NIOBIUM OXIDE IN ENVIRONMENTAL FRIENDLY OPTICAL GLASS

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Abstract

General properties of environmental friendly optical glasses are reviewed. Niobium oxide plays an important role as one of the components that are substituted for lead oxide. Conversion from lead containing glasses to most lead free glasses results in the less negative anomalous partial dispersion. But lead free glasses containing niobium oxide are able to attain almost the same relative partial dispersion values as conventional lead containing glasses. In addition, chemical durability, Knoop hardness and lower specific gravity are also enhanced.

Introduction

In recent years, the problem of global environmental destruction has been recognized worldwide. Water and soil pollution, caused by toxic waste disposal, cross-border toxic waste disposal, and insufficient disposal sites, are becoming significant problems.

Optical glasses are composed of various elements including the widely used important component "lead" which is regulated by the Water Pollution Prevention Law. Nowadays, with environmental preservation taken up as a critical problem, eliminating components that are toxic to the human body and that pollute the environment has become quite an important topic.

Ohara got a head start on the rest of the world and started developing lead free optical glasses in November 1990. In November 1995, from the perspective of the effective utilization of raw materials for the roughly 250 types of optical glasses in existence at that time, the focus was narrowed to 111 "recommended" types of glass useful for optical design. Then, in March 1997, lead-free designs were achieved for all recommended glass types. Within this development, niobium oxide was studied as the main substitute raw material for lead oxide for environmentally friendly optical glass. This paper describes the new roles for Nb_2O_5 in lead free glasses.

<u>Required Properties for Optical Glass</u>

Optical glass has long been used for lenses and prisms in optical components, primarily cameras, photocopiers, projectors, and binoculars. Various glass types, for meeting the requirements for a wide range of refraction, dispersion (the dependence of the refractive index on wavelength), and transmittance, were developed to match the optical design needs. Optical glasses have been used in the visible range from approximately 380 to 780 nm. The following should satisfy as standard requirements for lenses that make up optical systems.

(1) High transparency.
(2) Consistent optical constant such as "n_d" and "ν_d".
(3) High internal qualities (optical homogeneity, freedom from bubbles, devitrification and minimal strain).
(4) Good processing ability.
(5) Practical chemical durability.

In imaging systems, the most important parameters are the refractive index and dispersion. Optical glass is classified according to its refractive index at the 587.6nm helium-d line (n_d) and its dispersion characterized by the Abbe number (ν_d). The Abbe number is given by:

$$\nu_d = \frac{n_d - 1}{n_F - n_c} \qquad (1)$$

where n_F-n_C is the principal dispersion. The refractive indices n_F and n_C are measured at the hydrogen F line (486.1nm) and the hydrogen C line (656.3nm), respectively. Figure 1 shows the conventional diagram of optical glasses available in 1990, which are classified using the combination of n_d and ν_d. The refractive index n_d varies from approximately 1.4 to 2.0, while the Abbe number varies from 15 to 95.[1] The Abbe number shows the relation such that the smaller the number, the larger the dispersion and vice versa. As the diagram indicates, most of the conventional glasses include lead. Later, by 1997, all the recommended glass types were replaced with lead free glass types.

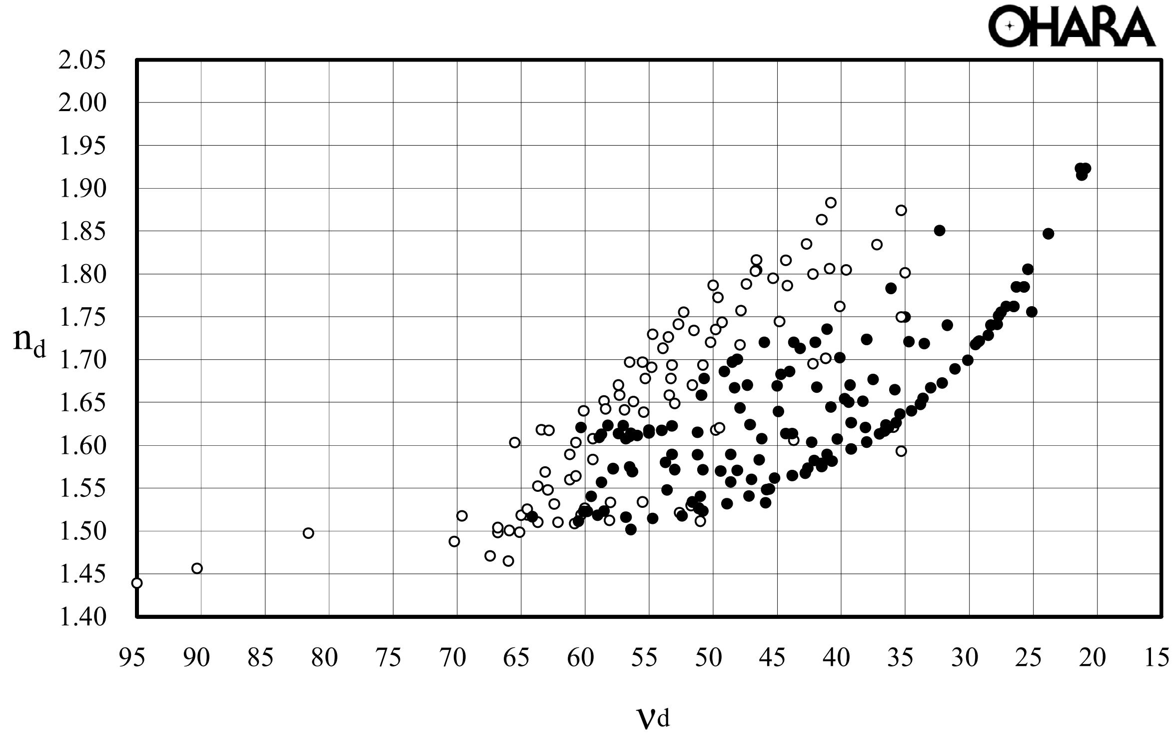


Figure 1: Conventional n_d /ν_d Diagram of Optical Glasses in 1990. ●= Lead containing glasses ○=Lead free glasses.

Relationship between Components of Optical Glass and Refractive Index

In addition to the typical metal oxides such as SiO_2, Na_2O and CaO, which create general glasses used for bottles and windows, etc., optical glasses need to contain heavy metal oxides such as Nb_2O_5, TiO_2, La_2O_3, Y_2O_3, Gd_2O_3, Ta_2O_5 in order to achieve the characteristics required in optical glasses. The refractive index (n) of optical glass is determined by the following Gladstone-Dale equation (2):

$$n - 1 = \frac{R}{V} \quad (2)$$

where *R* is the molecular refraction that is mainly influenced by the polarizability of O^{2-} ions, and *V* is the molecular volume that is influenced by the number of O^{2-} ions per unit volume. Dispersion, in the wavelength regions having negligible absorption, is expressed by the following Drude-Voigt equation (3):

$$n - 1 = \frac{N_1 e^2}{2\pi m} \Sigma \frac{f_1}{{\nu_{01}}^2 - \nu^2} \quad (3)$$

where N_l is the number of O ions per unit volume, e and m are the charge and mass of the electron, v_0 is eigenfrequencies of absorption of O ions, f_1 is the oscillator strength and v is the frequency of the light.[2] These parameters are dependent on the types and proportions of components

According to Ohara's experiments, the relationship between each oxide component, n_d and n_F-n_C are shown in Figure 2. It expresses the change in n_d and n_F-n_C when 1% by weight of the SiO_2 is replaced with another component. The rate of the change is influenced by the base composition, but the positions in the chart of the components relative to each other do not change much. From Figure 2, even among the various components used in optical glass, PbO is positioned with high refractive index and dispersion. In order to provide the same n_d and n_F-n_C in lead free glasses, it is necessary to use Ta_2O_5 ZrO_2 Nb_2O_5 and TiO_2. But Ta_2O_5 is expensive as optical material and ZrO_2 has a higher tendency to crystallize. To that effect, PbO is mainly substituted with Nb_2O_5 and TiO_2.

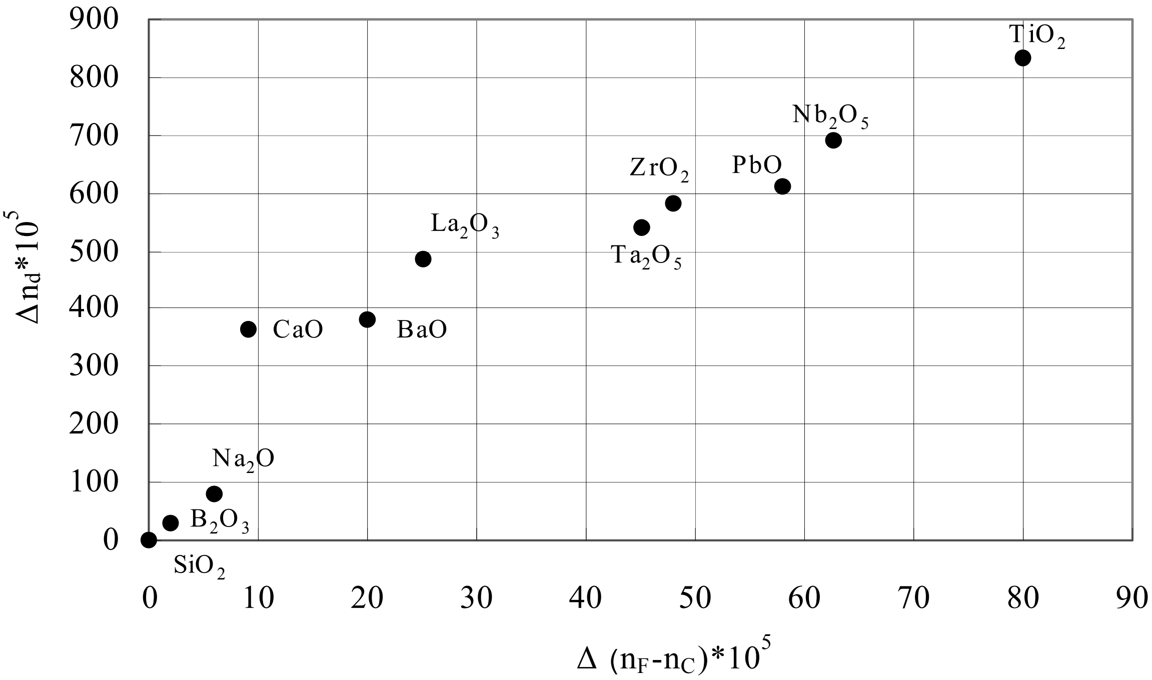


Figure 2: Change in optical constants by component substitution.

<u>Differences in Properties Between Lead Containing Glasses and Lead Free Glasses</u>

In conventional optical glasses, lead oxide is commonly used. Lead containing glasses have a lower tendency to crystallize, have a low material cost, are effectively produced with high refraction and high dispersion, and a small amount of lead oxide doping avoids solarization.[3]

For these and other reasons, lead oxide is used in many types of optical glasses. In some types of lead oxide based glasses, the content can be as high as 80% by weight.[1] Many characteristics of optical glass, such as the refractive index and dispersion, are greatly dependent on the types and proportions of components. Figure 3 shows different systems of optical glasses that can be classified by their chemical composition.

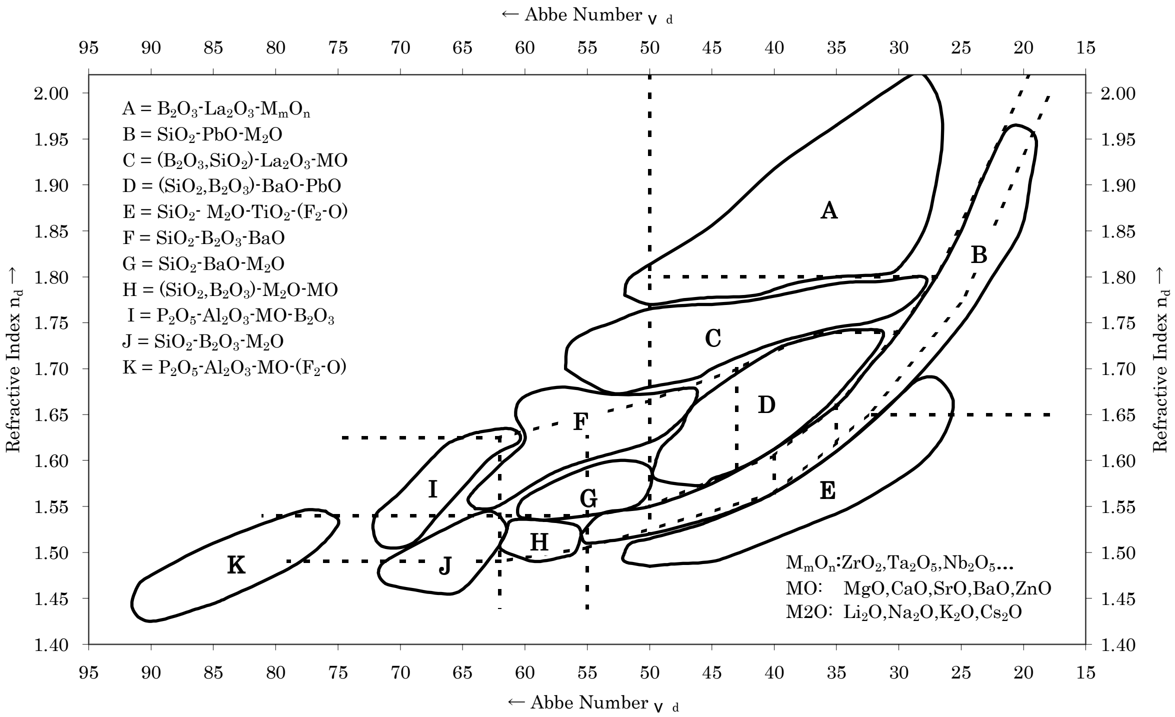


Figure 3: Glass systems of optical glasses in the n_d -ν_d diagram [1].

The conversion of lead containing glasses to lead free glasses causes several variations of characteristics such as relative partial dispersion and internal transmittance. Furthermore the variation in thermal properties are also affected by factors related to the manufacturing process, such as melting, whether the presence of devitrification is absent or not, degree of homogeneity, etc. In other words, when lead oxide is eliminated from the conventional glasses, it is necessary to review the manufacturing process as well as the entire compositions.

Development of Lead free Glass Having Negative Anomalous Partial Dispersion

One of the greatest difficulties that arises from trying to eliminate lead oxide from the composition of optical glass is creating glass with negative anomalous partial dispersion. As Figure 4 shows, by using a suitable combination of optical glasses having different Abbe numbers, the imaging flaw called chromatic aberration can be eliminated or at least reduced in lens systems. The residual chromatic aberration, which remains for the uncorrected colors, is referred to as the secondary spectrum.[4] This effect is particularly disadvantageous for high-performance optics, since it impairs the imaging sharpness. Correction of an impaired secondary spectrum, particularly at the short wavelength region is desired in the design of optical lenses. Such secondary spectrum problems can be reduced by a substantial degree by combining flint glass having large negative anomalous partial dispersion with crown glass as shown in figure 4.

The relative partial dispersion, $\theta_{x,y}$, is used as a scale for measuring the anomalous partial dispersion in optical glass. $\theta_{x,y}$ and is the ratio of a partial dispersion to the principal dispersion, for example:

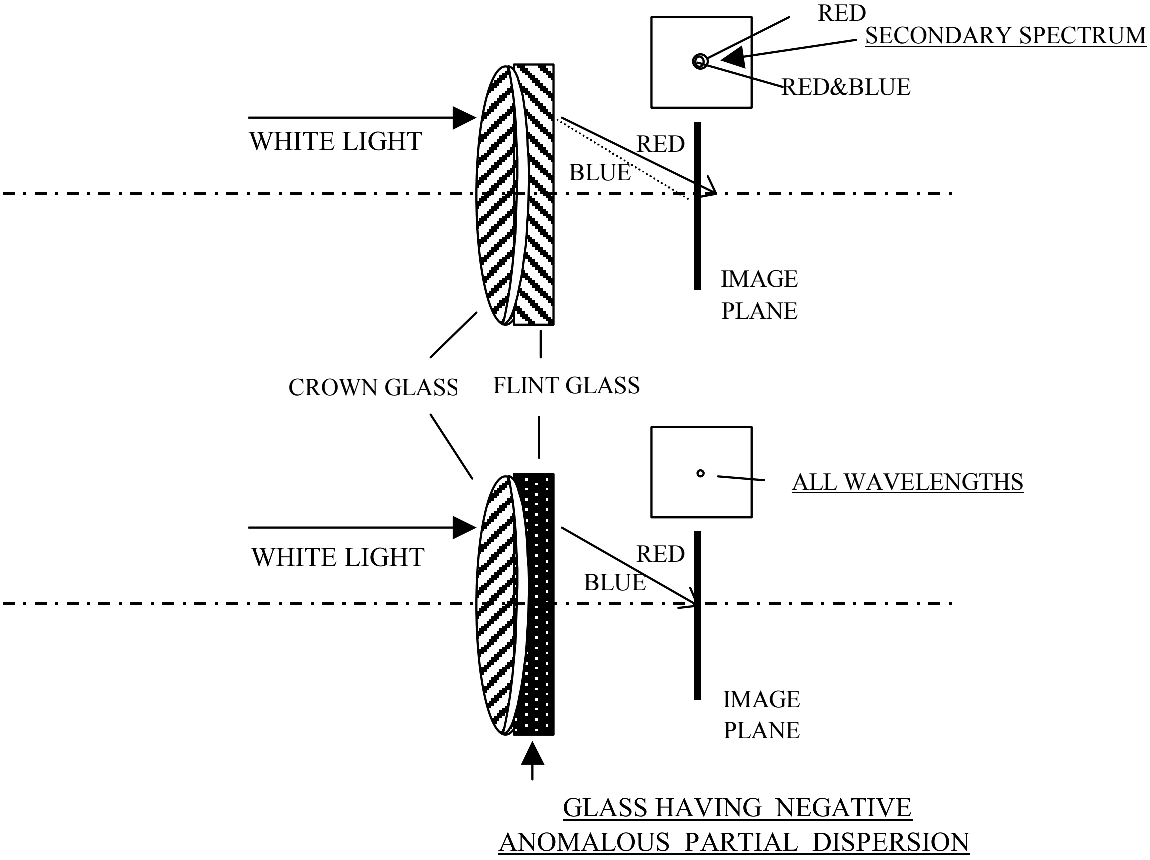


Fig.4: Achromatic lens systems.

$$\theta_{x,y} = \frac{n_x - n_y}{n_F - n_c} \tag{4}$$

Like the Abbe number, the relative partial dispersion is an important material constant for an optical glass. As Figure 5 indicates, glass types can be plotted in a graph of $\theta_{g,F}$ .vs. ν_d. Normal glass types tend to lie along a straight line between the two points which would be plotted for two of Ohara's glass types NSL7 (ν_d=60.5, $\theta_{g,F}$ =0.5436)and PBM2(ν_d=36.3, $\theta_{g,F}$ =0.5828). The majority of glasses satisfy an approximately linear relationship between $\theta_{g,F}$ and the ν_d according to equation (5) stated below:

$$\theta_{g,F}=a_{g,F}+b_{g,F} \bullet \nu_d \text{ (Standard straight line)} \tag{5}$$

Glasses that do not satisfy this equation are referred to as glasses having anomalous partial dispersion. The equation must then be expanded by an additional correction term: $\Delta\theta_{g,F}$:

$$\theta_{g,F}=a_{g,F}+b_{g,F} \bullet \nu_d + \Delta\theta_{g,F} \tag{6}$$

Depending on whether $\Delta\theta_{g,F}$ is greater or less than "0", the glasses are then referred to as glasses having positive or negative anomalous partial dispersion. Particularly achieving negative anomalous partial dispersion is very important to correct the secondary spectrum in the visible blue region. Especially for high dispersion flint glasses, where the smaller $\theta_{g,F}$ provides less secondary spectrum distortion. In this normal line (formula 5,6), $a_{g,F}$ =0.6415 and $b_{g,F}$ =-0.0016.

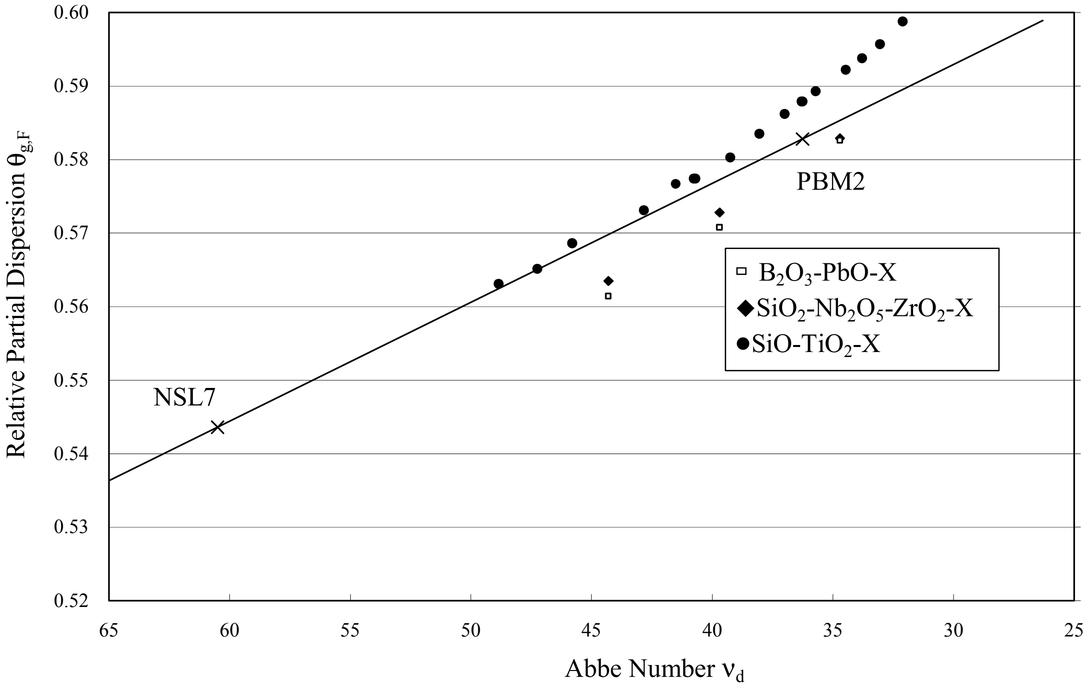


Figure 5: Change in the values of $\theta_{g,F}$ and ν_d upon exchanging glass systems.

In flint glasses, lead oxide plays a vital role in producing a negative anomalous partial dispersion. The B_2O_3-PbO system such as encountered in Ohara's glass types BPH8, BPH5, BPM51 shows significant negative anomalous partial dispersion. However, since it is thought that the characteristic of showing negative anomalous partial dispersion with high dispersion is a unique property of B_2O_3-PbO system,[1] it has been difficult up until now to eliminate lead oxide. The lead-free flint glasses, for example the glass system SiO_2-TiO_2, show the opposite behavior - positive anomalous partial dispersion. As environmentally friendly optical flint glasses having negative anomalous partial dispersion, the glass system SiO_2-GeO_2-Ta_2O_5 was introduced.[5] This flint glass however is economically disadvantageous because, in order to achieve the desired negative anomalous partial dispersion, it requires a large amount of GeO_2 and Ta_2O_5, materials which are very expensive. In addition, this glass is difficult to melt and therefore, it is hard to obtain material homogeneity.

In niobium containing glass systems, Ohara found that the SiO_2-Nb_2O_5-ZrO_2 system for Ohara's glass types S-NBH8, S-NBH5, S-NBM51 has negative anomalous partial dispersion.[6,7] These glasses attained almost the same values for $\theta_{g,F}$ as conventional lead containing flint glasses as shown in Table I. Niobium oxide is effective for increasing the negative anomalous partial dispersion property of the flint glasses if the amount of niobium oxide is above 20%. As a result, niobium oxide plays a vital role in environmental friendly glass having negative anomalous partial dispersion.

Table I Comparison of glass systems for relative partial dispersion values

Glass systems	Glass types	ν_d	$\theta_{g,F}$	$\Delta\theta_{g,F}$
B_2O_3-PbO-X	BPH8	34.7	0.5826	-0.0027
	BPH5	39.7	0.5708	-0.0065
	BPM51	44.3	0.5614	-0.0084
SiO_2-Nb_2O_5-ZrO_2-X	S-NBH8	34.7	0.5834	-0.0019
	S-NBH5	39.7	0.5737	-0.0036
	S-NBM51	44.3	0.5633	-0.0065
SiO_2-TiO_2-X	S-TIM2	36.3	0.5879	0.0051
	S-TIL25	40.8	0.5774	0.0019
	S-TIL1	45.8	0.5686	0.0012

Benefits of Niobium Oxide Containing Environmentally Friendly Optical Glasses

Improved Chemical Durability. The major advantage of niobium containing glasses over lead containing glasses is superior chemical durability. The possibility of hazing or staining on the glass surface is drastically decreased. Table II shows the comparison of chemical durability between the two glass systems. In this table one can see that the higher the grade, the worse the durability. The details of the measurement of the chemical durability have been stated in the International Standard Organization paper ISO [8424].

As the effect of the composition on chemical durability for optical glasses, it is well known that the lead ions in glass are easily migrated in nitric acid solution. The substitution of lead oxide by niobium oxide increases the chemical durability. Niobium containing glass shows chemical stability since niobium ions are less active than lead ions in glass. This improvement helps to keep the polished surfaces unchanged after the cleaning process even in a high temperature and high humidity environment.

Improved Mechanical Strength. “Hardness“ is an important factor of “ Mechanical Strength “. Table II shows the comparison of Knoop hardness between the two glass composition systems. The higher value means the higher the hardness. The details of the measurement of the Knoop hardness have been stated in the ISO paper [9385]. The niobium containing glasses can be machined more easily and therefore, scratches and surface imperfections can be avoided.

Lower specific gravity. Lower specific gravity is one of the most remarkable improvements of lead-free optical glass. By using lenses made of the lighter glasses the total weight of an optical device can be reduced.

In general, for conventional optical glasses, the higher the refractive index, the higher the lead oxide content of the glass composition and the higher the specific gravity as shown in Table II. When replacing the heavy element such as lead with the relatively light element such as niobium, the higher the refractive index of the glass, the greater is the specific gravity reduction ratio. The price of niobium oxide as a raw material is expensive even for an optical material, but through its low specific gravity, the increased cost of raw material is alleviated in the glass price per volume.

Table II Glass systems for optical properties

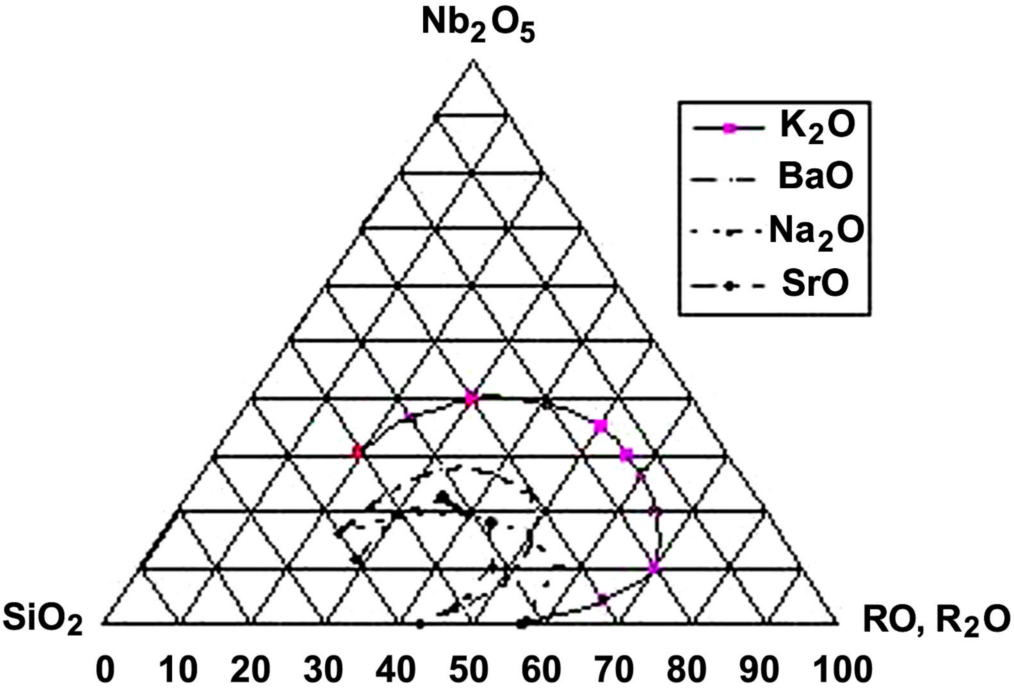
Glass Systems		B_2O_3-PbO-X			SiO_2-Nb_2O_5-ZrO_2-X		
Glass Types		BPM51	BPH5	BPH8	S-NBM51	S-NBH5	S-NBH8
Chemical Property	Acid Resistance(Surface)Group [SR]*ISO8424	53.2	52.2	53.2	1.0	1.0	1.0
Knoop Hardness[HK] *ISO9385		420 [4]	440 [4]	450 [5]	570[6]	580 [6]	590 [6]
Specific Gravity		3.24	3.49	4.20	2.93	3.02	3.19
Refractive index[n_d]		1.61340	1.65412	1.72047	1.61340	1.65412	1.72047
PbO(wt%)		32	39	55	0	0	0
Nb_2O_5(wt%)		0	0	0	12	21	32

*Status of standardization

<u>Problem of Niobium Oxide Containing Environmentally Friendly Optical Glasses</u>

Whether a melt of specific composition vitrifies or crystallizes depends on the composition and the cooling rate. When the cooling rate holds constant, the compositional range to form a glass is called the glass-forming region. Since there is a tendency for the glass-forming region to widen when multiple elements are used, we should consider that it does not necessarily match practical usage.

As Figure 6 shows, lead oxide has an unusual characteristic such that the glass forming tendency of even binary PbO-SiO_2 system leads to lead oxide content of more than 60 wt%. So it is possible for lead containing glasses to achieve a very high refractive index. However, niobium oxide has a narrower glass-forming region than lead oxide does. It shows that the glasses tend to crystallize stronger when the content of niobium oxide is more than 40 wt%. In order to prevent the crystallization for niobium containing glasses with high refractive index, it is necessary to adjust the refractive index by using additional elements like titanium oxide. However, since titanium oxide has the fundamental absorption in the range of the near ultraviolet, the absorption limit moves toward longer wavelength compared with lead containing glass as shown in Figure 7. This makes the glass slightly yellowish. Some extra attention in material selection is required just in case the optical system is designed for use at the short wavelength part of the visible range.



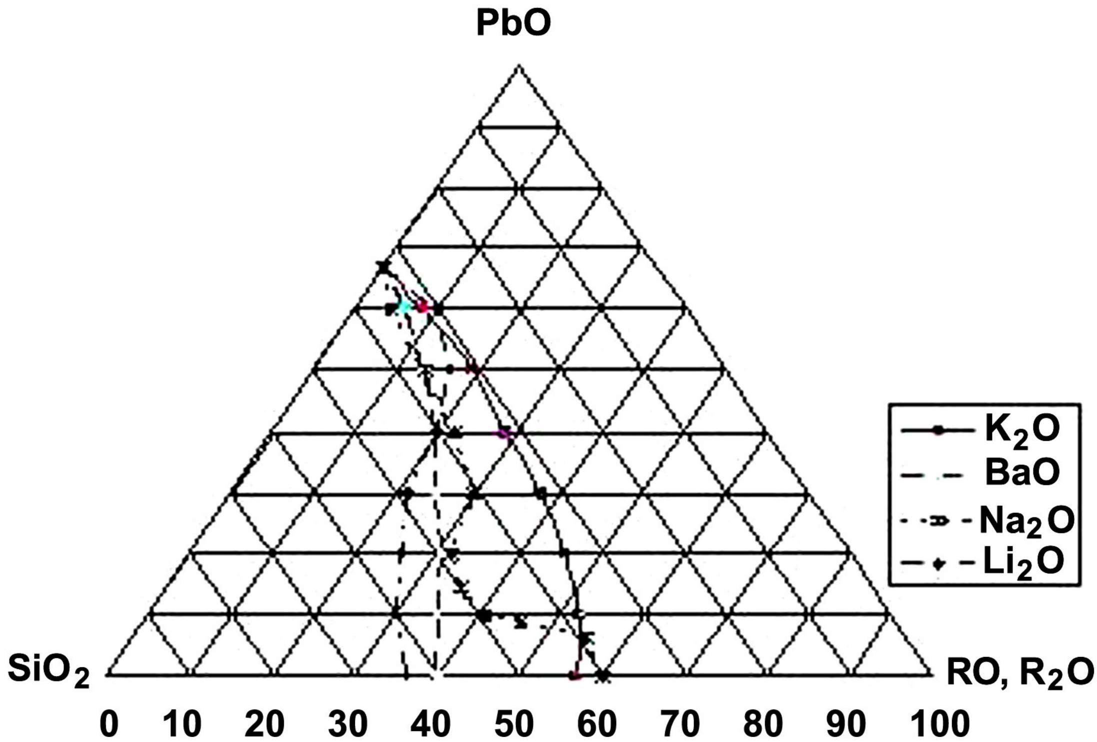


Figure 6: Glass-forming region of three components systems [2].

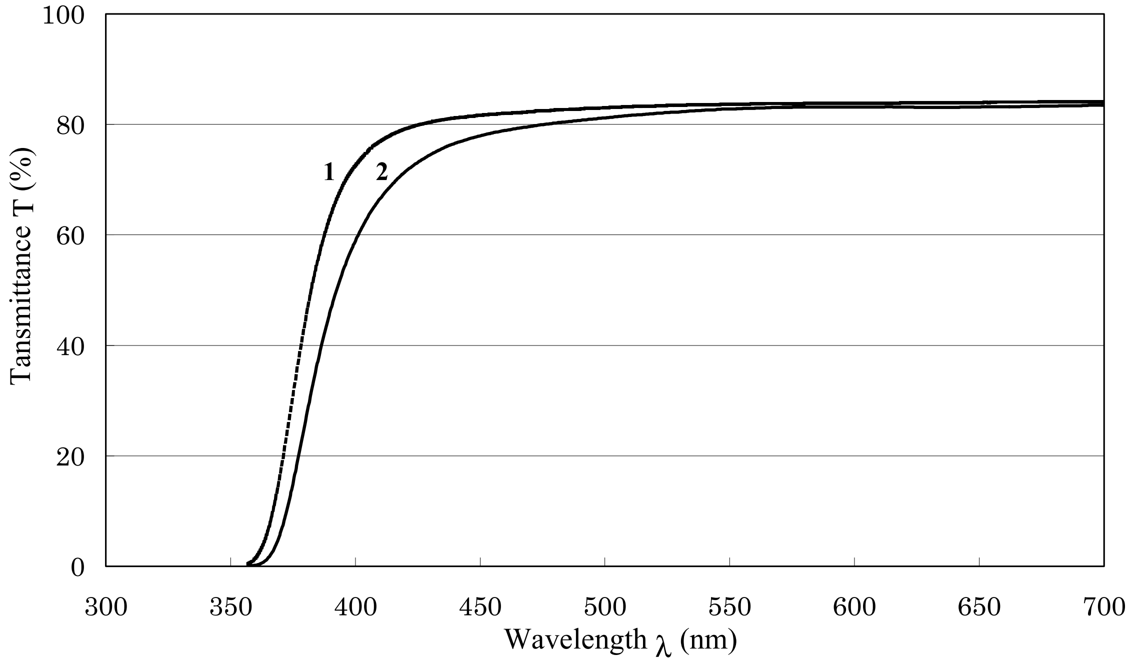


Figure 7: Transmittance with 10 mm path length (n_d =1.8466 ν_d =23.8).
1, SiO_2-PbO-X; 2, SiO_2-TiO_2-Nb_2O_5-X.

Conclusion

Niobium oxide plays an important role as one of the components that are substituted for lead oxide. Niobium oxide containing glasses are effective in attaining almost the same relative partial dispersion values as conventional lead containing glasses. In addition, chemical durability, Knoop hardness and lower specific gravity are also enhanced.

In the optical industry, the development of lead free products has become such an important consideration that it is also part of the marketing strategy. As a result, the demand for niobium oxide has doubled over the past ten years. If there will be sufficient supply of high-quality low-cost niobium oxide, then the demand for niobium oxide for optical glasses is expected to increase further.

Future development of optical materials with special characteristics is desirable to accompany cost reductions including those in manufacturing methods and higher performance optical system design. Even now, there are some special optical glasses for which the desired characteristics cannot be obtained without lead oxide.[8] However, solving various factors one by one with the cooperation of optical designers in order to provide optical materials free of toxic substances is a critical corporate principle for Ohara.

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