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Structure and Chemistry of Sol-Gel Derived* Transparent Silica Aerogel

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ABSTRACT

Transparent silica aerogels are being studied because of their excellent thermal insulation properties for window glazing materials. The chemistry of the base catalyzed $Si(OC_2H_5)_4$ sol-gel process to produce transparent aerogels is presented. The results of a factorial design set of experiments are discussed in which five process parameters are simultaneously varied. The goal of these experiments was to optimize the process conditions and to analyze the importance of various parameters in improving the properties of the aerogel.

A novel technique of ambient temperature supercritical drying of alcogels is described. In this process, supercritical drying occurs at $\leq 40^{o}C$ instead of at $\geq 270^{o}C$ and $\geq$ 1700 PSI (12 MPa), by substituting CO_2 for alcohol in the alcogel. The time of drying is reduced from 2-3 days to 8-10 hours. It is shown that light scattering, microstructural properties and other characteristics of aerogels produced by this process and by the high temperature supercritical drying are similar.

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INTRODUCTION

Aerogel is a microporous silica material containing a high fraction of voids (up to 97% by volume). It is transparent rather than translucent because the pore and particle sizes are smaller than the wavelength of light; therefore, it transmits rather than scatters light.

Aerogels were first made by Kistler[1-2] in 1931, but their application as transparent insulating material has attracted attention only recently.[3-7] Silica aerogels, prepared by base catalyzed hydrolysis and condensation of $Si(OCH_3)_4$ have been used in Chevenkov radiation detectors.[8-11] Here, aerogels with index of refraction between 1.02 and 1.10 replaced the pressurized cryostatic gas-systems with low index of refraction. Since $Si(OCH_3)_4$, the starting material for transparent silica is extremely toxic, it is desirable to utilize alternative materials to insure the commercial viability of transparent aerogels. Tetra ethyl ortho silicate, TEOS, $Si(OC_2H_5)_4$, seems to be the logical choice. Schmitt[3-4] prepared aerogels based on $Si(OC_2H_5)_4$ hydrolysis and condensation using acid catalysis. However, the aerogels are not as clear as obtained by base catalysis of $Si(OCH_3)_4$. Also, the alcogels shrink during removal of the alcohol which further reduces the optical transparency. A base catalyzed hydrolysis and gelation of $Si(OC_2H_5)_4$ combines the desirable properties of base catalysis with a low toxicity starting material. However Schmitt[4] reported that aerogel synthesis by base catalyzed $Si(OC_2H_5)_4$ was not possible because base catalyzed $Si(OC_2H_5)_4$ gave white powdery material instead of a transparent aerogel. Russo and Hunt reported the base catalysis of $Si(OC_2H_5)_4$.[12] In this paper we report the results of our studies of the base catalyzed hydrolysis and condensation of $Si(OC_2H_5)_4$ to optimize the desired transparency, strength and stability of silica aerogels.

The overall goals of the research program are to improve the optical and thermal properties of aerogel, develop methods to protect it from environment, discover less expensive synthesis methods, and develop a technology base for production of transparent aerogels. Using a factorial design set of experiments, process parameters have been varied over a wide range of conditions to achieve the desired properties of the

aerogel.

EXPERIMENTAL

Methods and Materials

Commercial $Si(OC_2H_5)_4$ was used without distillation. C_2H_5OH was 200 proof without water. NH_4OH and NH_4F was analytical grade. Viscosity was measured by Brookfield viscometer with small sample adapter and thermostatic control. Light scattering intensity measurements as a function of angle of scattering, were performed during gelation and after drying of aerogels as described earlier.[6-7] Optical transmission was obtained using Perkin Elmer Lamda 9 UV/VIS/NIR spectrophotometer.

The aerogel production has two segments: 1) hydrolysis and condensation of alkoxides giving alcogels, 2) removal of alcohol from the alcogels to achieve aerogel. These are discussed below.

Hydrolysis and Gelation from $Si(OC_2H_5)_4$

Both acid and base catalyzed hydrolysis and condensation reactions give alcogels from alcohol solutions of alkoxides according to reactions

$$Si(OC_2H_5)_4 + 4H_2O \xrightarrow{\text{catalyst}} Si(OH)_4 + 4C_2H_5OH$$

$$nSi(OH)_4 \rightarrow nSiO_2 + 2nH_2O$$

We used ammonia and ammonium fluoride as the catalyst for the gelation in the hydrolysis reaction.

Supercritical Drying of Alcogels

The alcogel structure contains more than 90% by volume fine pores containing alcohol. This alcohol must be removed to obtain aerogel.

Because the radius of the pores in the alcogel is extremely small, the the surface tension at the interface between liquid and gas is extremely high. To prevent damage to the gel structure due to these high interfacial forces, drying is done under supercritical conditions, where interfacial forces are minimum. For ethyl alcohol, supercritical conditions are 270°C and 1700 PSI pressure. Therefore, the process requires a high temperature and high pressure system. The autoclave used for supercritical drying is computer controlled with data acquisition capability up to 300°C and 3000 PSI. Typical drying conditions are 270°C and 1700 PSI and the heating rate is 0.2 to 0.5°C/min. The pressure release is at high temperature and the typical time is 48 hours. These requirements make the process expensive and slow (total drying time is 2 to 3 days for each batch).

Near Ambient Temperature Drying:

Performing the supercritical drying at near ambient temperature not only simplifies the requirements from those of high temperature drying but also reduces the time for drying and makes the process much more economical. Based on the critical constants of some common fluids[13], CO_2 seems to be the most practical choice. The cost of liquid CO_2 bottle is low ($6.00 per 50 lb. bottle). It has been successfully used in critical point drying of biological samples for scanning electron microscopy. N_2O, on the other hand, has not been used successfully for biological samples.[13] Other fluids which seem attractive are Freons 13, 23, and 116. However, they are relatively more expensive. Water and alcohols are obviously poor choices. We have used CO_2 substitution followed by supercritical drying and have compared the properties of aerogels dried by both methods; CO_2 drying at 40°C and 1200 PSI and high temperature drying at 270°C and 1700 PSI. The results are discussed below.

RESULTS AND DISCUSSION

Light Scattering of Alcosol, Alcogel and Aerogels:

Light scattering intensities for the gelling solutions were obtained

during and after gelation. During gelation, scattering intensity increases with time and reaches a limiting value (Figure 1). This observation is consistent with light scattering intensity from the nucleation and growth of silica particles with subsequent gel formation. The light scattering intensity reaches a limiting value when the microstructural changes cease. However, on drying the alcogel, light scattering intensity increases from the limiting value by a factor of 10 to 20 depending on the shrinkage, heterogeneity, etc., in the aerogel. A theoretical estimate based on the change of index of refraction between air and alcohol for the two materials[15] gives roughly a factor of 10 change in scattering intensity. Therefore, the change in scattering intensity arises from both intrinsic changes and from structural changes during drying. The changes in light scattering intensity during drying are similar for both the CO_2 dried and high temperature dried aerogels.

Process Optimization using Factorial Design:

Using a factorial design set of experiments process parameters were varied over a wide range of conditions to explore the properties of aerogel. Concentration of the alkoxide, water content, amounts of alcohol, ammonia and ammonium fluoride in the alcosol mixture, were simultaneously varied. Light scattering, optical transmission spectra, rheology, pH, shrinkage, surface area and transmission electron microscopy of the final aerogels were studied for the optimization. The results were represented by using a polynomial equation containing the parameters and displayed using contour plots (Figure 2). These calculations gave an evaluation of the significance and importance of the parameters and the direction of change to optimize the process. For example, it is concluded from Figure 2 that to improve the light scattering (i.e., increasing the negative log of the scattered intensity) the temperature of gelation and the concentration of NH_4OH has to be lower than what was used. In addition, at gelation temperatures higher than 35°C, the light scattering can not be improved by the variation of NH_4OH, (as indicated by the dotted line at the top in the figure 2).

Contour plots with other parameters helped to optimize the process conditions. We have achieved a formulation which produces aerogel comparable to that produced using $Si(OCH_3)_4$. A final optimization will be done to determine the exact process conditions for the desired properties of the aerogel.

Optical Spectra

Transmission spectra (figure 3A and 3B) show that in the visible region, the transparency of the aerogels dried by the two methods is very similar. The difference in the NIR region is probably due to water absorption bonds. Since in CO_2 drying, the aerogels are subjected to temperatures $\leq 40^oC$ compared to $\geq 270^oC$ in the high temperature supercritical method, water peaks are more pronounced in the CO_2 dried sample (Figure 2B). Water peaks have been reported[14] between 700-900, 900-1150, 1350-1800 and 1800-2200 nm. After heating the CO_2 dried aerogels in air at 250^oC for 2-3 hours, certain water peaks disappear (between 1700-1800 nm, Figure 4A and 4B), and other peaks are sharpened and reduced in overall intensity. The fine structure in some of the water peaks disappears, suggesting desorption of water from certain sites. The spectra of aerogels dried by CO_2 method, after further heating becomes similar to that for the high temperature supercritically dried aerogels (compare figure 3A and 4C), confirming our other observations that the two drying methods produce similar quality aerogels. Figure 5 shows the comparison of high temperature supercritically dried base catalyzed TMOS aerogel with CO_2 dried base catalyzed TEOS aerogel (4 mm thick).

Reproducibility and Quality of Aerogels in CO_2 drying

The ease of operation, reproducibility and repeatability of supercritical CO_2 drying of aerogels is far better than that of high temperature supercritical drying. The incidence of cracking or fracture of aerogels is significantly lower using the CO_2 method. The batch to batch reproducibility in drying is also improved. Above all, there is a marked time saving from 2 to 3 days for the high temperature process, to 8-10 hours for the CO_2 method. In addition, the equipment for the CO_2 method is simpler and less expensive than that required for the high

temperature supercritical drying.

SUMMARY AND CONCLUSIONS:

Optical transmission, light scattering, and other data show that CO_2 supercritical drying produces aerogels similar in quality to those produced by high temperature supercritical drying.

The reproducibility of the CO_2 drying method is far better than that of the high temperature supercritical drying.

CO_2 supercritical drying is simpler and less expensive because it is done at $\leq 40^oC$ and 1200 PSI instead of at $\geq 270^oC$ and $\geq$ 1700 PSI. The CO_2 method also saves significant time in the drying process.

By exploring a wide range of process variables by a factorial design set of experiments, we have achieved a base catalyzed $Si(OC_2H_5)_4$ aerogel similar in quality to the one prepared by $Si(OCH_3)_4$.

Supercritical drying may offer a unique opportunity in ceramic processing for controlling pore and particle sizes in gels, thereby providing a better control of the microstructure.

ACKNOWLEDGEMENTS

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Figure Captions

1. Light scattering intensity from a base catalyzed alcosol during gelation as a function of time.

2. Contour plots of the dependence of intensity of light scattering (L.S.) on temperature and ammonia content at H_2O: TEOS ratio of 8:1; NH_4F, 1.6×10^{-3}m and $V_{TEOS}/V_{total} = 0.15$. The inner scale gives the scaled change of the variable.

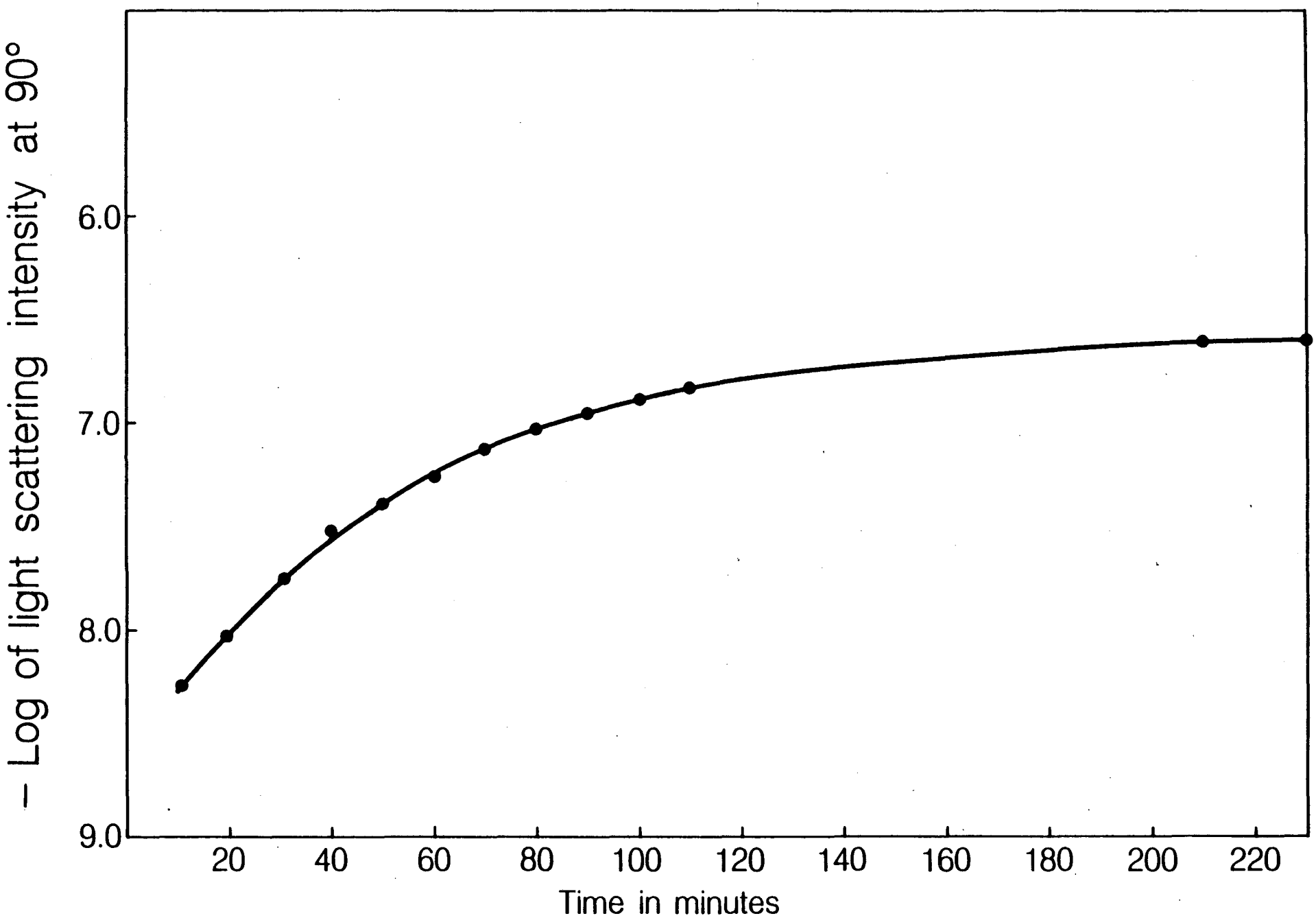
3. Transmission spectra of (A) base catalyzed $Si(OC_2H_5)_4$ aerogel prepared by high temperature supercritical drying; (B) base catalyzed $Si(OC_2H_5)_4$ aerogel prepared by CO_2 supercritical drying (3 nm thick).

4. Transmission spectra of (A) base catalyzed $Si(OC_2H_5)_4$ aerogel dried by CO_2 supercritical drying; (B) spectra of the same aerogel after heating for 3 hours in air at 250°C; (c) spectra of the same aerogel after heating for 4 hours in air at 450°C (samples 3 nm thick).

5. Transmission spectra of base catalyzed $Si(OCH_3)_4$ (TMOS) aerogel dried by the high temperature supercritical method (dashed line) and base catalyzed $Si(OC_2H_5)_4$, (TEOS) aerogel dried by the CO_2 method and heated to 450°C for 4-5 hours; both samples are 4 mm thick.

February 21, 1985

CS:



Light scattering intensity changes with time

Figure 1

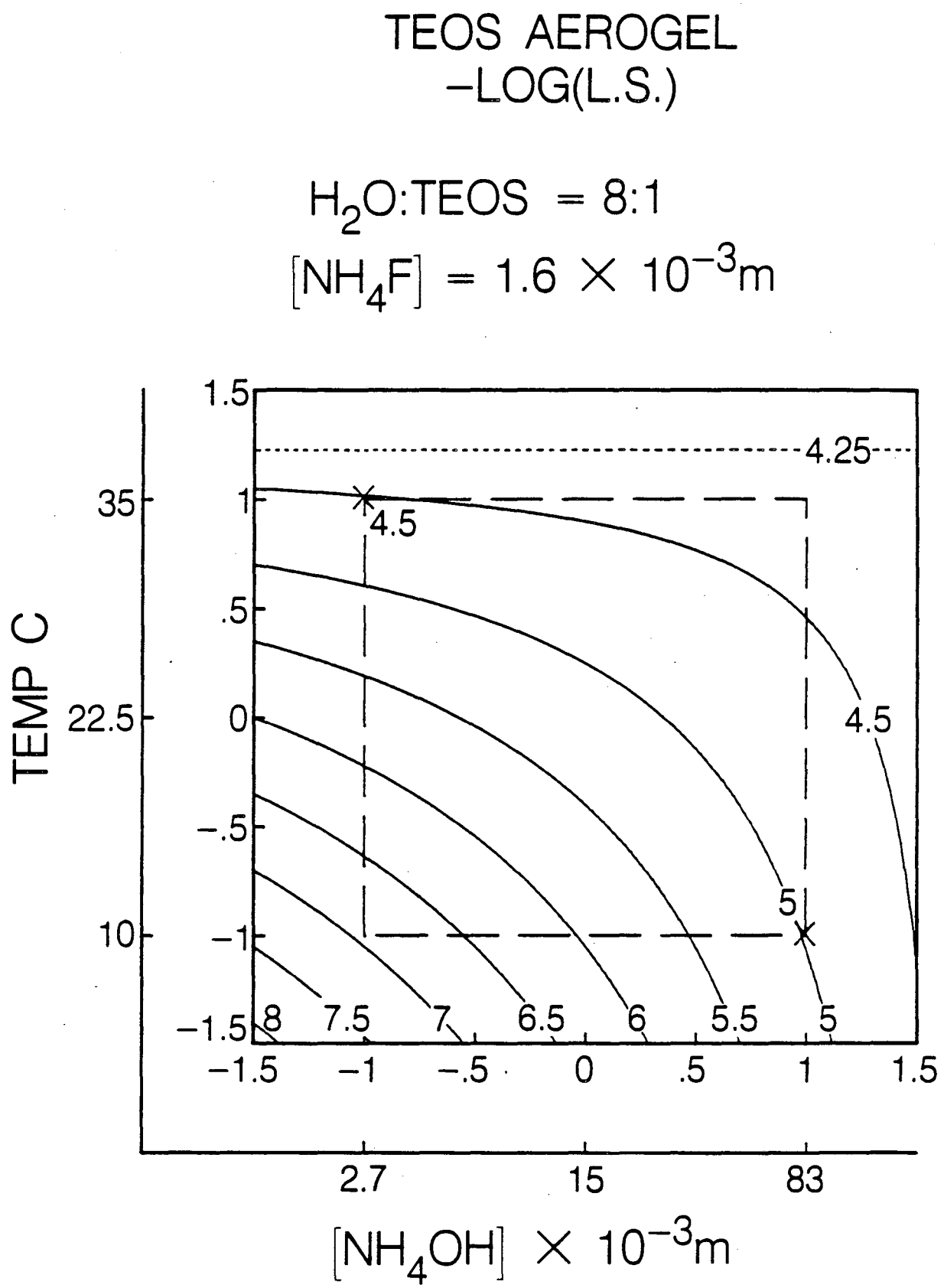

TEOS AEROGEL
−LOG(L.S.)
H2O:TEOS = 8:1
[NH4F] = 1.6 × 10−3m
TEMP C
35
22.5
10
1.5
1
.5
0
−.5
−1
−1.5
4.25
4.5
4.5
5
8
7.5
7
6.5
6
5.5
5
−1.5
−1
−.5
0
.5
1
1.5
2.7
15
83
[NH4OH] × 10−3m

Figure 2

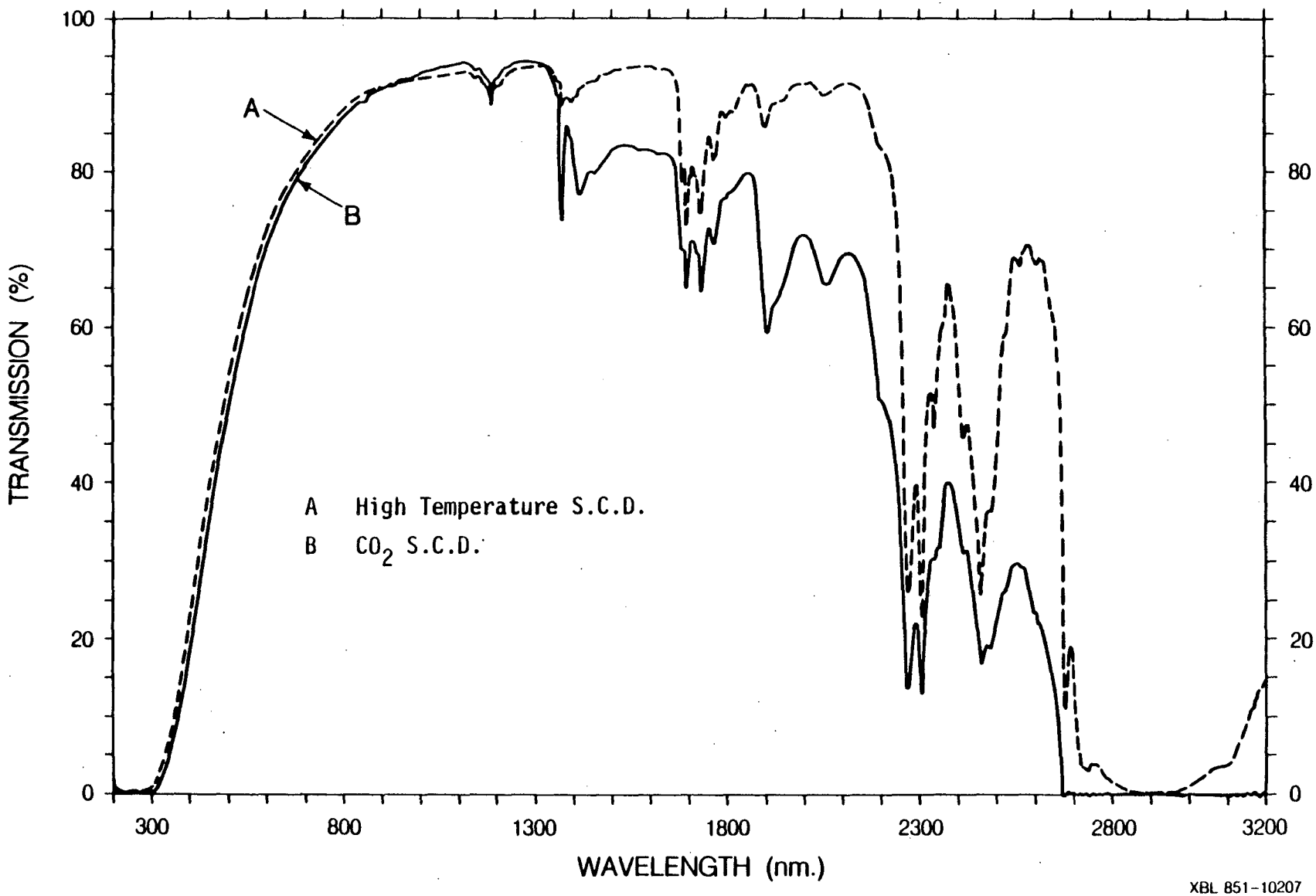

TRANSMISSION (%)
100
80
60
40
20
0
A
B
A High Temperature S.C.D.
B CO_2 S.C.D.
300
800
1300
1800
2300
2800
3200
WAVELENGTH (nm.)
XBL 851-10207

Figure 3

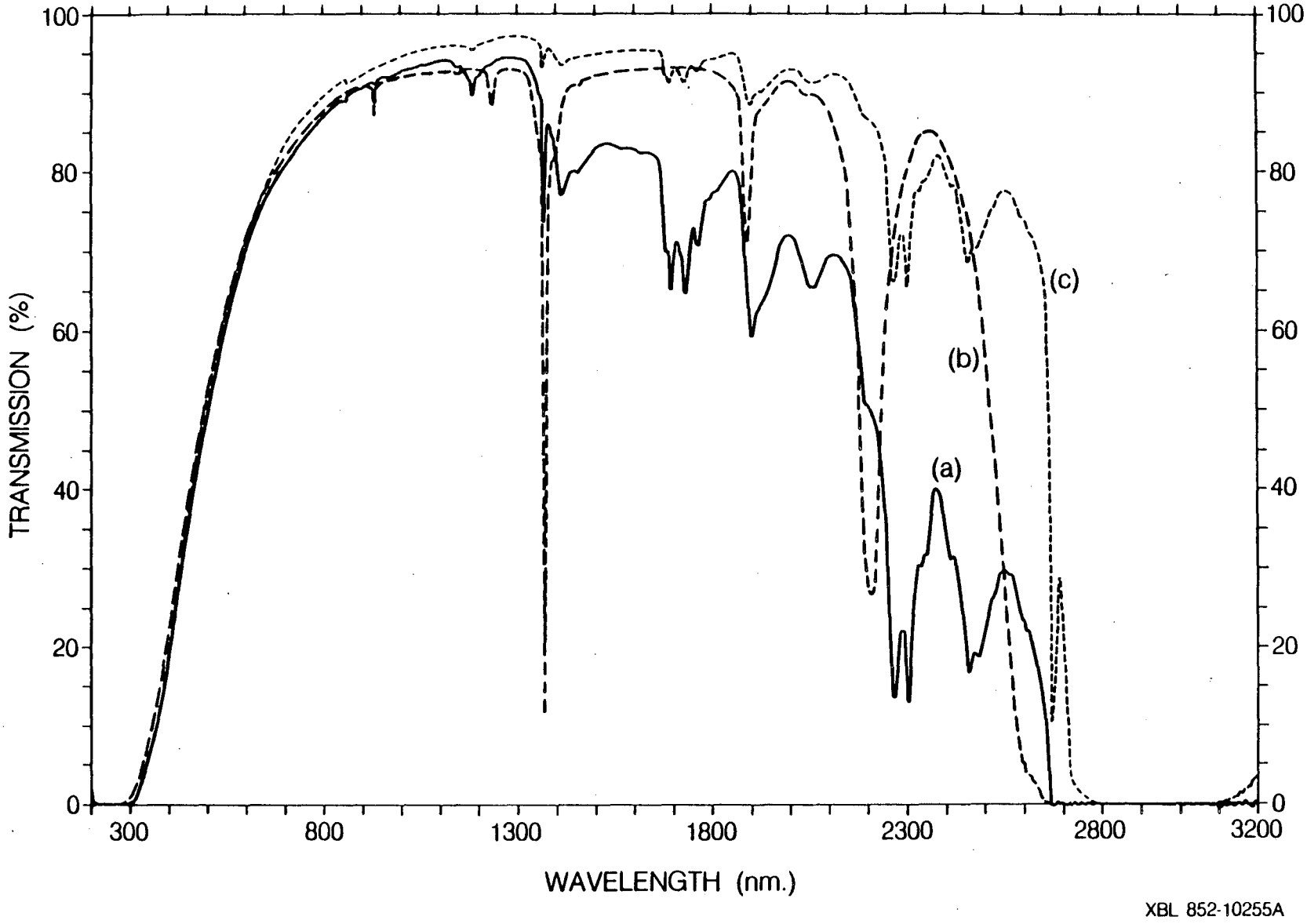

100
80
60
40
20
0
TRANSMISSION (%)
300
800
1300
1800
2300
2800
3200
WAVELENGTH (nm.)
(a)
(b)
(c)
XBL 852-10255A

Figure 4

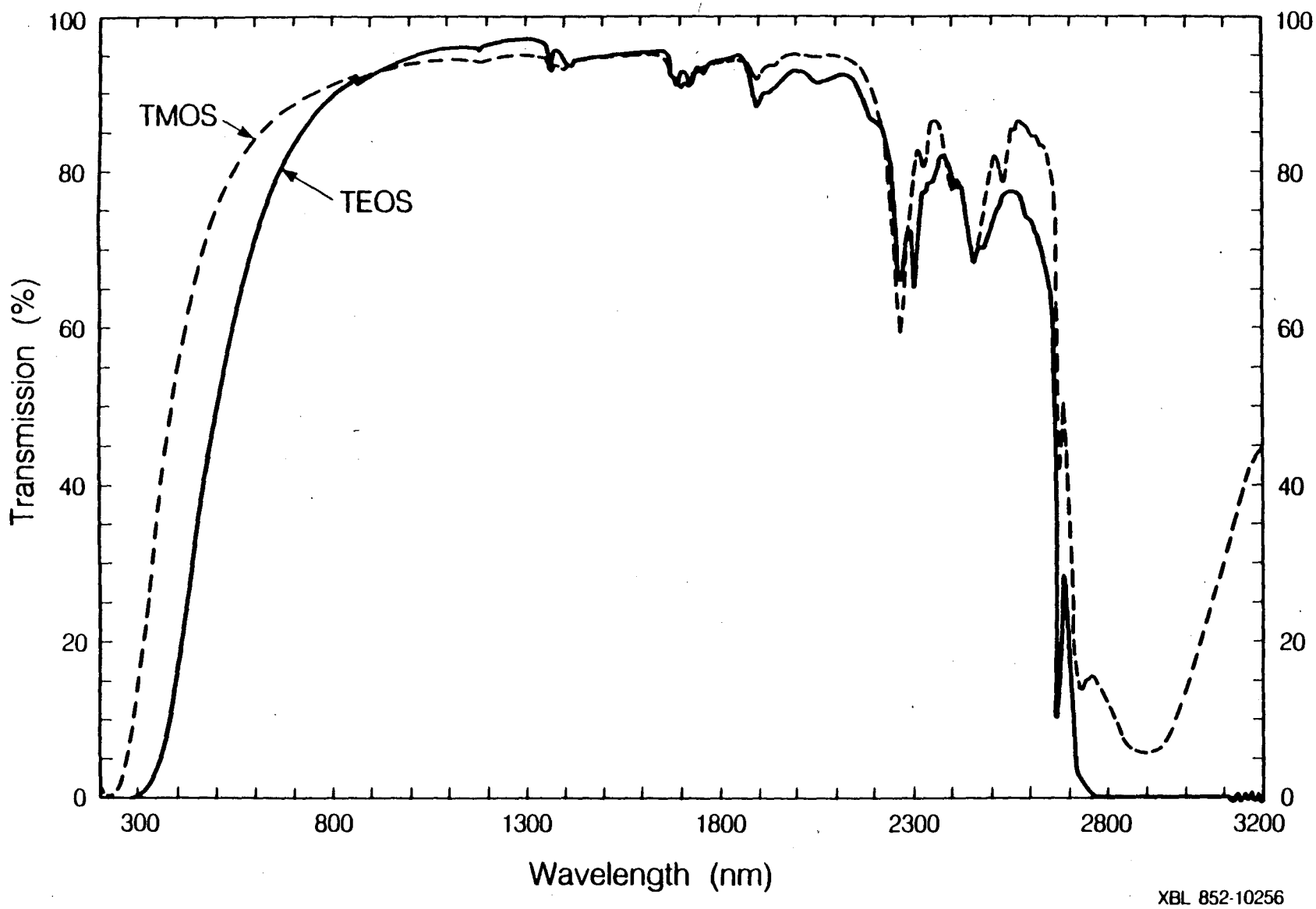

TMOS
TEOS
Transmission (%)
Wavelength (nm)
100
80
60
40
20
0
300
800
1300
1800
2300
2800
3200
XBL 852-10256

Figure 5

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