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Beibei Xu,[1,2] Ping Chen,[1] Shifeng Zhou,[1,a)] Zhanglian Hong,[1] Jianhua Hao,[2] and Jianrong Qiu[1,3,a)]

[1]*State Key Laboratory of Silicon Materials and Department of Materials Science and Engineering, Zhejiang University, Hangzhou, Zhejiang 310027, People's Republic of China*
[2]*Department of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Hong Kong, People's Republic of China*
[3]*State Key Laboratory of Luminescence Materials and Devices, and Institute of Optical Communication Materials, South China University of Technology, Guangzhou, Guangdong 510640, People's Republic of China*

Enhanced broadband near-infrared luminescence has been observed in Bi-doped oxyfluoride glasses excited from UV to near-infrared regions with the addition of AgCl. Enhancement factors depend greatly on excitation wavelength and maximal enhancement factor over three times occurs at the excitation wavelength around 320, 640, and 800 nm. Ag species play dual functions. The mechanism of the enhancement is discussed in depth combing the energy transfer from Ag^+, molecular-like, nonplasmonic Ag species, Bi^{3+} and Bi^{2+} to near-infrared bismuth active centers, and the redox reaction of Bi species with Ag species. These results offer a valuable way to enhance the near-infrared luminescence efficiency of Bi-doped glasses, and the dual functions of Ag species may also be employed to enhance luminescence of rare-earth and transition metal ions doped materials. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4804256]

I. INTRODUCTION

With the rapid development of optical communication technology and the dramatic increase of the capacity of information transmission, Bi-doped materials with ultra-broadband near-infrared (NIR) luminescence covering the whole optical fiber communication windows have attracted considerable interest at present. To date, many kinds of Bi-doped NIR luminescence materials have been reported.[1–11] However, the absorption cross section of Bi near-infrared active centers (BNIA) in glasses is $\sim 10^{-20}$ cm^2,[12] which limits the efficiency of NIR luminescence. Generally, sensitizers such as Yb^{3+} have routinely been employed to enhance the quantum efficiency.[13,14] However, Yb^{3+} can only sensitize NIR luminescence with limited excitation wavelength at around 980 nm.

Recently, surface plasmon resonance (SPR) effect of Ag nanoparticles has been used to enhance the luminescence of rare-earth ions doped materials.[15] Besides, Ag^+ and molecular-like, nonplasmonic Ag species (ML-Ag) can also enhance the luminescence of rare-earth ions doped materials through energy transfer.[16,17] Since the luminescence of Ag^+ and ML-Ag are based on the transition of 4d electrons, they present broad fluorescence bands from UV to NIR region under different excitation wavelengths.[16–19] Bi-doped oxy-fluoride silicate glasses show broad absorption from UV to NIR region and enhanced luminescence in contrast to silicate glasses; moreover, oxyfluoride glasses are able to comprise the best advantages of fluoride glasses and oxide glasses.[20] Thus, we aim to test the feasibility of enhancing NIR

luminescence by doping Ag in Bi-doped oxyfluoride silicate glasses in the present work. Excitingly, it is found that the doping of AgCl can enhance NIR luminescence within the excitation wavelengths from UV to near-infrared region, which is of great significance. The mechanism of the enhancement is discussed in detail. These results deepen our understanding of the interaction between Bi and Ag species which will be of great benefit to the applications of Bi-doped materials.

II. EXPERIMENTAL PROCEDURE

Glass samples with the compositions (in mol%) of $10NaF-20MgF_2-20Al_2O_3-50SiO_2-xBi_2O_3-yAgCl$ (A: $x = 0$, $y = 1.0$; B: $x = 0.5$, $y = 0$; AB: $x = 0.5$, $y = 1.0$) were prepared by the melt-quenching method using analytical grade reagents NaF, MgF_2, Al_2O_3, SiO_2, Bi_2O_3, and AgCl as raw materials. The 20 g batches corresponding to glasses A, B, and AB were mixed homogeneously in agate mortar. Then they were melted in covered corundum crucibles at 1550 °C for 30 min in air. The melts were cast onto a stainless steel plate. Finally, the obtained glasses were cut and polished into the same size. All the glass samples were used without further heat-treatment.
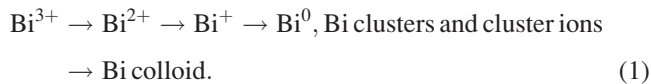
The excitation (PLE), photoluminescence (PL) spectra, and the fluorescence decay curves in both visible and near-infrared region were measured on an FLS920 fluorescence spectrophotometer (Edinburgh Instrument, Ltd., UK). A continuous-wave 450W Xe lamp and 980 nm laser diodes were used as the exciting sources. Absorption spectra were recorded using a UV3600 UV-Vis-NIR spectrophotometer (Shimadzu Corp., Japan). All the measurements were taken at room temperature.

a)Authors to whom correspondence should be addressed. Electronic addresses: sfzhou@zju.edu.cn and qjr@zju.edu.cn.

III. RESULTS AND DISCUSSION

Fig. 1(a) presents NIR PL spectra of glasses B and AB excited by 600 nm. Excitingly, with the addition of AgCl, NIR luminescence is enhanced and the peak position shows a blue-shift. Fig. 1(b) displays that the enhancement factor depends greatly on excitation wavelength. In the excitation wave-lengths around 320, 640, and 800 nm, factors over three times are obtained, while in the range around 260, 480, and 980 nm, no apparent enhancement can be observed. The rule of the enhanced luminescence does not match at all with that of the SPR enhanced luminescence, ruling out the possibility of plasmon enhancement definitely.

Absorption spectra of all glasses are shown in Fig. 2. No SPR absorption peak of Ag nanoparticles is observed (usually centered at $400 + 20$ nm[16]), indicating that there is no Ag nanoparticles in glasses. Two bands at around 490 and 700 nm appear in both glasses B and AB. The upper inset is the difference of the absorption of glass AB from that of glass B. With the addition of AgCl in Bi-doped glass, absorption in the range of 300–430 nm and 560–1000 nm increases with a dip in 680 nm; however, the absorption between 430 and 560 nm decreases, which is similar to the change tendency of the enhancement factor in Fig. 1(b). As previously reported, when the temperature is above 1000 °C, Bi^{3+} ions of Bi_2O_3 will transform to Bi species of lower valence states by the auto-thermo reduction[21] as follows:

$$Bi^{3+} \rightarrow Bi^{2+} \rightarrow Bi^+ \rightarrow Bi^0, Bi \text{ clusters and cluster ions}$$
$$\rightarrow Bi \text{ colloid.} \tag{1}$$

As the standard reduction potential (E^o) of $AgCl/Ag^0$ is lower (0.22233 eV) than that of Bi^{3+}/Bi^0 (0.31 eV),[22] the addition of AgCl will be of benefit to the reduction of Bi^{3+} at the initial stage of the melting of glass precursor. With the increase of melting time, more free Ag^+ will form in glasses. As E^o of Ag^+/Ag^0 is higher (0.80 eV) than that of Bi^{3+}/Bi^0,[22] some Ag^+ will be reduced to Ag^0 single atom and then aggregate to form ML-Ag, such as Ag_2^+ and Ag_3^{2+}.[17] Earlier research suggested that BNIA may be Bi species of low valence state, like Bi^+, Bi^0, Bi_5^{3+}, Bi_8^{2+} (Refs. 2–9, 23, and 24) and several types of BNIA contribute to the absorption bands at around 490 and 700 nm together,[23] while Bi atom clusters and metals have absorption at around 465 nm.[25,26] Thus, with the reduction of Ag^+, the decrease of the absorption at around 465 nm and the increase of the
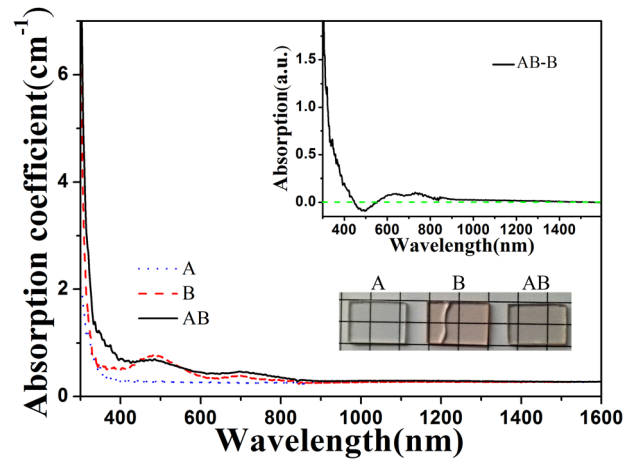

FIG. 2. Absorption spectra of glasses A, B and AB. The upper inset is the difference of the absorption of glass AB from that of glass B. The lower inset is the photographs of the glass samples.

absorption in 560–1000 nm reveal the oxidization of some Bi atom clusters and colloid into some kinds of BNIA. It is confirmed by the color change of the glass samples as shown in the lower inset. Single Ag-doped glass is completely transparent, and single Bi-doped glass is pink, while the color of Ag and Bi co-doped glass becomes a little lighter than that of single Bi-doped glass. Similar observation has been reported before that due to the higher E^o of $S_2O_8^{2-}/SO_4^{2-}$ (2.01 eV) than that of Bi^{3+}/Bi^0; the addition of proper concentrations of $K_2S_2O_8$ in glass leads to the oxidation of Bi metal clusters and the enhancement of NIR emission with the decrease of the absorption at around 465 nm.[26] As previously reported, some charged ML-Ag has absorption in the UV region[19] and an increase of the absorption at around 300–400 nm has been observed in Eu^{3+}-doped silicate glasses co-doped with Ag due to the presence of ML-Ag, such as Ag_2^+.[17] Combined with the redox equilibrium of Ag and Bi species in glasses, the increase of the absorption in the range of 300–430 nm in Ag and Bi co-doped glasses in contrast to single Bi-doped glass further confirms that some Ag^+ is reduced and aggregate to form very small ML-Ag, such as Ag_2^+.

To reveal the origin of this enhancement, we examined the visible excitation and emission spectra of glasses A and AB as presented in Fig. 3. When excited by 260 nm, single Ag-doped glass shows luminescence at around 300 and 400 nm originating from isolated Ag^+,[16,19] and the shoulder
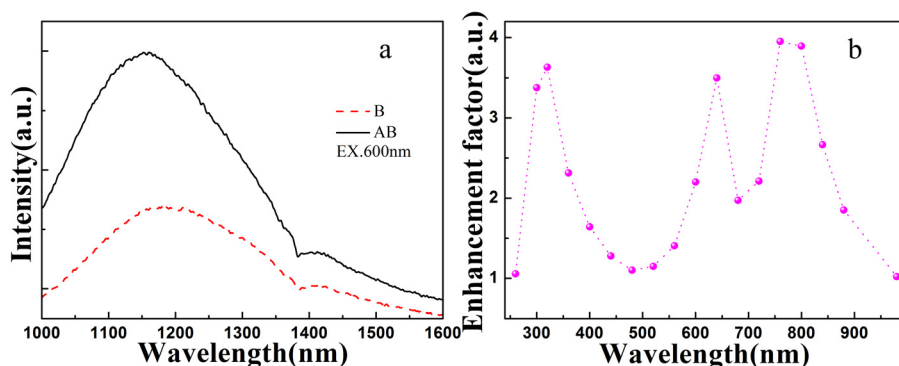

FIG. 1. (a) NIR PL spectra of glasses B and AB excited by 600 nm. (b) Enhancement factor as a function of excitation wavelength.
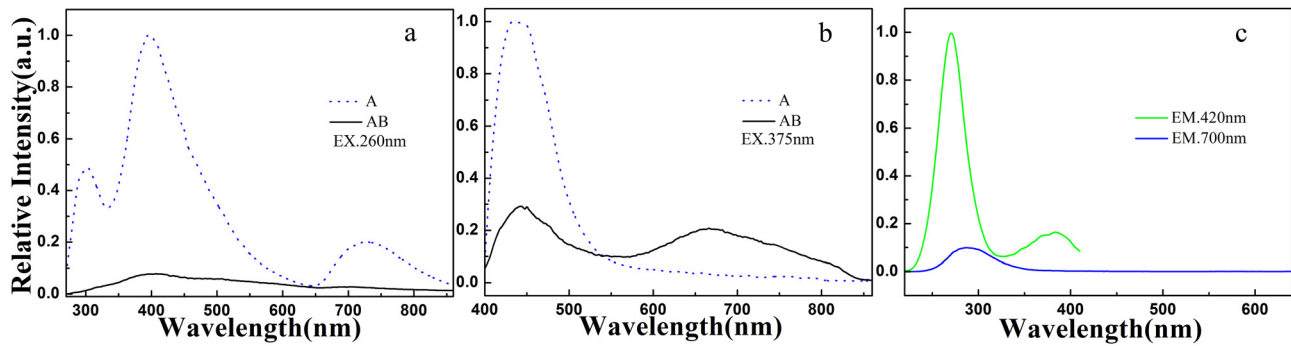
FIG. 3. (a)–(b) PL spectra of glasses A and AB. The excitation wavelengths are 260 and 375 nm, respectively. (c) PLE spectra of glass A monitored at 420 and 700 nm, respectively.

at around 500 nm indicates the presence of Ag^+-Ag^+ pairs.[19] Emission at around 740 nm may be due to ML-Ag, such as Ag_4^{2+}.[18] Single Ag-doped glass shows luminescence at around 440 nm originating from Ag_2^+ when excited by 375 nm.[19] By contrary, the luminescence related to these Ag species in Ag and Bi co-doped glass is much weaker. The decrease of luminescence at around 300 and 400 nm indicates that the content of Ag^+ is lower in Ag and Bi co-doped glass, which is consistent with the discussion in Fig. 2 that some Ag^+ is reduced with the oxidization of Bi metal clusters. Moreover, the absorption of BNIA also contributes to the weakness of the luminescence from Ag species in Figs. 3(a) and 3(b) indicating the probable energy transfer from Ag^+ and ML-Ag to BNIA. In Fig. 3(b), the emission peak at around 670 nm in Ag and Bi co-doped glass excited by 375 nm.[27] In Fig. 3(c), for single Ag-doped glass, when monitored at 420 nm, two peaks related to Ag^+ and Ag_2^+ are observed at 270 and 375 nm, respectively.[19] The excitation peak at 290 nm when monitored at 700 nm originates from Ag^+ implying that there may be an energy transfer from Ag^+ to Ag_4^{2+}. Thus, in Ag and Bi co-doped glass, ML-Ag is most probably Ag_2^+ and Ag_4^{2+}.

To prove the above discussion, we measured the decay curves of the luminescence of glasses as shown in Fig. 4. In Fig. 4(a), the emission at 400 nm of single Ag-doped glass shows single exponential decay with lifetime of 37.71 μs. When the glass is co-doped with Bi, the emission shows bi-exponential decay with fast and slow components of 2.16 and 31.83 μs. The fast decay is attributed to Bi^{3+},[28] and the slow component is attributed to Ag^+.[17] In Fig. 4(b), the

emission at 500 nm of single Ag-doped glass shows bi-exponential decay with fast and slow components of 1.40 and 16.26 μs which change to 1.45 and 14.23 μs when co-doped with Bi. The fast component is ascribed to Ag_2^+, and the slow ones are related to Ag^+-Ag^+ pairs.[19] The mean lifetime is calculated by the equation: $\tau_m = \int_{t_0}^\infty I(t)/I_{max}dt$, where $I(t)$ is the luminescence intensity at time t and $I_{max} = I(t_0)$ is the maximum of $I(t)$. The mean lifetime of glasses A and AB are 2.79 and 2.41 μs. In Fig. 4(c), the emission at 1200 nm of single Bi-doped glass can only been fitted by bi-exponential decay with fast and slow components of 54.07 and 399.99 μs due to the existence of several types of BNIA, while the emission of Ag and Bi co-doped glass shows three exponential decay with components of 17.75, 108.66, and 532.52 μs. The mean lifetime of glasses B and AB are 185.59 and 158.29 μs. The redox reaction leads to the change of the concentration of Ag and Bi species compared with that of single Ag-doped and Bi-doped glasses, which has large effect on the lifetime of the emission of BNIA centers and Ag species. Therefore, the efficiency of the energy transfer cannot be figured out by the decays of the emissions, and the change of the lifetime cannot explain the energy transfer between Ag and Bi species. Nevertheless, as shown in Fig. 4(c), the different exponential relationship of Ag and Bi co-doped glass from that of single Bi-doped glass confirms that there is energy transfer Ag species to BNIA.

Figs. 5(a) and 5(b) present the visible excitation and emission spectra of glasses B and AB. Single Bi-doped glass shows luminescence in the blue-green and orange-red region originating from Bi^{3+} and Bi^{2+},[27,28] respectively. Compared

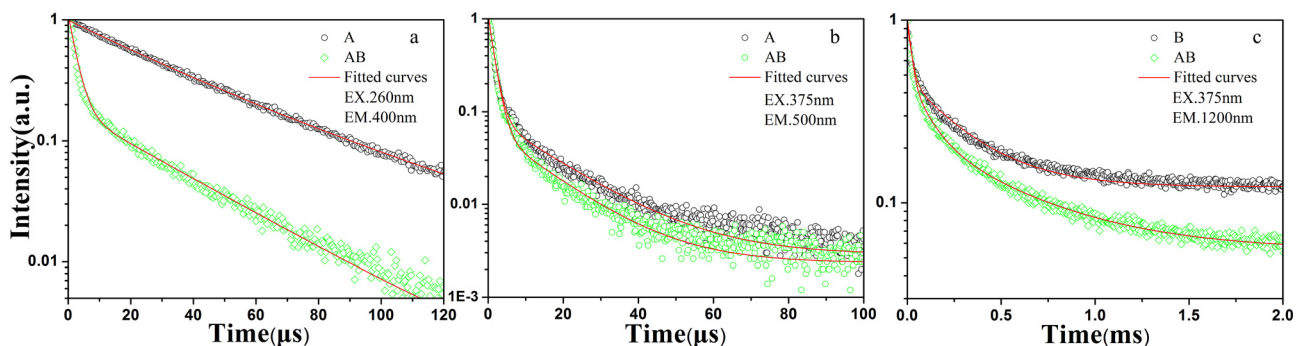FIG. 4. Decay curves of (a) Glasses A and AB ($\lambda_{ex} = 260$ nm, $\lambda_{em} = 400$ nm); (b) Glasses A and AB ($\lambda_{ex} = 375$ nm, $\lambda_{em} = 500$ nm); (c) Glasses B and AB ($\lambda_{ex} = 375$ nm, $\lambda_{em} = 1200$ nm).
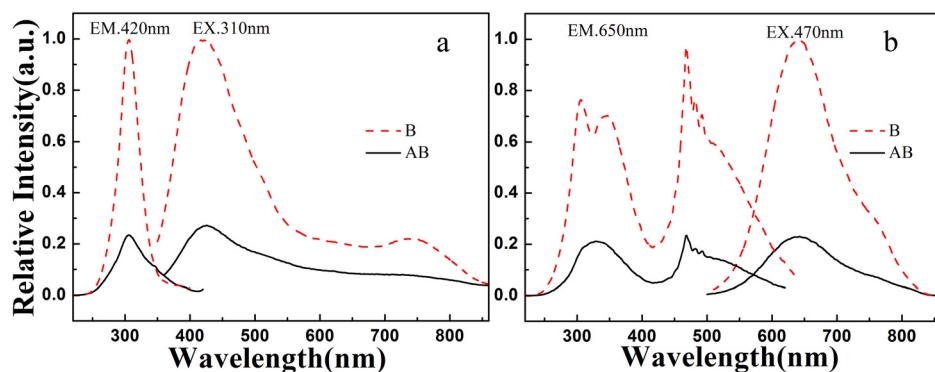
FIG. 5. PLE and PL spectra of glasses B and AB. (a) The excitation wavelength is 310 nm, the monitored emission wavelength is 420 nm. (b) The excitation wavelength is 470 nm, the monitored emission wavelength is 650 nm.

with that of single Bi-doped glass, the intensity of all the visible luminescence of Ag and Bi co-doped glass decreases. E^o of Bi^{5+}/Bi^{3+} (2.00 eV) is much higher than that of Ag^+/Ag^0,[22] thus Bi^{3+} cannot be oxidated by Ag^+. As the absorption in the range of 300–430 nm and 560–1000 nm increases in Ag and Bi co-doped glass in contrast to that of single Bi-doped glass, thus the decrease of the intensity of the visible luminescence may be due to the increased absorption in the region. Besides, we cannot rule out the possibility of the increase of the energy transfer from Bi^{3+} and Bi^{2+} to BNIA.

PLE spectra of glasses B and AB monitored at 1200 nm are presented in Fig. 6. Compared with single Bi-doped glass, the intensity of Ag and Bi co-doped glass is much stronger, and a strong broadband peaked at around 330 nm appears which is consistent with the large enhancement at around 330 nm in Fig. 1(b). The sharp peaks at 466 nm are caused by Xe lamp used in our measurement. The excitation spectra monitored at 1100 and 1300 nm of glass co-doped with Ag and Bi also show a strong broadband at around 330 nm as that monitored at 1200 nm which is not observed in single Bi-doped glass. The excitation band at around 330 nm in Fig. 6 of Ag and Bi co-doped glass is similar to the combined excitation bands of visible Bi active centers and Ag species in the region implying that there is energy transfer from visible Bi active centers and Ag species to BNIA.

Till now, the special origin of NIR luminescence in Bi-doped glasses is still unclear. Furthermore, there are many types of Ag and Bi species in glasses and redox reaction exists
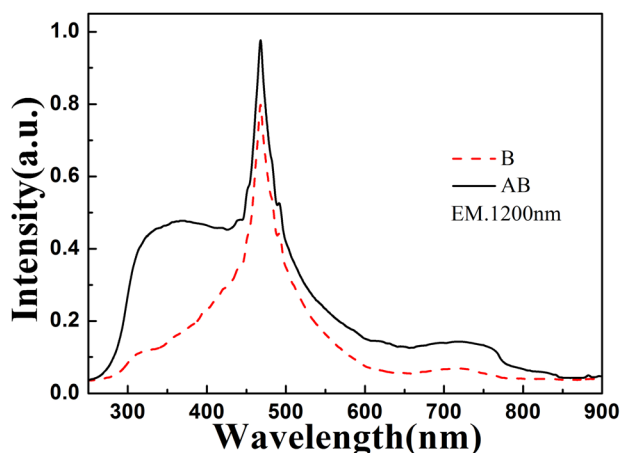
among them. Though the reduction potential can help us understand the tendency of the redox reaction, the thermodynamic properties and optical basicity of glasses during melting process will also influence the redox reaction between Ag and Bi species. Consequently, it is not easy to understand the change tendency of enhancement factor in Fig. 1. Further research on the glass host, the type of the Ag compounds, the concentration of dopants, the melting time, and heat-treatment process is needed to comprehend the change of the NIR luminescence. Nevertheless, a closer look at the luminescence properties reveals that the enhancement is due to the energy transfer from Ag species (Ag^+, ML-Ag) to BNIA and the increase of some kinds of BNIA with the oxidation of Bi atom clusters. And there may also be energy transfer from visible Bi active centers to BNIA. It is hoped that by controlling the chemical equilibrium of different Ag and Bi species in glasses, optimized luminescence properties can be obtained.

IV. CONCLUSION

In conclusion, by the addition of AgCl, NIR luminescence of Bi-doped oxyfluoride silicate glass is enhanced non-resonantly from UV to near-infrared region. On one hand, it is ascribed to the energy transfer from Ag^+ and molecular-like, nonplasmonic Ag species (Ag_2^+ and Ag_4^{2+}), and the probable increased energy transfer from Bi^{3+} and Bi^{2+} to near-infrared bismuth active centers. On the other hand, it is attributed to the increase of some kinds of near-infrared bismuth active centers resulting from the oxidation of Bi metal clusters and colloid. These results extend our comprehension of the interaction between bismuth species and Ag species in glasses and offer a significant method to enhance the NIR luminescence of Bi-doped glass. It may find some applications in fiber amplifiers and lasers.

FIG. 6. PLE spectra of glasses B and AB. The monitored emission wavelength is 1200 nm.

[1]H. Sun, J. Yang, M. Fujii, Y. Sakka, Y. Zhu, T. Asahara, N. Shirahata, M. Ii, Z. Bai, J. Li, and H. Gao, Small **7**, 199 (2011).

[2]S. Zhou, N. Jiang, B. Zhu, H. Yang, S. Ye, G. Lakshminarayana, J. Hao, and J. Qiu, Adv. Funct. Mater. **18**, 1407 (2008).

[3]H. Sun, Y. Sakka, M. Fujii, N. Shirahata, and H. Gao, Opt. Lett. **36**, 100 (2011).

[4]L. Su, H. Zhao, H. Li, L. Zheng, G. Ren, J. Xu, W. Ryba-Romanowski, R. Lisiecki, and P. Solarz, Opt. Lett. **36**, 4551 (2011).

[5]B. Xu, S. Zhou, M. Guan, D. Tan, Y. Teng, J. Zhou, Z. Ma, Z. Hong, and J. Qiu, Opt. Express **19**, 23436 (2011).

[6]H. Sun, A. Hosokawa, Y. Miwa, F. Shimaoka, M. Fujii, M. Mizuhata, S. Hayashi, and S. Deki, Adv. Mater. **21**, 3694 (2009).

[7]S. Zhou, H. Dong, H. Zeng, J. Hao, J. Chen, and J. Qiu, J. Appl. Phys. **103**, 103532 (2008).

[8]B. Xu, D. Tan, M. Guan, Y. Teng, J. Zhou, J. Qiu, and Z. Hong, J. Electrochem. Soc. **158**, G203 (2011).

[9]M. A. Hughes, T. Akada, T. Suzuki, Y. Ohishi, and D. W. Hewak, Opt. Express **17**, 19345 (2009).

[10]S. Zhou, H. Dong, H. Zeng, G. Feng, H. Yang, B. Zhu, and J. Qiu, Appl. Phys. Lett. **91**, 061919 (2007).

[11]K. Zhang, S. Zhou, Y. Zhuang, R. Yang, and J. Qiu, Opt. Express **20**, 8675 (2012).

[12]Y. Fujimoto and M. Nakatsuka, Jpn. J. Appl. Phys., Part 2 **40**, L279 (2001).

[13]J. Ruan, Y. Chi, X. Liu, G. Dong, G. Lin, D. Chen, E. Wu, and J. Qiu, J. Phys. D: Appl. Phys. **42**, 155102 (2009).

[14]J. Ruan, E. Wu, H. Zeng, S. Zhou, G. Lakshminarayana, and J. Qiu, Appl. Phys. Lett. **92**, 101121 (2008).

[15]V. A. G. Rivera, S. P. A. Osorio, Y. Ledemi, D. Manzani, Y. Messaddeq, L. A. O. Nunes, and E. Marega, Jr., Opt. Express **18**, 25321 (2010).

[16]J. Li, R. Wei, X. Liu, and H. Guo, Opt. Express **20**, 10122 (2012).

[17]J. Li, J. Chen, R. Wei, and H. Guo, J. Am. Ceram. Soc. **95**, 1208 (2012).

[18]J. J. Velázquez, V. K. Tikhomirov, L. F. Chibotaru, N. T. Cuong, A. S. Kuznetsov, V. D. Rodríguez, M. T. Nguyen, and V. V. Moshchalkov, Opt. Express **20**, 13582 (2012).

[19]J. A. Jiménez, S. Lysenko, and H. Liu, J. Appl. Phys. **104**, 054313 (2008).

[20]B. Xu, D. Tan, S. Zhou, Z. Hong, K. Sharafudeen, and J. Qiu, Opt. Express **20**, 29105 (2012).

[21]Y. Zhang, Y. Yang, J. Zheng, W. Hua, and G. Chen, J. Am. Ceram. Soc. **91**, 3410 (2008).

[22]*CRC Handbook of Chemistry and Physics*, Electrochemical Series, edited by P. Vanýsek and D. R. Lide (CRC, London, 2002), pp. 21–22.

[23]B. Xu, S. Zhou, D. Tan, Z. Hong, J. Hao, and J. Qiu, J. Appl. Phys. **113**, 083503 (2013).

[24]H. Sun, B. Xu, T. Yonezawa, Y. Sakka, N. Shirahata, M. Fujii, J. Qiu, and H. Gao, Dalton Trans. **41**, 11055 (2012).

[25]M. Peng, C. Zollfrank, and L. Wondraczek, J. Phys. Condens. Matter **21**, 285106 (2009).

[26]S. P. Singh and B. Karmakar, Opt. Mater. **33**, 1760 (2011).

[27]M. Hamstra, H. Folkerts, and G. Blasse, J. Mater. Chem. **4**, 1349 (1994).

[28]G. Blasse and A. Bril, J. Chem. Phys. **48**, 217 (1968).