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Optical Properties and Structure of $BaO-TiO_2-SiO_2$ Glass Ceramics

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ABSTRACT

Nanocrystallized glasses with the composition of $(50-x)BaO-xTiO_2-50SiO_2$ (x=10, 15, 16.7 and 20) have been prepared by heat-treatment at T_x (crystallization onset temperature) for 3 h, and their optical properties, photoluminescence (PL), XRD and Raman spectra have been examined. The absorption edges of the glasses were red-shifted and the absorption coefficient increased with an increase of TiO_2. The glass subjected to the heat-treatment showed a dense formation of $Ba_2TiSi_2O_8$ crystals. The XRD and Raman results show that the nanocrystallized glasses formed fresnoite phase up to TiO_2 concentrations of 15 mol%. Furthermore, blue luminescence with a peak at the wavelength of around 470 nm was observed in the nanocrystallized glass, demonstrating the optical multifunctional nanocrystallized material such as non-linear optics and photo-luminescence. It is thought that the blue luminescence from the $Ba_2TiSi_2O_8$ nanocrystallized glass originated from the presence of Ti^{4+} incorporated into the fresnoite-type structure.

Key words*: *Nanocrystallized glass, $Ba_2TiSi_2O_8$ (fresnoite), Photoluminescence

1. Introduction

Fresnoite $Ba_2TiSi_2O_8$, belonging to the P4bm group, has TiO_5 square pyramidal structure, which is the origin of the polarizability of this crystal.[1] In addition, since $Ba_2TiSi_2O_8$ crystal shows piezoelectric properties,[2,3] this crystal is thought to be a candidate for surface-acoustic-wave devices.[4,5] Since $Ba_2TiSi_2O_8$ crystal also shows pyroelectric,[6] ferroelectric,[7] fluorescence,[8,9] and non-linear optical properties,[10] $Ba_2TiSi_2O_8$ single crystal compositions and crystallized glasses (glass-ceramics) containing $Ba_2TiSi_2O_8$ crystallite have been studied since the 1960s. One of the interesting properties of $Ba_2TiSi_2O_8$ is its polarizability along the c-axis. Unlike a single $Ba_2TiSi_2O_8$ crystal, the polarizability of $Ba_2TiSi_2O_8$ phase in crystallized glasses, specifically in the surface of crystallized glass, can be controllable by heat-treatment. Several studies on $Ba_2TiSi_2O_8$ crystallized glasses have been performed to assess polarizability using conventional melt-quenching,[11,12] sputtering,[13-16] and the sol-gel method,[17] because high polarizability of $Ba_2TiSi_2O_8$ phase is favorable for its application to piezoelectric, ferroelectric, and non-linear optical materials. For practical applications of non-linear optical materials, transparent crystallized glass, which contains $Ba_2TiSi_2O_8$ crystallite without the light propagation loss, is desired. There are, however, a few reports about transparent $BaO-TiO_2-SiO_2$ (BTS) crystallized glass,[9,18,19] and the nominal compositions of glasses in previous reports were around a stoichiometric composition of $Ba_2TiSi_2O_8$: $40BaO-20TiO_2-40SiO_2$[9,19] or $33.3BaO-16.7TiO_2-50SiO_2$.[18] Because the crystallization behavior in a glass matrix depends on the composition of the glass as well as on the heat-treatment conditions during crystallization, the overall crystallization tendency of BTS glass in a glass forming region is worthy of investigation. Because the optical properties, second harmonic generation (SHG) and photoluminescence (PL), are very sensitive to heat-treatment conditions, it is interesting to examine the crystallization behavior of BTS glass and to clarify correlations between its optical properties and its structures.

For the present study, BTS glasses with different chemical composition were prepared. The BTS crystallized glasses were prepared by heat-treatment at crystallization onset temperature for 3 h and the crystallization behavior was analyzed using X-ray diffraction (XRD). The Relationship between structure and optical properties in the nanocrystallized glasses with $Ba_2TiSi_2O_8$ crystals was examined using Raman, UV-vis and photoluminescence (PL).

2. Experimental procedure

2.1. Preparation of $BaO-TiO_2-SiO_2$ (BTS) glass and the crystallized glass

The $BaO-TiO_2-SiO_2$ (BTS) glasses were prepared by a conventional melt-quenching method with starting materials of $BaCO_3$ (99.9%), TiO_2 (99.9%) and SiO_2 (99.9%). Batches were mixed and melted in a platinum crucible in an electric furnace at 1550°C for 1 h, and the glass melt was poured on

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Table 1. Glass Composition, Crystallization Onset Temperature, T_x, Crystallization Peak Temperature, T_p, Density of the Present BaO-TiO_2-SiO_2 (BTS) Glasses

	Composition (mol %)			T_x (°C)	T_p (°C)	Density ($g \cdot cm^{-3}$)
	BaO	TiO_2	SiO_2			
BTS-1	30	20	50	849.76	868.43	3.88583
BTS-2	33.3	16.7	50	838.30	867.23	3.95647
BTS-3	35	15	50	835.97	863.42	3.99997
BTS-4	40	10	50	817.53	849.46	4.13193

a steel plate using a mold press quenching method. Obtained glasses were annealed at their respective temperatures of glass transition, T_g, for 30 min, and then cut and mechanically polished to obtain the mirror surface. The glass samples were heat-treated for 3 h on an alumina plate in a tubular furnace under an ambient atmosphere at crystallization onset temperature, T_x, which was determined by differential thermal analysis (DTA). After the heat-treatment, the furnace was allowed to cool without temperature control.

2.2. Measurement

Crystallization onset temperature, T_x, and crystallization peak temperature, T_p, were estimated by DTA at a heating rate of 10°C/min using TG-DTA 60 (SHIMADZU). The crystalline phases and crystal sizes in the crystallized glasses were examined using an X-ray diffraction (XRD) machine equipped with Cu-Kα radiation (RIGAKU MiniFlex). The density of the sample was measured by the Archimedes method. Absorption spectra were measured using a UV-vis (Agilent 8453). The vibration characteristics of the crystallized glasses were determined by Raman scattering (BRUKER FT-RAMAN Spectrometer FRA 106/S). The PL measurement for the samples was performed using ultraviolet (UV) lamps with wavelengths of 254 nm, 312 nm and 365 nm, and using a spectrofluorometer with a Xenon lamp as the excitation source at room temperature.

3. Results and Discussions

3.1. BaO-TiO_2-SiO_2 (BTS) precursor glass

The obtained transparent BaO-TiO_2-SiO_2 (BTS) glasses were colorless or slightly yellowish. In the alkali (alkaline earth)-titanate-silicate glasses, if the ratio of TiO_2 : alkali (alkali earth) exceeds 1, and when the amount of TiO_2 exceeds the amount of alkali metal oxides, TiO_2 separates as rutile, or possibly as anatase.[20,21] The fact that the ratio of TiO_2 : alkali (alkaline earth) is important for the system of alkali-titanate-silicate glasses is further confirmed by the fact that a number of physical properties such as electrical, optical properties and density are affected by the ratio.[23] Table 1. shows the temperature of crystallization onset, T_x, and crystallization peak, T_p, of the BTS glasses in the present study. The value of density values are also shown in the same table. T_x and T_p of the glasses increased approximately in parallel with increasing TiO_2 content, whereas the density was strongly dependent on the amount of TiO_2. The effect of an increase of T_x and T_p is that TiO_2 improves the meltability of glasses, chiefly due to the formation of eutectics with SiO_2 and $BaCO_3$.[22] Decrease of density of the glasses are the reason that the density of BaO (5.7 $g \cdot cm^{-3}$) is larger than TiO_2 (4.23 $g \cdot cm^{-3}$).[23] Fig. 1 shows the absorp-

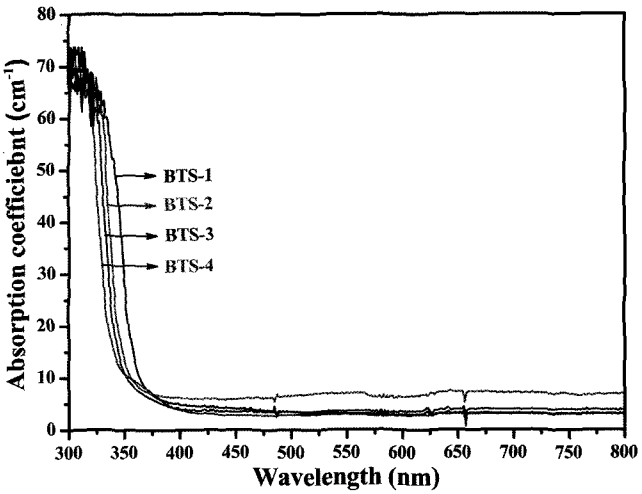

Fig. 1. Absorption spectra of (50-x)BaO-xTiO_2-50SiO_2 (x=10, 15, 16.7, 20) glasses.

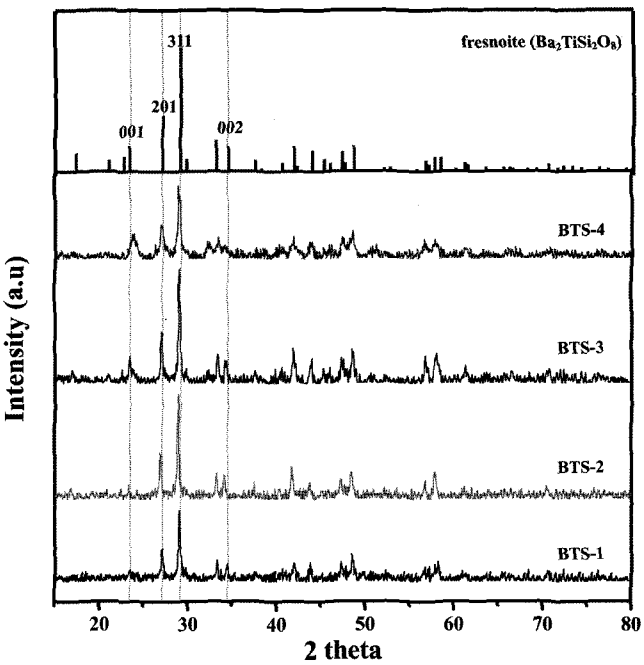

Fig. 2. Powder XRD patterns for the BTS glasses heat-treated at T_x for 3 h.

Table 2. The Analysis of Lattice Deformation from XRD Data, Heat Treated for 3 h at T_x

	Main phase	Standard 2θ (deg.)	Measured 2θ (deg.)	Δ(2θ) (deg.)	FWHM (deg.)	Deformation (%)	Orientation Index(OI)
BTS-1	BTS ($Ba_2TiSi_2O_8$)	29.00	29.060	0.060	0.306	0.03382	0.24916
		26.99	27.080	0.090	0.329	0.01326	
		33.19	33.260	0.070	0.282	0.00721	
BTS-2	BTS ($Ba_2TiSi_2O_8$)	29.00	28.920	0.080	0.282	0.04509	0.22991
		26.99	26.900	0.090	0.306	0.01326	
		33.19	33.220	0.030	0.306	0.00309	
BTS-3	BTS ($Ba_2TiSi_2O_8$)	29.00	29.040	0.040	0.329	0.02254	0.33333
		26.99	27.040	0.050	0.282	0.00736	
		33.19	33.340	0.150	0.306	0.01546	
BTS-4	BTS ($Ba_2TiSi_2O_8$)	29.00	28.980	0.980	0.329	0.55234	0.10016
		26.99	27.020	0.030	0.447	0.00442	
		33.19	33.420	0.230	0.282	0.02370	

tion spectra of the $(50-x)BaO-xTiO_2-50SiO_2$ (x=10, 15, 16.7, 20) glasses as a function of wavelength. Absorption coefficients were calculated by following equation.

$$\frac{I}{I_0} = e^{-ax}$$

where, I_0 is the intensity (or power) of the incident light and I is the intensity of the light, after passing through the material, a is the absorption coefficient and x is the thickness of the sample. The absorption edges of the glasses were red-shifted and the absorption coefficient increased with increasing concentrations of TiO_2.

3.2. XRD analysis

BTS crystallized glasses were obtained by heat-treatment at T_x, which was determined by DTA, for 3h. Fig. 2 shows XRD patterns of BTS-1, 2, 3 and 4 crystallized glasses almost match the diffraction pattern of fresnoite $Ba_2TiSi_2O_8$ (JCPDS No. 022-0513). To analyze the lattice deformation according to TiO_2 contents, the full-widths at half maximum (FWHM) and deviations $\Delta(2\theta)$ of peak positions from the XRD data of the three glass–ceramics were calculated using the equation below.[24]

$$\varepsilon(\Psi,\varphi) = \frac{\Delta(2\theta)(\Psi,\varphi)}{2\tan(\theta_0)}$$

where, $\varepsilon(\Psi, \varphi)$ is the deformation of the correspondent planes, $\Delta(2\theta)$ represents the deviations of peak position, and θ_0 is the standard diffraction angle, respectively. The deformations of the lattice in different planes were calculated and listed in Table 2. It can be seen that in the glass-ceramics with $BaTiSi_2O_8$ phase, the deformation of the crystal lattice was much larger than that of the glass-ceramics with fresnoite single phase. It can be seen from Table 2 that the full-widths at half maximum (FWHM) were approximately from 0.282° to 0.329° in the main first peak (311), indicating that the sizes of crystal in the glass-ceramic samples increased with increasing TiO_2. The FWHM of the (002) diffraction peak, however, was from 0.141 to 0.259 in all present BTS crystallized glass, indicating that average grain sizes were almost the same in the BTS glasses obtained in the present study. The deviation range of peak positions for the four glass–ceramic samples has a variation from 0.034°~0.007° to 0.552°~0.024° and BTS-2 shows the least variation. In the present study, the lattice deformation is demonstrated through XRD data based on internal stress, because the deformation could be caused by a mismatch between the thermal expansion coefficient of the glass and that of the crystal phase, and a larger deformation means that the crystals are subject to a greater stress. Hence, it is proposed that deformation is due to the internal stress between the glass and the crystal or crystals.

The relative degree of orientation in $Ba_2TiSi_2O_8$ crystallized phase can be estimated using the ratio of the intensity of (311) peak, I_{311}, which is the main peak of the $Ba_2TiSi_2O_8$ single crystal samples, and that of the (002) c-orientated peak, I_{002}. In this study, an orientation index (*OI*) of fresnoite is defined as below:

$$OI = \frac{I_{002}}{I_{311}}$$

The relation between orientation index and composition change is shown in Table 2. With the exception of that of the BTS-4 crystallized glass, the *OI* of the BTS crystallized glasses showed surface crystallization, and the I_{002}/I_{311} ratios for the crystallized glasses are more than 0.2, and more than the estimated value of the $Ba_2TiSi_2O_8$ single crystal sample, which is 0.2. In particular, the I_{002}/I_{311} ratio of BTS-3 is 0.33, which is the largest value among all the BTS crystallized glasses in the present study. In the case of BTS-4, the I_{002}/I_{311} ratio is 0.1. This clearly shows that both surface and bulk crystallization, which is an unusual crystallization, occurred in BTS-4 with heat-treatment at T_x. It is thought that the BTS-3 with c-oriented crystallized phase showed the largest optical non-linearity among all crystallized glasses in the present study. This is because the ten-

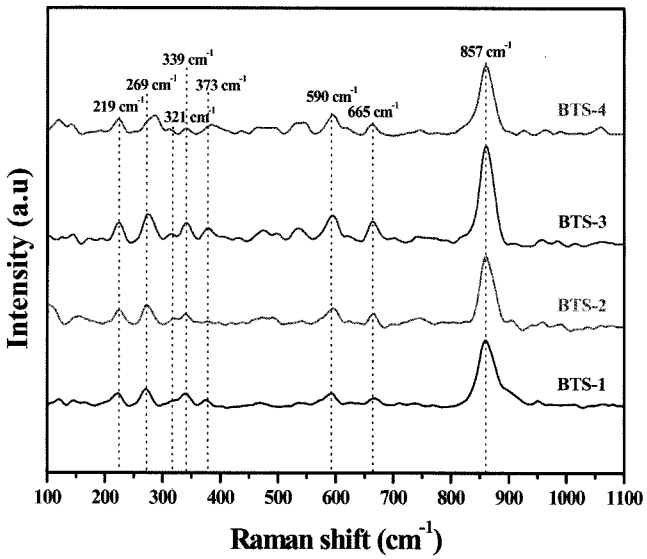

Fig. 3. Raman spectra of glass-ceramics crystallized at each crystallization temperature for 3 h.

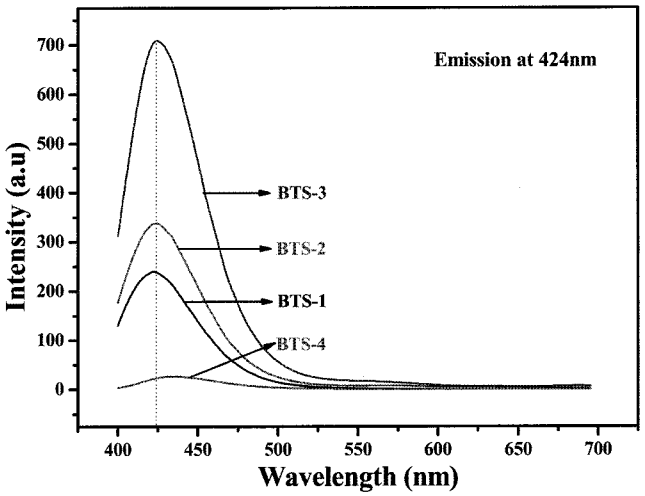

Fig. 4. Excitation and photoluminescent spectra for the BTS glass and $Ba_2TiSi_2O_8$ nanocrystallized glasses, BTS-1, 2, 3 and 4.

dency of the effect of glass composition on optical non-linearity is similar to that of the I_{002}/I_{311} ratio, or the c-orientation in the crystallized phase.[21] Despite some differences in the degree of transparency among the crystallized glasses, the results clearly show that there is a strong correlation between the orientation along the polar c-axis in the fresnoite phase and the optical non-linearity, which was demonstrated in the $BaO\text{-}TiO_2\text{-}GeO_2$ crystallized glass system.[25]

3.3. Raman analysis

Fresnoite is considered a silicate mineral with a specific $[TiO_5]$ pyramid and layered $[Si_2O_7]$ structure. Fig. 3 shows the Raman spectra of BTS-1~4 glass–ceramics heat treated at each T_x for 3 h. According to previous research on the Raman spectrum of fresnoite crystal,[26,27] the band around 857 cm^{-1} and 590 cm^{-1} can be respectively assigned to the A_1-mode of the short Ti-O bond and to the $v(TiO_4)$ mode, and the band at 665 cm^{-1} can be assigned to the vibration of v(Si-O-Si) mode. First, the broad band around 857 cm^{-1} can be assigned to the stretching mode of the short Ti-O^* bond (O^* denotes an apical oxygen), to the Ti-O bonds (O denotes a non-bridging oxygen), and to the terminal SiO_3 groups.[27] With decreasing TiO_2 content, the band around 858 cm^{-1} becomes narrow and the strongest peak, at 857 cm^{-1} which is assigned to the vibration of the short Ti-O bond, becomes increasingly distinct. Further, the band at 321 cm^{-1} splits into several peaks at 219 cm^{-1}, 269 cm^{-1}, 339 cm^{-1} and 373 cm^{-1} due to the translational and bending modes of the Si_2O_7 and TiO_5 group, excluding BTS-4.[26] All the sharp peaks agreed well with the Raman spectrum of $Ba_2TiSi_2O_8$ crystal in BTS-1, 2 and 3.[26,27] Therefore, it is confirmed that $Ba_2TiSi_2O_8$ crystal precipitated around TiO_2 contents ranging from 20 mol% to 15 mol%. Incomplete precipitation of $Ba_2TiSi_2O_8$ crystal was observed in BTS-4 with a TiO_2 content of 10 mol%, which has weak peaks at 369 cm^{-1}, 339 cm^{-1}, 373 cm^{-1}. This result was caused by surface and bulk crystallization, as can be seen in the XRD results.

3.4. PL analysis

Since the demand for luminescent material for use in field emission displays (FED) and the plasma display panels (PDP) has recently increased, the exploitation of luminescent compounds, particularly blue luminescent compounds, has significantly increased. It has been reported that the fresnoite crystal exhibits a broad blue luminescence in the range of about 400 nm~600 nm.[8] It is expected that the transparent $Ba_2TiSi_2O_8$ nanocrystallized glasses fabricated in this study also have the potential to be used as a blue luminescent material. Therefore, the luminescence properties of the $Ba_2TiSi_2O_8$ nanocrystallized glasses were also examined in this study. Fig. 4 shows the luminescence spectra for the transparent $Ba_2TiSi_2O_8$ nanocrystallized glass heat treated at T_x for 3 h for all samples from BTS-1 to BTS-4. The excitation was carried out using a 248 nm Xeon lamp. The broad emission of blue light with a peak around 470 nm was observed in the nanocrystallized glasses. 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, and the intensity was progressively greater for BTS-1, 2 and 3. This increase of PL intensity also accords with the XRD and Raman spectra results. The luminescent intensity of BTS-4, however, shows an abnormal tendency. Furthermore the emission peak of sample BTS-4 is not matched with that of the compositions, which lies at 435 nm. This is thought to be due to the effect of the bulk crystallization and surface crystallization discussed in the XRD results. 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.[8] However, Gaft et al. reported the emis-

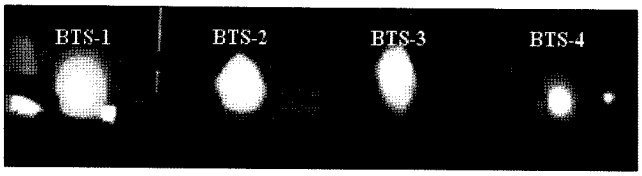

Fig. 5. SHG for $Ba_2TiSi_2O_8$ each glass ceramics. The incident laser light (λ=1064 nm) came from the rear side of the picture.

sion of blue light in benitoite ($BaTiSi_3O_9$) having three-membered silicate rings (Si_3O_9) and six-coordinated Ti^{4+} by UV excitation.[28] They suggested that the blue PL in the benitoite corresponds to the $^3T_{1u} \rightarrow {}^1A_{1g}$ transition of the TiO_6 luminescence center.[29] In addition, the excitation and PL spectra of the $Ba_2TiSi_2O_8$ nanocrystallized glasses in this study (Fig. 4) bear considerable analogy with those of the $BaTiSi_3O_9$ crystal.[28] Therefore, it is considered that the blue emission of PL of the $Ba_2TiSi_2O_8$ nanocrystallized glasses is coming from the presence of Ti^{4+} incorporated into the fresnoite-type structure.[19]

5. Conclusion

The optical and structural properties of (50-x)BaO-xTiO_2-50SiO_2 (x=10, 15, 16.7, 20) glasses containing fresnoite crystals ($Ba_2TiSi_2O_8$) were investigated in this study. First, BTS-1, 2 and 3, the nanocrystallized samples nearly stoichiometric to $Ba_2TiSi_2O_8$, were obtained through heat-treatment. The nanocrystallized glasses fabricated at T_x for 3 h feature visual transparency and I_{002}/I_{311} ratios greater than 0.2 and greater than the estimated value of $Ba_2TiSi_2O_8$ single crystal structure, which is 0.2. Raman spectra peaks at 219 cm^{-1}, 269 cm^{-1}, 339 cm^{-1} and 373 cm^{-1} show the translational and bending modes of the Si_2O_7 and TiO_5 groups. The broad emission of blue light with a peak around 470nm was observed in the nanocrystallized glasses. According to the XRD, Raman and PL results, BTS-3 shows the highest properties of fresnoite, followed in decreasing order by BTS-2 and BTS-1. All of the tested crystallized glasses showed surface crystallization. BTS-4 showed bulk and surface crystallization at the same time. The XRD, Raman and PL results of BTS-4 are not precisely matched with those of fresnoite crystal. This result is thought to result from the fact that BTS-4 is a non-stoichiometric composition, because the mole fraction of TiO_2 is smaller than BaO, and because the ideal stoichiometric mole fraction of fresnoite is 2BaO-TiO_2-2SiO_2. Fig. 5 shows the SHG for each of the $Ba_2TiSi_2O_8$ glass ceramics. The incident laser light (λ=1064 nm) came from the rear side of the picture.

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