ELSEVIER

# Long lasting phosphorescent properties of Ti doped ZrO$_2$

Yan Cong[a,b], Bin Li[a,*], Bingfu Lei[a,b], Wenlian Li[a]

[a]*Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics,*
*Chinese Academy of Sciences, Changchun 130033, PR China*
[b]*Graduate School of the Chinese Academy of Sciences, Chinese Academy of Sciences, Beijing 100039, PR China*

## Abstract

A novel long-lasting afterglow phosphor ZrO$_2$:Ti is prepared by the conventional solid-stated method and their luminescent properties are investigated. A bluish white strong and broad emissive band, which is attributed to originate from the recombination of electrons trapped by F$^+$ centers and the holes created in Valence band, is observed under 254 nm UV irradiation. The identical color long afterglow, which lasts about 1 h, is found in the ZrO$_2$:Ti phosphor after removing the 254 nm UV light. The mechanism of the long lasting phosphorescence (LLP) has been discussed based on the thermoluminescence (TL) results. The replacement of Zr by Ti produces more anion vacancies, resulting in the enhanced photoluminescence (PL) and LLP of ZrO$_2$:Ti sample. These results indicate that ZrO$_2$:Ti phosphor has potential promising applications.
© 2007 Elsevier B.V. All rights reserved.

*Keywords:* ZrO$_2$; Long-lasting phosphor; Titanium ions

## 1. Introduction

LLP phosphor is a kind of energy-storing material which can light up for a long time in the darkness after irradiation with sunlight or artificial light. Due to this special property, they are widely used in lots of areas, such as emergent lighting, traffic signs, multidimensional optical memory, and luminous paint, etc [1,2]. The beginning study on the LLP materials was focused on sulfide phosphors. However, some of them are extremely sensitive to moisture and luminescent intensity can not meet requirement of practical applications. To overcome above problems, the interest of researchers was switched to rare earth ion doped alkali earth aluminates from alkali earth sulfides [3,4]. This kind of materials has better formability and longer persistent time compared to sulfide phosphors. Up to date, the most efficient LLP phosphors are still based on alkali earth aluminates. In recent years, many new phosphors based on different hosts are reported and their mechanisms are discussed [5–8]. But the progress in developing the LLP phosphors with excellent optical properties is still slow due to the lack of the mechanisms of long afterglow.

Metal oxide-based materials have superior electrical, chemical and mechanical characteristics. They have demonstrated preferable choice for host materials [9–11]. Among them, ZrO$_2$ has attracted special attention because of its potential advantages such as chemical stability which makes them promising candidates for host materials, and related studies have been reported [11–13]. Recently, there are several reports on mechano-luminescence from stress-activated ZrO$_2$:Ti, and intense visible light and afterglow were observed [14]. In this paper, we present a Ti doped ZrO$_2$ phosphor prepared by a traditional solid-state reaction method, and a bluish white afterglow was observed. Luminescent studies provide useful information about the electronic excitations and defects in the sample. Based on the research results, we also try to discuss the mechanisms of long afterglow.

## 2. Experiment

### 2.1. Sample Preparation

The powder samples were prepared using the traditional solid-state reaction method. Analytical grade ZrO$_2$ and TiO$_2$ were used as starting materials. Those mixed powder materials were homogenized thoroughly ground with agate

---

*Corresponding author. Tel.: +86 431 6176935; fax: +86 431 6176935.
E-mail address:* lib020@ciomp.ac.cn (B. Li).

pestle in an agate mortar, and then sintered at 1250 °C for 3 h in an air atmosphere and in a reducing atmosphere, respectively. The $TiO_2$ dopant level is from 0 mol% to 0.5 mol%.

## 2.2. Measurements

The emission and excitation spectra were measured on a Hitachi F-4500 fluorescence spectrophotometer equipped with a 150 W Xenon lamp as the excitation source. The afterglow emission spectra and afterglow intensity decay curves were measured on the same Hitachi F-4500 fluorescence spectrophotometer. All the samples were exposed to 254 nm light for 5 min before the measurement. The thermoluminescence (TL) spectra were measured on FJ-427A TL meter (Beijing Nuclear Instrument Factory). Before measuring, the powder samples were exposed for 1 min to standard UV lamp peaking at 254 nm, then the radiation source was removed and the heating rate was fixed at 2 °K/s. All measurements were carried out at room temperature except for the TL spectrum.

## 3. Results and discussions

### 3.1. PL properties of Ti doped ZrO2 and pure ZrO2

Pure $ZrO_2$ and Ti doped $ZrO_2$ was obtained by sintering at 1250 °C for 3 h in the air. The as-obtained $ZrO_2$ sample emitted bluish white lights under excitation of UV light and the identical color long afterglow with chromaticity coordinates of $x = 0.22$ and $y = 0.33$ was observed after removing the excitation lights. Fig. 1 shows the excitation, emission and afterglow emission spectra of pure $ZrO_2$, respectively. As can be seen, the excitation spectrum showed a broad band with two weak peaks at 255 nm (4.88 eV) and 292 nm (4.25 eV). The excitation is originated
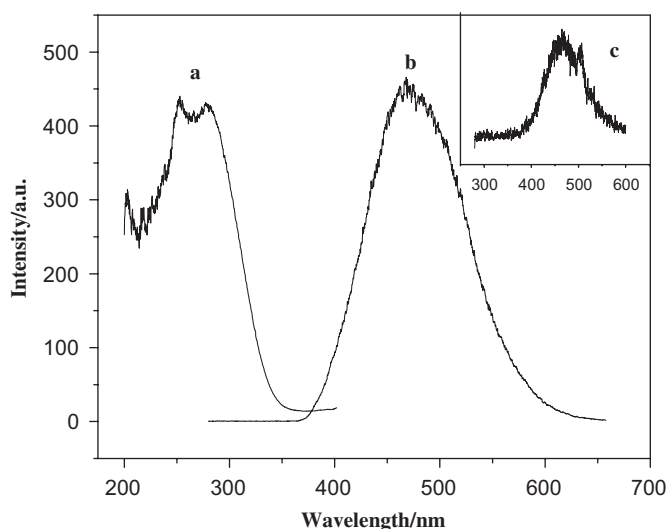
from electron transfer from the valence band (VB) to the local mid-gap states which is singly occupied anion vacancies (i. e., $F^+$ centers) [15–17]. The close resemblance of the emission and afterglow emission spectra suggests that the afterglow of $ZrO_2$ involves the same excited mechanism. The emission spectrum showed a broad band centered at 471 nm, which is assigned as excited states of F centers transfer to the ground state. The emission band is distinctly an extrinsic band with 4.88 eV excitation [16]. The shape of the emission spectrum did not exhibit significant changes as a function of excitation energy (254–292 nm), time or temperature. These results indicated that the spectrum is a normal Gaussian distribution band. The similar phenomenon is observed for the Ti doped $ZrO_2$. But the intensity of emission and afterglow emission increased strongly (shown in Fig. 2), this emission is attributed to compensating anion vacancies [17]. As shown in Fig. 3, electrons excited from VB to $F^+$ centers are trapped by the $F^+$ centers, creating F centers and holes. Then the recombination of F centers with holes creates the excited states of the emitter. These excited emitters transfer to the ground state giving out the light emission. We can describe the emission according to the following reaction:

$$e^- + F^+ + hv_1(4.88\,eV) \rightarrow F + h^+$$
$$F + h^+ \rightarrow (F^+)^* \rightarrow F^+ + hv_2(2.63\,eV) \qquad (1)$$
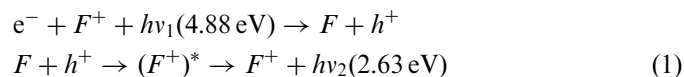
According to the discussion above, the emission is greatly affected by the concentration of the F centers (the number of anion vacancies). When $TiO_2$ was introduced into the sample and sintered in a sealed crucible, mixture valence states of Ti ($Ti^{4+}$, $Ti^{3+}$) ions with different ratio exist together in the samples. Each two $Ti^{3+}$ ion substituting a $Zr^{4+}$ ion produces one anion vacancy for charge compensation, so there is a higher concentration of anion vacancies in $ZrO_2$:Ti than that in the pure $ZrO_2$. Therefore the emission at 471 nm for $ZrO_2$:Ti is increased significantly.
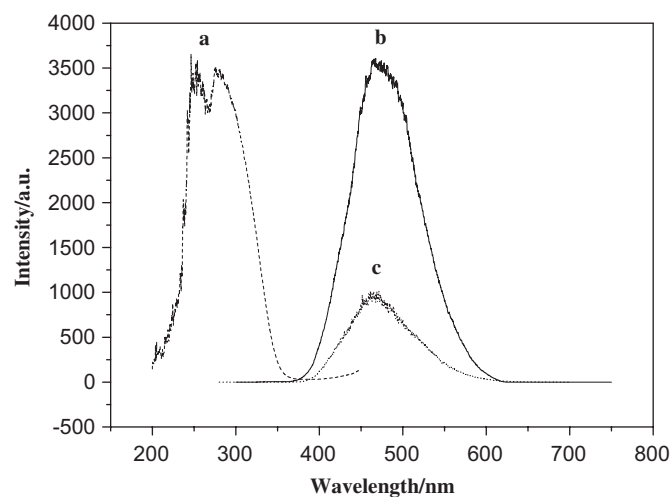


Fig. 1. PL spectra of pure $ZrO_2$: (a) excitation spectrum of $ZrO_2$ ($\lambda_{em} = 471$ nm), (b) emission spectrum of $ZrO_2$ ($\lambda_{exc} = 254$ nm), (c) afterglow emission spectrum of $ZrO_2$ ($\lambda_{exc} = 254$ nm).



Fig. 2. PL spectra of $ZrO_2$:0.5%Ti: (a) excitation spectrum of $ZrO_2$:0.5%-Ti ($\lambda_{em} = 471$ nm), (b) emission spectrum of $ZrO_2$:0.5%Ti ($\lambda_{exc} = 254$ nm), (c) afterglow emission spectrum of $ZrO_2$:0.5%Ti ($\lambda_{exc} = 254$ nm).
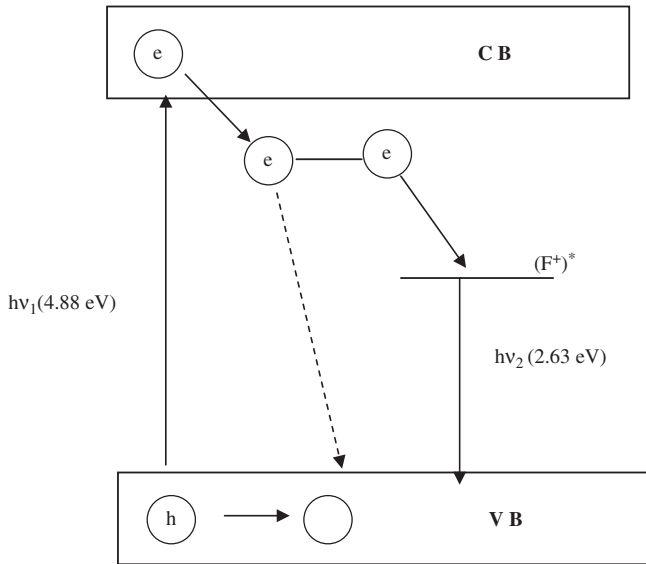
Fig. 3. The scheme of luminescence process induced by 4.88 eV (254 nm) excitation.

When the sample sintered in reducing atmosphere (CO gas is produced by kryptol in high temperature), the intensity is also increased. This phenomenon further confirmed that the concentration of anion vacancies greatly affect the intensity of the sample. It is found that the luminescence intensity and afterglow of the phosphors were enhanced with an increase of doped Ti concentration, reaching a maximum when the concentration of Ti is 0.5 mol%, and then decreased due to the concentration quenching effect.

The effect of sintering temperature on the emission intensity is also investigated. It is well known, the crystal-lite size of the sample increases with the increasing of the sinter temperature. The reduction of the band gap which contributed to the decrease of the quantum confinements of carriers reinforces the absorption coefficient. More electrons are excited to create F centers due to the increase of the absorption coefficient. So the samples sintered at higher temperature ($>700\,^{\circ}$C) present higher emissive intensity.

### 3.2. LLP properties of Ti doped $ZrO_2$ and undoped $ZrO_2$ phosphors

M. Akiyama et al. suggested that the same luminescence center is involved in the mechanoluminescence and photoluminescence [14]. In our present work, we have also proved that the introduction of Ti in the $ZrO_2$ lattices is responsible for the increase of the photoluminescence intensity based on the PL measurement. Furthermore, systematical investigations have been made on a series of comparative experiments, and a conclusion can be given that the introduction of $Ti^{3+}$ ions into the $Zr^{4+}$ lattices is more reasonable than the $Ti^{4+}$ in $Zr^{4+}$ lattice to be responsible for the increase of PL and TL in our samples

based on the observed results. As shown in Fig. 1 and Fig. 2.

An important result of the present work is that we observed obvious enhanced bluish white LLP in Ti doped $ZrO_2$. As shown in Fig. 1 and Fig. 2, both afterglow and normal emission spectra are similar in emission shape and maximum peak under 254 nm excitation, but emission intensity of the afterglow is reduced. The similar luminescent properties indicate that the radiating centers in both cases are the same.

Fig. 4 shows the decay curves of the phosphorescence of the Ti doped $ZrO_2$ and the pure $ZrO_2$ phosphors sintered in the air and in reduction atmosphere, respectively. The afterglow from the samples lasted for about one hour after the removal of the 254 nm UV light. The Ti doped sample sintered in the air demonstrates the stronger afterglow emission and the longer lifetime than other samples. When sintered in reduction atmosphere the Ti doped sample has a great reduction on the emission intensity and persistent time. The afterglow decay curves of the Ti-free $ZrO_2$ samples, which are sintered in the air and in reduction atmosphere, respectively are very similar. These phosphorescence characteristics are evaluated based on the decay times which are calculated using a curve-fitting technique. The decay curves can be well fitted by exponential equation [18]: $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where $I$ is the luminescence intensity; $A_1$ and $A_2$ are two constants; $t$ is the time; $\tau$ is defined as the decay time for the exponential components. The results are shown in Table 1. It is obvious that $ZrO_2$:Ti can be considered as two decay process and the pure $ZrO_2$ is considered as three decay process.

### 3.3. Possible mechanism of the occurrence of long afterglow

The mechanism of afterglow is rather complicated and unknown exactly till now. Generally, the LLP is assumed to be due to the thermostimulated recombination of holes
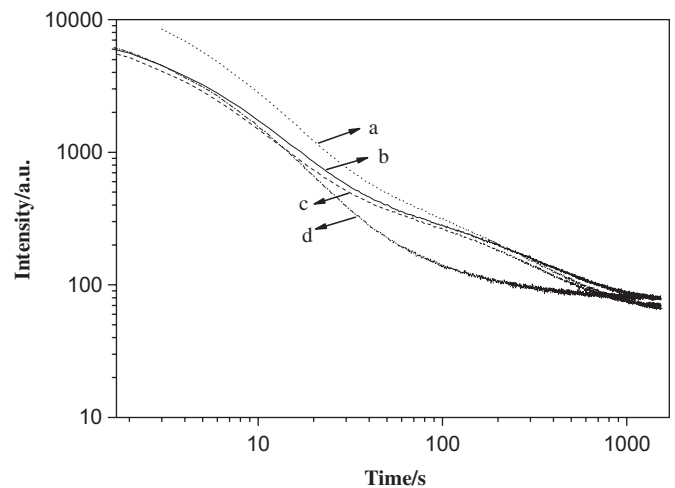


Fig. 4. Afterglow intensity decay curves of the $ZrO_2$ doped with $TiO_2$ sintered in the air (a) and in reduction atmosphere (d), the undoped $ZrO_2$ sintered in the air (b) and in reduction atmosphere (c), respectively.

Table 1
Decay times of the phosphorescence of Ti-doped $ZrO_2$: sintered in the air (a), in reduction atmosphere (b), undoped $ZrO_2$ sintered in the air (c) and in reduction atmosphere (d)

| Compounds | Decay lifetimes (s) | | |
| --- | --- | --- | --- |
| | $T_1$ | $T_2$ | $T_3$ |
| a | 139.28 | 6.92 | — |
| b | 15.83 | 2.89 | — |
| c | 10.97 | 206.21 | 2.63 |
| d | 9.63 | 183.22 | 2.32 |

and electrons which are in a metastable state at room temperature [19]. A luminescent activator which serves as an electronic donor absorbs incident energy, then the excited electrons or holes move to the trap centers and be trapped by the trap centers (defect centers). When these trapped electrons are released by heat at room-temperature and recombined with other trapped electrons or holes, LLP take place.

Based on the discussion above, we think that vacancies of oxygen and zirconium in the pure $ZrO_2$ are created during the synthesis process ($ZrO_2 \rightarrow V_O^{\bullet\bullet} + V''''_{Zr}$), and in the Ti doped $ZrO_2$, different valence states of $Zr^{4+}$, $Ti^{3+}$ in host lattice form the defects and vacancies [16]. When $Zr^{4+}$ is replaced by $Ti^{3+}$ ion, the defects with negative charge $Ti'_{Zr}$ is formed to be hole trapping centers with $V_{Zr}^{4+}$ together, the $V_O^{\bullet\bullet}$ can act as electron trapping centers. Based on this fact, the addition of $Ti^{3+}$ ion into $ZrO_2$ host and the zirconium and/or oxygen vacancies created in the sample are responsible for the bluish white afterglow in this kind of phosphor. Besides, $V_O^{\bullet\bullet}$ may also serve as F-center which is electron traps. The released energy transferring to the activator ions has a slow released ratio (as shown in Fig. 4), resulting in the afterglow happened. All of the supposition mentioned above could be testified by the TL spectra.

It was also reported by M. Akiyama et al. that tens of seconds afterglow and TL peaks were observed [14]. In our work, we extended the afterglow persistent time to about one hour, and we studied the PL and LLP properties of $ZrO_2$:Ti in a view to practical application as LLP material. The results show that the introduction of Ti in the $ZrO_2$ lattice is the reason for the increase of the TL intensity (One must bear in mind that in fact all "undoped" $ZrO_2$ contain traces of Ti).

Fig. 5 displays the TL spectra of the Ti doped $ZrO_2$ and the pure $ZrO_2$ phosphors. As shown in Fig. 5, there are at least two types of traps present in undoped $ZrO_2$ samples because there are two peaks in the TL spectra. Comparing with pure $ZrO_2$ sintered in the air, it is found that the peak at 67 °C was enhanced, and the peak at 126 °C was obviously reduced, while pure $ZrO_2$ sintered in the reduction atmosphere. So we conclude that the peak at 67 °C is caused by $V_O^{\bullet\bullet}$, the peak at 126 °C probably is of $V_{Zr}^{4+}$ origin. When the pure $ZrO_2$ sample sintered in
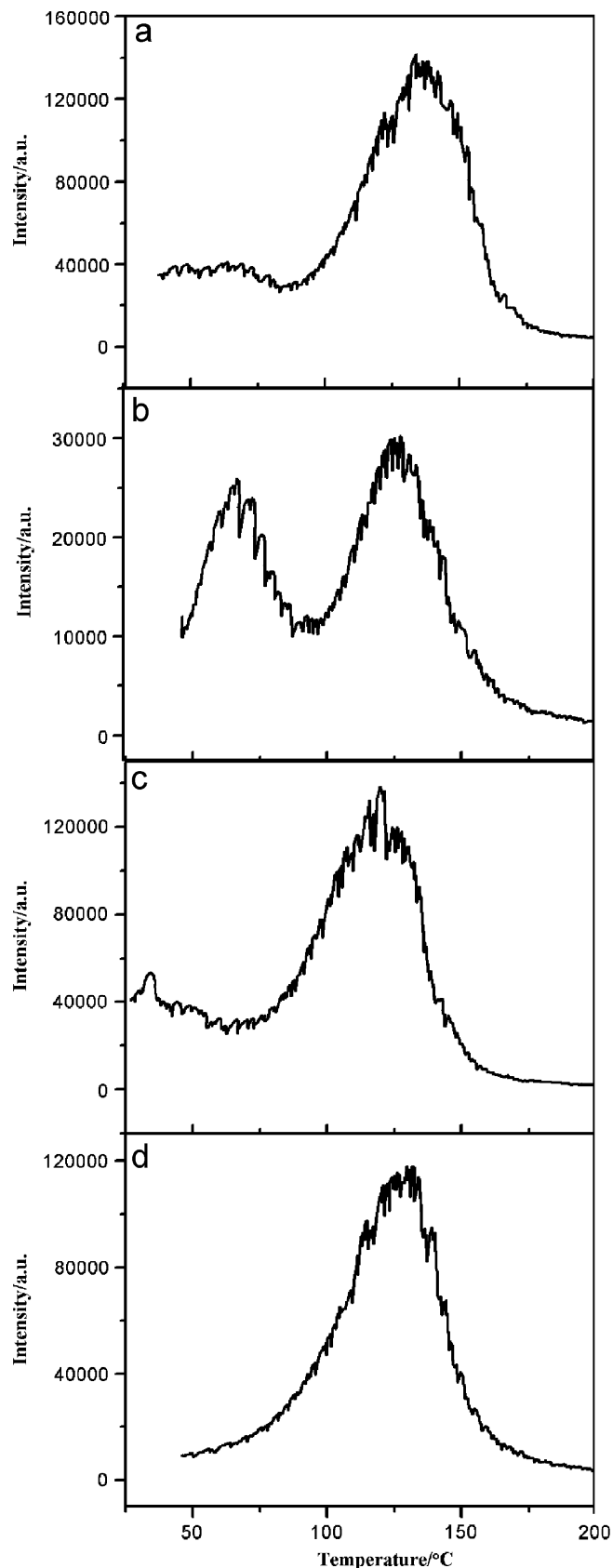


Fig. 5. TL curves of the pure $ZrO_2$ sintered in the air (a) and in reduction atmosphere (b), the Ti doped $ZrO_2$ sintered in the air (c) and in the reduction atmosphere (d).

reduction atmosphere, the number of the $V_O^{\bullet\bullet}$ will increase and the $V_{Zr}^{4+}$ will reduce. To confirming oxygen vacancies playing a role of trapping, ZrO$_2$:Ti codoped with additional Mg$^{2+}$ phosphor has also been synthesized and their TL properties have been investigated. It is found that the introduction of excess 0.5 mol% Mg$^{2+}$ ions can greatly reduce the 126 °C TL peak, and enhance the 67 °C TL peak. We think the addition Mg$^{2+}$ ions may induce some intrinsic defects, such as oxygen vacancy, resulting in higher LLP emission intensity of the sample. The peak of $V_O^{\bullet\bullet}$ of Ti doped ZrO$_2$ sample sintered in reduction atmosphere almost disappeared. It maybe due to the Ti reducing from Ti$^{4+}$ to Ti$^{3+}$ will consume up $O^{\bullet\bullet}$ ($2Ti^{4+} + O^{\bullet\bullet} \rightarrow 2Ti^{3+}$). It is clear that the TL peaks of the Ti doped ZrO$_2$ and the undoped ZrO$_2$ are different, indicating that the introduction of Ti into ZrO$_2$ yields different traps.

## 4. Summary and conclusion

In conclusion, a novel phosphor, Ti doped ZrO$_2$, has been synthesized by a conventional solid-state reaction method. The blush white PL of the phosphor with a strong and broad emission band at 471 nm, attributed to the recombination of trapped electrons in F$^+$ centers and holes in VB, is observed. The identical color LLP with persistent time of 1 h is found after removed the UV irradiation. The replacement of Zr by Ti results in the enhanced LLP.

## Acknowledgments

## References

[1] M. Kowatari, D. Koyama, Y. Satoh, K. Linuma, S. Uchida, Nucl. Instrum. Methods A 480 (2002) 431.
[2] J. Qiu, K. Miura, H. Inouye, Appl. Phys. Lett. 73 (1998) 1763.
[3] T. Matsuzawa, Y. Aoki, N. Takeuchi, Y. Murayama, J. Electrochem. Soc. 143 (1996) 2670.
[4] E. Nakazawa, T. Mochida, J. Lumin. 72 (1997) 236.
[5] D. Jia, W. Jia, X. Wang, Appl. Phys. Lett. 80 (2002) 1535.
[6] X. Wang, Z. Zhong. Z. Tang, Y. Lin, Mater. Chem. Phys. 80 (2003) 1.
[7] B. Lei, Y. Liu, Z. Ye, C. Shi, J. Solid State Chem. 177 (2003) 1333.
[8] M. Yamazaki, Y. Yamamoto, S. Nagahama, et al., J. Non-Cryst. Solids 241 (1998) 71.
[9] Y.J. Liu, R.O. Claus, J. Am. Chem. Soc. 119 (1997) 5273.
[10] Y. Du, M.S. Zhang, Y. Shen. Q. Chen, Z. Yin, Appl. Phys. A 76 (2003) 171.
[11] F. Gu, S.F. Wang, C.F. Song, M.K. Lu, Y.X. Qi, G.J. Zhou, D. Xu, D.R. Yuan, Chem. Phys. Lett. 372 (2003) 451.
[12] M. Garcia-Hipolito, C. Falcony, M.A. Aguilar-Frutis, J. Azorin-Nieto, Appl. Phys. Lett. 79 (2001) 4369.
[13] S. Wang, F. Gu, M. Lu, W. Zou, S. Liu, G. Zhou, D. Xu, D. Yuan, Opt. Mat. 27 (2004) 269.
[14] M. Akiyama, C. Xu, K. Nonaka, Appl. Phys. Lett. 81 (2002) 457.
[15] S.E. Pajfe, J. Llopis, Appl. Phys. A. 59 (1994) 569.
[16] N.G. Petrik, D.P. Tayor, T.M. Orlando, J. Appl. Phys. 85 (1999) 6770.
[17] G. Stapper, M. Bernasconi, N. Nicoloso, Phys. Rev. B. 59 (1999) 797.
[18] T. Katsumata, T. Nabae, K. Sasajima, S. Komuro, T. Morikama, J. Electrochem. Soc. 9 (1997) L243.
[19] J. Qiu, K. Miura, H. Inouye, S. Fujiwara, T. Mitsuyu, K. Hirao, J. Non-Cryst. Solids 185 (1999) 244.