

STRUCTURAL DEPENDENCE OF THIRD-ORDER OPTICAL NONLINEARITY OF $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-AgX}$ (X=Cl, Br, I) CHALCOHALIDE GLASSES

X. ZHENG^{a*}, H. TAO^a, F. CHEN^c, H. GUO^b, C. LIN^c, X. ZHAO^a

^aKey Laboratory of Silicate Materials Science and Engineering (Wuhan University of Technology), Ministry of Education, Luoshi Road 122, Hongshan District, Wuhan, Hubei 430070, P.R. China

^bState Key Laboratory of Transient Optics and Photonic, Xi'an Institute of Optics and precision Mechanics, Chinese Academy of Science (CAS), Xi'an, Shanxi 710119, PR China

^cCollege of Information Science and Engineering, Ningbo University, Ningbo 315211, PR China

$\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-AgX}$ (X=Cl, Br, I) chalcocalide glasses were prepared and their microstructures were investigated by Raman scattering method. Third-order optical nonlinearities were also characterized utilizing the Z-scan method at the wavelength of 800nm. The halogens compositional dependences of third-order optical nonlinearities of these glasses were discussed from the structural point of view. Among the different additives of silver halides, AgBr was demonstrated to have largest contribution to a larger n_2 and smaller FOM simultaneously in the studied glass system, which indicating that Br-containing chalcocalide glasses would be more suitable for the application in all-optical switching devices.

(Received April 18, 2011; Accepted June 10, 2011)

Keywords: Chalcocalide glasses; Raman spectroscopy; Z-scan; Nonlinear optics

1. Introduction

According to the Miller's rule [1], third-order optical nonlinear susceptibility, $\chi^{(3)}$, can be enhanced by the augment of the linear refractive index, n_0 . As heavy metal elements, such as Ag, Pb, etc., and halogens (Cl, Br, I), play an important role in increasing the linear refractive indices distinctly, AgX(X=Cl, Br, I)-containing chalcocalide glasses are expected to possess prominent third-order optical nonlinearities. Dong et al. [2] have shown large third-order optical nonlinearities in $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-AgCl}$ chalcocalide glasses, and investigated the compositional dependence of $\chi^{(3)}$ in these glasses. However, to our best knowledge, systemic investigations that focused on how halogens affect third-order optical nonlinearities in chalcocalide glasses are scarce.

In this paper, $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-AgX}$ (X=Cl, Br, I) chalcocalide glasses were prepared, their third-order optical nonlinearities were studied through standard Z-scan technique at the wavelength of 800nm, and the influence of halogens on third-order optical nonlinearities were also discussed from the structural point of view. These works will allow improvements in efforts to optimize the compositions in Ag-containing chalcocalide glasses that more suitable for the application in future optoelectronic and optics device.

*Corresponding authors: zhengxl0615@hotmail.com

2. Experimental details

Homogeneous $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-AgX}$ ($\text{X}=\text{Cl, Br, I}$) chalcogenide glass samples were obtained by well established melt-quenching technique using high-purity Ge, Ga, S (all of 5N) and AgX ($\text{X}=\text{Cl, Br, I}$) (all of 3N) as raw materials. Details of the preparations were similar to our previous works [3].

To analyze the halogens compositional dependence of third-order nonlinearities from structural point of view, two glass compositions were designed for the following investigation, i.e. series a: $50\text{GeS}_2\cdot 25\text{Ga}_2\text{S}_3\cdot 25\text{AgX}$ ($\text{X}=\text{Cl, Br, I}$) (all in mol%, hereinafter labeled as GGAgCl-a, GGAgBr-a, and GGAgI-a, respectively), and series b:

$50\text{GeS}_2\cdot 15\text{Ga}_2\text{S}_3\cdot 35\text{AgX}$ ($\text{X}=\text{Cl, Br, I}$) (all in mol%, hereinafter labeled as GGAgCl-b, GGAgBr-b, and GGAgI-b, respectively).

Optical absorption was recorded with a spectrophotometer (Shimadzu UV-1601) in the visible and near-infrared region (Vis-NIR). Refractive index n_0 was measured using a Spectro-Ellipsometer (Woollam W-VASE32TM) between 400 and 1300nm wavelength. Raman characterization was conducted using the back (180°) scattering configuration by the micro-Raman spectrometer (Renishaw RM-1000), a He-Ne laser ($\lambda=632.8\text{nm}$) was used as an excitation source.

Third-order optical nonlinearities were determined on the bases of Z-scan measurement using pump laser beam of 200fs duration generated from a mode-locked Ti:Sapphire laser (Coherent Mira 900-D) at 800nm, the detailed experimental setup used has already been described in Ref.[4]. The estimated error of Z-scan method is $\pm 15\%$. No changes were observed under microscopy between the as-prepared samples and ones after laser irradiation, indicating that no obvious photo-induced phenomena occurred during the optical experiments.

3. Results

The linear optical absorption spectra of two series glasses in Vis-NIR region are shown in Fig. 1, and almost no absorption exists at the femtosecond laser operation wavelength of 800nm. The spectra of both two series glasses exhibit an obvious red-shift of the visible cutting-off edge with the contained halogens varied from Cl to I, this can be interpreted from polarizability. It is known that the short-wavelength absorption edge of the glass is ascribed to the electrical transition between valence bands and conduction bands [5]. Due to the increased polarizability of halogens from Cl to I, the required excitation energy of electronic transition is smaller, just showing distinct red-shift of visible cut-off edge. In addition, as shown in the curves insert of Fig. 1, refractive indices of both two series glasses increase monotonously with the contained halogens varied from Cl to I. This variation also results from the polarizability and atomic mass differences of halogens.

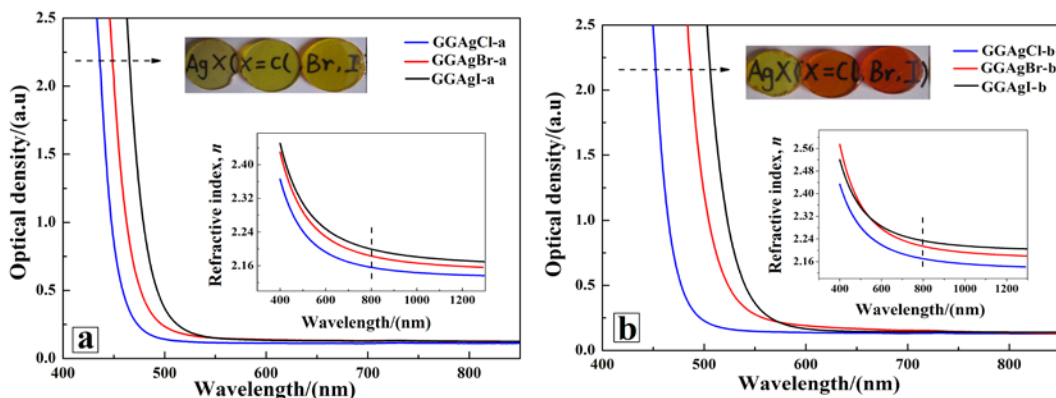


Fig.1 Vis-NIR absorption spectra and dispersive curve of refractive index (insert) of (a) series a glasses and (b) series b glasses

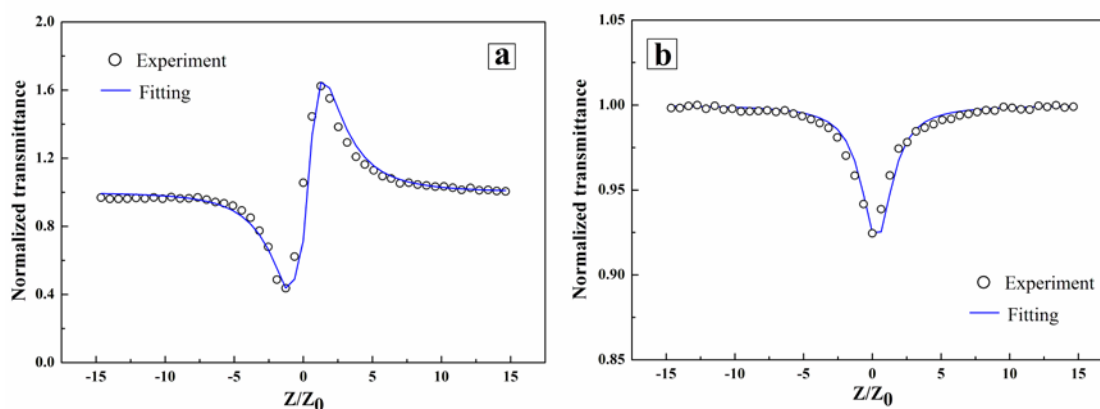


Fig.2 Z-scan signals and fitting curves of the 50GeS₂·25Ga₂S₃·25AgCl glass in the conditions of (a) close aperture measurement and (b) open aperture measurement.

Fig. 2 shows Z-scan signals of the 50GeS₂·25Ga₂S₃·25AgCl glass in the conditions of closed aperture (CA) and open aperture (OA) measurements, respectively. Here, the Z-scan measurements were carried out at the power density of $I_0 \sim 2.9 \text{ GW/cm}^2$, the aperture

linear transmittance of $S \sim 0.05$, and the beam waist radius of $\omega_0 \sim 20 \mu\text{m}$. Using the well-established method described in Ref. [4], experimental signals in Fig. 2 were fitted, and nonlinear absorption coefficient β and nonlinear refractive index n_2 were also calculated.

The Z-scan measurement results of both two series glasses are summarized in Table 1. It can be seen that the β for both two series glasses increases monotonously with the contained halogens varied from Cl to I. However, the variation trends of the n_2 for two series glasses are different. For Series a glasses, the n_2 increases monotonously from GGAgCl-a to GGAgI-a. Whereas for Series b glasses, the n_2 increases firstly and then decreases from GGAgCl-b to GGAgI-b, and GGAgCl-b possesses the smallest n_2 .

The Raman spectra of both two series glasses are shown in Fig. 3. The strongest peak at 340 cm^{-1} was attributed to the symmetrical stretching vibration (ν_1) mode of $[\text{Ge}(\text{Ga})\text{S}_{4/2}]$ tetrahedra [6]. The shoulder sited at 432 cm^{-1} is ascribed to the vibrational mode of the two inner sulfurs of the two edge-shared $[\text{Ge}(\text{Ga})\text{S}_{4/2}]$ tetrahedra [7]. With the addition of different silver halides, some distinct changes can be observed on the Raman spectra of both two series glasses.

In the case of 50GeS₂·25Ga₂S₃·25AgX (X=Cl, Br, I) glasses, the obvious bands at around 270 cm^{-1} on the Raman spectra (see Fig. 3a) are assigned to the symmetrical bending

Table 1. Linear and nonlinear optical parameters of the GeS₂-Ga₂S₃-AgX (X=Cl, Br, I) glasses.

Sample	n_0 (800nm)	E_{opt} (eV)	β (10^{-11} m/W)	n_2 (10^{-11} esu)	FOM^a
GGAgCl-a	2.16	2.63	0.60	0.82	0.606
GGAgBr-a	2.18	2.54	1.54	1.16	1.113
GGAgI-a	2.20	2.46	7.18	1.51	3.981
GGAgCl-b	2.17	2.53	1.06	1.00	0.877
GGAgBr-b	2.21	2.31	4.46	2.78	1.356
GGAgI-b	2.22	2.23	11.49	1.97	4.942

^a $FOM = 2\beta\lambda/n_2$

vibration (ν_3) mode of $[\text{S}_{3/2}\text{Ge}(\text{Ga})-(\text{Ga})\text{GeS}_{3/2}]$ ethane-like structural units (s.u.). This band is generally found in Ga-rich chalcogenide glasses and results from the S/Ga ratio for Ga_2S_3 is 1.5, which is less than 2 in $[\text{GaS}_{4/2}]$ tetrahedra, therefore inducing the deficiency of sulfur in the glass [8]. The additional different halogens, which play the role of sulfur compensator, leads to the breaking of $[\text{S}_{3/2}\text{Ge}(\text{Ga})-(\text{Ga})\text{GeS}_{3/2}]$ s.u. into $[\text{Ge}(\text{Ga})\text{S}_{3/2}\text{X}]$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) mixed-anion tetrahedra. However, the molar ratio of halogens to Ga is 1/2, less than 1, so incomplete substitution of $[\text{S}_{3/2}\text{Ge}(\text{Ga})-(\text{Ga})\text{GeS}_{3/2}]$ s.u. for $[\text{Ge}(\text{Ga})\text{S}_{3/2}\text{X}]$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) tetrahedra occurs, which results in the obvious bands at around 270cm^{-1} . Due to the formed $[\text{Ge}(\text{Ga})\text{S}_{3/2}\text{X}]$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) tetrahedra, some distinct changes can be also observed on the spectra with the addition of different silver halides. On the spectrum of GGAgCl-a glass, due to the similarity of S and Cl, the vibrational mode of $[\text{Ge}(\text{Ga})\text{S}_{3/2}\text{Cl}]$ tetrahedra is overlapping to that of $[\text{Ge}(\text{Ga})\text{S}_{4/2}]$ tetrahedra where located at around 340cm^{-1} [9]. On the spectrum of GGAgBr-a glass, as the vibrational mode of $[\text{Ge}(\text{Ga})\text{S}_{3/2}\text{Br}]$ tetrahedra is situated at around 260cm^{-1} , strengthening and shifting of the band at 270cm^{-1} toward lower frequency could be observed. On the spectrum of GGAgI-a glass, the little prominence at around 235cm^{-1} is ascribed to the vibrational mode of $[\text{Ge}(\text{Ga})\text{S}_{2/2}\text{I}_2]$ tetrahedra, indicating that the formed mixed-anion tetrahedra are mainly $[\text{Ge}(\text{Ga})\text{S}_{2/2}\text{I}_2]$. This is consistent with the previous Raman studies of I-containing chalcohalide glasses [10].

In the case of $50\text{GeS}_2\cdot 15\text{Ga}_2\text{S}_3\cdot 35\text{AgX}$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) glasses, as the molar ratio of halogens to Ga is 7/6, more than 1, complete substitution of $[\text{S}_{3/2}\text{Ge}(\text{Ga})-(\text{Ga})\text{GeS}_{3/2}]$ s.u. for $[\text{Ge}(\text{Ga})\text{S}_{3/2}\text{X}]$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) tetrahedra occurs, which results in the disappearance of bands at 270cm^{-1} on the Raman spectra (see Fig. 3b). Three distinct changes can be observed on the spectra with the addition of different silver halides. First, $[\text{Ge}(\text{Ga})\text{S}_{(4-x)/2}\text{X}_x]$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) ($x>1$) tetrahedra were formed because of the larger affinity of $\text{Ge}(\text{Ga})-\text{X}$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) bonds when more AgX ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) is added. So the bands at around 250cm^{-1} on the spectra of GGAgBr(I)-b glasses should be ascribed to the vibrational mode of $[\text{Ge}(\text{Ga})\text{S}_{(4-x)/2}\text{X}_x]$ ($\text{X}=\text{Br}, \text{I}$) tetrahedra, and the vibrational mode of $[\text{Ge}(\text{Ga})\text{S}_{(4-x)/2}\text{Cl}_x]$ tetrahedra is still overlapping to that of $[\text{Ge}(\text{Ga})\text{S}_{4/2}]$ tetrahedra where located at around 340cm^{-1} . Second, a flat curve between 200cm^{-1} and 250cm^{-1} could be observed on the spectrum of GGAgI-b glass, which indicating that some more complex mixed-anion $[\text{Ge}(\text{Ga})\text{S}_{(4-x)/2}\text{I}_x]$ ($x>2$) tetrahedra were formed. At lastly, a slightly strengthening and broadening of shoulder between 380 and 420cm^{-1} were observed on the spectra of GGAgBr(I)-b glasses, which might be relative to the vibrational mode of more complex Br(I)-containing s.u..

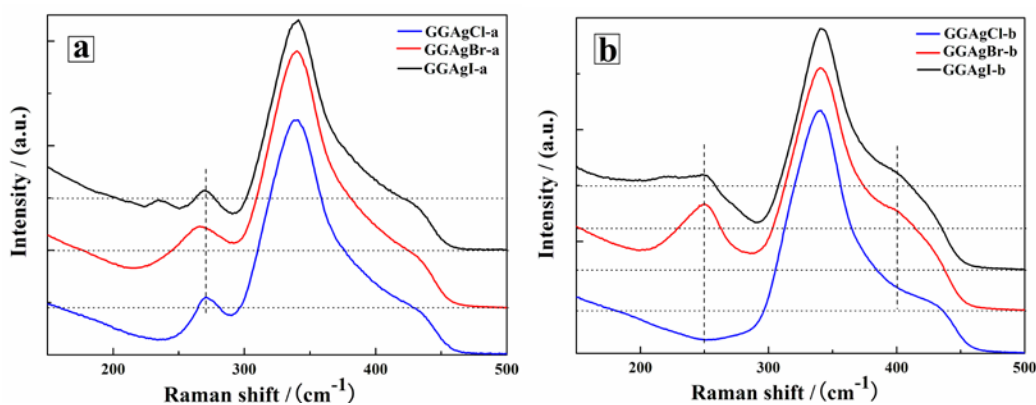


Fig. 3. Raman spectra of (a) series a glasses and (b) series b glasses

4. Discussion

According to the semiempirical Miller's rule, a large third-order optical nonlinearity can be expected in a glass with large n_0 . As listed in Table 1, the n_0 of both two series glasses increases monotonously with the contained halogens varied from Cl to I. So the third-order optical nonlinearities in Series b glasses do not obey the Miller's rule, indicating that some other factors play a more important role in halogens dependence of third-order optical nonlinearities of the studied glass system.

The structural evolution of both two series glasses were analyzed according to the abovementioned Raman spectra. In the case of series a glasses, the glassy network is constituted mainly by $[\text{Ge}(\text{Ga})\text{S}_{4/2}]$, $[\text{Ge}(\text{Ga})\text{S}_{3/2}\text{X}]$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) tetrahedra, and $[\text{S}_{3/2}\text{Ge}(\text{Ga})-(\text{Ga})\text{GeS}_{3/2}]$ s.u.. In the case of series b glasses, the glassy network is constituted mainly by $[\text{Ge}(\text{Ga})\text{S}_{4/2}]$ and $[\text{Ge}(\text{Ga})\text{S}_{(4-x)/2}\text{X}_x]$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) tetrahedra. There are two main structural factors that influence the third-order optical nonlinearities. First, the order of electronegativity is $\text{Cl} > \text{Br} > \text{I}$ [11], therefore the order of bond polarity is $\text{Ge}(\text{Ga})-\text{Cl} > \text{Ge}(\text{Ga})-\text{Br} > \text{Ge}(\text{Ga})-\text{I}$. As weaker covalent bonds will have larger electron cloud's distortion degree under femtosecond laser pulse, the contribution of covalent bonds that contained in $[\text{Ge}(\text{Ga})\text{S}_{(4-x)/2}\text{X}_x]$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) tetrahedral to n_2 is $\text{Ge}(\text{Ga})-\text{I} > \text{Ge}(\text{Ga})-\text{Br} > \text{Ge}(\text{Ga})-\text{Cl}$ [12]. Second, it is known that an integrated and homogeneous glassy network with less structural defectiveness is more beneficial to the enhancement of n_2 [13]. As the terminator of the glassy network, the addition of halogens originated from silver halides induces the degradation of integrity of glassy network and more structural defectiveness are formed, and this degradation effects become more obvious with the contained halogens varied from Cl to I, due to the increased atomic radii from Cl to I.

So these two factors mentioned above have contradictive effects on the contribution to n_2 with the contained halogens varied from Cl to I. For series a glasses, the first factor has more profound influence, so the n_2 increased monotonously from GGAgCl-1 to GGAgI-1. However, in the case of series b glasses, as the high content of silver halides, the second factor will be more preferential gradually, especially in the GGAgI-b glass due to the large atomic radius of I, so the n_2 increases firstly and then decreases from GGAgCl-2 to GGAgI-2. In addition, compared the corresponding n_2 of two series glasses, it can be found that $[\text{S}_{3/2}\text{Ge}(\text{Ga})-(\text{Ga})\text{GeS}_{3/2}]$ s.u. makes no considerable contribution to n_2 . Judging from the discussion mentioned above, it can be deduced that compared with the Miller's rule, the structural evolution plays a more important role in the variation of third-order optical nonlinearities in the studied glassy system.

Generally, figure of merit $FOM = 2\beta\lambda/n_2$ is considered to be a criterion to analyze the suitability of a non-linear material for all-optical switching devices, and $FOM < 1$ is expected. As listed in Table 1, the values of FOM for both two series glasses increase monotonously from GGAgCl to GGAgI, due to the strongly increased nonlinear absorption at the wavelength of 800nm. GGAgCl and GGAgBr glasses have relatively small FOM around 1, and for the consideration of n_2 , we anticipated that GGAgBr glass have the optimal third-order optical nonlinearities. To our best knowledge, it is firstly demonstrated that Br-containing chalcogenide glasses have the best third-order nonlinearities among the same composition glasses that contained different halogens. This conclusion will be valuable for the search of new materials that more proper considering the requirement of nonlinear optical devices.

5. Conclusions

The third-order optical nonlinearities of $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-AgX}$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) chalcogenide glasses were characterized utilizing the Z-scan method at the wavelength of 800nm. From the discussion related to the structural dependences of third-order optical nonlinearity of these glasses, it can be deduced that $[\text{Ge}(\text{Ga})\text{S}_{(4-x)/2}\text{X}_x]$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) mixed-anion tetrahedra that possess high hyperpolarizability, and an integrated and homogeneous glassy network without any structural defects are more beneficial to the enhancement of third-order optical nonlinearity. Among these glasses that contained different silver halides, $50\text{GeS}_2\cdot 15\text{Ga}_2\text{S}_3\cdot 35\text{AgBr}$ has a relatively large n_2 and small FOM simultaneously, which indicating that Br-containing chalcogenide glasses would be more suitable for requirement of all-optical switching devices.

Acknowledgements

This work was financially supported by the NSFC (Nos. 60807034, 60907039 and 60808024); the SRF for ROCS, SEM; NSG Foundation; the Opening Research Fund of State Key Laboratory of Transient Optics and Photonics.

References

- [1] R. C. Miller, *Appl. Phys. Lett.* **5**, 17 (1964).
- [2] G. P. Dong, H.Z. Tao, X.D. Xiao, C.G. Lin, Y.Q. Gong, X.J. Zhao, S.S. Chu, S.F. Wang, Q.H. Gong, *Opt. Express* **15**, 2398 (2007).
- [3] H.Z. Tao, X.J. Zhao, C.B. Jing, *J. Mol. Struct.* **697**, 23 (2004).
- [4] Y.F. Chen, Q.H. Nie, T.F. Xu, S.X. Dai, X.S. Wang, X. Shen, *J. Non-Cryst. Solids* **354**, 3468 (2008).
- [5] M. Seki, K. Hachiya, K. Yoshida, *J. Non-Cryst. Solids* **315**, 107 (2003).
- [6] G. Lucovsky, F.L. Galeener, R.C. Kezer, R.H. Geils, H.A. Six, *Phys. Rev. B* **10**, 5134 (1974).
- [7] S Sugai, *Phys. Rev. B* **35**, 1345 (1987).
- [8] X.F. Wang, S.X. Gu, J.G. Yu, X.J. Zhao, *Solid State Commun.* **130**, 459 (2004).
- [9] H.Z. Tao, X.J. Zhao, C.B. Jing, H. Yang, S. Mao, *Solid State Commun.* **133**, 327 (2005).
- [10] H.T. Guo, H.Z. Tao, Y.B. Zhai, S. Mao, X.J. Zhao, *Spectrochim. Acta A* **67**, 1351 (2007).
- [11] J.A. Dean, *Lange's Handbook of Chemistry* (in Chinese), The Scientific Press, Beijing (1991).
- [12] I. Kang, S. Smolorz, T. Krauss, F. Wise, B.G. Aitken, N.F. Borrelli, *Phys. Rev. B* **54**, 641 (1996).
- [13] G.P. Dong, H.Z. Tao, S.S. Chu, S.F. Wang, X.J. Zhao, *Optics Commun.* **270**, 373 (2007).