Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Non-Crystalline Solids 348 (2004) 103–107
JOURNAL OF NON-CRYSTALLINE SOLIDS
www.elsevier.com/locate/jnoncrysol

GeO_2–PbO–Bi_2O_3 glasses doped with Yb^{3+} for laser applications

L.R.P. Kassab [a,*], L.C. Courrol [a], V.D.D. Cacho [c], S.H. Tatumi [a], N.U. Wetter [b], L. Gomes [b], N.I. Morimoto [c]

[a] *Laboratório de Vidros e Datação, FATEC-SP, Praça Cel. Fernando Prestes 30, CEP 01124-060, São Paulo, SP, Brazil*
[b] *Centro de Lasers e Aplicações, IPEN-CNEN, São Paulo, SP, Brasil*
[c] *LSI, Departameto de Engenharia de Sistemas Eletrônicos, EPUSP, São Paulo, SP, Brasil*

Abstract

Glasses of heavy metal oxide GeO_2–PbO–Bi_2O_3 doped with different concentrations of Yb^{3+} were prepared as materials for IR emission. Absorption and fluorescence emission spectra were measured. The spectroscopic properties and laser parameters are calculated; the disagreement between the reciprocity method and Fuchtbauer–Ladenburg formula in calculations of Yb^{3+} emission cross-sections is discussed using the radiation trapping effect. GeO_2–PbO–Bi_2O_3 glass doped with Yb^{3+} is a promising material for laser action at 1021 nm, with properties similar to other known glasses (phosphate and tellurite laser glasses) used as active laser media; the high absorption cross-section (of 1.5×10^{-20} cm^2) and the large emission bandwidth (of 70 nm) are properties appropriate for short pulse generation.

PACS: 42.70.−a

1. Introduction

The heavy metal oxide glasses [1,2] have attracted interest for optoelectronics and photonics applications because of their optical properties such as refractive indices, optical non-linearities and infrared transmittance up to 8 μm providing the possibility to develop more efficient lasers and fiber optic amplifiers at longer wavelengths than available from other oxide glasses. The broad infrared transmission is a consequence of the small field strengths and relatively large masses of the components of these glasses that generally contain more than 50% of heavy metal oxides, such as PbO and Bi_2O_3 [3,4]. In these glasses the usual vitrifying elements are oxides of germanium, gallium and tellurium [5]. In this work we report the optical properties of Yb^{3+} ions in GeO_2–PbO–Bi_2O_3 glasses (produced at the Laboratory of Glasses and Datation at FATEC-SP). The emission bands of Yb^{3+} doped glasses generate tunable laser emission, as well as ultra-short pulse (of about femtoseconds) and the location of the absorption band (900–1000 nm) is suited for pumping with na InGaAs laser diode. To our knowledge there are no studies of the optical property of Yb^{3+} in these glasses. The literature recently presented the optical properties of Nd^{3+} [6,7] in binary and ternary glasses based on GeO_2, PbO and Bi_2O_3. GeO_2–PbO–Bi_2O_3 glasses have a transmission window from 400 nm up to 4.5 μm and refractive index = 2.0; recently Miller et al. observed that glasses in this system are potential candidates for fiber optic amplifiers and oscillators [8,9].

In this work Yb^{3+} spectroscopic properties are investigated in a ternary composition of GeO_2–PbO–Bi_2O_3 glasses (GPB1) suggested by Balda et al. [7]; the laser parameters I_{min} (minimum pump intensity), I_{sat} (pump saturation intensity) and β_{min} (minimum fraction of Yb ions that are excited to balance the laser gain) are

* Corresponding author.
E-mail address: kassablm@osite.com.br (L.R.P. Kassab).

0022-3093/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2004.08.244

calculated and the effect of radiation trapping is discussed [10].

2. Experiment

Batches of 12 g were prepared by mixing 99.99% elements. Different concentrations of Yb^{3+} (shown in Table 1) were added to the ternary lead bismuth gallate composition ($62.5GeO_2$–$12.5PbO$–$25.0Bi_2O_3$ (mol%)) or GPB1 suggested by Balda et al. [7]. The powders were melted in an alumina crucible (with impurities of 0.01%) at 1050 °C, for 1 h, quenched in heated brass molds, in air, annealed for 1 h at 420 °C (considering the transition temperature) and then cooled to room temperature, inside the furnace. Samples were examined through an optical microscope to confirm the complete melting of rare-earths. The samples produced are transparent, homogeneous and stable against crystallization. For concentrations greater than $(6.9 \pm 0.1) \times 10^{20}$ ions/cm^3 of Yb^{3+} we observe a loss of transparency. Therefore the solubility limit of Yb^{3+} in this heavy metal oxide glass, considering the current melting scheme employed, is approximately $(6.9 \pm 0.1) \times 10^{20}$ ions/cm^3. Finally the samples were polished for absorption, emission and lifetime measurements. The absorption spectra were measured using a spectrometer (Carry 500), at room temperature, in the range of 900–1200 nm. Emission measurements were performed by optically pumping the samples with an AlGaAs laser diode (Optopower A020) of 968 nm; the emission was analyzed with monochrometer and detected by a Ge detector. Front surface exciting technique, perpendicular to the sample thickness and close to its edge was utilized to minimize reabsorption due to radiation trapping [10]. Errors in these measurements are estimated to be ±5%, based on the signal to noise ratio. The lifetimes of the excited Yb^{3+} ions were measured using pulsed laser excitation (4 ns) from an Optical Parametric Oscillator (OPO from Opotek) pumped by a frequency doubled Nd:YAG laser (Quantel) and a InSb detector (Judson) with appropriate emission filter. Errors are also estimated to be of ±5%. Because of the spectral overlap of the emission and absorption bands of Yb^{3+}, radiation trapping [10] makes the measured lifetime longer than that of a single isolated ion. To reduce the effect of the radiation trapping due to self absorption, the samples used in the lifetime measurements had thickness of 0.6 mm [11].

Table 1
Spectroscopic properties and laser performance parameter of GPB1 glasses doped with different concentrations of Yb^{3+}

Yb^{3+} (10^{20} ions/cm^3)	σ_{abs} (λ_p) (10^{-20} cm^2)	τ_f (±5%ms)	I_{min} (kW/cm^2)
0.23 ± 0.01	1.8 ± 0.1	0.44	2.1 ± 0.4
0.58 ± 0.01	1.6 ± 0.1	0.47	2.2 ± 0.5
1.16 ± 0.02	1.5 ± 0.1	0.54	2.0 ± 0.4
2.31 ± 0.05	1.5 ± 0.1	0.54	2.0 ± 0.4
4.63 ± 0.09	1.5 ± 0.1	0.50	2.2 ± 0.5

3. Results

The two usual methods to obtain the emission cross-section of Yb^{3+}:$^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition are the reciprocity method (RE) [12] and the Fuchtbauer–Ladenburg (F–L) formula [13]. The second one requires knowledge of the radiative lifetime and of the emission line shape as follows:

$$A_R = \frac{8\pi c n^2 (2J'+1)}{\lambda_p^4 (2J+1)\rho} \int k(\lambda) d\lambda \quad (1)$$

$$\sigma_{em}(\lambda) = \frac{\lambda^4 g(\lambda) A_R}{8\pi n^2 c} \quad (2)$$

where A_R represents the spontaneous emission probability, c the velocity of light, n the refractive index, λ_p the absorption peak wavelength (977 nm), ρ the concentration of Yb^{3+} ions, $k(\lambda)$ the absorption coefficient, J and J' the total momentum for the upper and lower levels and $g(\lambda)$ the normalized line shape function of the measured fluorescence transition of Yb^{3+}. However, accurate experimental determination of the fluorescence spectrum, easily affected by radiation trapping, is difficult, as the emission line width increases. The reciprocity method avoids this effect of radiation trapping because it is obtained from the absorption cross-section spectrum (σ_{abs}) using the relation given by [12]:

$$\sigma_{em}(\lambda) = \sigma_{abs}(\lambda) \frac{Z_l}{Z_u} \exp\left(\frac{E_{zl} - hc\lambda^{-1}}{kT}\right) \quad (3)$$

where k and E_{zl} represent Boltzman's constant and the zero line energy that is defined as the energy separation between the lowest components of the upper and lower states, respectively; in the high temperature limit, the ratio of the partition functions (Z_l/Z_u) simply becomes the degeneracy weighting of the two states. Fig. 1 presents the emission and absorption cross-sections for Yb^{3+} doped GPB1 glasses; the emission cross-sections are calculated using the reciprocity method (RE) and the Fuchtbauer–Ladenburg (F–L) formula. Based on cumulative errors associated with the spectra, and energy level assignments we estimate that the emission cross-sections are accurate to ±18% in F–L method and to ±9% in RE method. However the discrepancies of the emission cross-sections calculated by RE and F–L are mainly due to the radiation trapping [11]. Table 1 shows some of the spectroscopic properties; τ_f is the fluorescence lifetime obtained fitting the measured lifetime to single exponential and σ_{abs} (λ_p) the absorption cross-section at the absorption peak wavelength (λ_p = 977 nm); I_{min}

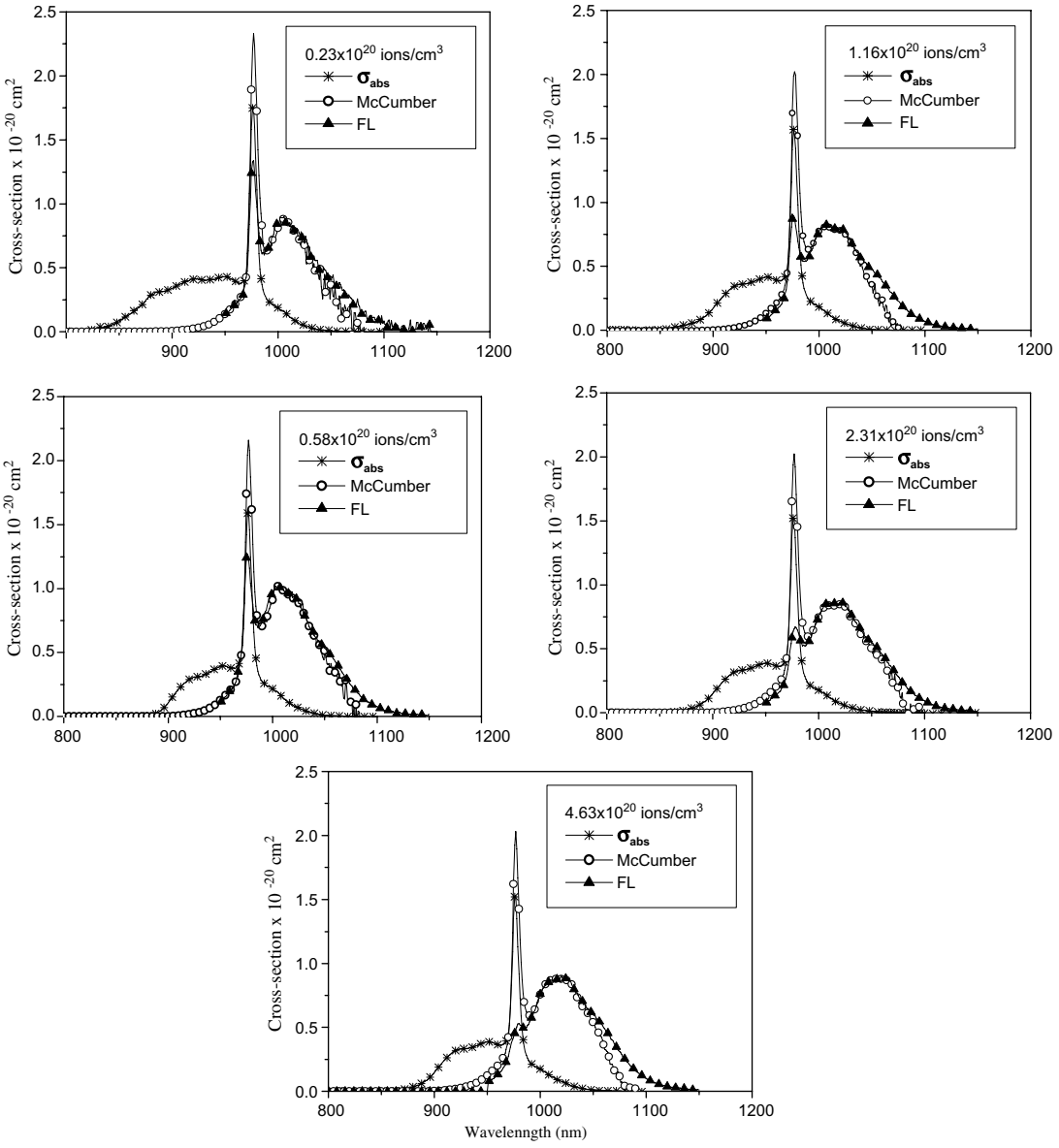

Fig. 1. Absorption and emission cross-sections spectra (calculated using RE and F–L methods) for GPB1 glasses doped with different concentrations of Yb^{3+}.

is a laser parameter that is the minimum pump intensity which is a measure of the ease of pumping the laser material to get laser action [14]:

$$I_{\min} = \beta_{\min} I_{\text{sat}}, \tag{4}$$

where

$$\beta_{\min} = \frac{\sigma_{\text{abs}}(\lambda_{\text{ext}})}{\sigma_{\text{em}}(\lambda_{\text{ext}}) + \sigma_{\text{abs}}(\lambda_{\text{ext}})}, \tag{5}$$

$$I_{\text{sat}} = \frac{hc}{\lambda_{\text{p}} \tau_{\text{f}} \sigma_{\text{abs}}(\lambda_{\text{p}})}. \tag{6}$$

In the equation above, $\sigma_{\text{em}}(\lambda_{\text{ext}})$ and $\sigma_{\text{abs}}(\lambda_{\text{ext}})$ are, respectively, the emission and the absorption cross-sections at the extraction wavelength ($\lambda_{\text{ext}} = 1021$ nm); this is the wavelength for which $I_{\min}$ is smallest. We remark that, at 1021 nm, the absorption cross-section is 10 times smaller than the one at 1007 nm (this is the wavelength that corresponds to the emission cross-section of the secondary peak). Concerning the emission cross-sections, the differences between them, at 1021 nm and 1007 nm, are within the experimental errors. So, 1021 nm is chosen as the extraction wavelength for the calculation of $I_{\min}$.

I_{sat} is the pump saturation intensity that characterizes the pumping dynamics and the $\beta_{\min}$ parameter is defined as the minimum fraction of Yb ions that must be excited to balance the gain exactly with the ground-state absorption at λ_{ext}. We remark that at 7.5 W of cw diode pump power there was no visible fracture of the samples, even in the absence of cooling.

4. Discussion

From Fig. 1 we observe a good agreement (to within ±13%) between RE and F-L methods at the secondary peak. However there are differences in the emission cross-sections of the primary peak (σ_{emp} at 977 nm) and the ratio of the secondary (at 1007 nm) to primary peak emission cross-section ($\sigma_{ems}/\sigma_{emp}$). These results are presented in Table 2. If $(\sigma_{emp})_{RE}$ is the emission cross-section calculated by reciprocity method and $(\sigma_{emp})_{FL}$ the one calculated by F–L equation, from Table 2 we observe: $(\sigma_{emp})_{RE}$ is larger than $(\sigma_{emp})_{FL}$; considering the ratio of the secondary to primary peak, $(\sigma_{ems}/\sigma_{emp})_{FL} > (\sigma_{ems}/\sigma_{emp})_{RE}$ and $(\sigma_{ems}/\sigma_{emp})_{RE}$ remains approximately constant whereas $(\sigma_{ems}/\sigma_{emp})_{FL}$ increases with Yb^{3+} concentration. These facts can be attributed to radiation trapping, as reported by Zhang and Hu [15] in Yb tetraphosphate glasses; radiation trapping increases with sample thickness, refractive index and concentration. As shown in Fig. 1 there is a spectral trap in the primary emission peak (at 977 nm) and this explains the greater differences between FL and RE methods at this peak $(\sigma_{emp})_{RE} > (\sigma_{emp})_{FL}$ in Table 2; the strong fluorescence trapping decreases the measured emission at 977 nm and increases the fluorescence effective linewidth ($\Delta\lambda_{eff}$), as the bands are normally broadened ($\Delta\lambda_{eff} = 70$ nm up to 1.16×10^{20} ions/cm^3 of Yb^{3+} and $\delta\lambda_{eff} = 84$ nm, for larger doping levels). With the increase of Yb^{3+} concentration, the fluorescence trapping increases, the fluorescence peak at 977 nm is completely reabsorbed and disappears, whereas the secondary one increases and the emission line broadening occurs: consequently $(\sigma_{ems}/\sigma_{emp})_{FL}$ increases. This explains the disagreement (Fig. 1) between the two methods at wavelengths greater than 1030 nm. Zhang and Hu [15] proposed that radiation trapping can be evaluated by the parameter rtc (radiation trapping coefficient) also used recently by Bell et al. [16] and defined as follows: $((\sigma_{ems}/\sigma_{emp})_{FL} - (\sigma_{ems}/\sigma_{emp})_{RE})/(\sigma_{ems}/\sigma_{emp})_{RE}$. The results of rtc calculations are presented in Table 2. Hence radiation trapping depends on concentration and occurs even for smaller doping levels; similar results for the rtc parameter were reported in Yb tetraphosphate glasses [15] and in phosphate glasses [16]. Radiation trapping also increases with the thickness; for example Dai et al. [17] observed that the measured fluorescence lifetime increases 30% when the thickness increased from 0.3 mm to 4 mm, even at Yb^{3+} concentration of 0.2 mol%. For doping levels of 6 mol% the increase is of about 44%. In our case the samples were 0.6 mm thick; even though we observe that the measured fluorescence lifetimes tend to increase with Yb^{3+} concentration (Table 1) and in most cases are longer than the radiative lifetime (0.44 ms), calculated using Eq. (1); these facts also indicate the presence of some radiation trapping [16,18]. To minimize the radiation trapping effect other studies are being performed in GPB1 glasses doped with Yb^{3+}.

From the point of view of laser operation, it is generally desirable for the emission cross-section to be as large as possible for greater gain, for the fluorescence lifetime to be long to permit greater pulsed power, and for the absorption cross-section at the pump wavelength to be as large as possible to allow for efficient diode pumping; these considerations indicate that laser parameters should be as small as possible. We observe that Yb^{3+} doped GPB1 glasses have a larger absorption cross-section, at 977 nm, and that the laser parameter I_{min} is within the acceptable limits, always less than 4.5 kW/cm^2 [14]. For comparison we present, in Table 3, the spectroscopic properties and the I_{min} parameter of some laser glasses

Table 2
Comparison between RE and F–L equation in calculations of Yb^{3+} emission cross-sections for GPB1 glasses; rtc = $((\sigma_{ems}/\sigma_{emp})_{FL} - (\sigma_{ems}/\sigma_{emp})_{RE})/(\sigma_{ems}/\sigma_{emp})_{RE}$. (radiation trapping coefficient)

Yb^{3+} (10^{20} ions/cm^3)	σ_{emp} ($\times 10^{-20}$ cm^2)		σ_{ems} ($\times 10^{-20}$ cm^2)		$\sigma_{ems}/\sigma_{emp}$		rtc
	RE	FL	RE	FL	RE	FL	
0.23 ± 0.01	2.3 ± 0.2	1.3 ± 0.2	0.9 ± 0.1	0.9 ± 0.2	0.4 ± 0.2	0.7 ± 0.3	0.8
0.58 ± 0.01	2.2 ± 0.2	1.3 ± 0.2	1.0 ± 0.1	1.0 ± 0.2	0.5 ± 0.2	0.8 ± 0.3	0.6
1.16 ± 0.02	2.0 ± 0.2	0.9 ± 0.2	0.8 ± 0.1	0.8 ± 0.2	0.4 ± 0.2	0.9 ± 0.3	1.3
2.31 ± 0.05	2.0 ± 0.2	0.7 ± 0.1	0.8 ± 0.1	0.9 ± 0.2	0.4 ± 0.2	1.3 ± 0.3	2.3
4.63 ± 0.09	2.0 ± 0.2	0.5 ± 0.1	0.9 ± 0.1	0.9 ± 0.2	0.5 ± 0.2	1.8 ± 0.3	2.6

Table 3
Spectroscopic properties and the I_{min} parameter of Yb^{3+} ion in some laser glasses, in the YAG laser crystal and in the GPB1 glass, doped with 1.16×10^{20} ions/cm^3 of Yb^{3+}

Materials	σ_{em} (10^{-20} cm^2)	λ_{ext} (nm)	I_{min} (kW/cm^2)	σ_{abs} (λ_p) (10^{-20} cm^2)	τ_f (ms)
QX [19]	0.7	1018	1.8	0.5	2.00
FP [20]	0.5	1020	0.8	0.4	1.20
YTG [21]	2.4	1024	0.8	1.6	0.90
YAG [14]	2.0	1031	1.5	0.8	1.08
GPB1	0.8	1021	2.0	1.5	0.54

[19–21] and the YAG laser crystal [14], together with the GPB1 glass, doped with 1.16×10^{20} ions/cm^3 of Yb^{3+}; it has an emission cross-section larger than Yb:QX (a commercial phosphate laser glass from Kigre Incorp) [19] and FP glasses [20] and an absorption cross-section, at 977 nm, comparable to Yb:YTG, a tellurite laser glass [21]; the fluorescence lifetime is, however, the smallest. $I_{min} = (2.0 \pm 0.4)$ kW/cm^2 indicates the ease of pumping the material to get laser action.

5. Conclusion

The emission cross-sections were calculated using RE and F–L method and agreement between them was observed at the secondary peak; the discrepancies were mainly due to radiation trapping. GPB1 glasses doped with Yb^{3+} have spectroscopic properties suitable for laser action at 1021 nm, comparable to other known laser glasses used as active media: for 1.16×10^{20} ions/cm^3 of Yb^{3+} the absorption cross-section, at 977 nm, is of 1.5×10^{-20} cm^2, the emission cross-section, at 1021 nm, is of $(0.8 \pm 0.2) \times 10^{-20}$ cm^2 and the possibility of getting laser action is revealed by $I_{min} = 2.0$ kw/cm^2. The large fluorescence effective linewidth of 70 nm, as well as the absorption cross-section are important features for short pulse generation.

Acknowledgment

We would thank the support from CNPQ and FAPESP.

References

[1] W.H. Dumbaugh, Phys. Chem. Glasses 27 (1986) 119.
[2] W.H. Dumbaugh, Phys. Chem. Glasses 27 (1978) 121.
[3] D. Coleman, S.D. Kackson, et al., J. Opt. Soc. Am. B 19 (2002) 1982.
[4] J. Heo, C.G. Kim, Y.S. Kim, J. Am. Ceram. Soc. 78 (5) (1995) 1285.
[5] D. Lezal, J. Pedlikova, P. Kostka, J. Bludska, M. Poulain, J. Zavadil, J. Non-Cryst. Solids 284 (2001) 288.
[6] R. Balda, J. Fernández, M. Sanz, A. Oleaga, A. de Pablos, J.M.F. Navarro, Journal of Non-Crystalline Solids 256–257 (1999) 271.
[7] R. Balda, J. Fernández, M. Sanz, et al., Phys. Rev. 61 (2000) 3384.
[8] A. Miller, K. Nassau, K.B. Lyons, et al., J. Non-Cryst. Solids 99 (1988) 289.
[9] J.E. Canale, R.A. Condrate, K. Nassau, et al., J. Ca. Ceram 55 (1986) 50.
[10] D.S. Sumida, T.Y. Fan, Opt. Lett. 19 (1994) 1343.
[11] M.J. Weber, J.E. Lynch, et al., IEEE J. Quantum Electron. 19 (1983) 1600.
[12] D.E. McCumber, Phys. Rev. 136 (1964) A954.
[13] P.F. Moulton, J. Opt. Soc. Am. B 3 (1986) 125.
[14] L.D. Deloach, S.A. Payne, L. Smith, W.L. Kway, W.F. Krupke, J. Opt. Soc. Am. B 11 (1994) 269.
[15] L. Zhang, H. Hu, J. Non-Cryst. Solids 292 (2001) 108.
[16] M.J.V. Bell, W.G. Quirino, S.L. Oliveira, D.F. de Sousa, L.A.O. Nunes, J. Phys.: Condens. Matter 15 (2003) 4877.
[17] S. Dai, J. Yang, L. Wen, L. Hu, Z. Jiang, J. Luminescence 104 (2003) 55.
[18] H. Yin, P. Deng, J. Zhang, F. Gan, J. Non-Cryst. Solids 210 (1997) 243.
[19] R. Koch et al., Opt. Commun. 134 (1997) 175.
[20] V. Petrov, U. Griebner, D. Ehrt, W. Seeber, Opt. Lett. 22 (1997) 408.
[21] C. Jiang, F. Gan, J. Zhang, P. Deng, G. Huang, Mater. Lett. 41 (1999) 209.