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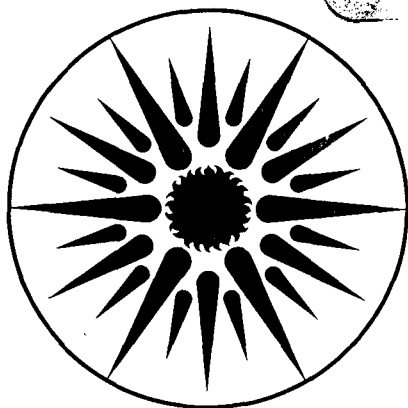# LB Lawrence Berkeley Laboratory
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Comparison of Ethyl Versus Methyl Sol-Gels for Silica Aerogels Using Polar Nephelometry*

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ABSTRACT

The transparency of silica aerogels has been improved by varying the molar ratio of starting ingredients, temperature of gelation and drying procedure. A reduction in light scattering greater than 70% has been obtained for acid catalyzed tetraethylorthosilicate (TEOS) aerogels, and 23% for base catalyzed tetramethylorthosilicate (TMOS) aerogels. The success rate for aerogels has been improved by coating the molds with a releasing agent before drying to eliminate cracking. A transparent base catalyzed TEOS aerogel has been produced using NH_4OH and NH_4F as catalysts.

INTRODUCTION

Porous optical materials, or aerogels, exhibit excellent insulating properties because of their high porosity and small pore size. Nonevacuated aerogel at ambient temperatures can provide a thermal resistance (R value) of approximately 7 for each inch of thickness, and 15 per inch with a low grade vacuum (0.1atm) [1]. Significant energy savings can result if conventional window glazings are replaced by aerogel glazings [2]. However, aerogels scatter light, albeit only weakly and nearly isotropically. This type of scattering does not produce distortion nor blur images viewed through the material (Figure 1), but the transparency of aerogel is reduced by light scattering. Polar nephelometry, or light scattering measurements provide a means of determining gel homogeneity and therefore optical quality.

In most of the earlier aerogel research, tetramethylorthosilicate (TMOS) was used as the starting alkoxide [3-6]. The alkoxide hydrolyzes to silicic acid and rapidly condenses forming silicon dioxide (SiO_2). During the condensation reaction, the molecules grow to colloidal particles. Once they reach a certain size, depending on the pH and temperature, they are bound together by siloxane links (Si-O-Si) leading to gelation [3]. A less toxic silicon alkoxide, tetraethylorthosilicate (TEOS) was investigated in this work. We produced both TMOS and TEOS gels in order to compare their characteristics, and to determine optimum starting recipes (molar ratio of initial reagents) and gelation conditions. Light scattering intensity was recorded after varying the pH, temperature, and molar ratio of the starting material, from the time of mixing the reagents and throughout the gelation process. In addition, light scattering provided a means of quantifying gel changes after super-critical drying. Alcogels are dried above the critical point in order to avoid a liquid-vapor interface during drying which would destroy the gel structure because of surface tension [7].

PROCEDURE

Aerogels examined in this work were produced with the silicon alkoxides TEOS and TMOS (Aldrich Chemical Co). Each alkoxide is first diluted 1:1 with either ethanol or methanol, respectively in order to increase its stability against self hydrolysis (3). Depending on the recipe, the proper volume of alcohol, water and catalyst is mixed, cooled to a temperature of 7°C, and added to the dilute alkoxide mixture. For TMOS recipes, NH_4OH is used as the catalyst, whereas HCl and HF are required to catalyze TEOS gels. Table 1 lists the optimum molar ratios and gelation conditions for both TEOS and TMOS gels as determined by this work.

Small (30ml) beakers were chosen as light scattering cells and represent the volume and shape of our alcogels/aerogels. Once the alcosol is poured into the beakers, one of three gelation temperatures is chosen; 20°C, 7°C or -7°C. After gelation at the lower temperatures, the alcogels are placed at room temperature for aging. Our aging procedure is simply to place the alcogels in pure alcohol and monitor light scattering versus time.

NEPHELOMETRY

The nephelometer (Figure 2) serves to quantify the amount of scattered light from gels as a function of change in preparation. Briefly, one of four wavelengths is chosen for the light scattering measurements from two available lasers. The particular line is chosen in order to obtain a situation in which only single scattering occurs (8,9); very low extinction of the primary beam through the alcogel or aerogel sample. For most aerogels, only the 6328A line of the HeNe laser satisfied this condition. The alcogels can be measured with either HeNe or HeCd laser lines. The nephelometer is calibrated before each experiment using a dilute suspension of $0.085\mu m$ polystyrene latex spheres (Duke Scientific Co., Palo Alto, CA). The incident laser beam passes through a polarizer oriented 45 degrees to the scattering plane. In this case, equal intensity is provided in both the parallel and perpendicular polarizations. A series of polarizers and filters are chosen for the detection path before a shutter and photomultiplier tube. This detector assembly is scanned through a 180 degree arc and the intensity of scattered light in the horizontal or vertical polarization is recorded. Light scattering curves are digitized by a computer, (HP 9133, Hewlett Packard, Palo Alto, CA). Figure 3 presents an example of the scattered intensity in the parallel and perpendicular polarizations from a TEOS alcogel. These shapes are characteristic of the patterns produced by Rayleigh scattering.

Although an approximately 160 degree scan is recorded for each measurement of light scattering, the intensity at 90 degrees is used to compare and plot changes in light scattering versus time. A typical graph showing the log-log plot for light scattering intensity at 90 degrees versus time, during a TEOS gelation is shown in Figure 4. The scattering increases very slowly initially, then increases sharply as the gelation point is approached and then attains a limiting value. The final plateau region is used to compare changes in light scattering as preparation conditions are varied. Although the top portion of the curve maintains a slight slope indicating continued increases in light scattering, >90% of the final value of scattering occurs for this TEOS alcogel within 24 hours of gelation. The gelation point is defined as that time in which the solution meniscus does not move when the mold is tipped (±10min). At this time the viscosity increases rapidly and solidification occurs (7).

AUTOCLAVE DRYING

Alcogels must be dried in a pressure vessel above the critical point. Surface tension generated by a liquid-vapor interface is strong enough to break the linked particles and densify the material. By drying the alcogel above the critical point, the liquid vapor interface is avoided. After supercritical drying, the surface of the aerogel is covered with alcohol groups and the material is predominantly hydrophobic (3). When the aerogel is heated to further increase transparency and cooled in the atmosphere, the surface becomes covered with hydroxyl groups

rendering the material more hydrophilic.

The autoclave system is similar to that described in reference 10. However, several modifications in the system and drying procedure warrant mention. The Hewlett Packard microcomputer was interfaced to the autoclave to control the temperature ramp. A micrometering valve (Autoclave Engineer, Erie, PA) was installed in the depressurization lines to precisely control the pressure release cycle. The supercritical conditions are chosen as 265 ° C and a pressure of 12.7 MPa for both TEOS gels in ethanol and TMOS gels in methanol. In this case, the temperature and pressure are well above the critical values so that slight fluctuations in the system will not lead to a liquid vapor interface.

A slow temperature ramp (0.2 ° C/min) is employed to reach the supercritical temperature. During heating, alcohol expansion generates the necessary pressure, and a pressure control valve keeps the pressure constant once the desired pressure is obtained. After the critical temperature is reached, the pressure is reduced over a five hour period. A dry nitrogen purge similar to that used by Schmitt is used to flush the system in order to remove all remaining traces of condensible vapors (10). The curves in Figure 5 show the temperature and pressure response for a typical run.

DISCUSSION

Initially, many of the gels cracked during aging and drying. The reason for the cracking was that the alcogels, once formed and during aging, shrink slightly. In a clean mold (glass), the alcogel adheres to the walls and cannot shrink uniformly. Therefore, stresses are developed in the gel which lead to cracking. To overcome this problem, we investigated various releasing techniques. The optimum method involved heating the molds to 260 ° C and spraying a teflon particle-based agent (Miller-Stephenson Chemical Co.) over the mold. Once sprayed and excess material is removed, the coated molds are again heated to 260 ° C for approximately two minutes. The second heating is not suggested by the manufacture but was found to provide better resistance to the alcohol based gels. Whenever possible, the alcogels are removed from the molds and dried openly in the autoclave.

Initially, we measured light scattering from gels that had the starting molar ratios for both TMOS and TEOS as listed in the literature (3,4,10). We quickly realized that the molar ratio recommended by other groups as optimum is dependent on the particular laboratory procedures. Therefore, literature recipes were used only as a starting point and subsequently varied to find an optimum using polar nephelometry.

ACID CATALYZED TEOS GELS

Schmitt's (10) recipe was used as a starting point to produce transparent TEOS aerogels. For these acid catalyzed TEOS gels, we found that the pH of the solution can be varied between 1-2 without having a substantial affect on the intensity of residual scattering (<5%). Solutions mixed outside this pH range either did not gel, or if gelled, were milky white and not suitable as aerogel material.

The volume of water was found to directly influence residual light scattering. The initial TEOS recipe (10) was changed by varying the amount of water by up to 15%. Although the overall molar ratio of all compounds was affected, changing the molar ratio by varying the ethanol or alkoxide did not affect the gel transparency as significantly as directly changing the water content. Schmitt found that a more transparent aerogel resulted as the initial alkoxide concentration was increased (10). In the present work, the initial water content was found to have a larger influence on gel transparency. Curve a in Figure 6 shows that a 15% increase in water from the literature value (STD) provides an approximate 12% increase in scattered light whereas a 15% reduction in water leads to a 10% decrease in light scattering. Each data point in Figure 6 represents the average from three separate experiments, measured when the gels exhibited approximately 95% of its final scattering intensity. As the water content was decreased further, the gels

became soft and fragile, and could not support themselves. Increasing the water produced a more rigid or brittle, highly scattering gel. These results hold for both the alcogel and aerogel material.

The temperature of gelation had a significant affect on residual light scattering for TEOS recipes (Figure 6). For all TEOS recipes, lowering the gelation temperature reduced the amount of residual light scattering. From curve b, a decrease of approximately 40% in light scattering is obtained by gelling a TEOS alcosol at 7°C compared to 21°C. A decrease of approximately 68% is obtained by gelling the alcosol at -7°C (cf. curve c). Therefore, we have been able to reduce the scattering from TEOS aerogels by reducing the water content and temperature of gelation. The overall reduction in light scattering was greater than 70%. Importantly, a particular recipe gelled at a lower temperature does not attain the light scattering level of the same recipe gelled at a higher temperature, even when the lower temperature gel is subsequently aged at a higher temperature (21°C). The optimum molar ratio and gelation conditions as listed in Table 1 for acid catalyzed TEOS gels refers to point x in Figure 6.

An inverse relationship between water content and gelation time was found. Schmitt's recipe (10) required about 1.5 hours for gelation whereas 3.25 and 0.8 hours were required to gel the lower and higher water content (15%) samples, respectively. However, we found that very small changes in the procedure will substantially effect the gelation time. For example, by diluting the silicon alkoxide with the appropriate alcohol and then mixing the same recipe, the gelation time increased by approximately 25%. Gelation time is also affected by open area of the mold; the larger the open area, the shorter the gelation time. As expected, the gelation time is increased as temperature is reduced; the alcosol placed at -7°C required on the average 28 hours to gel, and 12 hours to gel at 7°C. In both cases, the alcogels were placed at 21°C, ten hours after gelation.

BASE CATALYZED TMOS GELS

Base catalyzed TMOS recipes (3,4) provide better optical quality gels than acid catalyzed TEOS recipes. The main difference is likely due to the pH range at which the different alcosols are mixed. The best TMOS aerogels are produced at a basic pH of 8.6, compared to an acidic pH of 1.2 for TEOS gels. At low pH, small particles and pores are favored because the charge of the colloid is low and particles make contact when small in size. The gels are unstable and tend to shrink and densify. At higher pH, the charge of colloid is greater so that particles grow to a larger diameter before making contact. This case should result in stable gels with larger particles and a more homogeneous particle size distribution (7). Nitrogen adsorption (BET) measurements show that the average surface area is less for TMOS aerogels indicating larger particle sizes. The average surface area measured for TMOS is 620 m^2/g compared to an average of 880 m^2/g for acid catalyzed TEOS aerogels.

The water content in TMOS recipes also has a marked affect on residual light scattering (Figure 7). Increasing the water content 20% resulted in a 14% increase in light scattering, whereas a 20% decrease in water gave an 18% improvement (curve a). The water content could be varied more in the TMOS recipes than in the TEOS recipes, and still result in good quality aerogel material. The molar ratio accepted as optimum for a transparent TMOS aerogel in this work is listed in Table 1.

Residual light scattering in TMOS gels is not strongly influenced by temperature of gelation (Figure 7). Only a 9% decrease in light scattering occurs by gelling the alcosol at 7°C (curve b) relative to 21°C, and a 16% decrease by gelling the alcosol at -7°C (curve c). These results follow the different chemistry involved in the two gelation systems (7). Base catalyzed solutions normally tend to form a more homogeneous particle size distribution with larger particle and pore sizes before linking occurs. In addition, the rate of hydrolysis is usually faster than the rate of condensation in the base catalyzed case; in contrast to acid catalyzed gelation. Reduced temperatures seems to provide a similar mechanism for TEOS gels. When gelation is slowed by the lower temperature, the hydrolysis may become more complete providing larger particles before linking occurs in the acid catalyzed system. Finally, because the solubility of silica is proportional to

temperature (7), smaller particles should result at the lower temperatures, which partially explains a reduction in light scattering intensity for all gels.

BASE CATALYZED TEOS AEROGELS

We investigated the possibility of producing transparent base catalyzed TEOS aerogels. Importantly, the optimum molar ratio for TMOS gels can not be used to produce a TEOS gel. In addition, a transparent base catalyzed TEOS gel could not be obtained by simply adjusting the pH with NH_4OH; the base catalyst used for TMOS gels. We found that a TEOS gel could be produced by adjusting the pH to 8 with NH_4OH and then adding micro-molar concentrations of NH_4F. The TEOS alcogels and aerogels produced using this procedure are comparable to the acid catalyzed TEOS gels, but not as good as the base catalyzed TMOS gels. An intensive program using a factorial design approach is underway to determine the optimum molar ratios of all starting materials for a base catalyzed TEOS aerogel.

AGING

All TEOS alcogels continue to show increases in light scattering with time (cf. figure 4). In contrast, all TMOS alcogels maintain the same light scattering level from the first day of gelation. A possible explanation for this behavior is that the TEOS acid catalyzed network contains a larger particle size distribution in which case Ostwald ripening strongly influences residual light scattering. In contrast, if the TMOS base catalyzed gels comprise a more homogeneous particle size network, Ostwald ripening would be less. Ostwald ripening is the dissolution of smaller particles and subsequent deposition of silica on larger ones (7). Again, BET measurements indicate larger particle sizes in TMOS gels, and larger particles are less soluble (7). In addition, several of the TEOS gels exhibited light scattering behavior characteristic of Rayleigh scattering with large scale density inhomogeneities (11,12). This behavior was not observed in the base catalyzed TMOS aerogels.

Aging or increase in light scattering is negligible for aerogels; no changes in measured light scattering occurred even after several months from drying. However, an aerogel that has been heated to 500°C initially shows a decrease in light scattering but then increases beyond its initial value with time. Aerogels heated to 500°C are more hygroscopic and absorb water from the atmosphere, which may account for the increase in light scattering.

SHRINKAGE

TEOS gels shrink considerably compared to very minimal shrinkage of TMOS gels. Initially, shrinkage would lead to cracking in the gel structure both before and after drying. However, this problem was eliminated when treated molds were employed. TEOS alcogels were found to decrease by 10 - 12% in volume during the gelation and aging processes. In contrast, shrinkage in TMOS alcogels cannot be measured. In most cases, TMOS gels do not shrink enough to be released from the molds and cannot be dried openly in the autoclave. These results are consistent with Iler in that low pH-catalyzed gels tend to form smaller particles and pores, which shrink and densify. The higher pH-catalyzed gels are more stable (7).

TEOS gels also exhibit substantial shrinkage during the supercritical drying procedure. The decrease in volume during drying is approximately 25%, which means greater than one-third reduction in volume from gelation to final product. This one third reduction in volume occurs for the TEOS aerogels using the optimum recipe in Table 1. For recipes with a higher molar ratio of water, the shrinkage was greater. Again, in contrast, TMOS gels shrink negligibly during drying and sometimes are difficult to remove from the mold. In the worst case, shrinkage in TMOS was less than 4% by volume between the final aerogel material and the initial alcosol volume.

CONCLUSION

An improvement in aerogel transparency was obtained by reducing the water content and gelation temperature. Our work demonstrated that acid catalyzed TEOS aerogels exhibit inferior optical quality and shrink considerably compared to the base catalyzed TMOS aerogels. Even though we have been able to reduce the light scattering in acid catalyzed TEOS aerogels by more than 70% and in base catalyzed TMOS aerogels by 23%, our best TEOS aerogel exhibits 9 times more light scattering than our TMOS aerogels. It is probable from these results that the acid catalyzed TEOS gels exhibit a heterogeneous particle and pore size distribution compared to a more homogeneous distribution for the base catalyzed TMOS gels. The difference in transparency cannot be due to particle or pore size alone, because the BET measurements show TMOS gels to contain the larger particles.

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FIGURE CAPTIONS

(Figure 1)
Photograph of one-centimeter thick TMOS aerogel.

(Figure 2)
Block diagram of polar nephelometer used to monitor light scattering intensity from gels. M, mirrors; PMT, photomultiplier tube; O, scattering angle from 0 to 160 degrees.

(Figure 3)
Polarization dependent light scattering intensity versus angle. Numbers in parenthesis represent full scale sensitivity. l, perpendicular; ll, parallel polarization.

(Figure 4)
Light scattering intensity versus time during a TEOS gelation. See text for discussion.

(Figure 5)
Pressure and temperature cycle for super-critical drying.

(Figure 6)
Light scattering intensity of TEOS alcogels versus temperature and percent change in water volume from initial (STD) recipe (9).

(Figure 7)
Light scattering intensity of TMOS alcogels versus temperature and percent change in water volume from initial (STD) recipe (2).
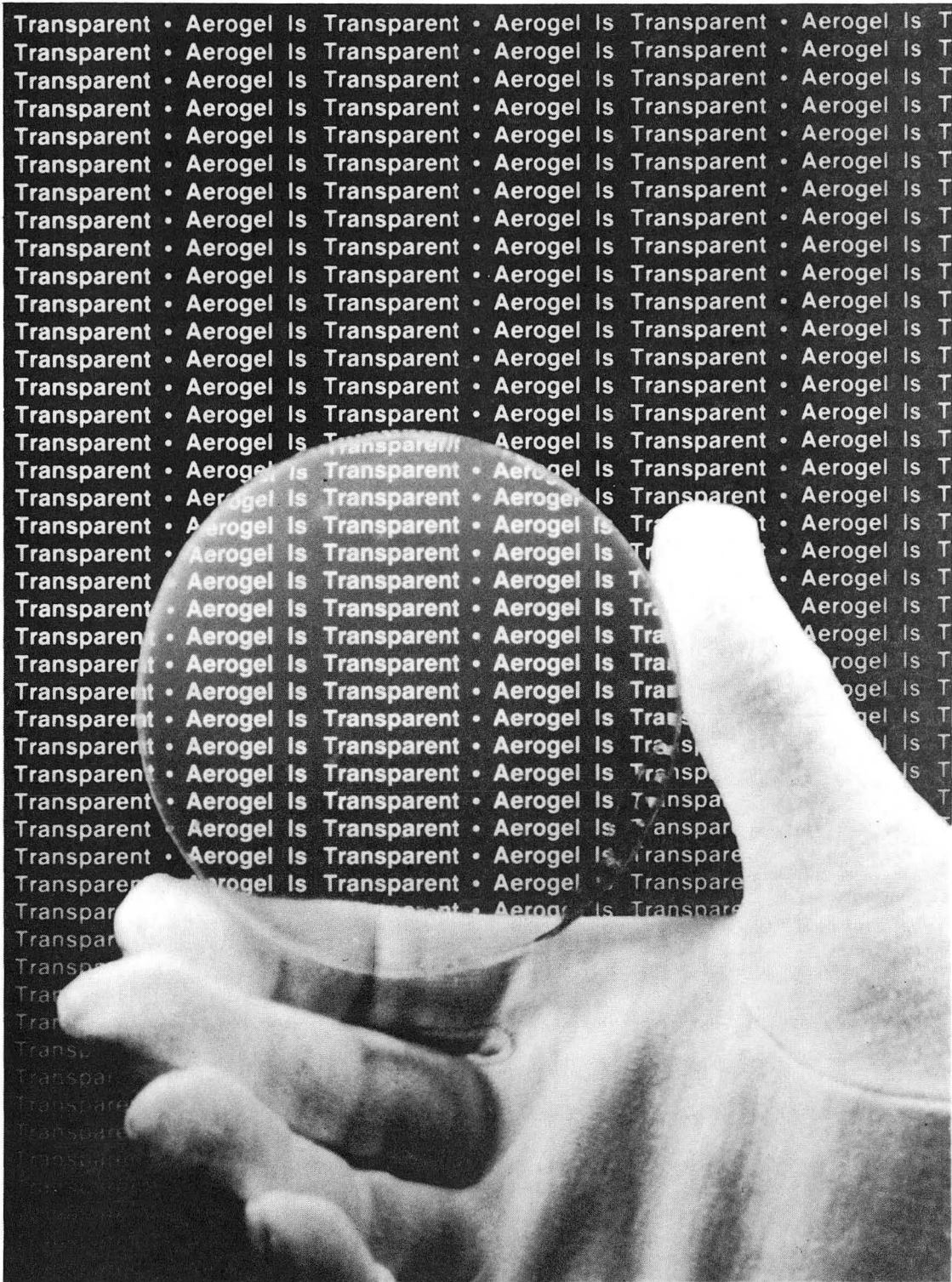
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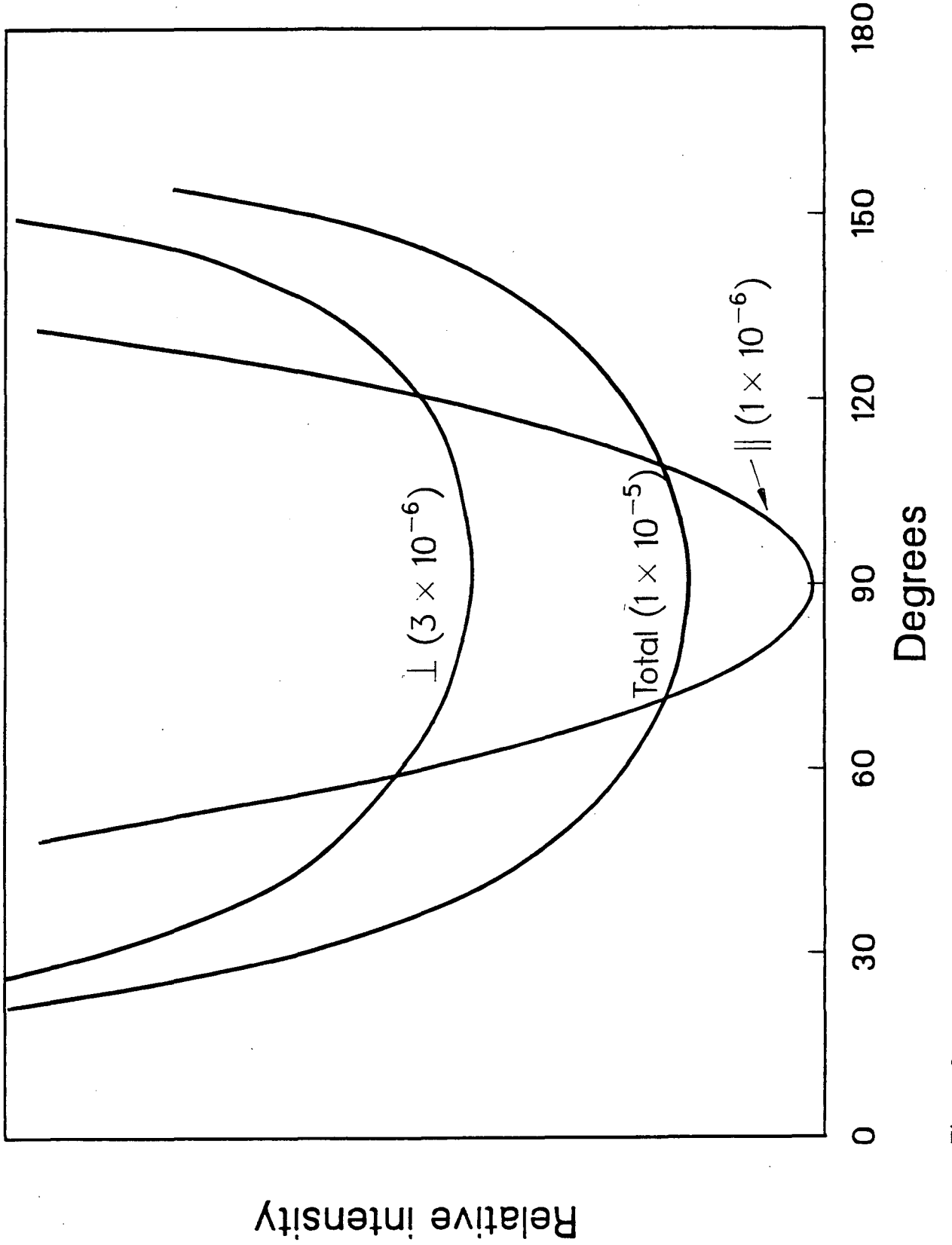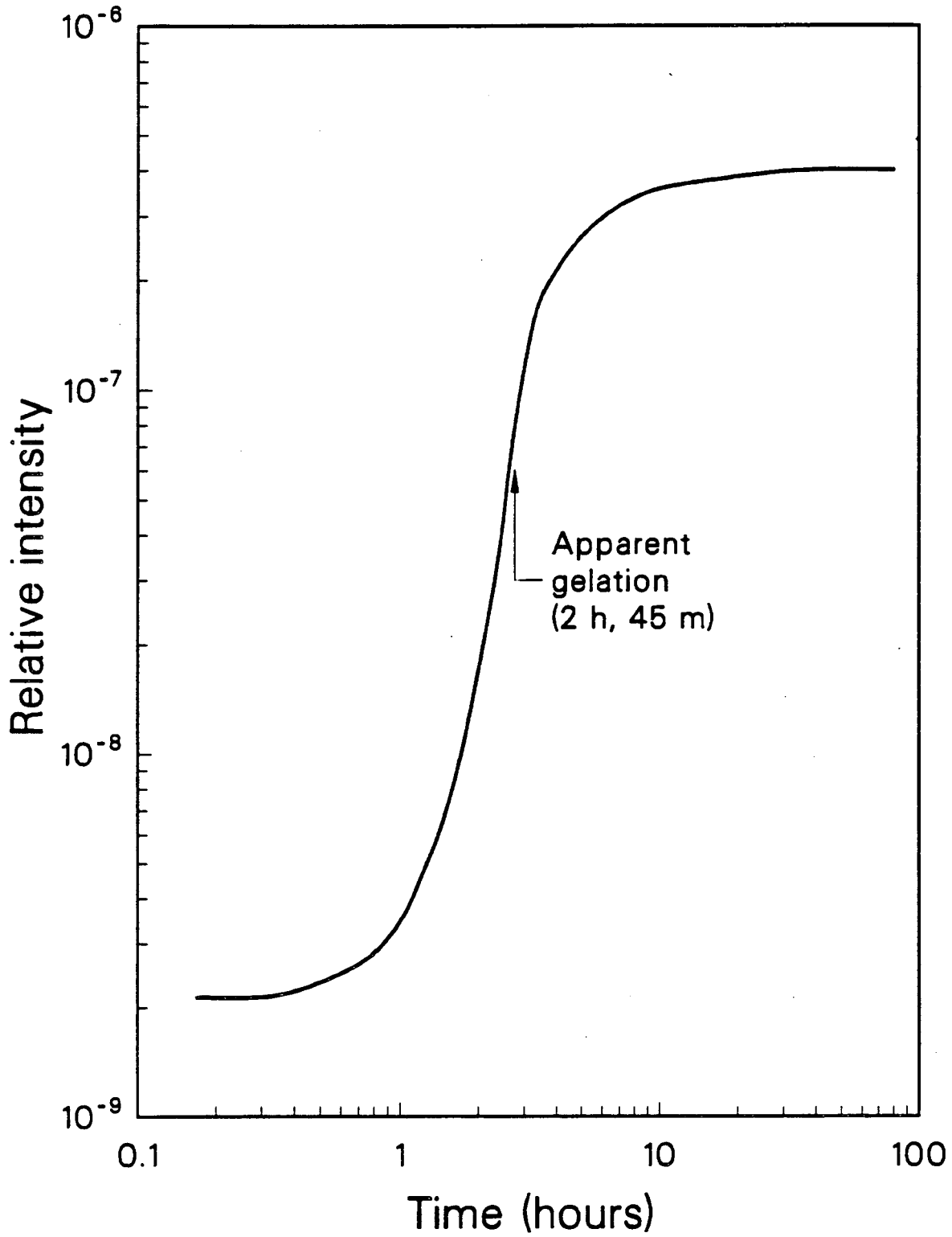
Figure 2

XBL 854-9522

⊥ (3×10^{-6})

Total (1×10^{-5})

∥ (1×10^{-6})

Relative intensity

Degrees
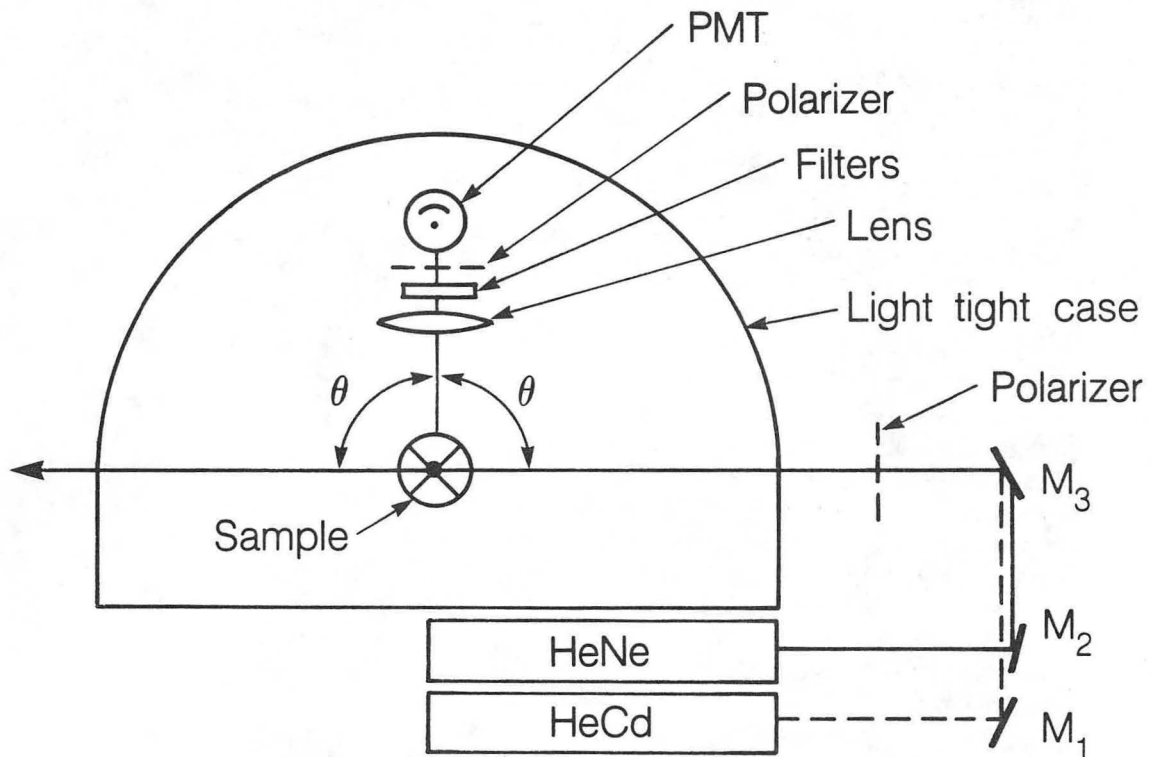
XCG 854-204

Figure 3

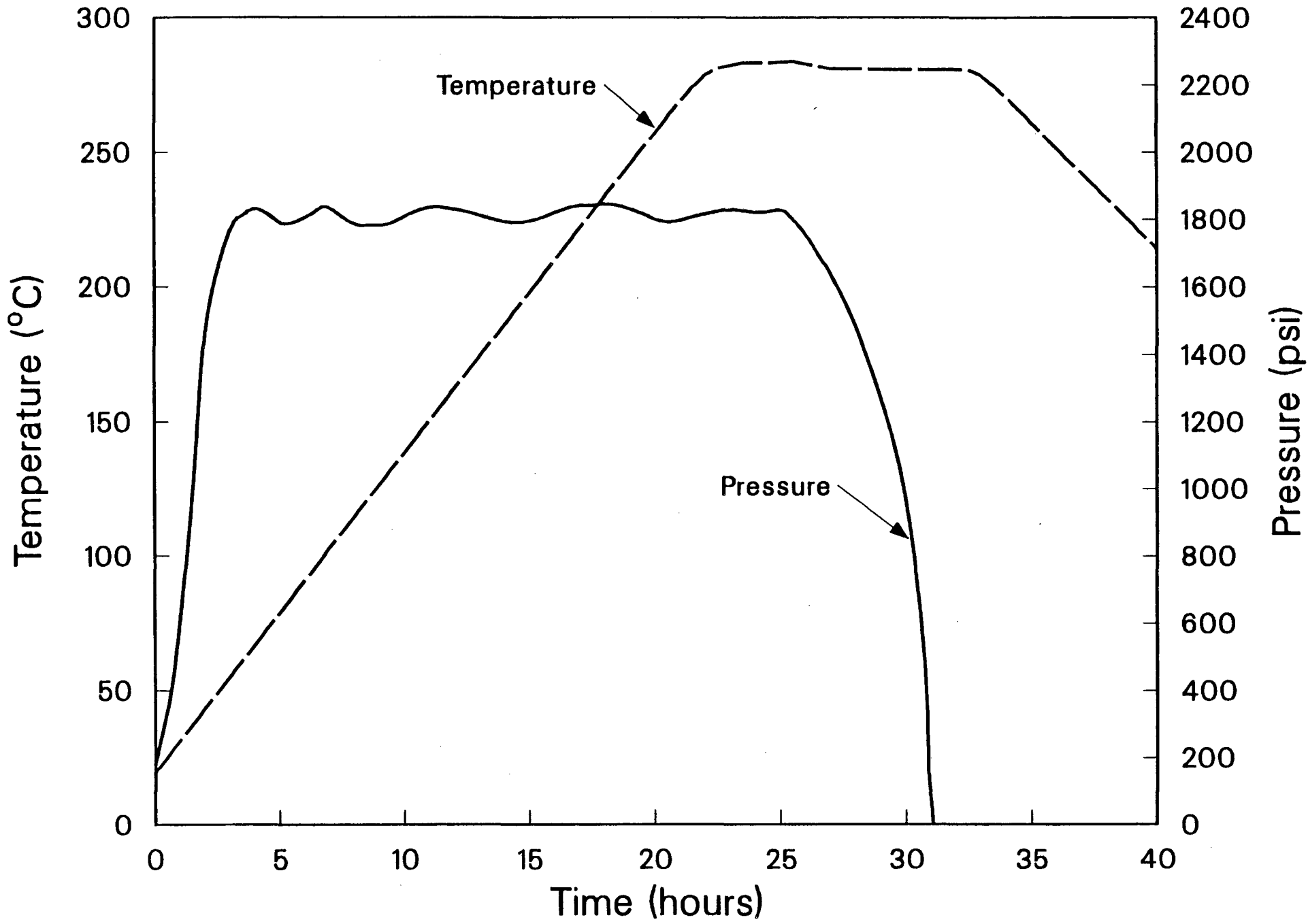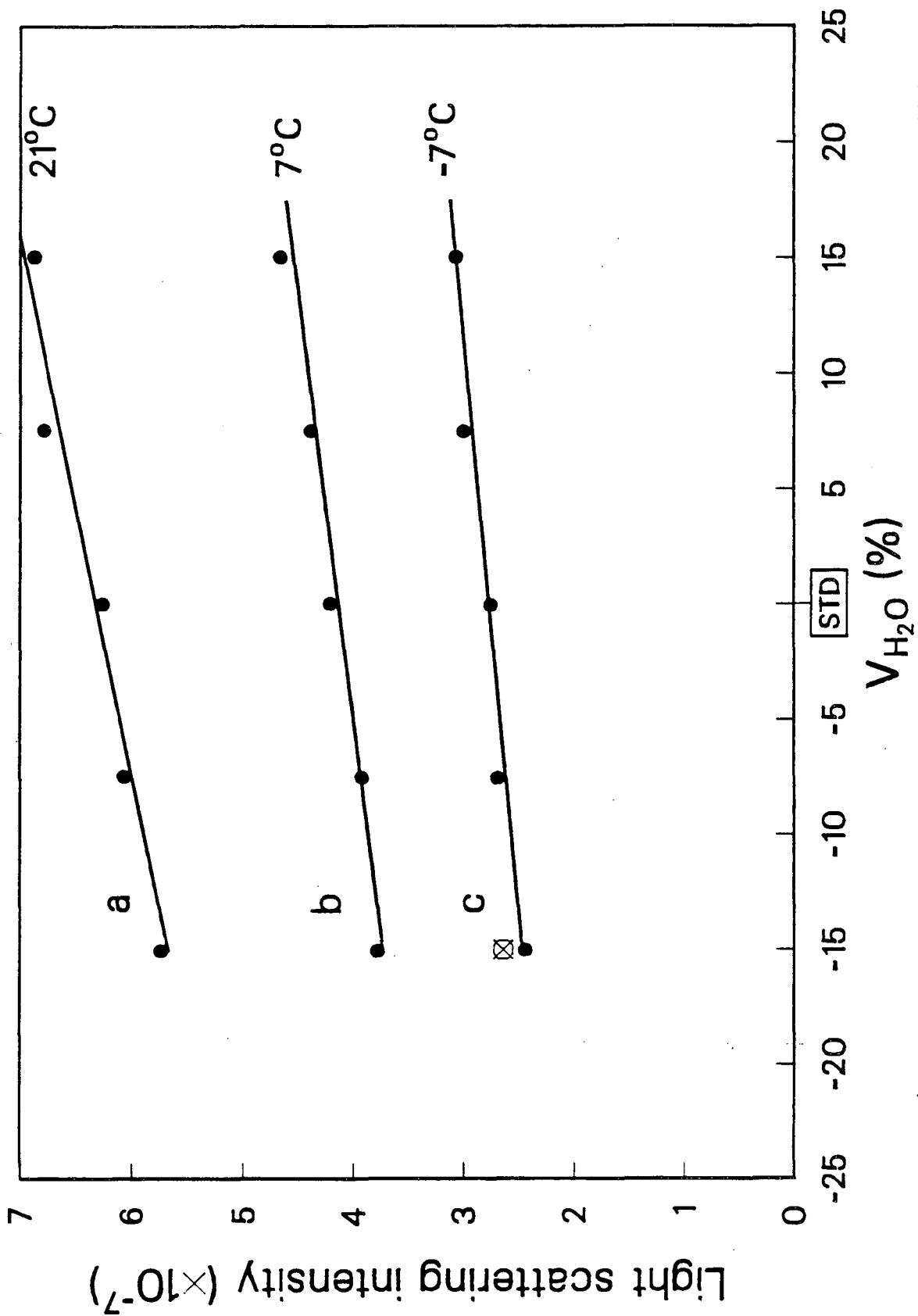Figure 4   XCG 854-205

Figure 5

XCG 854-203

Figure 6

XCG 864-206
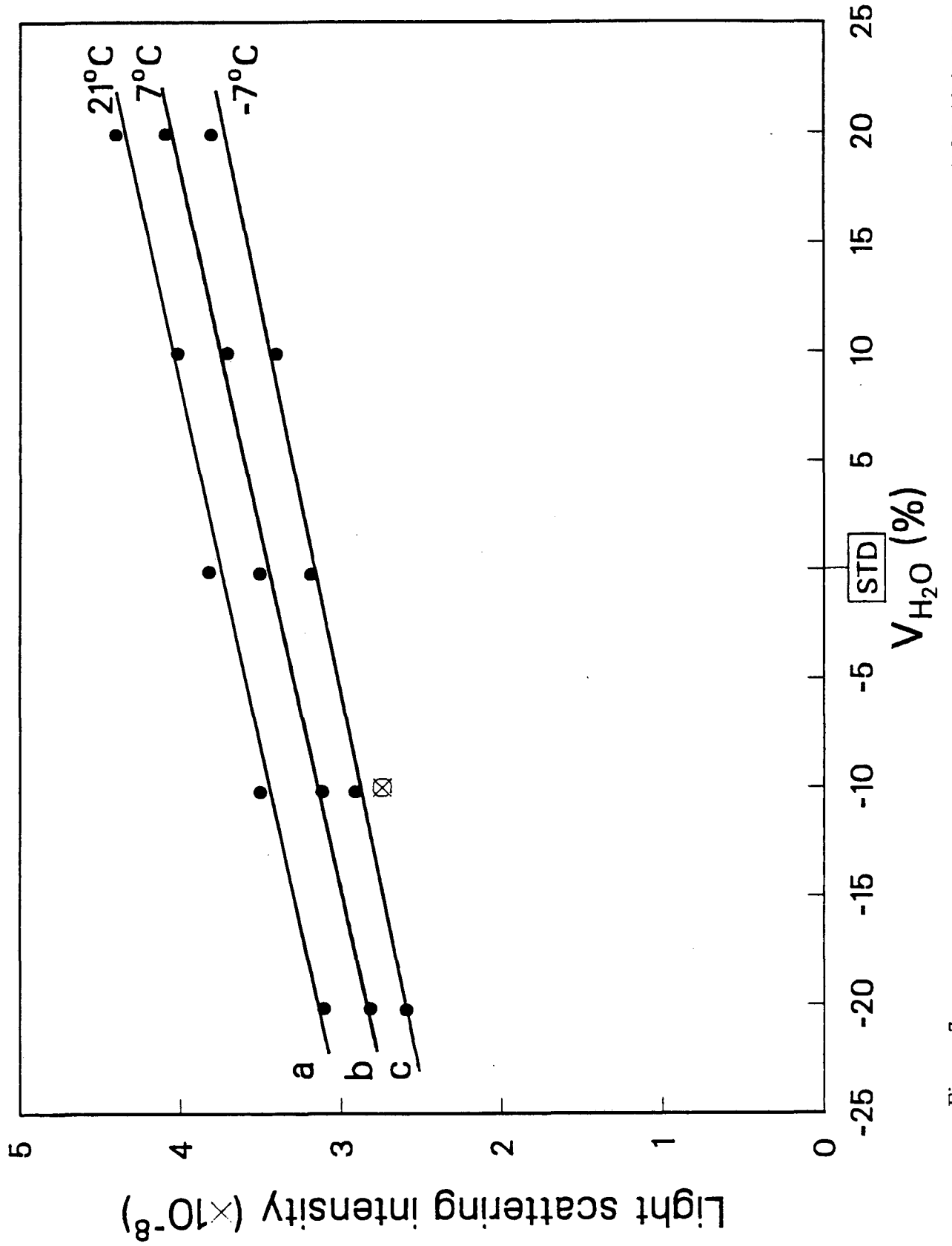
Figure 7

XCG 854-207

Table 1

Molar ratio, gelation conditions and characteristics for transparent aerogels

Alkoxide/Alcohol	X_{Alk}	X_{H_2O}	X_{Alc}	X_{Cat}	$T(^oC)$	t(hrs)	ρ (g/cm^3)	Sc (m^2/g)
TEOS/EtoH	.0857	.4366	.4677	.0018 HCL .0083 HF	-7	28	0.14	880
TMOS/MeOH	.0774	.2538	.6686	.00013 NH$_4$OH	21	¯ 1	0.11	620

X ≡ molar ratio   T ≡ gelation temperature
Alk ≡ silicon Alkolide   t ≡ gelation temperature
Alc ≡ Alcohol S_c ≡ surface area
Cat ≡ Catalyst
ρ ≡ density

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