Second-order optical nonlinear and luminescent properties of $Ba_2TiSi_2O_8$ nanocrystallized glass

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The optical properties of $Ba_2TiSi_2O_8$ nanocrystals in transparent crystallized glasses were investigated. The transparent nanocrystallized glass with $Ba_2TiSi_2O_8$ crystals having a particle size of ~200 nm was fabricated by crystallization (at 760 °C for 1 h) of a glass with the stoichiometric composition of $Ba_2TiSi_2O_8$, i.e., $40BaO \cdot 20TiO_2 \cdot 40SiO_2$ glass. Both visible second-harmonic generation (green light, 532 nm) and luminescence (blue light, ~470 nm) could be observed in the transparent $Ba_2TiSi_2O_8$ nanocrystallized glass, demonstrating the optical multifunctional nanocrystallized material. It was suggested that the blue luminescence from the transparent $Ba_2TiSi_2O_8$ nanocrystallized glass originated from the oxygen-related defects of the SiO_4 unit in the $Ba_2TiSi_2O_8$ nanocrystals. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1879114]

Recently, functional nanosized inorganic crystals, i.e., nanocrystals, embedded in a glass matrix have received much attention, because these are candidates for ferroelectric,[1] magnetic,[2] fluorescent,[3] and nonlinear optical materials.[4,5] For instance, Wang *et al.* reported the upconversion luminescence of Yb^{3+}, Er^{3+} codoped-$(Pb,Cd)F_2$ nanocrystals in a fluoroaluminosilicate glass.[3] In addition, the second-order optical nonlinearity was clarified in the transparent glass-ceramics consisting of nonlinear optical nanocrystals in the $Li_2B_4O_7$-$SrBi_2Ta_2O_9$[1] and K_2O-Nb_2O_5-TeO_2 systems.[5] Although it is recognized that such nanocrystallized materials have a great potential for advanced photonic devices, the second-harmonic (SH) wave output from these nanocrystallized glasses are very low, because the particle size of the crystals is much smaller than its coherent length (generally ~10 μm), and the SH intensity is proportional to the particle size. Furthermore, there is no report about transparent nanocrystallized materials with both excellent nonlinear optical and luminescent properties. In order to achieve a high optical performance in a nanocrystallized glass, the following three requirements are indispensable: (1) transparency of the nanocrystallized glass, (2) large volume fraction of nanocrystals in the glass matrix, and (3) development of the nanocrystals with a high optical performance.

We focused on the fresnoite ($Ba_2TiSi_2O_8$) crystal,[6] because a glass with the stoichiometric composition of $Ba_2TiSi_2O_8$ indicates an extremely high nucleation rate, and the size of the $Ba_2TiSi_2O_8$ crystal formed by crystallization in the glass is limited to ~700 nm.[7] Recently, Takahashi *et al.* demonstrated that the fresnoite-type crystals possess very large second-order optical nonlinearities, comparable to that of the $LiNbO_3$ single crystal.[8,9] In this study, we succeeded in fabricating transparent $Ba_2TiSi_2O_8$ nanocrystallized glasses, and observed a large second-order optical nonlinearity in these nanocrystallized glasses. Furthermore, an obvious blue luminescence was found in the nanocrystallized glass by UV excitation, demonstrating that these nanocrystallized glasses have a significant potential as both nonlinear optical and luminescent materials.

The glass composition used in this study was $40BaO \cdot 20TiO_2 \cdot 40SiO_2$, which is the stoichiometric composition of the $Ba_2TiSi_2O_8$ crystal. The glasses were prepared using a conventional melt-quenching method. Commercial powders of reagent grade $BaCO_3$, TiO_2, and SiO_2 were mixed and melted in a platinum crucible at 1550 °C for 1 h in an electric furnace. The batch weight was 20 g. The melts were poured onto an iron plate and pressed to a thickness of about 1 mm with another iron plate. Refractive index of glass sample was measured at room temperature using an ellipsometer at a wavelength of 632.8 nm (He–Ne laser). The glass plates were mechanically polished to obtain a mirror surface using a diamond slurry and CeO_2 powder and then heat treated at various temperatures, T_{HT}, to obtain the transparent nanocrystallized glasses. The heat treatment was performed in a tube furnace. The temperature was maintained within ±1 °C. Crystallization was carried out by heating the glass at 5 °C/min to T_{HT}, holding at T_{HT} for 1 h, and then cooling slowly to room temperature. The SH intensity of the nanocrystallized glass was measured by Maker fringe techniques.[10] A fundamental wavelength of a Q-switched Nd^{3+}: yttrium–aluminum–garnet (YAG) laser at a wavelength of 1064 nm was used as the incident light. Details of the second-harmonic generation (SHG) measurement are described elsewhere.[8,9] Confirmation of photoluminescence and its spectral measurement for the samples were carried out using an ultraviolet (UV) lamp with a wavelength of 254 nm and a spectrofluorometer with a xenon lamp as the excitation source, respectively, at room temperature.

Optical absorption spectra for the precursor glasses subjected to the heat treatment at T_{HT}=760–780 °C for 1 h are shown in Fig. 1. The glass sample heat treated at T_{HT}

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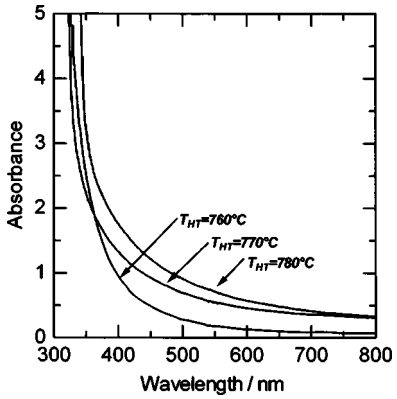

FIG. 1. Optical absorption spectra in the wavelength region of 300–800 nm for the glass samples heat treated at T_{HT}=760–780 °C for 1 h.

=760 °C maintained a good transparency in the visible region. However, for T_{HT}=770 and 780 °C, the samples became slightly opaque. Figure 2 shows the SEM image of the cross section of the heat-treated precursor glass at T_{HT} =760 °C. In Fig. 1, it is confirmed that the crystal particles with a diameter of ~200 nm, less than the wavelength of visible light, are very densely and uniformly precipitated in the sample. These crystal particles were confirmed to be $Ba_2TiSi_2O_8$ crystals based on the XRD measurement. Thus, we succeeded in fabricating an optically transparent $Ba_2TiSi_2O_8$ nanocrystallized glass by careful heat treatment of the precursor glass.

The refractive index for the precursor glass at the wavelength of 632.8 nm was measured to be ~1.77, which was close to that of the $Ba_2TiSi_2O_8$ single crystal (~1.76).[11] According to Beall and Duke,[12] the intensity of the light based on Rayleigh scattering is described by the following equation:

$$I(\theta) = \frac{(1+\cos^2\theta)}{r^2}\frac{8\pi^4}{\lambda^4}a^6\left(\frac{M^2-1}{M^2+2}\right)I_0,$$

where I is the intensity of the scattered light, θ is the scattering angle, r is the distance from the scattering source, λ is

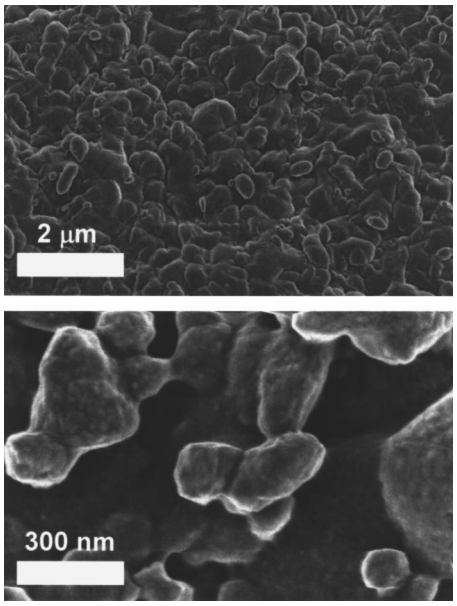

FIG. 2. SEM image of the cross section of the transparent $Ba_2TiSi_2O_8$ nanocrystallized glass fabricated at T_{HT}=760 °C for 1 h.

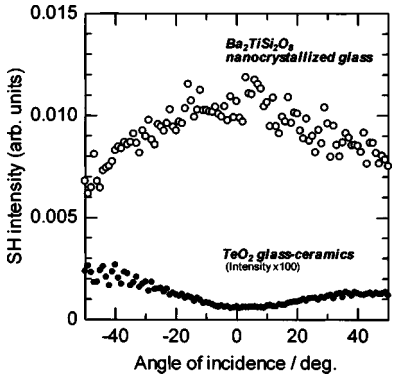

FIG. 3. Maker fringe patterns for the transparent $Ba_2TiSi_2O_8$ nanocrystallized glass fabricated at T_{HT}=760 °C for 1 h (open circle) and the $15K_2O\cdot15Nb_2O_5\cdot70TeO_2$ glass ceramics (closed circle). The fabrication of the $15K_2O\cdot15Nb_2O_5\cdot70TeO_2$ glass ceramics was carried out using the procedure described in Ref. 5.

the wavelength of the light, a is the radius of the particle in the medium, M is the ratio of the refractive index of the particle to that of the medium, and I_0 is the intensity of the incident light. From this equation, one can realize that both the smallness of the crystals in the glass matrix, and the closeness of the refractive index of the crystals to that of the matrix are required for the glass-ceramic materials to be transparent. Thus, in this study, the fabrication of the $Ba_2TiSi_2O_8$ nanocrystallized glass with a good transparency is achieved by the precipitation of the nanosized $Ba_2TiSi_2O_8$ crystalline particle and the closeness of the refractive index between the crystal and precursor glass.

The Maker fringe pattern for the transparent $Ba_2TiSi_2O_8$ nanocrystallized glass fabricated at T_{HT}=760 °C for 1 h is shown in Fig. 3. The data for the transparent $15K_2O\cdot15Nb_2O_5\cdot70TeO_2$ glass ceramics are also included in Fig. 3. A clear green light, corresponding to the SH wave (532 nm), could be observed coming from the transparent $Ba_2TiSi_2O_8$ nanocrystallized glasses, demonstrating that the nanocrystallized glass has a function of wavelength conversion based on a second-order optical nonlinearity. The maximum SH intensity of ~1/100 compared to the intensity of the reference (Z-cut α-quartz single crystal) was accomplished in the transparent $Ba_2TiSi_2O_8$ nanocrystallized glass. This SH intensity is $\sim10^3$ times greater than the intensity of the transparent nanocrystallized glasses achieved so far, e.g., the transparent $15K_2O\cdot15Nb_2O_5\cdot70TeO_2$ glass ceramics.[5] Takahashi *et al.* reported that the large optical nonlinearity for the $Ba_2TiSi_2O_8$ crystal (~10 pm/V) originated in the sequence of the pyramidal TiO_5 units along the c-axis in the fresnoite-type structures.[9] In addition, the halo pattern, which is a characteristic of amorphous material, could not be observed in the powder XRD pattern for the transparent $Ba_2TiSi_2O_8$ nanocrystallized glass. Moreover, it is reported that in the $40BaO\cdot20TiO_2\cdot40SiO_2$ glass, the volume fraction of the $Ba_2TiSi_2O_8$ crystals reached 1 by the crystallization at >750 °C for 1 h.[7] These suggest that the precursor glass almost completely convert into the $Ba_2TiSi_2O_8$ phase by the crystallization. Consequently, the transparent $Ba_2TiSi_2O_8$ nanocrystallized glass meets the three requirements already mentioned. Therefore, the evolution of such a large SHG for the nanocrystallized glass was accomplished in this study.

Since the importance of luminescent material for use in field emission displays (FED) and the plasma display panels

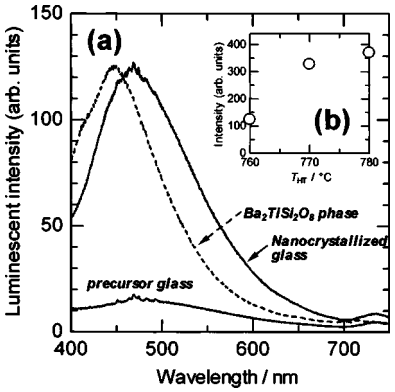

FIG. 4. (a) Luminescent spectra for the precursor glass, the transparent $Ba_2TiSi_2O_8$ nanocrystallized glass ($T_{HT}=760$ °C), and $Ba_2TiSi_2O_8$ polycrystalline phase synthesized by a solid-state reaction; (b) dependence of the blue luminescent intensity in the samples fabricated at $T_{HT}=760$–780 °C for 1 h on the heat treatment temperature.

(PDP) have recently increased, the exploitation of a luminescent compound, particularly a blue luminescent material, has significantly occurred. It has been reported that the fresnoite crystal exhibits a broad blue luminescence in the range of about 400–600 nm.[13] It is expected that the transparent $Ba_2TiSi_2O_8$ nanocrystallized glasses fabricated in this study also have the capability as a blue luminescence material. Therefore, we also examined the luminescent properties for the $Ba_2TiSi_2O_8$ nanocrystallized glasses. Figure 4(a) shows the luminescent spectra for the precursor glass, the transparent $Ba_2TiSi_2O_8$ nanocrystallized glass ($T_{HT}=760$ °C), and the $Ba_2TiSi_2O_8$ polycrystalline phase synthesized by a solid-state reaction are shown in Fig. 4. The broad emission of blue light with the peak at ~470 nm was observed in the precursor and the nanocrystallized glasses. This feature agrees with that of Blasse's report.[13] It was also seen by the naked eye that these transparent $Ba_2TiSi_2O_8$ nanocrystallized glasses exposed to UV light ($\lambda=254$ nm) showed a clear blue luminescence was observed. The blue luminescent intensity at 470 nm as a function of heat treatment temperature, T_{HT} is shown in Fig. 4(b). The luminescent intensity is increased with T_{HT}. It is considered that the increase of luminescent intensity is due to the increase of the volume fraction of the $Ba_2TiSi_2O_8$ nanocrystals.

The mechanism of the blue luminescence in the $Ba_2TiSi_2O_8$ crystal is still controversial; it has been proposed that the pyramidal TiO_5 unit is the probable origin of the luminescence, because some compounds with six-coodinated Ti^{4+} do not show any luminescence at room temperature.[13] On the other hand, Gaft *et al.* recently reported a blue luminescence by UV excitation in benitoite ($BaTiSi_3O_9$) with TiO_6 octahedra.[14] A point in common between these minerals is the existence of the SiO_4 tetrahedral unit in the crystal. It is known that the pure and doped-silica glasses fabricated by a sol-gel method and a mesoporous silica possess a blue photoluminescence around 450 nm, and these luminescences originate from the oxygen-related defects of the SiO_4 units in the glasses.[15–17] Therefore, it is suggested that the blue luminescence from the transparent $Ba_2TiSi_2O_8$ nanocrystallized glass and the fresnoite crystal is also due to the oxygen defect center of the $Ba_2TiSi_2O_8$ crystals. However, in the $Ba_2TiSi_2O_8$ phase via a solid-state reaction, the peak position of the luminescence lies at ~450 nm, 20 nm shorter than that of the nanocrystallized glass. Although the reason for this is still unclear, it may be concerned with the difference in the preparation process of the samples.

Fujiwara *et al.* succeeded in creating the periodic structure of nonlinear optical nanocrystals by laser-induced nanocrystallization in the K_2O–Nb_2O_5–TeO_2 glass.[18] A silicate glass showing nanocrystallizaion has a great potential for use in a photonic device and fiber application. Therefore, it is strongly expected that the transparent $Ba_2TiSi_2O_8$ nanocrystallized glass is an excellent candidate for photonic devices with an ordered nanostructure and second-order optical nonlinearity. Such an investigation is now in progress.

In summary, we succeeded in fabricating an optically transparent $Ba_2TiSi_2O_8$ nanocrystallized glass from a glass with the stoichiometric composition of the $Ba_2TiSi_2O_8$ crystal using a careful heat treatment at $T_{HT}=760$ °C for 1 h. It was observed that the $Ba_2TiSi_2O_8$ crystalline particles with the diameter of about 200 nm were densely formed in the nanocrystallized glass. A very large second-order optical nonlinearity, strong green light of SHG, was confirmed from the nanocrystallized glass. In addition, a visible blue luminescence with a peak at ~470 nm was also confirmed in this sample. It was demonstrated that the transparent $Ba_2TiSi_2O_8$ nanocrystallized glass made in this study possessed both a large optical nonlinearity and photoluminescence, i.e., an optical multifunctional nanocrystallized material. Furthermore, it was suggested that the blue luminescence from the transparent $Ba_2TiSi_2O_8$ nanocrystallized glass originated from the oxygen-related defects in the $Ba_2TiSi_2O_8$ nanocrystals.

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[1] G. S. Murugan, K. B. R. Varma, Y. Takahashi, and T. Komatsu, Appl. Phys. Lett. **78**, 4019 (2001).
[2] M. Zayat, F. Monte, M. P. Morales, G. Rosa, H. Guerrero, C. J. Serna, and D. Levy, Adv. Mater. (Weinheim, Ger.) **15**, 1809 (2003).
[3] Y. Wang and J. Ohwaki, Appl. Phys. Lett. **63**, 3268 (1993).
[4] D. Li, Y. Lin, L. Zhang, and X. Yao, J. Non-Cryst. Solids **261**, 273 (2000).
[5] R. Sakai, Y. Benino, and T. Komatsu, Appl. Phys. Lett. **77**, 2118 (2000).
[6] P. B. Moore and J. Louisnathan, Science **156**, 1361 (1967).
[7] A. A. Cabral, V. M. Fokin, E. D. Zanotto, and C. R. Chinaglia, J. Non-Cryst. Solids **330**, 174 (2003).
[8] Y. Takahashi, Y. Benino, T. Fujiwara, and T. Komatsu, Appl. Phys. Lett. **81**, 223 (2002).
[9] Y. Takahashi, Y. Benino, T. Fujiwara, and T. Komatsu, J. Appl. Phys. **95**, 3503 (2004).
[10] P. D. Maker, E. W. Terhune, M. Nisenoff, and C. M. Savage, Phys. Rev. Lett. **8**, 21 (1962).
[11] S. Haussühl, J. Eckstein, K. Recker, and F. Wallrafen, J. Cryst. Growth **40**, 200 (1977).
[12] G. H. Beall and D. A. Duke, J. Mater. Sci. **4**, 340 (1969).
[13] G. Blasse, J. Inorg. Nucl. Chem. **30**, 2283 (1968).
[14] M. Gaft, L. Nagli, G. Waychunas, and D. Weiss, Phys. Chem. Miner. **31**, 365 (2004).
[15] P. Yang, C. F. Song, M. K. Lu, J. Chang, Y. Z. Wang, Z. X. Yang, G. J. Zhou, Z. P. Ai, A. Xu, and D. L. Yuan, J. Solid State Chem. **160**, 272 (2001).
[16] C. F. Song, M. K. Lu, S. F. Wang, D. Xu, D. R. Yuan, and G. J. Zhou, Inorg. Mater. **39**, 1326 (2003).
[17] Y. C. Lee, Y. L. Liu, J. L. Shen, I. J. Hsu, P. W. Cheng, C. F. Cheng, and C. H. Ko, J. Non-Cryst. Solids **341**, 16 (2004).
[18] T. Fujiwara, R. Ogawa, Y. Takahashi, Y. Benino, and T. Komatsu, Phys. Chem. Glasses **43C**, 213 (2002).