Preparation and properties of anti-glare glass doped with rare earth ions Ce^{3+}, Sm^{3+} and Ho^{3+}

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Glare proof glass is a functional glass material which absorbs ultraviolet and blue light being harmful to the human eyes while maintaining a high overall transmittance. In this paper, silicate glasses with different amounts of Ce^{3+}, Sm^{3+} and Ho^{3+} were prepared by high temperature melting method, and their expansion coefficient, refractive index, density and transmission spectrum were measured. The results showed that when the doping concentration of three rare earth ions Ce^{3+}, Sm^{3+} and Ho^{3+} in silicate matrix is 1.5 wt%, 31.1 wt% and 2.3 wt%, the glass samples have a large absorption in ultraviolet and blue light regions, and the glare can be prevented.

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1. Introduction

Based on the current technology condition, a simple anti-glare way is to transform the mirror reflection into diffuse reflection by coarsening the surface structure to achieve the purpose. Special glass manufacturer Schott launched the first commercial high-strength anti-glare glass on June 5, 2012. It has excellent anti-glare properties and excellent physical properties, resulting in a series of anti-glare glass in electronics [1]. The field of display devices has been widely used. The most commonly used method is Chemical etching [2], which uses a mixed solution of sulfuric acid and fluoride to chemically etch the glass surface. This method is often applied to an environment where the equipment is less demanding. But the disadvantage is that it is difficult to handle chemical corrosion residues, and excessive acid etching results in a decrease in the overall transmittance. Foreign technicians have also applied a coating method for glass [3]. The microscopic protrusions are processed on the surface of the uneven micro-structures to perform nano-level operations, coated the multiple composite film with a graded index of refraction, which is combined with conventional etching to achieve anti-glare purposes. This type of process technology requirements are relatively high, it is difficult to apply to the needs of the general public. The advantages are outstanding and the disadvantages are obvious. It is the development of anti-glare structure in the prior art.

Among the light waves that constitute glare, the blue and ultraviolet regions are the main components. This article aims to solve the problem of anti-glare by changing the glass formulation and doping with rare earth elements that reduce such light waves. It not only avoids the disadvantages of the prior art that requires high processing difficulty, and surface roughness affects the transmittance, but also can reduce costs in large scale production to put it into use. By this means, the purpose and effect of the experiment were achieved.

2. Experimental process

The materials needed for the experiment are SiO_2, HBO_3, Na_2CO_3, $NaNO_3$, K_2CO_3, Al_2O_3 and TiO_2. This study chose silicate glass as the base material. Using high temperature melting method, the temperature is 1430 °C. Melting process will last for 20 min and the annealing temperature of releasing its internal stress is 500 °C, holding time 4h, completing glass fire, and processing and making it meet the test requirements. In order to understand the properties of glass products, the spectrophotometric determination was carried out by using the ultraviolet-visible spectrophotometer (Ultima IV, PerkinElmer, Waltham, America). The thermal expansion coefficient was measured by using the horizontal dilatometer (HTV). The density was measured by the HYDMDB-II and the refractive index was measured by the abbe refractometer (wzs-1).

3. Results and analysis

3.1. Performance and analysis of single-doped Ce^{3+} silicate glass samples

In experiments, the absorption range of trivalent terbium ions in silicate glass is in the range of 200-360 nm.

In this range, it is an important wavelength band that constitutes "glare"-the ultraviolet region. And Ce^{4+} have the very wide absorption band in practical applications, which will cause the glass to be significantly colored yellow and be deepening as the concentration increasing. So we place it in an oxidizing atmosphere. The silicate glass with a composition of (wt%) 83.5%SiO_2-1.8B_2O_3-13.2Na_2O-1.5TiO_2-xCeO_2 was selected as the glass formulation, and different concentrations of CeO_2 were set to determine the optimum amount thereof. The amount of 1.2 wt%, 1.3 wt%, 1.4 wt%, 1.5 wt% and 1.6 wt% of CeO_2 in the glass composition was numbered C1, C2, C3, C4 and C5 respectively. A set of transparent, uniform, bubble-free glass samples was made. And use a spectrophotometer for scan testing to get a set of spectra:

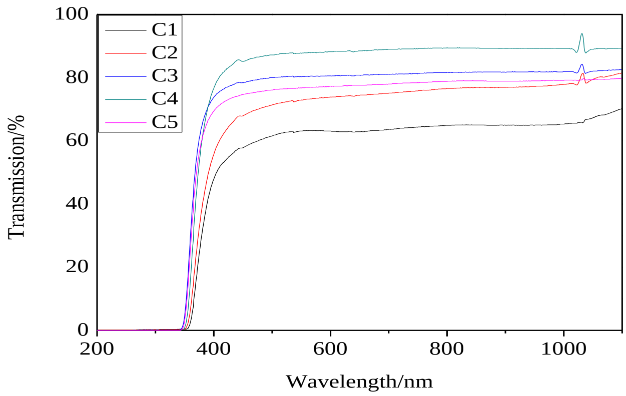

Fig. 1. Transmission spectra of C1-C5 at 200-1100 nm

Because of its unique electronic layer mechanism $4f^1 5s^2 5p^6 5d^1 6s^1$, Cerium can lose two electrons of 6s level and one electron on f layer to form Ce^{3+}, and can also lose two electrons of 6s level and two electrons on f layer to form Ce^{4+} [4]. For trivalent ions, the electric dipole transition from the 4f ground state to the 5d excited state is allowed, and its oscillator strength is strong. For different concentrations of CeO_2 doped glass samples in the 200-1100 nm transmission line graph, from the figure, we can obtained that the samples are maintained at more than 88% transmittance in the visible light range. As the wavelength decreasing, in the wavelength band of the ultraviolet wavelength region, there is a noticeable drop, which has a good absorption effect on the main wavelength band that produces glare. With the addition of Ce^{3+} concentration range of 1.2 wt% to 1.6 wt%, the glass achieved the highest transmittance at 1.5 wt%, and once again increased to 1.6 wt%, there was a partial drop in the visible light transmittance. While ensuring the absorption of blue light, and there is no bad effect on the transmission of visible light, the 1.5 wt% of Ce^{3+}can be selected as the optimum doping concentration.

3.2. Performance and analysis of single-doped Sm^{3+} silicate glass samples

We have solved the problem of UV interception well. Then, considering the problem of long wave blue light with wavelength in the range of 450-475 nm, the silicate glass with (wt%) 83.5%SiO_2-1.8B_2O_3-13.2Na_2O-1.5TiO_2-ySm_2O_3 of glass composition was selected as the objects of study. Setting different concentrations of Sm_2O_3 determined its optimal concentration. A group of transparent, uniform and bubble free glass samples were prepared by using the mass fraction of Sm^{3+} in the glass component being 31.1-31.5 wt%, numbered as S0, S1, S2, S3 and S4, respectively.

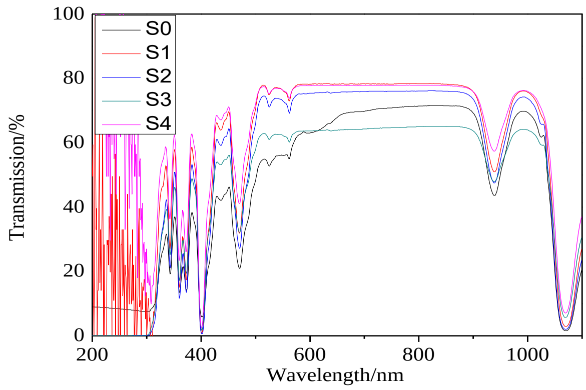

Fig. 2. Transmission spectra of S0-S4 at 200-1100 nm

The transmission spectrum of single doped Sm^{3+} glass is shown in Fig. 2. It can be seen from the Fig. 2 that Sm^{3+} have several absorption peaks between 300-500 nm and their positions are about 360 nm, 370 nm, 400 nm, 440 nm and 480 nm, which is roughly consistent with the absorption peaks reported in literature [5]. The absorption at 360 nm, 400 nm and 480 nm can reach 60-70 %, and the absorption of blue light is very good. This is because the common compounds of rare earth samarium are 2, 3 valence states, the outer electron distribution is: $4f^6$ $6s^2$, and the electron distribution outside the nucleus is 2, 8, 18, 24, 8, 2. The characteristic of rare earth ions is that the energy level of 4f is partially filled with electrons, and all the absorption of Sm^{3+} surrounded by $5s^2$ and $5p^6$ electrons are f-f electron transitions from ground state $^6H_{5/2}$ to each excited state. Through the analysis of the glass samples, it can be seen that when the concentration of Sm^{3+} is between 31.1-31.4 wt%, the overall transmittance of the glass decreases slowly with the increasing of the concentration, and the absorption of the glass increased with the increasing of the concentration. When the concentration is 31.4 wt%, the blue light reaches the maximum absorption, and the overall transmittance is in the minimum state about 60%. Then with the increasing of concentration, the overall transmittance increases slowly, and the absorption of blue light decreases. Considering the double factors of transmittance and absorption, the optimal concentration of Sm^{3+} is 31.3 wt%.

3.3. Performance and analysis of single-doped Ho^{3+} silicate glass samples

Because of the problem of long wavelength blue light, there is still a poor absorption effect in the short-wave blue light (wavelength range of 435-450 nm), so the selected group was the (wt%) 83.5%SiO_2-1.8B2O_3-13.2Na_2O-1.5TiO_2- zHo_2O_3 of silicate glass as the research object. Setting different concentrations of Ho_2O_3 determined the optimum concentration. The mass fraction of Ho_2O_3 in the glass component is 2.2 wt%, 2.3 wt%, 2.4 wt%, 2.6 wt% and 2.8 wt%, respectively. The numbers were H1, H2, H3, H4 and H5. Made a series of transparent, uniform, non-bubble glass samples.

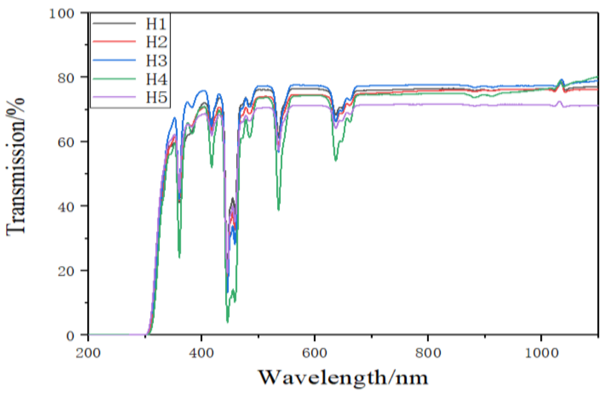

Fig. 3. Transmission spectra of H1-H5 at 200-1100 nm

The transmission spectrum of a single doped Ho^{3+} glass is shown in the graph, it can be seen from the figure that Ho^{3+} have multiple absorption peaks between 300 and 600 nm. The location are about 445 nm, 458 nm, 535 nm, 635 nm. The absorption rate at 445 nm and 458 nm can reach 60-70%. And the absorption of short wavelength blue light has an excellent effect. This is because of the rare earth element holmium whose atomic structure is $1S^22S^22P^63S^23P^63d^{10}4S^24P^64f5S^25P^66S^2$. After losing the electron, the outer electron of holmium is $4f^{10}5s^25p^6$. Among which the 5s and 5p shell are fully filled, while the 4f shell is partially filled, so the Ho^{3+} ion has a rich energy level structure. According to Hund rule, the ground state of Ho^{3+} is $5I^8$ energy level, which corresponding to six excited states: $5I^7$, I^6, $5I^5$, $5I^4$, $5F^5$ and $5F^4(5S^2)$ energy levels [6-9]. Through the analysis of samples with different doping concentration of glass, the concentration of Ho^{3+} lying from 2.2 wt% to 2.8 wt%, the absorption of glass in the blue increases first, and there is an absorption peak. The absorption rate of glass fluctuates at blue light, and the blue light absorption rate is 2.2 wt% < 2.8 wt% < 2.3 wt% < 2.4 wt% < 2.6 wt%. When the concentration is 2.6 wt%, blue ray has reached the maximum absorption, but the overall transmittance is too small, roughly 70%. After that, as the concentration increasing, the overall transmittance decreased slowly, and the absorption rate of blue light decreased. Considering the double factors of transmittance and absorptivity, 2.3 wt% is the best single mixing concentration of Ho^{3+}.

3.4. Improvement and performance analysis of three doped silicate glasses

Above, we studied the effects of rare earth ions alone on the absorption of ultraviolet and blue light. It is determined that the best anti-glare effect can be achieved when the doping concentration of Ce^{3+} is 1.5 wt%, the doping concentration of Ho^{3+} is 2.3 wt% and the concentration of Sm^{3+} is 31.3 wt%, and the absorption coefficient is considerable and the transmittance is high.

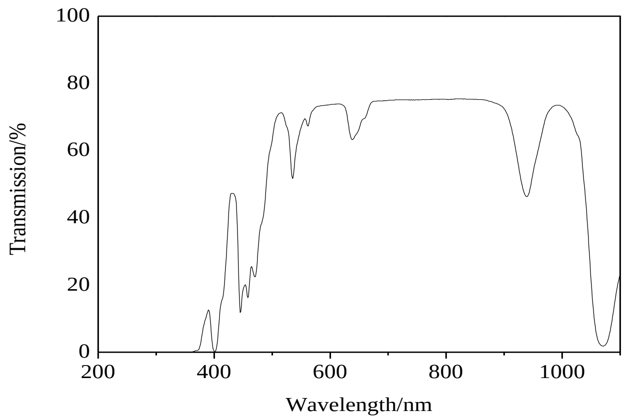

Fig. 4. Transmission spectra of rare earth ions in 200-1100 nm

As shown in Fig. 4, we have made triple-doped glass-proof glass samples in accordance with the optimal concentration in previous chapters. We have carried out spectroscopic tests and analyses. It is found that the final results are not up to the expected ideal due to the interaction between rare earth ions. First, the overall transmittance does not reach the expected results. Second, the absorption of short wave blue (435-450 nm) is not sufficient, and the improvement is not completed. Therefore, on this basis, we have improved the previous formulation. Considering that the absorption of long-wave blue light has exceeded the expected effect and the doping concentration of Sm^{3+} is the most in the whole formulation, the samarium ion is adjusted in the original formulation. It can improve the overall transmittance of glass while keeping the absorption effect of long-wave blue light. So, on the basis of the glass composition of (wt%) 83.5%SiO_2-1.8B_2O_3-13.2Na_2O-1.5TiO_2-xCeO_2-ySm_2O_3-zHo_2O_3, we adjust the optimum concentration of Sm^{3+} from 31.0 wt% to 31.5 wt% and the concentration of Ce^{3+} doped 1.5 wt%, Ho^{3+} remains unchanged at 2.3 wt%, and numbered T0, T1, T2, T3, T4, T5 respectively.

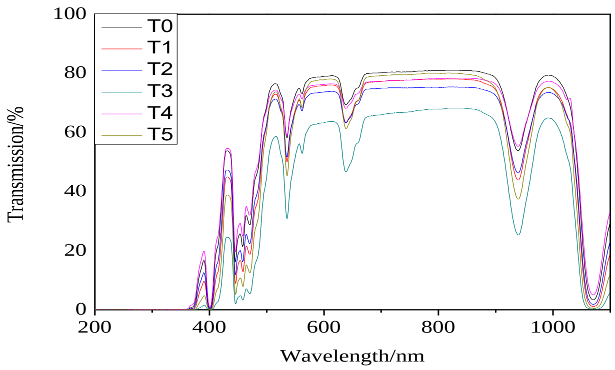

Fig. 5. T0-T5 Transmission spectra of rare earth ions in 200-1100 nm

When the absorption coefficient of long wave blue light is maintained, the overall transmittance is mainly considered. From the analysis of Fig. 5, it can be seen that when the concentration of Sm^{3+} is 31.1 wt%, the transmittance is higher and the absorption of long wave blue light is better. Although we have shown in subsection 2.3 wt% that holmium ion has a good absorption effect on short wave blue light, but after doping two other rare earth ions, we want to control the absorption of short wave blue light below 40%. Then the overall transmittance of the glass will be very sacrificial, and the effect is not obvious. Therefore, we have decided to introduce new ions on the basis of the original, and to absorb the short-wave blue light with high transmittance. Due to the existence of three absorption peaks in the ultraviolet and near ultraviolet regions of Bi^{3+}, and considering the interaction between rare earth ions, we have added Bi^{3+} to the above original formulation, and the effect is remarkable.

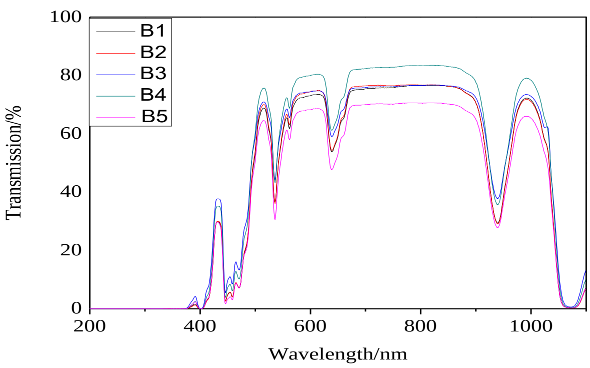

Fig. 6. B1-B5 transmission spectrum in 200-1100 nm

Fig. 6 is basing on that the glass composition is 83.5%SiO_2-1.8B_2O_3-13.2Na_2O-1.5TiO_2-xCeO_2-ySm_2O_3-zHo_2O_3-mBi_2O_3(wt%), setting the concentration is 1.1 wt%, 1.3 wt%, 1.5 wt%, 1.7wt% and 1.9 wt% respectively. A group of transparent, uniform, non-bubble-free glass samples were prepared by numbering B1, B2, B3, B4 and B5. From the image, we can see that with the addition of Bi^{3+}, the absorption of short-wave blue light has obviously progress. The above figure shows that when the concentration is 1.5 wt%, the blue light can be controlled to about 35%, and the overall transmittance is 80%. Therefore, 1.5 wt% is the best doping concentration for Bi^{3+}.

3.5. The basic properties of glass are studied

We choosing the B1-B5 as the samples, measured their density and refractive index.

Table 1. The density and refractive index of B1-B5

	B1	B2	B3	B4	B5
density	3.2316	3.2424	3.2518	3.2582	3.291
refractive index	1.605	1.614	1.622	1.632	1.639

4. Density

In order to ensure the accuracy of the measurement, the density of each sample was measured three times, and the average value of the sample was recorded as the density value of the sample. According to the data in the Table 1, the density of glass samples increases with the increase of Bi^{3+} content. The density of glass samples is mainly affected by two factors: the volume of internal network structure and the filling degree of external network. Bi^{3+} has a larger radius, which can widen the network structure and only fill the gap. Therefore, with the increase of glass content, the density of the sample increases.

5. Refractive index

The refractive index of B1-B5 is also selected as sample, and its refractive index is measured. It can be seen from Table 1. With the increasing of Bi_2O_3 concentration, the refractive index of glass sample increases gradually. The lowest refractive index is 1.605 and the highest is 1.639, which is higher than the refractive index of matrix silicate glass, which indicates that the refraction index of glass is obviously increased by adding Bi_2O_3. The main factor affecting the refractive index of glass samples is the ionic radius, which determines the polarization degree. The larger the ionic radius, the higher the refractive index of glass system. Because the radius of Bi^{3+} belongs to the larger ionic radius, its ability of polarization is high, so the refractive index of the whole sample system will be increased by introducing the ion. To sum up, the addition of Bi_2O_3 to the glass samples promoted the increase of refractive index.

6. Coefficient of thermal expansion

The thermal expansion coefficients of the last three rare earth ions Ce^{3+}, Sm^{3+}, Ho^{3+} and Bi^{3+} were measured in the glare resistant glass samples with doping concentration in silicate matrix at 1.5 wt%, 31.1 wt%, 2.3 wt% and 1.5 wt%.

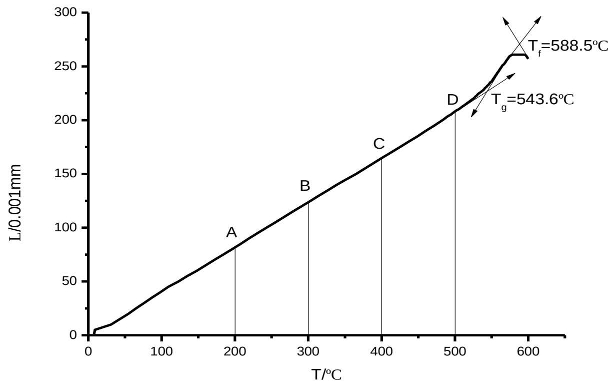

Fig. 7. The expansion curve of the sample

As is shown in Fig. 7, the elongation of the glass sample varies more evenly with the increasing of temperature in the range of 200 ℃ to 500 ℃. Therefore, the expansion coefficient of the glass sample is calculated by selecting the curve. The expansion coefficients of 200-300 ℃, 200-400 ℃, 200-500 ℃ are calculated respectively, and the average values of the three are calculated as the expansion coefficient of the sample. According to the data, the expansion coefficient of the glass sample is $\alpha=110.58\times10^{-7}$/℃. It can be seen from the picture that the transition temperature of the glass sample is about 543.6 ℃, and the softening temperature TF is about 588.5 ℃, which indicates that the glass sample has good thermal stability.

7. Conclusion

In this paper, the glare proof glass samples were prepared by using silicate as the substrate and doped with different moles of Ce^{3+}, Sm^{3+}, Ho^{3+} and Bi^{3+}. The thermodynamic properties, density, refractive index, absorption spectra and transmission spectra of each group of samples were determined.

1. By analyzing the absorption and transmission spectra of the sample C1-C5, when the amount of Ce^{3+} doped is 1.5 wt%, the cut off wavelength is up to 360 nm, and most of the absorption of ultraviolet light is realized. It can be determined that the optimum doping concentration.

2. The position of the absorption peak of Sm^{3+} is 400-470 nm by analyzing the transmission spectrum of sample S1-S5. When the doping concentration is 31.3 wt%, the transmittance at 400 nm is 5.6% and the transmittance of 470 nm is 49.9%. It can be determined the optimum doping concentration.

3. It can be determined by the analysis of the H1-H5 transmission spectrum of the samples. The glass samples absorbed at 445 nm, 460 nm, 535 nm, 635 nm after incorporation of Ho^{3+}. Based on the above basic ions, 2.3 wt% is added to the base ion, and the concentration gradient is obtained.

4. It can be determined that with adding the Bi^{3+}, there is a good absorption coefficient in the short wave blue light (434 nm), and with the increasing concentration of the Bi^{3+}, the absorption coefficient is very good. The absorption is firstly increased and then decreased, and 1.5 wt% could be taken as the best yield, and the short-wave blue light is controlled at about 35%. To sum up, when the doping concentration of three rare earth ions Ce^{3+}, Sm^{3+}, Ho^{3+}, Bi^{3+} in silicate matrix is 1.5 wt%, 31.1 wt%, 2.3 wt%, 1.5 wt%, the glass sample has a large absorption in ultraviolet and short-wave blue light regions, which can be used to prevent glare.

Acknowledgements

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