Decolorising of Crystal Glasses with Colorimetry

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Introduction

Lead crystal glass has many excellent properties. It is easy to melt, it is easy to process on machines and has outstanding optical properties like a high refractive index of about 1,545, a low Abbé number < 47, and a high light transmission in the visible range. Due to this high transmission, lead crystal glasses are easy to decolorise with NiO. Furthermore lead crystal glasses are easy to grind on machines because of their low hardness, and a successive acid polishing is possible.

Up to now, many efforts were undertaken to develop an equally suitable glass to substitute lead crystal glass. As yet, those efforts were not successful.

At the University of Applied Sciences of Nuremberg, it was possible to melt such a glass. The new lead and barium free crystal glass possesses the same good optical properties as lead crystal glass. The refractive index is higher than 1,55, and the Abbé number is lower than 47, with the transmission in the visible range comparable to lead crystal glass. To obtain these optical characteristics, the use of highly refractive oxides like TiO_2 and ZrO_2 is recommended. The use of TiO_2 in glasses leads to a yellowing of the glass. The cause of this is the shifting of the UV–absorption band of the glass towards the visible range and the existence of ferric complex chromophores.

In this work it is shown how a glass with a yellow shade can be decolorised. To assure a complete decolorising of the glass, series of melting processes with different colorising ions were carried out. The results of the obtained melting series were measured with a spectrometer to determine the color values and to quantify the colors. Knowing the exact relationship between the concentration of the coloring ions and the position of the color values, it is possible to calculate the right amount of the decolorising species for different percentage compositions. On the other hand, a quality assurance for the color of the crystal glasses can be attained. Fluctuations of the color generally are due to changing tonnage and cullet ratio leading to a variation of the iron content.

Color measurement

The aim of color measurement is the quantification of colors with numerical values. An impression of color results from different materials absorbing different parts of the visible light. For example, a green sample absorbs yellow and blue light and reflects the green fraction.

Basis of any color measurement is the determination of the transmission or reflection curve. The transmission curves in this test series were obtained with a spectrometer, and the color values were calculated with the aid of a special software. To quantify the colors, the Hunter system (also called Lab – system) was used.

The representation of all visible colors in the Hunter system forms a color orb consisting of various color levels perpendicular to the coordinate of brightness L. The brightness increases from the bottom (black = 0) to the top (white = 100). The coordinates a and b depict the color shade, where +a represents red, -a represents green, +b represents yellow and –b represents blue.

For the following measurements, the L–coordinate has been omitted, because the variations among the samples are very minor and the brightness has no consequence on the trend of the colors.

To compare different samples, it is very important to indicate the used method of measurement. The following specifications are crucial: measurement method, norm light used, angle of observation, standardization of the thickness, standardization of the reflection.

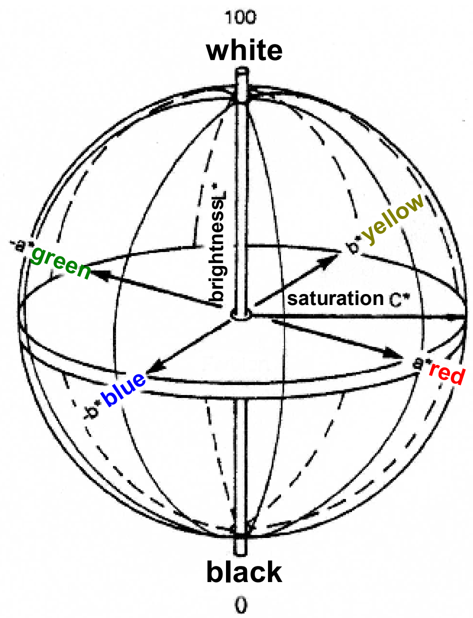

Figure 1 shows the Hunter color system which forms a color orb from -a (green) to +a (red), from -b (blue) to +b (yellow) and from L = 0 (black) to L= 100 (white).

Decolorising

In this work the emphasis is on the physical decolorising. The decolorisation generally results from contamination with iron. In crystal glasses, this contamination is in the range of 100 – 150ppm. To decolor a glass sample, we tried to additionally create the complementary color of the decolorisation in the glass. If this is attained, the glass seems to be colorless, whereby the reduction of total transmission is tolerated. Numerous references to existing literature on the subject of coloring effects of various elements in glasses can be taken in account to reach a decision which decolorising species can be used. For the titan crystal glass, a decolorisation based on the combination of Er_2O_3 and CoO was chosen. The following transmission curve of a 10% titan crystal glass justifies the selection of Er_2O_3 and CoO. This figure obviously shows that a slightly yellow shade can be expected.

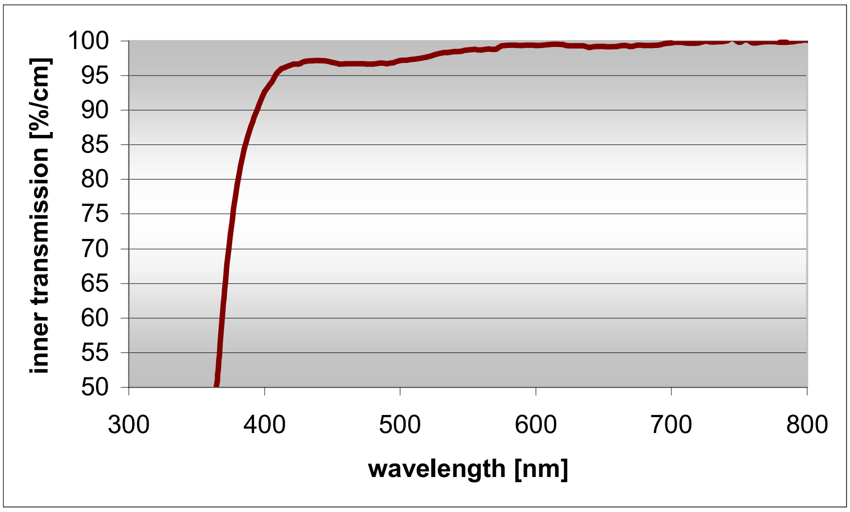

Figure 2 shows the transmission curve of a titan crystal glass containing 9% titanium.

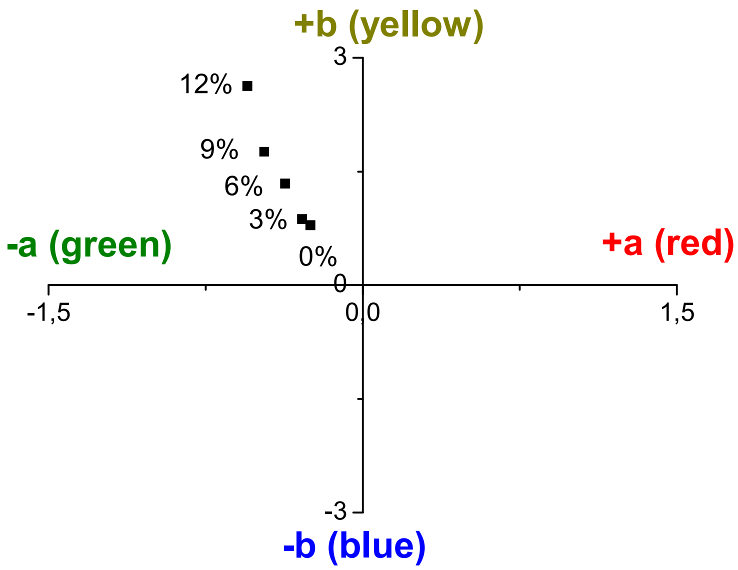

Figure 3 shows the color place of different titan crystal glasses.

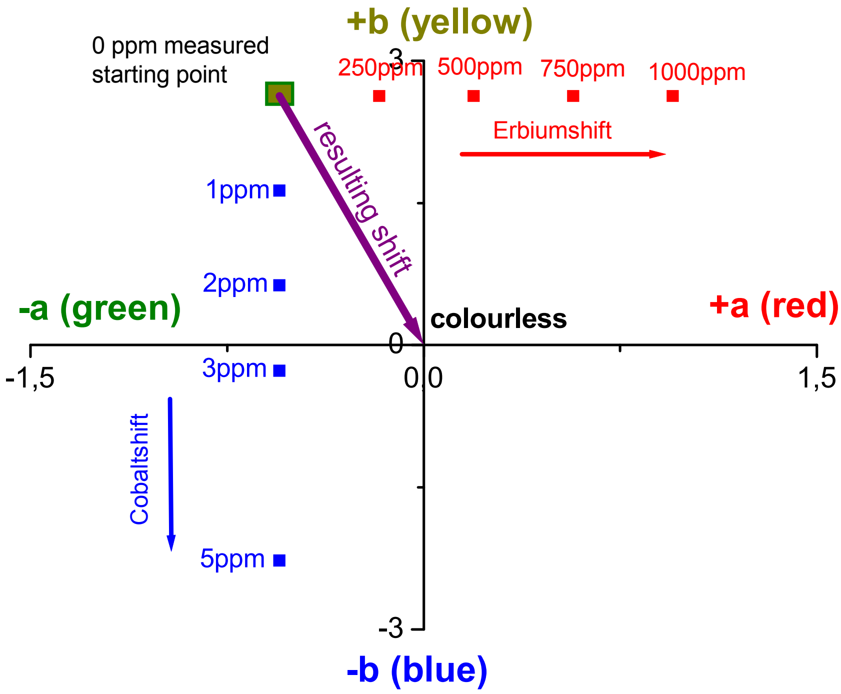

Figure 4 shows the principal steps of the decoloring .

The relationship between different TiO_2–contents and the color of the glass can be seen in figure 3. The use of TiO_2 shifts the color values to green and yellow. To reach the optical properties of lead crystal glass, it is necessary to add between 8 – 11 weight-% of TiO_2. The resulting color has to be decolored with suitable additives. Figure 4 shows the principal of the decoloring. The color place of the 0–sample is shifted to red by Er_2O_3, and to blue by CoO. Adding the correct amount of these two oxides, a colorless glass is obtained.

Results

Hereafter, the measured relations are shown. The transmission curves were measured and evaluated according to the following specifications: - 2° standardized observer, measurement range 380 – 780nm, Lab–color system, on 10mm standardized thickness, reflection correction.

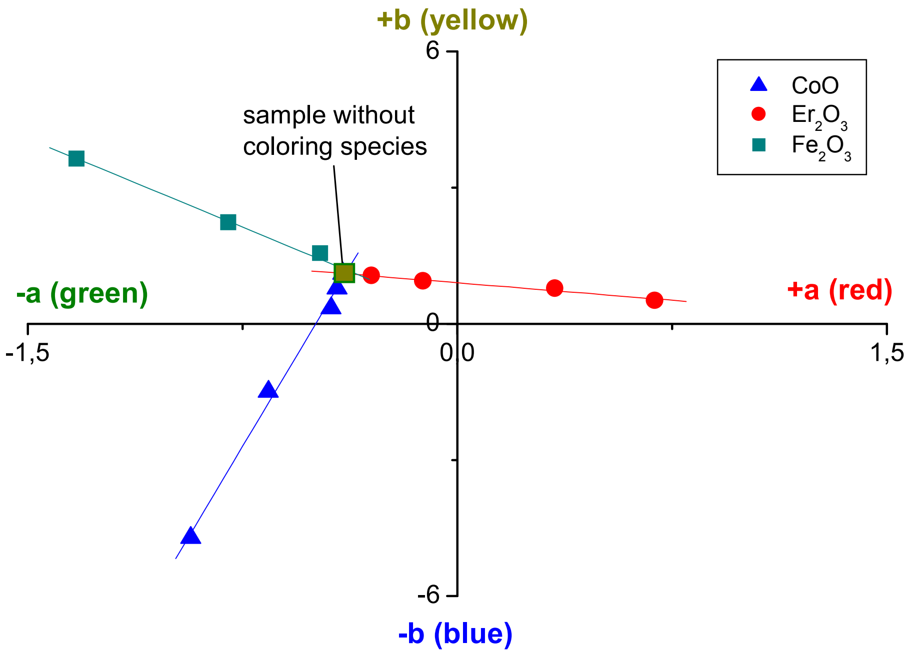

Figure5 shows the measured values for the erbium- cobalt and iron series.

As always, reality´s mechanisms are more complex than any theory. An addition of Er_2O_3 leads not only to a shift of the color values to red, but also to blue. Likewise, CoO shifts not only to blue, but also to green. The following graph will show the measured relations of the color shift and the concentration in ppm. On the one hand, the shifting of the respective a–value, and on the other hand the respective shift of the b–value can be observed.

The relation between the coloring and the concentration of the decolorising species is linear. Once this relationship is known, the decolorising of a titan glass sample can be calculated with the simple culmulative formulas below.

$$
\begin{aligned}
a(CoO, Er_2O_3) &= a_{measured} + \sum a_{Er_2O_3}, a_{CoO} \\
b(CoO, Er_2O_3) &= b_{measured} + \sum b_{Er_2O_3}, b_{CoO}
\end{aligned} \tag{1}
$$

The a– and b–values for Er_2O_3 and CoO are calculated using the fit equations of the measured values. The mentioned culmulative formulas are solved for a and b set to 0 (0 = colorless) leading to the required concentration.

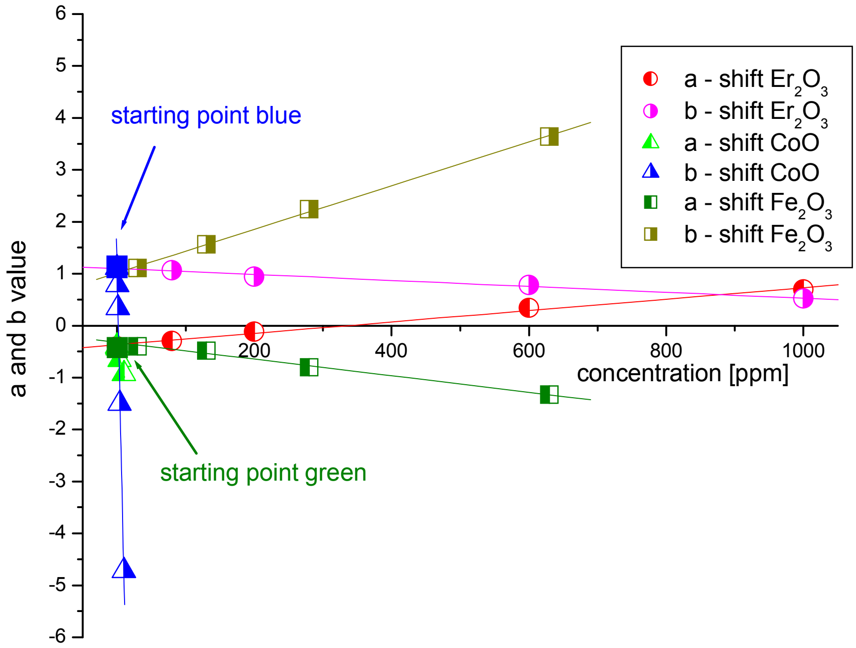

Figure 6 shows the measured values of the a– and b–coordinates as a function of the additive concentration in ppm.

Conclusion

Many experiments have shown that a satisfactory calculation of the amount of the decolourising species is possible using this approach. It has to be taken into account that with an increase in the cullet ratio, the iron content increases too. Extending the equation 1 with the a– and b–value of the respective iron content, it is possible to optimize the decolorising. With this method, a quality assurance with regard to the glass color is possible. Therefore, the deviation of the color from an ideal standard can be calculated with equation 2. Defining tolerances enable a permanent monitoring of the glass color.

$$\Delta E = \sqrt{\Delta a^2 + \Delta b^2 + \Delta L^2} \qquad (2)$$

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2 - Anni Berger-Schunn: Praktische Farbmessung, Muster-Schmidt Verlag, Göttingen, 1994

3 - C. R. Bamford: Colour Generation and control in glass, Elsevier Science Publishers B. V., 1977