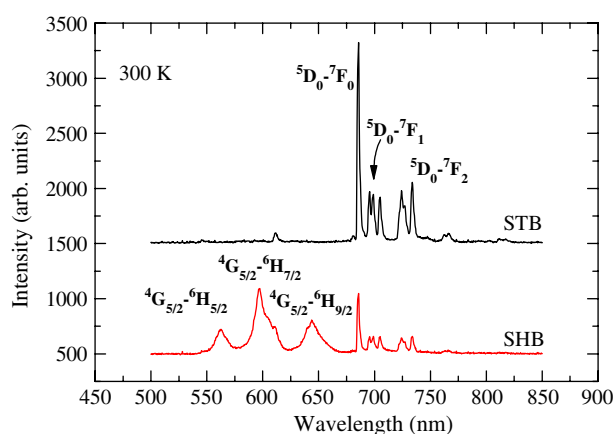
Figure 1. Room temperature PL spectra of Sm-doped strontium borates. STB stands for strontium tetraborate and SHB for strontium hexaborate host.

BO_4, are very important in reduction of RE^{3+} and optical properties of doped ions [9–11]. The basic structures of strontium borates could be expressed as $SrO \cdot nB_2O_3$ [11]. With different n values, different anion units are linked together, forming different networks. The number of triangularly coordinated boron atoms (BO_3) per tetrahedrally coordinated boron atom (BO_4) is equal to $n - 1$. In this study, we prepared two kinds of Sm-doped strontium borates, i.e., SrB_4O_7 (denoted as STB) and SrB_6O_{10} (SHB). According to the facts mentioned above, we have two different samples in which the ratios of anion units, between the numbers of BO_3 and BO_4, are different.

Figure 1 shows the low resolution PL spectra for the two samples STB and SHB. The three broadband emissions in the SHB originate from the transitions $^4G_{5/2}$–$^6H_{5/2}$, $^4G_{5/2}$–$^6H_{7/2}$ and $^4G_{5/2}$–$^6H_{9/2}$ of Sm^{3+} ions, respectively. The other narrow lines in the range 675–750 nm are due to the transitions of $4f^6$ electrons of Sm^{2+} ions. As can be seen in the figure, while almost no Sm^{3+} transitions are observed in the STB spectrum, two kinds of emissions are observed in SHB. This means that the Sm^{3+} ions are well reduced in the matrix SrB_4O_7, but partially reduced in the SrB_6O_{10} host. The reduction of RE ions in strontium borates is explained as follows: in STB, only the BO_4 tetrahedral anion units exist and form a tight three-dimensional network around cations by corner sharing. In this structure, Sm^{2+} ions are completely surrounded by nine oxygen atoms and are hard for oxygen to attack [12, 13]. This is the reason why the Sm ions are easily reduced and stable in the divalent state in the STB host. On the other hand, in SHB, BO_3 triangles and BO_4 tetrahedra co-exist and the number of the BO_3 units is expected to be twice the number of the BO_4 units according to the literature [8, 11]. It was reported that the host structure is less condensed and the Sm–O bond distance is longer with BO_3 units compared to the BO_4 tetrahedral units [9]. This means the Sm–O bond is loose and easily attacked by the oxygen in the BO_3 environment, resulting in hindering the reduction. Thus, we assume the Sm ions surrounded by BO_3 units are hard to reduce in air environment and remain in the trivalent states. The result of partial reduction shown in the spectrum SHB of figure 1 supports this assumption.

We can find some experimental results for x-ray-induced reduction of RE ions in other host material [5]. In this experiment, we also irradiated the SHB with x-rays for 15 h, expecting the reduction of unreduced Sm^{3+} (the x-ray-irradiated SHB is denoted by SHBX throughout the text). As shown in figure 2(a), while the Sm^{3+} emission intensity decreased
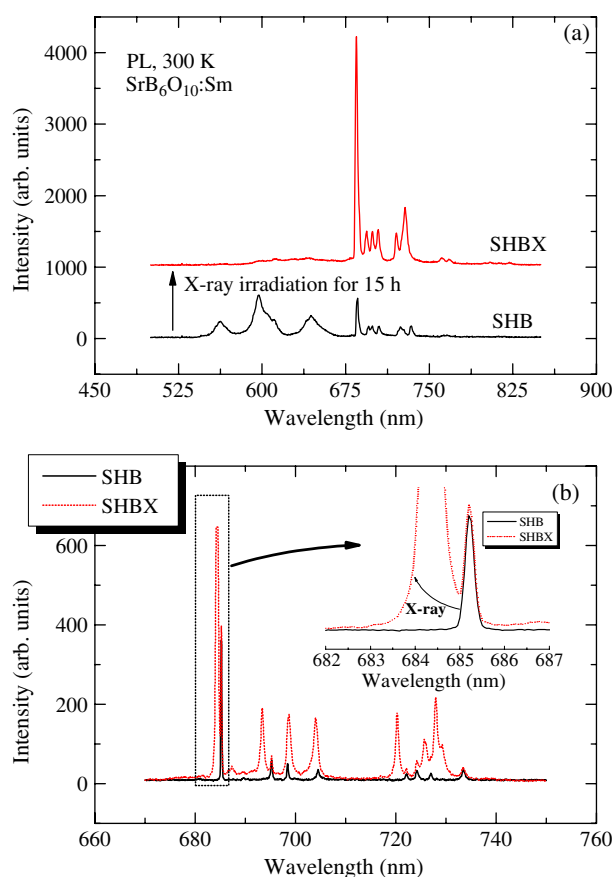
Figure 2. (a) PL spectra of SHB samples before and after x-ray irradiation. (b) High resolution PL spectra of SHB and SHBX. The inset shows the $^5D_0$–$^7F_0$ transitions of Sm^{2+} ions.

after the x-ray irradiation, Sm^{2+} intensity increased significantly. This is apparent evidence for the reduction of Sm^{3+} to Sm^{2+}. To the best of our knowledge, this is the first observation of x-ray-induced reduction in strontium borate host materials.

For a more detailed investigation, high resolution PL spectra were measured in the spectral range 670–750 nm, which corresponds to the region of transitions of Sm^{2+} ions, at room temperature (refer to figure 2). Though it is very weak in intensity compared with that of STB, the spectral shape and peak positions of Sm^{2+} in SHB are exactly the same as those of STB (the high resolution PL spectrum for STB is shown in figure 3). However, after the x-ray irradiation, totally new transition lines were generated at different positions in addition to the pre-existing lines, and the emission intensity overwhelms the pre-existing lines. The inset of figure 2(b) shows the enlarged details of $^5D_0$–$^7F_0$ transitions of Sm^{2+} ions in SHB and SHBX, respectively. The newly generated line after the x-ray irradiation appears at the high energy side (684.4 nm), 9 nm from the pre-existing line (685.3 nm).

Remembering the position 685.3 nm is exactly the same position as $^5D_0$–$^7F_0$ in STB in which only BO_4 tetrahedral units exist, we could deduce that the pre-existing transitions in SHBX originate from the transitions of Sm^{2+} surrounded by BO_4 units. On the other hand, the newly generated lines are presumed to originate from the BO_3 triangle unit environment.
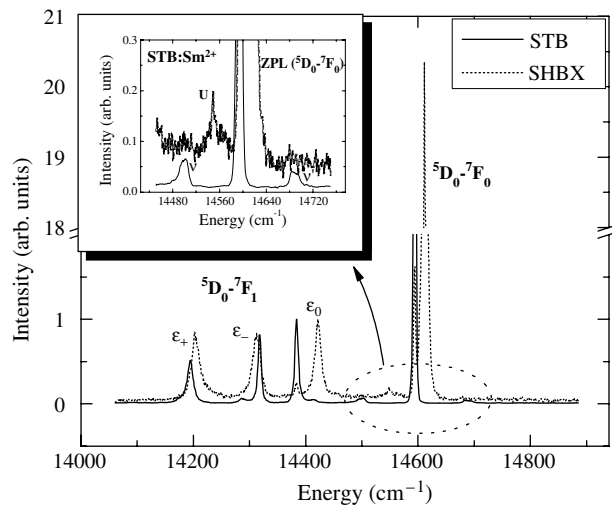
Figure 3. PL spectra of Sm^{2+}-doped STB and SHBX measured at room temperature. The inset shows the phonon side band around the ZPL.

Though some interpretations of the reduction of RE ions by x-ray irradiation were made in other materials, the detailed mechanism of x-ray-induced reduction is still unclear. We assume the reduction mechanism in this material as follows: when Sm ions are doped into the strontium borates, two Sm^{3+} ions substitute three Sr^{2+} ions in order to maintain the charge valence [10, 14]. Hence, a vacancy defect is formed inevitably at the Sr^{2+} site. This vacancy defect has two negative charges due to the absence of the Sr^{2+} ion. Thus, this vacancy site can act as an electron donor by transferring the electrons to Sm^{3+} ions, resulting in the reduction of Sm^{3+}. This process might easily happen in STB because of the short bond distance between Sm–O and stable structures of three-dimensional BO$_4$ units. On the other hand, with BO$_3$ triangle units in the SHB, the Sm–O bond is less tight and the distance is longer compared to the case of STB [9]. Since this might give a higher potential barrier between the defect centre and Sm^{3+}, it needs a high energy for electrons to overcome this potential barrier. We assume the x-ray could give a sufficient energy to electrons by which the electrons could be transferred to the Sm^{3+} ions, resulting in the reduction of Sm^{3+} ions as described in equation (1).

$$2\mathrm{Sm}^{3+} + \mathrm{V}_{\mathrm{Sr}}^{2-} \rightarrow 2\mathrm{Sm}^{2+} + \mathrm{V}_{\mathrm{Sr}} \tag{1}$$

where V$_{\mathrm{Sr}}$ is a vacancy generated by the absence of the Sr^{2+}. In this process, two non-bridging oxygens might be generated which provide the electrons. However, we cannot give apparent experimental evidence related to the assumption in this report. More detailed experimental research is needed.

Figure 3 is high resolution PL spectra of STB and SHBX measured at room temperature. We can see three sharp peaks in the 14 100–14 500 cm^{-1} range. These lines are attributed to the ^{5}D$_0$–^{7}F$_1$ transitions whose degeneracy is completely lifted by the crystal field. ε_0, ε_- and ε_+ correspond to three M_J components of ^{7}F$_{J=1}$, i.e., $M_J = 0, -1, +1$, respectively. Since the degenerated levels of ^{7}F$_1$ spilt into three levels in the site symmetry of C$_s$ or lower, we also assume the site symmetry of Sm^{2+} in these hosts to be C$_s$ as mentioned in the other literature [12]. The energy differences among these three lines can be characterized by the crystal field parameters. We calculated the crystal field parameters roughly according to the literature [15, 16] and the results are summarized in table 1.

Table 1. Energy positions of $^5D_0$–$^7F_1$ transitions and calculated crystal field parameters.

	Energy (cm^{-1})			Crystal field parameters	
	ε_0	ε_-	ε_+	B_{20}	B_{22}
STB	14 383	14 318	14 194	−423	253
SHBX	14 422	14 312	14 203	−548	222

It is known that, in C_{2v}, C_2 and C_s symmetries, the wavefunction describing the $M_J = 0$ component (ε_0) has a large electron distribution in the z axis and the other components ($\varepsilon_\pm$) along the x–y plane. Since the energy of the ε_0 component is directly proportional to the second order crystal field parameter B_{20}, the large value of $|B_{20}|$ means strong influences of crystal fields in the z direction. The result of table 1 shows that the Sm^{2+} ions doped in SHBX are more strongly influenced by the crystal field in the z direction compared with the case in STB. Though the crystallographic structure of SHB is not yet clear, the structure of STB is well known. In STB, Sr^{2+} (and Sm^{2+}) ions are surrounded by nine oxygen ions. Eight of the nine coordinating oxygen atoms are approximately on the corners of the cube, and the ninth is on one of the tetragonal axes [13, 17, 18]. We assume the large difference of $|B_{20}|$ values in the two samples (423 and 548) is due to the different atomic distances between the ninth oxygen, which is assumed to be on the z axis, and the Sm^{2+} ion.

The inset of figure 3 shows the high resolution PL spectra around the $^5D_0$–$^7F_0$ transitions of Sm^{2+} ions. The centre line is called the zero-phonon line (ZPL) and the two side bands (denoted ν and ν', respectively) are known as the phonon side bands, and are the result of the interaction between 4f electrons of the Sm^{2+} ions and vibrational modes of the lattice. The lines ν and ν' can be attributed to the transitions $|^5D_0, n\rangle \rightarrow |^7F_0, n + 1\rangle$ and $|^5D_0, n + 1\rangle \rightarrow |^7F_0, n\rangle$, respectively, where n is the quantum number of the phonon mode [19]. The electron–phonon coupling strength is described by the Huang–Rhys factor S. The measured energy displacement with the ZPL, which is the phonon energy, is about 94 cm^{-1} and the calculated Huang–Rhys factor is $S = 0.003$. On the other hand, we could hardly observe the phonon side band in SHBX and this also means the environments of Sm^{2+} ions in the two matrices are very different. We can see a sharp and weak peak U at 14 549 cm^{-1}. Though the origin of the peak is unclear at the moment, we assume the peak is attributed to the $^5D_0$–$^7F_0$ transitions of Sm^{2+} ions, which reside at different crystallographic sites. We can find similar results in other literature [19, 20].

Figure 4 shows the results of spectral hole burning experiments conducted for the two samples of STB and SHBX at room temperature. The curves R and B are the excitation spectra before and after the burning, respectively. The hole signal H is obtained by subtracting the intensity of B from that of R. The excitation spectrum was measured by monitoring the fluorescence of $^5D_0$–$^7F_0$, while scanning the $^7F_0$–$^5D_1$ band with a tunable dye laser. The $^7F_0$–$^5D_1$ band is composed of three transition lines which originated from the energy splitting of the $^5D_1$ level by the crystal field. The peaks denoted by $\delta_{0,-,+}$ are attributed to the transitions between the $M_J = 0, -1, +1$ sub-levels of $^5D_1$ and the $^7F_0$ ground state. The spectral shape is well fitted by the Lorentzian function and the line widths in STB and SHBX are 2.1 and 4.3 cm^{-1}, respectively. In general, the inhomogeneous line broadening is induced by the distribution of local environment and the spectral shape is expressed by the Gaussian function. Thus, these results suggest that almost no inhomogeneous line broadening occurs in these samples.

Curve H is the hole spectrum. The hole was burnt only on the peak of the δ_0 line in each sample. We can clearly see the holes in the other two lines, δ_- and δ_+. This means that the
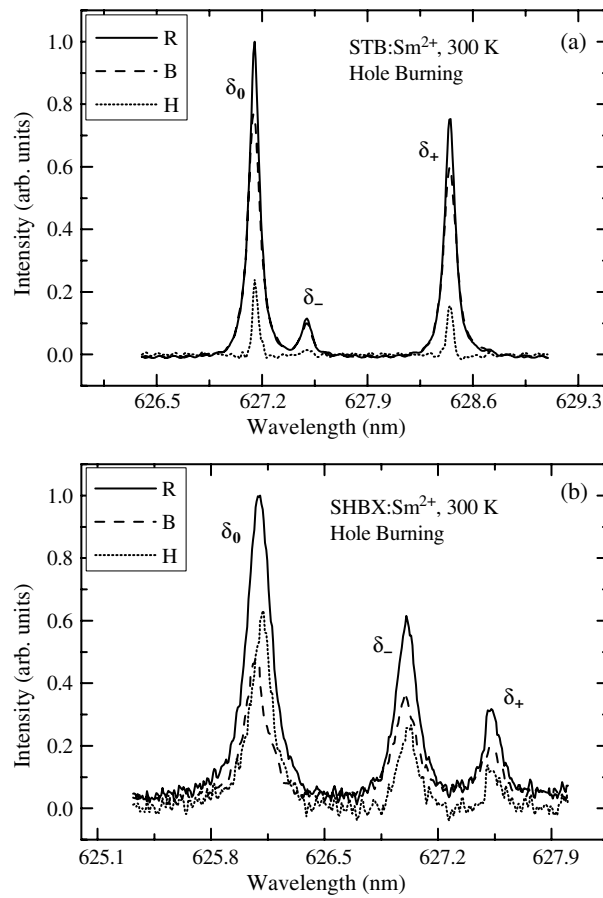
Figure 4. Room temperature hole burning of Sm^{2+}-doped (a) STB and (b) SHBX.

three transition lines originate from the ions, which occupy the same crystallographic sites. There are two possible mechanisms in the permanent spectral hole burning. One is that the Sm^{3+} ion acts as an electron trap in the hole burning. In this case, the excited Sm^{2+} ions are changed into Sm^{3+} ions and the electrons extracted from the burnt Sm^{2+} ions are trapped on the other Sm^{3+} ions. Consequently, the electron captured Sm^{3+} ions are changed into Sm^{2+} ions, resulting in the increase of Sm^{2+} emission in the other regions beside the burning position, which induce the anti-holes. When the other kinds of trap sites are involved in the hole burning we cannot see the anti-holes. As we can see in figure 4, no anti-hole structures were observed in this experiment and this means that the Sm^{3+} ions are not the main electron traps in both samples used in this experiment.

24% and 63% hole depths were measured for the 10 min burning with burning power of 10 W cm^{-2} in the STB and SHBX, respectively. So far, we can hardly find any results related to the hole burning experiment in the strontium borates. Mikhail *et al* observed the spectral hole in the Sm^{2+}-doped SrB_4O_7 single crystal at 80 K [18]. Though our experimental conditions are different from those of Mikhail *et al*, these values of 24% and 63% measured at room temperatures are much higher than their result of 5.25%. To the best of our knowledge, this is the first observation of room temperature hole burning in Sm^{2+}-doped strontium borates.

We also conducted the hole burning experiment with x-ray-irradiated STB and found the hole depth to be 15%, which is a smaller value compared to the result of STB itself. Similar experiments were conducted by Nogami *et al* for the Sm^{2+}-doped $Al_2O_3 \cdot SiO_2$ glasses [5]. In the literature, they reported that the hole burning rate and hole depth significantly increased after x-ray irradiation. In the process, the defect centres generated by the x-ray irradiation played an important role as electron traps. However, our result of x-ray irradiated STB shows contrary results, i.e., hole depth decreased after the x-ray irradiation.

Although the hole burning efficiencies are measured with high value, especially in SHBX, the detailed mechanisms are unclear at the moment. We presume the hole burning is the reverse process of reduction. That is, the electrons excited by the burning light are transferred again to the oxygen ions, forming the negatively charged vacancies V_{Sr}^{2-} that are described in equation (1).

4. Conclusions

Sm^{3+} ions doped in strontium hexaborate (SHB) were well reduced to Sm^{2+} ions by x-ray irradiation. After the x-ray irradiation, the Sm^{3+} ions surrounded by the BO_3 triangle units were easily reduced to Sm^{2+} ions and are assumed to occupy different crystallographic sites from the case of the ions surrounded by the BO_4 tetrahedral units. Spectral holes were observed at room temperature in both samples of STB and SHBX. The measured hole depths were 24% and 63% in STB and SHBX, respectively. As a result, we could obtain an effective and novel hole burning material based on the Sm-doped strontium borates with x-ray-induced reduction.

Acknowledgment

References

[1]   Hirao K, Todoroki S, Cho D H and Soga N 1993 *Opt. Lett.* **18** 1586
[2]   Kurita A, Kushida T, Izumitani T and Matsukawa M 1994 *Opt. Lett.* **19** 314
[3]   Nogami M 1999 *J. Non-Cryst. Solids* **259** 170
[4]   Jaaniso R and Bill H 1991 *Europhys. Lett.* **16** 569
[5]   Nogami M and Suzuki K 2002 *Adv. Mater.* **14** 923
[6]   Qiu J, Miura K, Suzuki T, Mitsuyu T and Hirao K 1999 *Appl. Phys. Lett.* **74** 10
[7]   Pei Z and Su Q 1993 *J. Alloys Compounds* **198** 51
[8]   Machida K, Adachi G and Shiokawa J 1979 *J. Lumin.* **21** 101
[9]   Liang H, Zeng Q, Hu T, Wang S and Su Q 2003 *Solid State Sci.* **5** 465
[10] Zeng Q, Pei Z, Wang S and Su Q 1998 *J. Alloys Compounds* **275** 238
[11] Block S and Piermarim G 1964 *Phys. Chem. Glasses* **5** 138
[12] Perloff A and Block S 1966 *Acta Crystallogr.* **20** 274
[13] Pan F, Shen G, Wang R, Wang X and Shen D 2002 *J. Cryst. Growth* **241** 108
[14] Pei Z, Zeng Q and Su Q 2000 *J. Phys. Chem. Solids* **61** 9
[15] Nishimura G and Kushida T 1988 *Phys. Rev.* B **37** 9075
[16] Tanaka M, Nishimura G and Kushida T 1994 *Phys. Rev.* B **49** 16917
[17] Blass G, Dirksen G J and Meijerink A 1990 *Chem. Phys. Lett.* **167** 41
[18] Mikhail P, Hulliger J, Schnieper M and ans Bill H 2000 *J. Mater. Chem.* **10** 987
[19] Zeng Q, Pei Z, Su Q and Huang S 1999 *Phys. Status Solidi* b **212** 207
[20] Zeng Q, Pei Z, Wang S and Su Q 1999 *Spectrosc. Lett.* **32** 895