Preparation and Optical Properties of CuCl-Doped Na₂O-B₂O₃-SiO₂ Glasses

Hiroyuki NASU, Shoji KANEKO, Keiji TSUNETOMO* and Kanichi KAMIYA

Department of Chemistry for Materials, Faculty of Engineering, Mie University, Kamihama, Tsu-shi 514

*Department of Electrical Engineering, Faculty of Engineering, Hiroshima University, Saijo, Higashi-Hiroshima-shi 724

CuCl ドープ Na₂O-B₂O₃-SiO₂ ガラスの作製とその光学的性質

那須弘行・兼子祥治・常友啓司*・神谷寛一

三重大学工学部分子素材工学科, 514 津市上浜町1515

*広島大学工学部電子物性工学大講座, 724 東広島市西条町

[Received February 26, 1990; Accepted January 24, 1991]

CuCl-doped Na₂O-B₂O₃-SiO₂ glasses were successfully obtained by the conventional melt-quenching method. Complete glassy bodies were obtainable up to 2 mol% CuCl. The CuCl microcrystals grew by heat-treatment at 450° or 500°C, and the mean radius of the microcrystals was proportional to one third power of heating duration. The exciton peaks were observable even at room temperature and the temperature dependence of the peak shift implied the significant influence of volume effect. Homogeneous and inhomogeneous widths of the exciton peaks were evaluated from the temperature dependence of Z₃ peak line width. The large inhomogeneous distribution seems to result from random structure of the matrix glasses and large microcrystal size distribution.

Key-words: CuCl-doped glasses, Optical properties, Microcrystal, Exciton, Coherent length

1. Introduction

The recent and remarkable development of optical communication and processing technologies stimulates the research and development of new materials to be available and functional for very fast optical systems. Materials with large optical nonlinearity are powerful candidates for the systems. Nonlinear polarizability of a material (P_{NL}) is expressed as

$$P_{NL} = \chi^{(2)} E^2 + \chi^{(3)} E^3 + \dots \quad (1)$$

where E is electric field, and $\chi^{(2)}$ and $\chi^{(3)}$ are second- and third-order nonlinear susceptibility. For all-optical or optoelectronic communication systems, optical Kerr effect, and optical bistability, in particular, caused by $\chi^{(3)}$ are quite significant. To obtain effective functions, large $\chi^{(3)}$ is naturally preferable. The studies of developing materials with large $\chi^{(3)}$ can be divided into two categories. One is the study of large homogeneous $\chi^{(3)}$ glasses, such as high-index glasses,¹⁻³⁾ and the other is that of the glasses containing metal or semiconductor microcrystals.⁴⁻⁷⁾ Although nonresonant-type $\chi^{(3)}$ of homogeneous glasses has been no more than 10^{-10} (esu), that of resonant-type CdS_xSe_{1-x}-doped glasses are in the order of 10^{-8} – 10^{-9} (esu)⁴⁾ in the visible region. In particular, $\chi^{(3)}$ caused by excitons are predicted to be much larger

than that of CdS_xSe_{1-x}-doped glasses.⁸⁾ Although the radius of exciton of the semiconductors is commonly larger than the microcrystals doped in glasses as quantum dots (<100 Å), excitons of some halides such as CuCl or CuBr seem to be formable due to the small exciton radius, even in quantum dots. Ekimov et al.⁹⁻¹¹⁾ prepared CuCl or CuBr-doped glasses and found exciton peaks at 4.2 K. Further they confirmed the existence of the quantum size effect of the doped microcrystals. However, the detailed informations, being important for practical use, such as the composition of the matrix glasses, temperature dependence of exciton peaks and the influences of glass matrix compared to crystal matrix, have not been enough cleared. Therefore, this work reports preparation and temperature dependence of exciton-peaks of CuCl-doped Na₂O-B₂O₃-SiO₂ glasses and influences of matrix on optical properties.

2. Experimental procedure

Commercially available analytical grade, Na₂CO₃, B₂O₃, SiO₂ were used as raw materials. The Na₂CO₃, B₂O₃ and SiO₂ powders were weighed to be 13Na₂O·54B₂O₃·33SiO₂ in mol%, and after mixed well, the batch was put into platinum crucible and decarbonated at 800°C for 30 min in air. Subsequently, the batches were melted at 1100°C for 1 h in air, and the melts were quenched between stainless steel plates. The quenched bodies were completely transparent and glassy. Then, the bodies were crushed by stainless steel die and milled by alumina pestle and motor. After milled, the powders passing through 60 mesh were used as raw matrix powders. Then, CuCl was weighed and mixed with the powder. The concentration of CuCl was varied from 0.5 to 15 mol% to the matrix glasses, but no microcrystals could be formed below 1 mol% CuCl even after heat-treatment. The mixed batches were melted using platinum crucibles from 1350°C to 1450°C for 5 min with covers of platinum, and then the melts were quenched between stainless steel plates. The quenched bodies containing CuCl less than 2 mol% were transparent and completely

glassy.

The glass samples were annealed at 450° or 500°C for various duration, so as to form microcrystals. The glasses after annealed were polished and optical spectra were measured by optical spectrometer (Cary 14) from liquid nitrogen temperature to room temperature. The CuCl films were prepared by vacuum evaporation for comparison.

3. Results and discussion

Glass forming region as a function of the concentration of CuCl is tabulated in Table 1 with final melting temperature. Complete homogeneous glasses were obtained to 2 mol% CuCl in the nominal composition as seen in the table, while the quenched bodies containing over 2 mol% CuCl were opaque, and CuCl large crystals precipitated, those identified from X-ray diffraction pattern.

Figure 1 shows the exciton peaks of CuCl polycrystalline film at 77 K for comparison. The peak at nearly 375 nm and that at nearly 383 nm are ascribed to $Z_{1,2}$ and Z_3 peaks, respectively. Both two peaks were quite sharp and position of the each peak were quite similar to those in literature.⁹⁾⁻¹¹⁾ The dependence of growth of exciton peaks of CuCl in the glass on annealing conditions measured at 77 K are shown in Figs. 2(a) and (b). The annealing temperatures were 500° and 450°C and the time was from 10 min to 84 h. In Fig. 2(a), the shoulder assignable to Z_3 peak could be seen even for 10 min heat-treatment, and the peak became sharper with increasing

Table 1. Glass forming region of x CuCl ($1-x$) ($13\text{Na}_2\text{O}\cdot 53\text{B}_2\text{O}_3\cdot 33\text{SiO}_2$ (mol%)) glasses as a function of x .

x	melting temperature	state of quenched bodies
1	1350°C, 1450°C	glass
2	1350°C, 1450°C	glass
3	1450°C	glass + partially crystal
5	1450°C	partially glass + crystal
7	1450°C	crystal
9	1450°C	crystal
10	1450°C	crystal
15	1450°C	crystal

Fig. 1. Exciton peaks of bulk CuCl at 77 K.

Fig. 2. Annealing time dependence of exciton peaks when annealed at 500°C (a) and 450°C (b), measured at 77 K.

heating time. Both $Z_{1,2}$ and Z_3 peaks shifted to longer wavelength as annealing time increased, the shift resulting from the increase of mean diameter of the microcrystals. On the other hand, the effect of annealing was not relatively effective at 450°C. Even after 3 h treatment, no Z_3 peak was detectable, and the 84h's treatment was necessary to obtain clear Z_3 peak. With respect to the red shift, both peaks likewise shifted to longer wavelength, resulting from the increase of microcrystal diameter as will be discussed below. After very long annealing enough to form CuCl crystals without quantum size effect, no difference in the peak positions of the exciton could be seen in CuCl films and in glass matrix. It is theoretically interpreted that the exciton absorption energy is mainly influenced by the mass of excitons and crystal radius, and that the energy is insensitive with small amounts of impurities.

Figure 3 depicts dependence of energies of the exciton peaks on the temperature of measurements for the sample annealed at 500°C for 3 h. As temperature increases, the Z_3 peak became broader, but, even at 249 K and at room temperature, the exciton peaks were observable. The is quite important for the future practical use of the materials as the exciton device at room temperature.

The mean diameter of the microcrystals was evaluated by the following. The observed blue shift (ΔE) at constant temperature is theoretically proportional to the reciprocal of square radius of microcrystals as $\Delta E \propto 1/a^2$.⁹⁾ Therefore, by fitting the blue shift of this work for $Z_{1,2}$ and Z_3 , one can evaluate mean diameter of the microcrystals in the present glasses. Specifically, $d\Delta E_{Z_{1,2}}/d(1/a)^2$ is evaluated from Ref. 11) as 19.9, and the average microcrystal radius (a) is calculated from

$$a = \frac{4.464}{(\Delta E_{Z_{1,2}} - \Delta E_{77\text{K}})^{1/2}}$$

(2)

Fig. 3. Temperature dependence of exciton peaks for the sample annealed at 500°C for 3 h.

Fig. 4. Radius of CuCl microcrystals as a function of one third power of annealing time.

Fig. 5. Temperature dependence of spectral $Z_{1,2}$ (a) and Z_3 (b) peak positions for the samples annealed at 500°C. Annealing times are denoted besides each line.

When the crystallization process undergoes in super-saturated melts and crystals grow at an expense of small crystalline particles, the mean radius of crystals depends on $t^{1/3}$, where t is annealing time (Lifshitz-Slyozov model¹³⁾). The radius of CuCl is plotted against $t^{1/3}$ in Fig. 4. One can point out the growth mechanism of CuCl microcrystals can be interpreted by Lifshitz-Slyozov model at 500° and 450°C, and the growth rate at 500°C is rather faster than that at 450°C.

Figures 5(a) and (b) show the temperature dependence of peak energies of $Z_{1,2}$ and Z_3 , respectively,

for the samples annealed at 500°C. As pointed out above, the crystal radius is dependent on one third of annealing time, and thus crystal diameter increases as annealing time increases. The redshift of peaks due to annealing can be interpreted by the increase of crystal diameter. As temperature increases, the peaks show blue shift. From the linear relationship between temperature and the blue shift (ΔE), one can calculate temperature coefficient of the shift. For bulk CuCl, $d\Delta E/dT = 1.3 \times 10^{-4}$ eV/K, which agrees with the data reported by Cardona.¹⁴⁾ For microcrystalline CuCl in the present glasses,

$d\Delta E/dT$ ranges $2.1\text{--}2.6 \times 10^{-4}$ eV/K, and no obvious dependence on the diameter can be seen. The value for bulk CuCl can be considered as temperature dependence of band gap and the present value seem to contain those of band gap and quantum size effect. Assuming that the band gap of microcrystals is the same as bulk, temperature dependence of quantum size effect is calculated as $0.8\text{--}1.3 \times 10^{-4}$ eV/K. According to Cardona,¹⁴⁾ $d\Delta E/dT$ is caused by two factors. One is volume effect, resulting from thermal expansion of lattice, and the other is explicit temperature effect, resulting from electron-phonon interaction. Volume effect should positively influence $d\Delta E/dT$, but the other should yield negative $d\Delta E/dT$.

The observed $d\Delta E/dT$ is positive and similar to that of the band gap. Thus, the positive temperature dependence of the quantum size effect can be attributed to the volume effect.

Figure 6 shows temperature dependence of the linewidth (Γ) of Z_3 peak. The line width can be expressed as

$$\Gamma = \Gamma_{\text{inh}} + \Gamma_{\text{h}} = \Gamma_{\text{inh}} + A / [\exp(B/k_B T) - 1] \quad (3)$$

where Γ_{inh} and Γ_{h} are inhomogeneous and homogeneous linewidth, respectively, and A and B are constants. By fitting this equation with the experimental values in Fig. 6, Γ_{inh} , A and B are estimated as 23.4 meV, 502 meV and 58.0 meV, respectively. Compared to the values for CuCl microcrystal in NaCl matrix,¹⁵⁾ Γ_{inh} in glasses (23.4 meV) is far larger than that in NaCl matrix (8.0 meV). That seems to result from the random structure of glass matrix and larger distribution of microcrystal size. 58.0 meV for B is well close to that in NaCl matrix, and thus the excitation process seems to be quite similar to the CuCl microcrystals in NaCl matrix.

Figure 7 depicts $\Delta E(Z_{1,2} - Z_3)$ as a function of temperature for the samples annealed at 500°C. Although some fluctuation can be seen, it can be said that $\Delta E(Z_{1,2} - Z_3)$ is almost independent of temperature. $\Delta E(Z_{1,2} - Z_3)$ is plotted against $1/a^2$ in Fig. 8 with the data in literature⁹⁾ for comparison. The deviation between solid and broken lines is due to the difference of the temperature. According to Ekimov et al.⁹⁾ the spectral position of Z_3 can be expressed as

$$\hbar\omega_{Z_3} = E_q - E_{\text{ex}} + 0.67 \frac{\hbar^2}{2M_{\text{sa}}} \pi^2 \quad (4)$$

where E_q and E_{ex} are energy gap and exciton energy, respectively, M_s is the exciton translational mass and a is mean radius of microcrystals. On the other hand, that of $Z_{1,2}$ is given by

$$\hbar\omega_{Z_{1,2}} = E_q - E_{\text{ex}} + 0.67 \frac{\hbar^2}{2M_{\text{ha}}} [\Psi(M_1/M_h)]^2 \quad (5)$$

where M_h and M_l are the mass of the heavy and light excitons, respectively, and $\Psi(M_1/M_h)$ is a root of the transcendental equation cited in Ref. 16). Thus, $\Delta E(Z_{1,2} - Z_3)$ can be expressed as

Fig. 6. Temperature dependence of the linewidth of Z_3 peak for the samples annealed at 500°C for 8h. The line was drawn by the least square fitting.

Fig. 7. The energy difference of $Z_{1,2}$ and Z_3 peaks, $\Delta E(Z_{1,2} - Z_3)$, as a function of temperature for the samples annealed at 500°C. Annealing times were denoted besides each line.

Fig. 8. $\Delta E(Z_{1,2} - Z_3)$ as a function of reciprocal of square mean diameter of microcrystals, $1/a^2$.

$$\Delta E(Z_{1,2}-Z_3) = \frac{0.67}{a} \left(\frac{h^2}{2M_h} [\Psi(M_l/M_h)]^2 - \frac{h^2\pi^2}{2M_s} \right) \quad (6)$$

Thus, when the masses of excitons are independent of the diameter, $\Delta E(Z_{1,2}-Z_3)$ could be linearly proportional to $1/a^2$. Above $a=15$ Å, $\Delta E(Z_{1,2}-Z_3)$ is linearly proportional to $1/a^2$ as expected when the masses are constant. However, below 15 Å, the experimental points deviated from the line. Ultimate interpretation on the deviation is so far difficult, but one may presume that the basic parameters of exciton are influenced by the microcrystal size, or that the quantum size effect changes to the relative motion of electrons and holes from center-of-mass motion when the size comes to be close to the Bohr radius of CuCl exciton (13.6 Å in diameter).¹²⁾

4. Conclusion

CuCl-doped Na₂O-B₂O₃-SiO₂ glasses were successfully prepared by conventional melt-quenching technique. The maximum content of CuCl to obtain complete homogeneous glasses is 2 mol%. The exciton peaks are observed at 77 K and even at room temperature. The microcrystal radius is dependent on one third power of annealing time, which clears the crystal growth process. The spectral exciton positions $Z_{1,2}$ and Z_3 are dependent on microcrystal size, and it proves the existence of quantum size effect. The temperature dependence of peak position is attributed to mainly volume effect. From the temperature dependence of Z_3 linewidth, inhomogeneous term is much larger than that of CuCl in NaCl matrix, presumably resulting from the random structure of glass matrix and larger crystal size distribution. Coherent length

of CuCl is evaluated to cover whole microcrystals from homogeneous term. The energy difference of $Z_{1,2}$ and Z_3 peak was linearly proportional to the reciprocal of square diameter of microcrystals ($1/a^2$), when a is larger than 15 Å. However, obvious deviation is noticed below $a=15$ Å, might being attributed to the change of exciton type.

References

- 1) D. W. Hall, M. A. Newhouse, N. F. Borrelli, W. H. Dumbaugh and D. L. Weidman, *Appl. Phys. Lett.*, **54**, 1293-95 (1989).
- 2) H. Nasu, Y. Ibara and K. Kubodera, *J. Non-Cryst. Solids*, **110**, 229-34 (1989).
- 3) H. Nasu, M. Nakamura, K. Kamiya, M. Kobayashi and K. Kubodera, *J. Am. Ceram. Soc.*, **73**, 1794-96 (1990).
- 4) R. K. Jain and R. C. Lind, *J. Opt. Soc. Am.*, **73**, 647-53 (1983).
- 5) J. Yumoto, S. Fukushima and K. Kubodera, *Opt. Lett.*, **12**, 832-34 (1987).
- 6) H. Nasu, K. Tsunetomo, Y. Tokumitsu and Y. Osaka, *Jpn. J. Appl. Phys.*, **28**, L862-64 (1989).
- 7) K. Tsunetomo, H. Nasu, H. Kitayama, A. Kawabuchi and Y. Osaka, *Jpn. J. Appl. Phys.*, **28**, 1928-33 (1989).
- 8) E. Hanamura, *Phys. Rev. B*, **37**, 1273-79 (1988).
- 9) A. I. Ekimov, Al. L. Efros and A. A. Onushchenko, *Solid State Comm.*, **56**, 921-24 (1985).
- 10) A. I. Ekimov, A. A. Onushchenko, A. G. Plyukhin and Al. L. Efros, *Sov. Phys. JETP*, **61**, 891-97 (1985).
- 11) A. I. Ekimov, Al. L. Efros, M. G. Ivonov, A. A. Onushchenko and S. K. Shumilov, *Solid State Comm.*, **69**, 565-68 (1989).
- 12) T. Itoh, Y. Iwabuchi and T. Kiriara, *Phys. Stat. Sol. (b)*, **146**, 531-43 (1988).
- 13) I. M. Lifshitz and V. V. Slesov, *Zh. Eksp. Theor. Fiz.*, **35**, 479 (1958).
- 14) M. Cardona, *Phys. Rev.*, **129**, 69-78 (1963).
- 15) Y. Masumoto, *Kotai Butsuri*, **24**, 937-40 (1989).
- 16) A. I. Ekimov, A. A. Onushchenko, A. G. Pluhin and Al. L. Efros, *Sov. Phys. JETP*, **61**, 891-97 (1985).
- 17) Y. Kayanuma, *Kotai Butsuri*, **24**, 551-58 (1989).