NIOBIUM OXIDE IN OPTICAL GLASS MANUFACTURE

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Introduction

Within recent years, niobium oxide has been widely used as a raw material for lanthanum borate glasses, which are typical optical glasses having high refractive indices and a relatively low value of optical dispersion. These types of glasses have been highly developed in recent decades and are now used extensively for camera lens systems, objective lenses of optical microscope, etc. The main reason for the wide use of niobium oxide is due to the rapidly increasing cost of tantalum oxide, which is often used for lanthanum borate glasses contributing to glass of high refractive indices and low optical dispersion. Since the early 1970's, the price of tantalum oxide has increased 700–800 percent, thus raising the cost of optical glasses containing tantalum oxide. Therefore, tantalum oxide has been gradually replaced by niobium oxide, which has similar optical property to tantalum oxide, and is less expensive. However, in comparison with tantalum oxide, a system containing niobium oxide has a limited glass forming region and is likely to be tinted slightly yellow. The substitution of niobium oxide for tantalum oxide is still only partial with progress depending on advances in compositional research and manufacturing methods. Ultimately, tantalum oxide is expected to be replaced to a great extent by niobium oxide except for glasses in the region of extremely low optical dispersion. Figure 1 shows a cross sectional view of a camera lens system using the optical glass containing niobium oxide. The lens shown with solid oblique lines is made of niobium and other lanthanum borate glasses.

Niobium oxide is not only a simple substitute for tantalum oxide, but is also used for ophthalmic lenses having high refractive indices, because it combines the advantages of high refractive index and relatively low value of specific gravity for a glass.

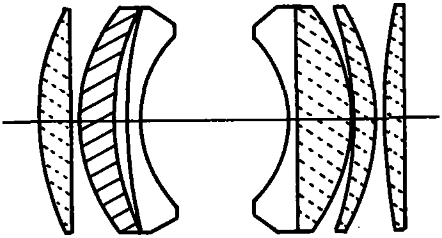

Figure 1. Lens system with niobium oxide containing glass.

Necessary Conditions for Optical Glass

Optical glasses are used as a material for lenses and prisms that are optical elements to transmit an image. Accordingly, they should satisfy standard requirements for transmission of a clear image.

1. Homogeneity
2. Transparency
3. Variety of optical constants

These are fundamental conditions governing transmission of an image. In addition to these conditions, optical glasses should have satisfactory chemical durability, mechanical properties, thermal properties, solarization and luminescence depending on the application.

Homogeneity

If inhomogeneous regions exist in a glass, the light is locally refracted and scattered and an image is not transmitted completely. Macroscopic inhomogeneities of optical glass comprise striations, bubbles, devitrification and stone, while the microscopic inhomogeneity is strain. The striations are a local inhomogeneities of glass composition. They disappear by stirring the glass melt during the melting process. The bubbles rise up to the melt surface and are released in the air during the melting process. The small entrapped bubbles are absorbed in the glass melt during the cooling process. Devitrification is partial crystallization ocurring during the cooling process which can be prevented by increasing the cooling rate. Stone is foreign matter entering the glass melt from outside sources during the melting process. The typical stone contaminent is a broken piece of brick from a melting furnace lining or material eroded from a crucible. These macroscopic inhomogenities may be detected and removed as substandard regions in the inspection process. Strain is the microscopic inhomogeneity of the refractive index which arises from inadequate cooling of the glass melt. A fine annealing process is required to eliminate such defects.

Transparency

In total transparency the incident light is not absorbed at all. If the light is absorbed selectively at a certain wavelength by a glass, the color of the image can not be reproduced completely. Therefore, optical glasses must be transparent over a wide region of wavelength acording to the usage. The optical absorption of glass consists of the fundamental absorption and the absorption by coloring impurities. In order to prevent the latter absorption purified raw materials that contain few coloring impurities should be used. Iron oxide is the most general coloring impurity. Even a very small amount of iron oxide colors the glass yellow. Oxides of the rare earth elements in raw materials, such as lanthanum oxide, ytterbium oxide, yttrium oxide, etc., often contain other lanthanides, which absorb the light in the visible region due to incomplete refining. The permissible maximum concentration of these coloring impurities depend on the composition of the glass. Glasses containing niobium oxide, titanium oxide, tungsten oxide and lead oxide have fundamental absorption in the ultraviolet region near the visible region. Consequently, even if these glasses contain extremely small amount of coloring impurities, they absorb the blue light of the visible region and are colored slightly yellow.

Variety of optical constants

The refractive index of a glass is dependent upon the wavelength of incident rays. Each incident ray having specific wavelength is focused on its own focal point through a lens. This is called chromatic aberration. It is impossible to avoid chromatic aberration by use of a single lens system. A combination of at least two lenses with different optical constants is essential to minimize the aberration.

As refractive index N is a function of wave-length, it is denoted with suffix corresponding to each wavelength of measuring rays specifically N_d, N_e, N_F, N_C ... etc., where d is the d line of helium, e is the e line of mercury, F and C are the F and C lines of hydrogen. Optical constants which indicating optical dispersion are the Abbe number $V_d = N_d - 1/N_F - N_C$, and the partial dispersion ratio $P_{xy} = N_x - N_y / N_F - N_C$, etc. Generally, optical glasses are classified using the combination of N_d and V_d as shown in Figure 2. Other than chromatic aberration, Seidel's five aberrations caused by the spherical surface of lenses are taken into consideration. Using a glass with high refracting power, the curvature of a lens can be reduced and then these aberrations are minimized.

In summary, approximately two hundred types of optical glasses with various optical constants are necessary to design a lens system having good performance.

Glass Forming Systems Containing Niobium Oxide

Glass forming region

Generally, when a melt is cooled rapidly, it forms into glass. On the other hand when melt is cooled slowly, it crystallizes or devitrifies at the solidifying or liquidus temperature. Whether a melt of specific composition forms into glass or crystallizes depends on the composition and the cooling rate. When cooling rate holds constant, compositional range to form a glass is called the glass forming region. The forming region changes with cooling rate in each system. If the system has a broad glass forming region, the wider will be its range of use. For example, in Figure 3 the glass forming regions of some three components systems B_2O_3-La_2O_3-M_nO_m are shown. They are B_2O_3-La_2O_3-Nb_2O_5, B_2O_3-La_2O_3-Ta_2O_5, B_2O_3-La_2O_3-ZrO_2, B_2O_3-La_2O_3-TiO_2, B_2O_3-La_2O_3-WO_3 and B_2O_3-La_2O_3-PbO. The B_2O_3-La_2O_3-Nb_2O_5 system is relatively

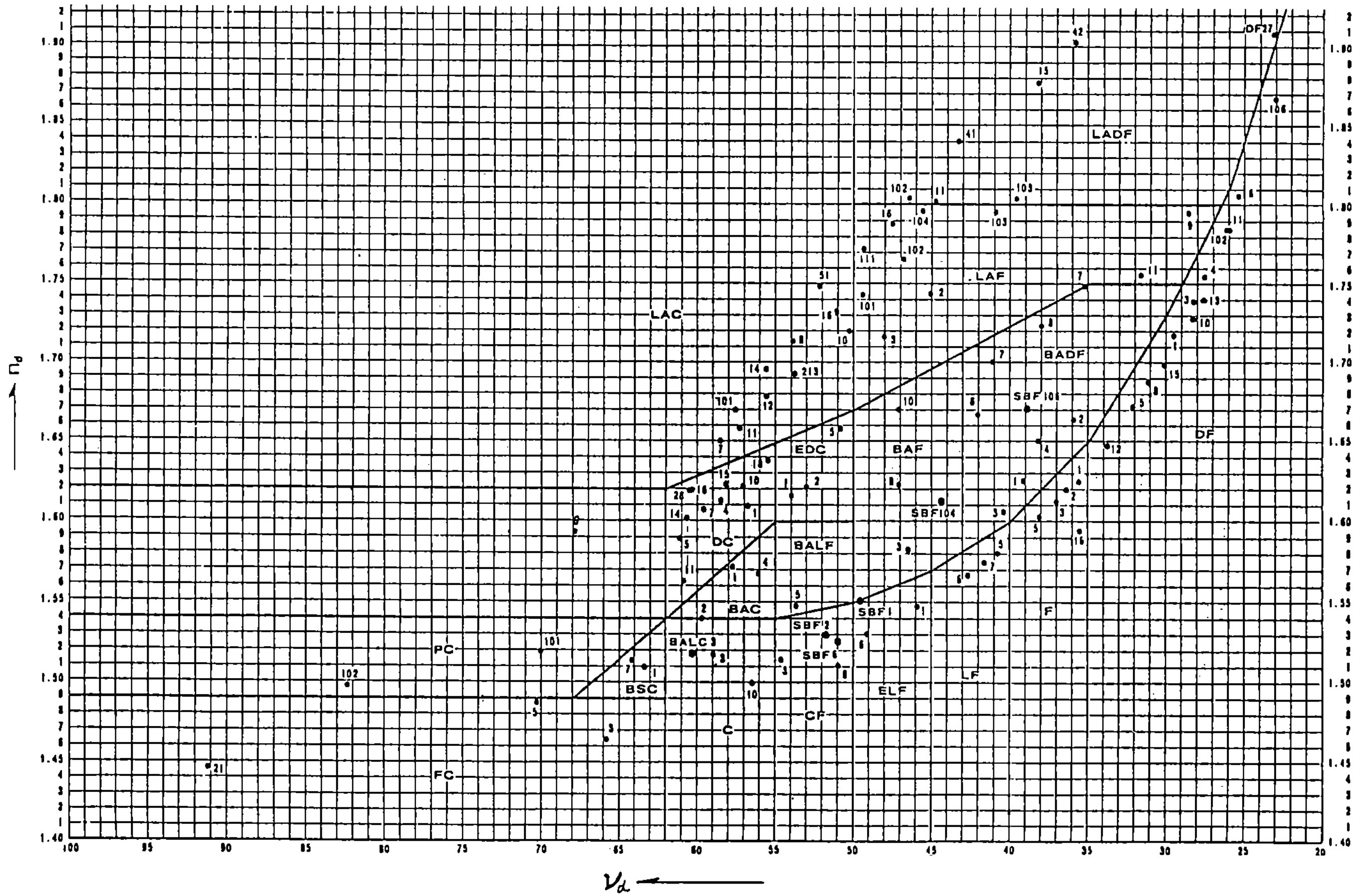

Figure 2 Diagram of optical glass

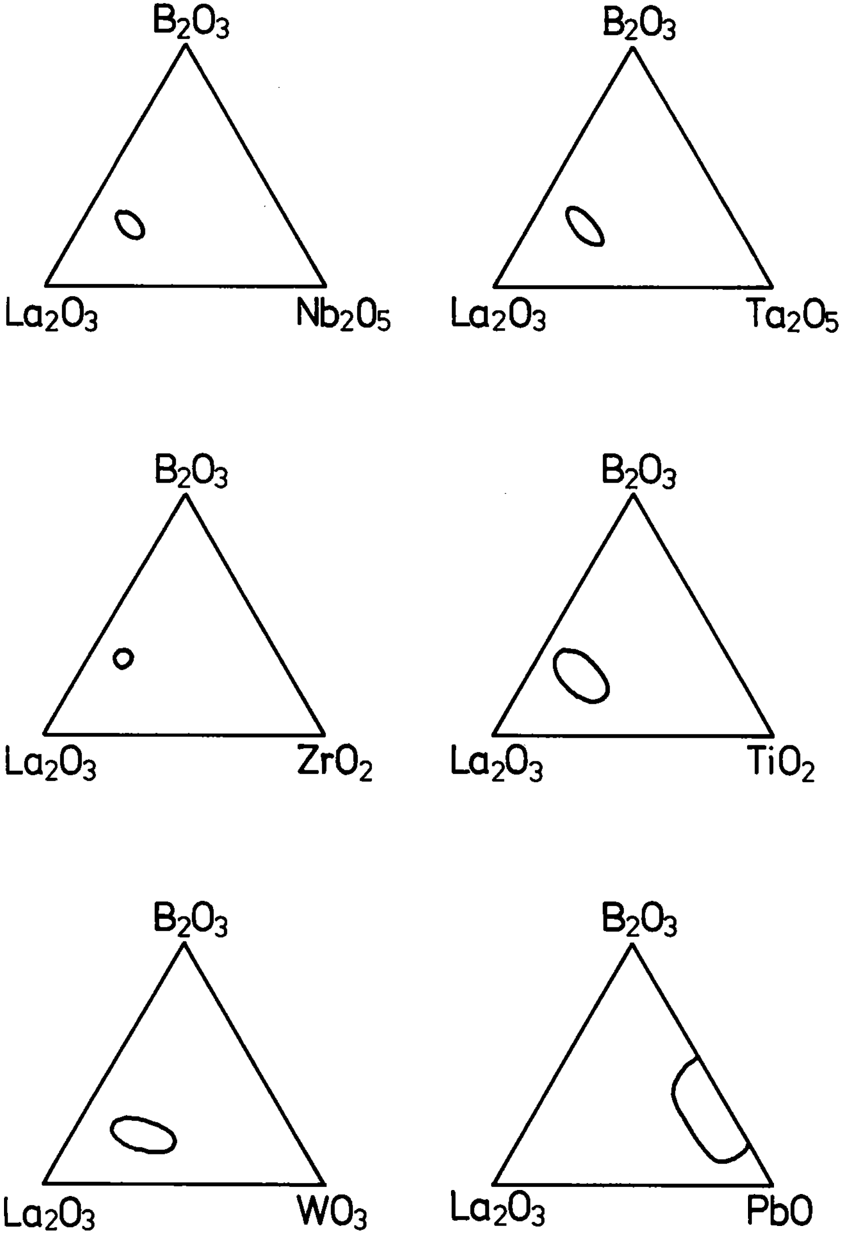

Figure 3. Glass forming region of three components systems.

narrow in comparison with other systems. Lanthanum borate glasses in practical use consist of more than three components and their glass forming regions broaden generally and do not necessarily correspond to that of the basic three components system.

The polyvalent metal oxides such as tantalum oxide, zirconium oxide and tungsten oxide are not used extensively in silicate and phosphate glasses but tend to be used in borate glasses. In contrast, niobium oxide is used in all three systems. For example, according to United States Patent (U.S.P.) 4,115,131, niobium oxide is contained in the range 22 percent to 70 percent in glasses based on the P_2O_5-B_2O_3-Nb_2O_5 system giving a refractive index of 1.57–1.98 and Abbe number of 18–46. According to U.S.P. 4,193,807 niobium oxide can be added in the range 22 percent to 50 percent'in the glass based on P_2O_5-PbO-Nb_2O_5 system yielding refractive index values of 1.75–2.13 and Abbe numbers of 17–28. These glasses are resistant to devitrification. Thus, niobium oxide has the advantage of forming glasses both in the phosphate and lanthanum borate systems.

Niobium oxide as a raw material

There are various impurities contained in the raw material of optical glasses that affect the properties of the glass, including optical properties, coloration and stability against devitrification.

If a raw material contains many impurities which strongly affect optical properties, it is not suitable as a raw material.

Secondly, it is necessary to minimize impurities such as iron oxide which color the glass. As mentioned previously, niobium oxide is one of the components which have the fundamental absorption of ultraviolet radiation near the visible region; therefore, niobium oxide containing glasses tend to color intrinsically under the influence of the coloring impurities. The intensity of coloration depends on the glass composition, and the permissible concentration for each glass is determined by experimentation.

It is hard to describe quantitatively the influence of the impurities on the resistance to devitrification, but there are some instances in which they affect the stability decisively.

In many cases, a very small amount of tantalum oxide is contained in niobium oxide as a raw material. Tantalum oxide is one of the components used in the lanthanum borate glasses and it has a similar properties to niobium oxide, therefore, its presence is not a serious problem. For example, in the glass with niobium oxide of 10 percent, if the raw material contains tantalum oxide of 0.1 percent, such content does not significantly affect the properties of the glass in common systems.

Various Properties of the Glass Containing Niobium Oxide

Chemical resistance

Chemical resistance of glass containing niobium oxide is considered good. For example, a comparison between two optical glasses which have the same optical constant, such as lead silicate glass and boro-phosphate glass containing 33 percent niobium oxide the dissolved amount of the former by the acid is 0.682 percent while that of the latter is merely 0.005 percent. That is, the niobium oxide containing glass has about one hundred times the resistance as the former. The resistance to acid was in the cited example measured according to the Japan Optical Glass Industrial Standard.

Specific gravity

In many optical glass forming systems, the specific gravity tends to increase as the refractive index increases due to the addition of dense components such as lanthanum oxide, lead oxide, zirconium oxide, tantalum oxide, titanium oxide and niobium oxide. These increase the specific gravity as they increase the refractive index. Among such components, niobium oxide, titanium oxide and zirconium oxide, have the advantage of increasing specific gravity at a lower rate than the other oxides. The relationship between specific gravity and refractive index in two systems, B_2O_3-ZnO-La_2O_3-ZrO_2-Nb_2O_5 and B_2O_3-ZnO-La_2O_3-ZrO_2-Ta_2O_5 shown in Figures 4 and 5 indicates that in comparison with tantalum oxide, niobium oxide is preferred for increasing refractive index without increasing specific gravity.

In a practical example, two lanthanum borate glasses may have the same optical constant, but one containing tantalum oxide and lead oxide has a specific gravity of 4.63 and the other containing niobium oxide has a specific gravity of 4.19 making it lighter by 10 percent. Similary, comparing two commercial dense flint glasses which have the same optical property, one containing about 60 percent lead oxide has a specific gravity of 4.48 whereas the other containing 41 percent niobium oxide has a specific gravity of 3.10 or 31 percent less.

Glass as with low specific gravity have the advantage of lightening and compacting the lense system and the optical system.

Optical properties

Niobium oxide is one of the most effective components for increasing the refractive index of glass. With respect to the Abbe number, niobium oxide increases it more than lead oxide, titanium oxide and tungsten oxide whereas it increases it less than lanthanum oxide, gadorinium oxide, yttorium oxide, ytterbium oxide, zirconium oxide and tantalum oxide. Therefore, niobium oxide is used in the broad, intermediate range, except for very low Abbe number range and very large Abbe number range in the diagram shown in Figure 6. The figure presents refractive indices and Abbe numbers of the three component system B_2O_3-La_2O_3-Nb_2O_5.

Transmittance

Because niobium oxide has the property of fundamental absorption of ultraviolet near the visible range, it turns the glass slightly yellow. Spectral transmission curves of the B_2O_3-ZnO-La_2O_3-ZrO_2-Nb_2O_5 system are shown in Figure 7. The absorption limit moves toward the visible range as the content of niobium oxide increases. The difference in transmittance between glass containing 15 percent niobium oxide and another containing tantalum oxide ranges from a few percent to several tens of percent. However, except for special uses, it is acceptable for normal optical glasses to transmit the visible rays only. Therefore, in the context of transmittance, glasses containing niobium oxide about up to 15 percent in the system shown in Figure 7, are usable.

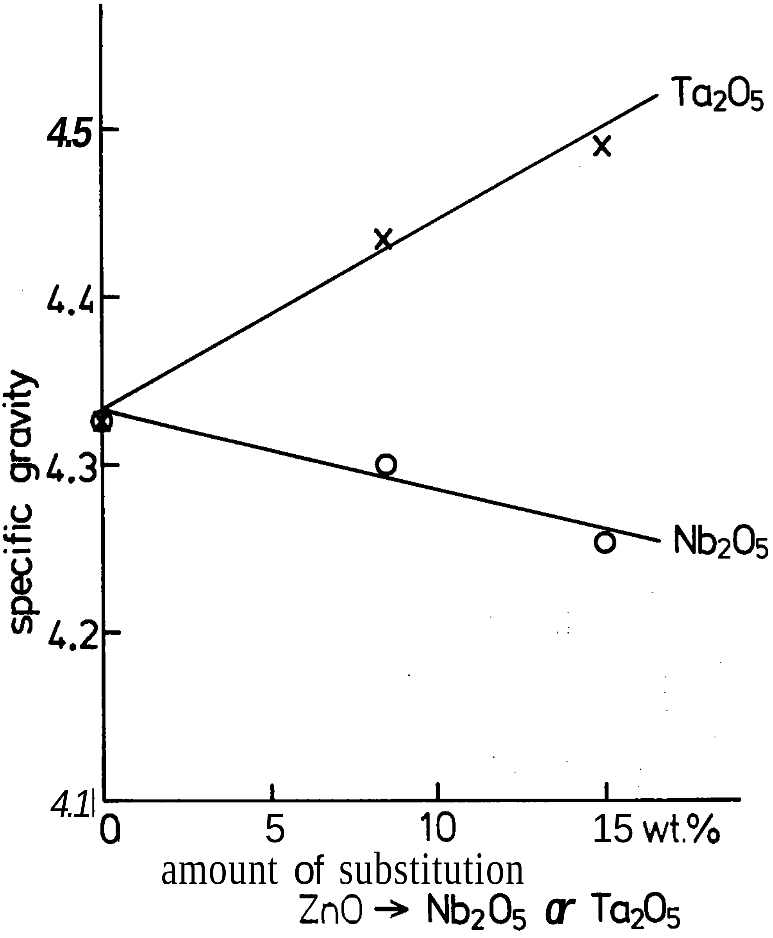

Figure 4. Relation between the substitution amount and the specific gravity in the system B_2O_3-ZnO-La_2O_3-ZrO_2-Nb_2O_5 or Ta_2O_5.

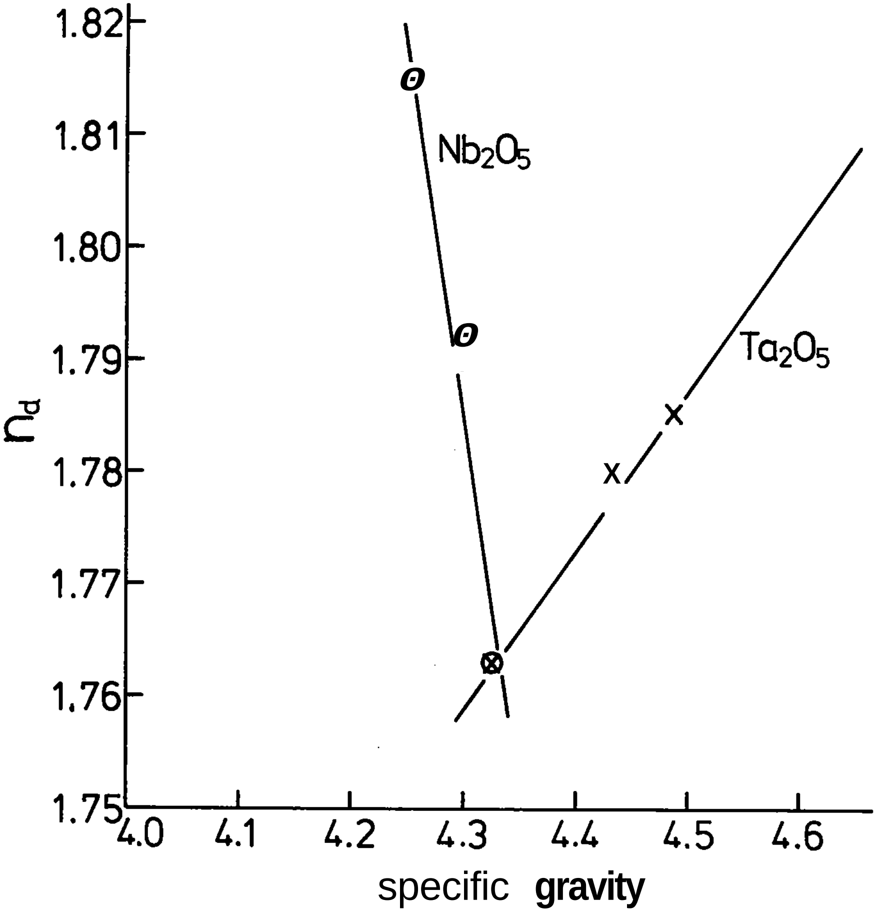

Figure 5. **Relation between the refractive index and the specific gravity in the system** B_2O_3-ZnO-La_2O_3-ZrO_2-Nb_2O_5 or Ta_2O_5.

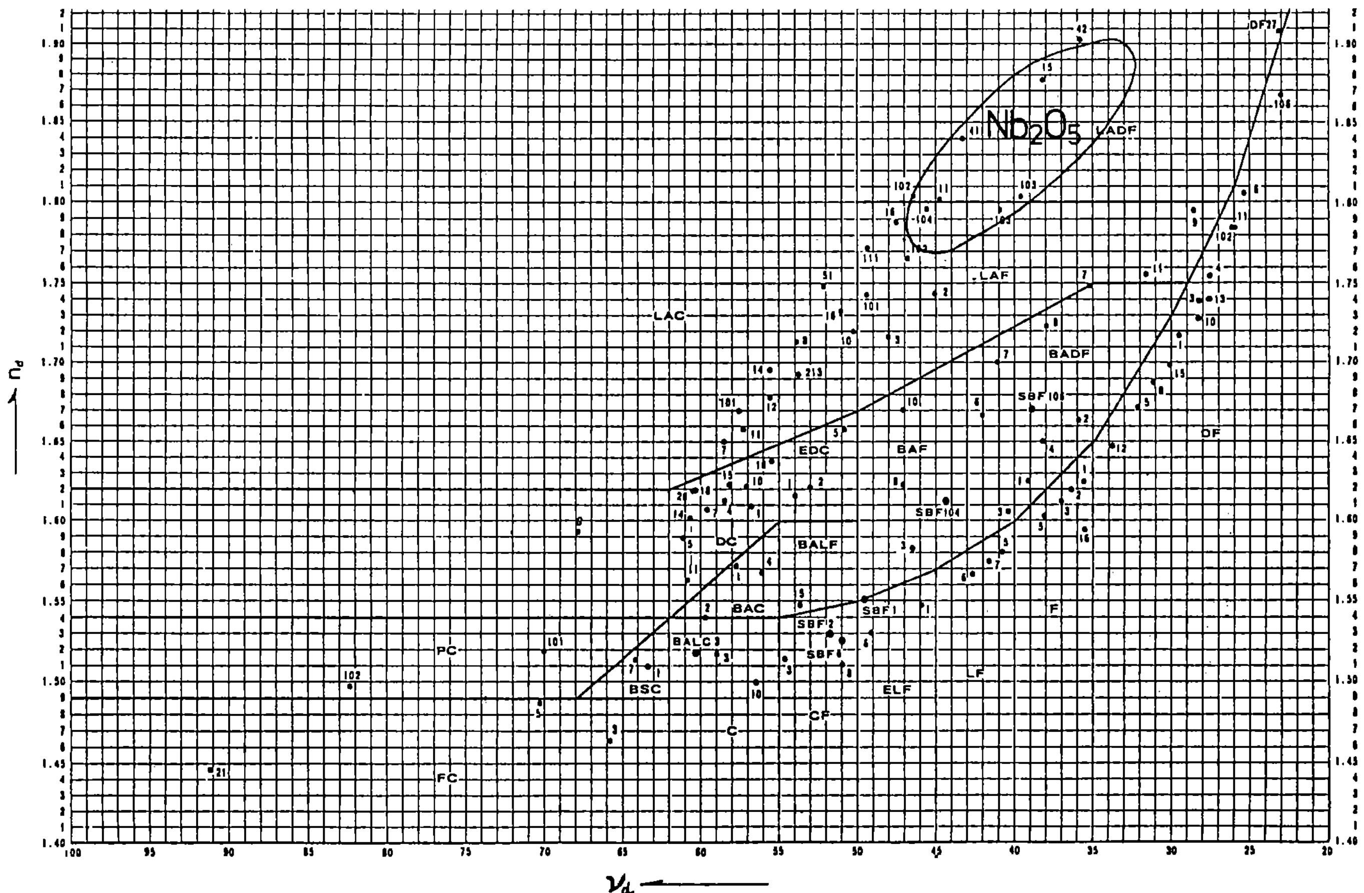

Figure 6 Optical properties of the three components system $B_2O_3-La_2O_3-Nb_2O_5$.

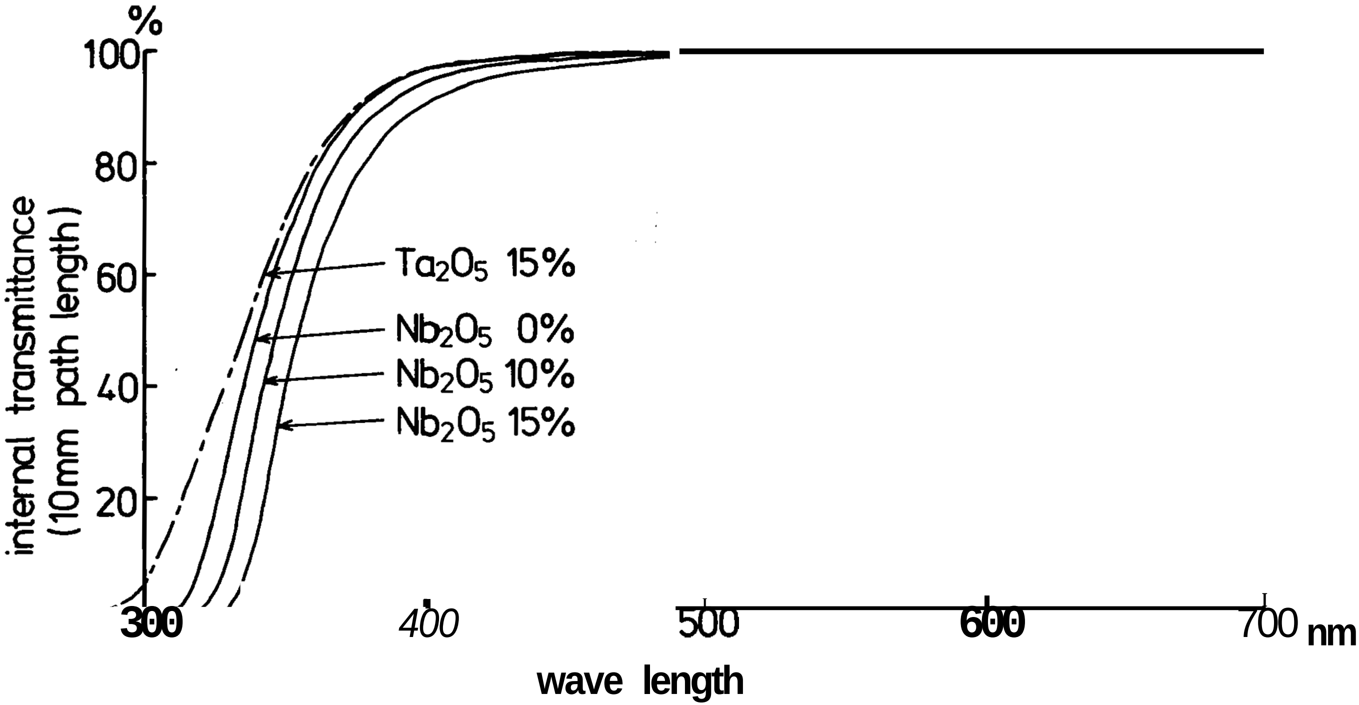

Figure 7. Internal transmittance with 10 mm path length in the system B_2O_3-ZnO-La_2O_3-ZrO_2-Nb_2O_5 or Ta_2O_5.

Conclusion

Since niobium oxide increases the refractive index without decreasing the Abbe number significantly, it is used in lanthanum flint glass and lanthanum dense flint glass.

Similarly, since 'it increases the refractive index without increasing the specific gravity, it is used in ophthalmic lenses having high refractive index and light weight. These lenses have a refractive index (N_d) of 1.70 and specific gravity of 3.0. Alternative optical glasses having the same refractive index have a specific gravity of 3.83 or 22 percent greater than the niobium oxide glasses. Moreover, in comparison with normal low refractive index ophthalmic lenses, it is possible to reduce the curvature of the lens. Thus, there exists an advantage in aesthetic terms such that swirl like images arising from multiple reflections between the two surfaces of the lens can be attenuated.

At present, the limitation of the extensive use of niobium oxide for optical glass is determined by the stability against devitrification and by the coloration of a glass. It is thought that the content of niobium oxide in glass and the amount in optical glass manufacturing will increase measureably as studies of the composition of optical glasses proceed and glasses which are stable against devitrification are developed. Similary, supply of raw material of high quality and of low price will stimulate adoption of niobium containing glasses.