Study on Ti content in Low thermal expansion silica glass based on IR reflectance spectra

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Abstract. Ultra-Low thermal expansion (ULE) silica glass with essentially zero coefficient of thermal expansion is one of the most promising achievements in glass technology in a few decades. The property of the low thermal expansion coefficient makes it a suitable candidate for optical systems to be used in critical environments like space or vacuum. In this paper, by the help of ICP-OES and Infrared reflectance spectra, we measured titanium content of different samples and its corresponding reflection spectrum. We compared the linear fitting relation of Ti content with reflectivity and of Ti content with integration area of Gaussian fitting peak with a weighted average wave centre in 923 cm⁻¹. Results show that the latter one has a better correlation coefficient. By the tests of the IR reflectance spectrum of samples, we can deduce the Ti content using the linear fitting result.

1. Introduction
Ultra-low thermal expansion is only part of properties of silica glasses containing titanium, but it’s the part that attracts the most attention. This characteristic makes it a suitable candidate for optics as well as mask substrates in which ultra-high geometrical stability is required during application like Extreme Ultraviolet Lithography (EUVL) and both orbital and terrestrial bound telescopes[1-3]. Series of studies indicated that the thermal expansion had a direct correlation with Ti concentration in the glass. Carapella[4] et al. mentioned the CTE for annealed Corning 7972 glass: CTE (ppb/K) = −55.1 × wt. %[TiO₂] + 407.9. Based on the above equation, the mean linear CTE of Corning Code 7972 glass is 0 ± 30 ppb/°C from 5°C to 35°C with a 95% confidence level.

An accurate control of titanium content in products will guarantee a stable coefficient of the thermal expansion. However the actual Ti concentration may fluctuate during the deposition process for many reasons like TiO₂ particles that didn’t deposit onto the glass ingot. This kind of defects in the deposition process will result in visible striae, which influence the quality of products[5-6]. Therefore, a fast and feasible measurement of the Ti concentration in the products is considerable needed during the industrial production process.

Nowadays, the most precise measurements of Ti concentration in the glass are ICP-OES and EPMA. Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES)[7] is a way to measure the bulk concentration of the test sample which must be ground and sifted through 200 meshes. Electron probe microanalysis (EPMA) is a kind of microanalysis, and the analysis area is just a few cubic micro-meters[8]. The sample must have a clean smooth polished surface. So the above test methods are in need for help of the testing facility. Not only does it cost a lot to machining and testing,
but it takes a while for the test results to be available. So find an easy and fast way to accurately value Ti concentration is widely demanded to satisfy the need of industrial inspection.

We demonstrated a fast and non-destructive testing method evaluating Ti concentration of ULE glasses using the Infrared reflection spectrum. This spectral test method widely used in glass research is sensitive to the arrangement of atoms and the strength of chemical bonds between atoms in the micro-structure. The structure of mirror reflection accessories is simple and reliable. Samples to be tested are easy preparing. The whole test process is swift and convenient, meanwhile basically not affected by the size of the sample. So it is an express verification method[9].

In this paper, we fabricated a serial of different Ti concentration TiO$_2$-SiO$_2$ ULE glass by CVD method. Ti concentrations of samples have been tested by ICP-OES. With the help of the IR reflection spectrum, we analysed the relationship between Ti concentration and spectrum characteristics. The results show that a linear correlation between Ti concentration with reflectivity at 931 cm$^{-1}$ and integration area of Gaussian fitting peak at 923cm$^{-1}$. By fitting the result of Ti concentration and the above two indices mathematically, we can speculate the Ti concentration of a sample non-destructively using the IR reflection spectrum.

2. Experimental

2.1 Sample preparation process

Samples were prepared by the Chemical Vapour Deposition (CVD) method under the same melting atmosphere. As shown in Figure 1, High-purity vapor state precursor containing Ti and Si react in the oxy-hydrogen flames to generate nanoparticles that are deposited onto the forming glass block and vitrified into glass. ULE silica glass samples with different titanium content were prepared by adjusting the amount of titanium precursors used in the preceding deposition process.

![Figure 1. Schematic diagram of CVD process](image)

2.2 Sample preparation and testing of ICP-OES

Ti concentration of selected glass samples were measured by Perkin Elmer Optima8000 full spectrum direct reading inductively coupled plasma emission spectrometer. The ICP-OES method for the measurement of titanium content in low expansion silica glass has been adequately studied by Yang[10] et al., more specific details can be referred in the paper.

2.3 Preparation and test of Infrared Reflectance Spectrum Samples

The thickness of double-sided polished sample is 0.8mm[11]. Measurement of infrared reflectance spectra of samples with different titanium contents in the wave number range of 400-1500cm$^{-1}$ implemented by using PerkinElmer spectrum 100 FT-IR Spectrometer.

3. RESULTS AND DISCUSSION

3.1 ICP-OES test results of titanium content

Test results of ICP-OES plasma emission spectrometry are as follows in Table1:
Table 1. Ti content of samples

| Sample number | 1   | 2   | 3   | 4   | 5   | 6   |
|---------------|-----|-----|-----|-----|-----|-----|
| Ti content (wt%) | 3.46 | 5.92 | 6.72 | 7.88 | 8.82 | 10.85 |

In the following study, the calibrated titanium content in Table 1 obtained by this test will represent the samples' titanium content.

3.2 Infrared reflection spectrum analysis of low expansion silica glass

Compared with results of silica glass, spectrogram of ULE silica glass has the following differences.

As can be seen in Figure 2, with the increase of titanium content in samples, the typical peak of ULE silica glass moves toward lower wavenumber and the intensity decrease in comparison with the characteristic peaks of silica glass at 1122 cm\(^{-1}\). Sanders[12] et al. considered that the peak near 1100 cm\(^{-1}\) in the high-frequency region related to the silicon oxygen stretching vibration. Zhou[11] et al. pointed that corresponding to the results of reflection spectrum analysis of silica glass. The characteristic peak at 1122 cm\(^{-1}\) in the mid-infrared reflectance spectrum of silica glass is determined by the change of bond angle of Si-O-Si structure. When the bond angle increases, the band shifts to higher-frequency wavenumber. Therefore, the bond angle of Si-O-Si structure decreases when titanium is doped in the sample, and the more titanium is doped in; the more bond angle decreases. This point of view has been proved by the comparison of X-ray diffraction data with IR spectroscopic[13].

The peak found between 400 and 600 cm\(^{-1}\) is related to bending (or "rocking") motions of the silicon-oxygen network. With the increase of titanium content, the peak at around 500cm\(^{-1}\) becomes broadening. This phenomenon is mainly caused by the bending vibration of the tetrahedron containing two non-bridging silicon oxygen bonds.

Sanders[12] et al. suggested that the peak near 950 cm\(^{-1}\) is assigned to the stretching vibrations of the silicon non-bridging oxygen. Because titanium dioxide is an intermediate oxide, on the one hand, it can form the network structure, but also can give free oxygen to break the network. So with the addition of Ti ions, the ULE Silica glass network results in local symmetry decrease with the formation of silicon non-bridging oxygen bonds.
3.3 Fitting and error analysis of titanium content and various spectral indices

There is a phenomenon that the reflectance index located at 931 cm\(^{-1}\) increase with the amount of titanium content in the sample. Results show that the reflectivity of samples at 931 cm\(^{-1}\) fitted with the content of titanium in linear. Although the relationship between them is obtained by linear fitting, we hope to get a better fitting effect through further mathematical analysis. By the help of Gaussian Peak separation, we got the integration area of the weighted average wave centre at 923cm\(^{-1}\), a linear relation between the Ti content and the integration area shows a best-fitting effect.

![Figure 3. Fitting curves of Ti content and reflectance at 931cm-1(a) Ti content and Gaussian peak integration area at 923cm-1(b)](image)

3.3.1 Linear fitting between reflectance and titanium content

First, scatter points of reflectance corresponding to characteristic peaks at 931 cm\(^{-1}\) of reflectance spectra of different titanium contents are drawn, and there is a linear relationship between these indices. Then we fitted the scatter points linearly. The fitting result is y=0.11989+0.00536x, R\(^2\)=0.956. The results are shown in Figure 3(a). The residual sum of squares is 0.3405.

According to Sanders [12] et al., the relationship between infrared reflectance spectra and alkali metal content in glass can be characterized by the following equation \( R = C_rTt_p \). In this equation \( C_r \) is the concentration of reemitting species. \( T \) represents the reemission efficiency; \( t_p \) means the penetration depth. So the reflectance \( R \) fits both the composition and penetration depth in linear. This fits the result of our research in theory. Corresponding to the results of this study, the formula can theoretically prove the reliability of the results obtained by linear fitting.

3.3.2 Linear fitting between Gaussian peak integration area and titanium content

In order to obtain a more accurate fitting relationship between the titanium content in the sample and the infrared reflectance spectrum data, we processed the characteristic peak data by recognition and fitting, calculated the integration area of the Gaussian fitting weighted average wave centre at 923cm\(^{-1}\). Shown in Figure 4, we have chosen the Gaussian peak fit result of the sample with a Ti content of 6.72%. Then we analysed the relationship between the titanium content and the peak integration areas of samples with Ti content from 3.46% to 10.85%. The final analysis result is \( y=648.45+45.55x \), \( R^2=0.97 \). This is shown in Figure 3(b). \( y \) is the area of the Gaussian fitting peak weighted average wave centre at 923cm\(^{-1}\) of the reflectance spectrum, and \( x \) is the content of Ti in the sample.
4. Conclusion
In this paper, we fabricated a serial of TiO$_2$-SiO$_2$ ULE glass with distinctive Ti concentrations by CVD method. With the help of ICP-OES and Infrared reflectance spectra, we measured Ti content of different samples and its corresponding characteristic spectrum. We concluded a linearly fitting result of Ti content, and the Gaussian peak areas with a weighted average wave centre located in 923 cm$^{-1}$. The relationship between peak area and titanium content is $y=648.45+45.55x$, $R^2=0.97$. This result has a better correlation coefficient than the linear fitting results between reflectivity and titanium content. By applying the fitting result, we can deduce the Ti content by measuring the IR reflectance spectrum of samples. So with the help of infrared reflectance spectroscopy we can measure the titanium content of samples rapidly and non-destructively to meet the requirements of product verification and analysis without using chemical analysis method.

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