AD-A192 301 DEVELOPMENT OF A HIGH EFFICIENCY Q-SWITCHED GLASS LASER VIA SOL-GEL PROCESSING(U) GELTECH INC ALACHUA FL W V MORESHEAD 14 FEB 88 AFOSR-TR-88-0096 1/1

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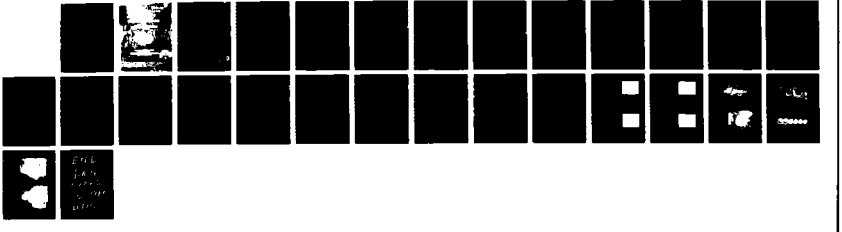

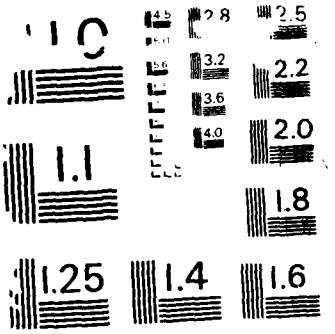

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AD-A192 301

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The sol-gel process is a logical choice for silica-based laser glasses, since it requires lower processing temperatures than traditional melt glass techniques, and allows good control of purity. This report describes attempts to prepare silica glasses containing neodymium or neodymium and erbium using sol-gel technology. A description of two different doping procedures is given, along with results. The materials produced were characterized and the spectral, thermal, and physical properties are reported. Fluorescence spectra and fluorescence lifetimes are given for three different materials prepared.

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The contractor, GELTECH, Inc., hereby certifies that to the best of its knowledge and belief, the technical data delivered herewith under Contract no. F49620-87-C-0087 is complete, accurate, and complies with all requirements of the contract.

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Introduction

Currently, neodymium doped glass matrix lasers show perhaps the greatest promise for high powered pulsed-laser applications. Recent developments in sol-gel glass technology have permitted the fabrication of high purity silica glasses at much lower temperatures than traditional melt glass techniques. The following report describes an attempt to apply this technology to the production of neodymium glasses in order to determine the possibility of producing a Nd:glass laser material with a high purity silica matrix. If successful this material would be expected to have properties superior to currently used glass laser materials.

Background

Current technology at GELTECH, Inc. makes it possible to prepare silica glass by the sol-gel process. In this process a silicon-containing precursor, such as tetramethyl or tetraethylorthosilicate, is hydrolyzed to form a sol. After complete homogenization, this sol is cast into molds where it sets into a very porous, wet gel having the shape of the mold. The gel is then dried to give a transparent, silica monolith (see picture 1). The resulting dry gel can be further heat-treated to strengthen it and at the same time reduce its porosity. Although this process removes most of the water, heating to temperatures necessary to fully densify the silica gel normally results in bloating of the sample due to residual water being trapped in the porous structure. If a dehydration step is carried out before the final densification, the bloating problem is avoided and fully dense glass can be obtained.[1] For a summary of the overall process see figure 1.

The sol-gel process lends itself to the incorporation of other elements into the glass in at least two different ways (see figure 1):

1. Doping by Impregnation: Impregnation of the stabilized but still porous pure silica.

2. Doping by Mixing: Addition of soluble salts of the elements desired to the other starting materials in the gel preparation.

This report describes work done using both of these methods. The initial work has been done using discs, since discs would bring fewer variables into the process at the beginning. Work was done meanwhile to begin to optimize the process for the production of rods (see picture 2.)

Doping by Impregnation

In order to control the doping of porous silica monoliths it was first necessary to quantify changes the gels undergo during the stabilization treatment. Figure 2 shows the changes in pore volume and surface area of the pure silica gels as a function of processing temperature. Measurements were made using a nitrogen adsorption/desorption technique on an Autosorb 6 (Quantachrome Corp.). Accompanying the change in porosity is a decrease in diameter, as shown in figure 3. Knowing the pore volume of the gel makes it possible to calculate the solution concentration of the salt necessary to give the desired percentage of metal oxide in the gel after further processing.

After doping a gel the same dehydration procedure used for pure silica was attempted in order to fully densify the glass. This was the expected route as described in the original proposal. However, the dehydration procedure currently used caused the gels to become white and opaque, as shown in picture 3. Even after modifying schedules and sources of dehydrating agent the same result was obtained. X-ray analysis of the white, opaque sample indicated that it was still amorphous, so as yet the exact cause of the white color and opaqueness are not known (see figure 4). Further attempts to avoid this problem by modifying experimental conditions yielded similar results.

Doping by Mixing

Because of problems encountered with the dehydration procedure used after doping gels by impregnation, and in order to explore alternatives, the

doping by mixing approach was also taken. This technique has permitted the preparation of neodymium doped silica monoliths up to stabilization without any problem. When the dehydration treatment is performed on these gels in the same way as with pure silica and Nd gels doped by impregnation, the same white, opaque material results. However, the presence of the neodymium salt from the beginning appears to influence the initial gel structure, and this has led to some promising results in an alternative approach.

At least two differences appear when the neodymium salt is added to the pure silica process:

First, the gels containing neodymium have repeatedly demonstrated an ability to withstand heat treatment much better than pure silica gels. Pure silica gels undergo serious surface cracking and sometimes breakage under conditions where the neodymium gels have repeatedly survived completely intact. At the present time it appears that the surface crack problem may be related to the pore structure of the gel. The presence of neodymium ions may be altering this structure. However, mapping of the actual pore structure of the gel is impossible by typical methods, such as microscopy or mercury porosimetry, because the pores are too small.[2,3]

A second difference, and even more important, is the fact that the neodymium gels have been able to withstand much higher temperatures than pure silica before beginning to foam (or bloat). This is important because it may make it possible to remove enough water in the process to be able to densify the glass without the dehydration treatment which has already shown to cause serious problems, as described above. Picture 4 shows Nd doped gels prepared at different processing temperatures.

Figure 5 shows the change in gel texture with respect to processing temperature for the neodymium gels. Figure 6 shows the accompanying trend in shrinkage. When porosity becomes very low the nitrogen adsorption technique is less reliable, so after treatment at temperatures above 900 to 1000°C other characterization techniques such as bulk density are necessary to understand the changes taking place in the gels. In figure 7 the bulk densities of the gels are reported as a function of the processing temperature. The densities were

measured using mercury displacement pycnometry. One problem which exists is the lack of knowledge of the theoretical density of the gels containing neodymium. However, one would expect to see a levelling off in the density curve, and a final density above 2.2 g/cc, the theoretical density of vitreous silica. For processing temperatures at or above 1075ºC the density is already greater than 2.2 g/cc. The decline in density at even higher temperatures can be explained by the sample beginning to bloat.

Optical properties of pure silica and neodymium gels are shown in figures 8a to 8d. Spectra were run on a Perkin Elmer Lambda 9 uv/vis/nir spectrophotometer. Figure 8a shows the spectrum of pure silica after drying, before any further dehydration / densification treatment. The absorption bands in the near infrared region are due primarily to the presence of OH, either bonded to silica or in water molecules adsorbed on the silica surface. Table 1 lists the prominent bands and their assignments. The removal of these bands after dehydration and subsequent densification is obvious from the spectrum in 8b.

Figures 8c & 8d show the spectra of neodymium gels before and after processing. The effect of the neodymium includes peaks in the visible region, as expected (300-800 nm). The initial loss in the uv cutoff in the low temperature neodymium gel is regained after processing.

Wavelength (nm)	Assignment
945	Si--OH Harmonic
1380	Si--OH Harmonic
1400	Si--OH Harmonic
1896	H--OH
2220	Si--OH Stretching/Bending
2730	Si--OH Free OH and OH--H

Table 1: Peak Assignments for Pure Silica, nir Spectra[4,5]

Thermogravimetric Analysis (TGA) was performed on a neodymium gel to study the changes taking place in the gels upon heating (see figure 9). An initial loss of water around 100ºC appears to be followed by a gradual loss in weight

as organic materials left from processing are burned out and the nitrate salt of neodymium decomposes to the oxide. The literature indicates that the decomposition of the nitrate salt is complete at 830ºC,[6] which agrees with the leveling off of the TGA curve above 800ºC. FTIR spectroscopy shows a change due to processing, which is presumably the loss of the nitrate. (see figures 10a & 10b).

In order to find out if and when crystallization may be taking place in the gels, a sample was analyzed by Differential Thermal Analysis (DTA). In this technique the temperature of the sample is recorded relative to a standard material, over the temperature range under consideration. Endothermic or exothermic processes taking place in the material will be represented as a valley or peak in the curve. Figure 11 shows a DTA curve for a neodymium gel doped by mixing and heated to moderate temperatures prior to being run. The initial endotherm corresponds to a loss of adsorbed water. The last exotherm is very likely the result of crystallization taking place in the gel. Since the sample is run as a powder crystallization is much more likely to occur than if it were a monolith. When heating a monolith, therefore, crystallization may be avoided by traversing very rapidly the temperature region indicated by the DTA curve to be the likely crystallization range.[7]

Gels having three different concentrations of neodymium have been prepared, and are shown in picture 5. The primary part of the work done to date has been with gels having five percent neodymium, although initial evidence indicates that gels having a lower neodymium content respond in a similar way during processing. Gels codoped with neodymium and erbium have also been prepared (see picture 6.) Upon heat treatment they appear to respond similarly to gels having Nd only.

The homogeneity of the neodymium gels has been measured using SEM EDXA. Preliminary data suggests that the center of the gel contains less neodymium than the edges, by a factor of three. This means that the neodymium is not actually being chemically incorporated into the network under the conditions of gel preparation. However, improvement of the homogeneity should be possible by altering the drying procedure.

The most critical initial evaluation of these materials to determine their suitability for laser materials is the decay time of their fluorescence emission. The decay times of various samples were measured for GELTECH by Litton Laser Systems in Apopka, Florida. A dye laser was used to focus light of 585 nm wavelength into the bulk of the samples, and the resulting fluorescence spectra were measured by focusing the output onto a fast photomultiplier. The fluorescence lifetimes were also measured at the peak intensity of the fluorescence spectrum for each sample using an oscilloscope to monitor the photomultiplier output. The results of these tests are shown in figure 12 a-d.[8] Fluorescence decay times are summarized in table 2. A Nd:phosphate rod was used as a reference.

Composition	Source	Fluorescence Lifetime (μsec)
9% Nd, Nd:Phosphate	Kigre, Inc.	170
5% Nd, Nd:SiO_2	GELTECH, Inc.	7
5% Nd, Nd:SiO_2 (with alternate treatment)	GELTECH, Inc.	7
4% Nd/1%Er, Nd/Er:SiO2	GELTECH, Inc.	8

Table 2: Fluorescence Lifetimes of GELTECH samples

Both porous and densified samples were given for testing to see what difference, if any, the porosity would have on the fluorescence behavior. The fluorescence decay times of the porous materials were similar to those of the fully dense, but the fluorescence spectra were difficult to measure due to a "bleaching effect" which caused the fluorescence signal to decay to the level of the detector noise after about five minutes of continuously pumping the sample with radiation.

It appears from the data that the GELTECH samples, as prepared, would not be satisfactory for a laser material due to the very short decay times. A second group of samples prepared by doping by impregnation but without further densification was submitted to Litton Laser Systems for analysis, and the results of those tests were very similar to the first group.[9]

These short decay times are consistent with results of Namikawa, et. al., who prepared neodymium doped pure silica by a chemical vapor deposition process. In this process neodymium and silicon chlorides are reacted in the vapor phase in the presence of oxygen gas, using a plasma torch, to produce the neodymium doped silica.[10] The decay times they measured were of two types, one very short but more intense, and another longer but of very low intensity. Neither was considered suitable for laser action. They concluded that the low solubility of neodymium oxide in a pure silica matrix caused the neodymium ions to cluster together and cause concentration quenching to occur.[11] This low solubility of Nd_2O_3 is cited as a reason why fused silica had not been made to lase with Nd^{+3}.[12] Stone and Burrus[13] report the successful incorporation of neodymium into fused silica fibers which lased at 1.08 μm, but the concentration of Nd was less than one weight percent.

Although sol-gel processing requires substantially lower temperatures for densification compared to temperatures required to melt glass, the work done during phase 1 seems to indicate that the neodymium ions still have a tendency to cluster in the silica matrix, and that unless another component is added to the matrix which will prevent the clustering of Nd^{+3} ions, laser action will be impossible. Because of these problems, evidently inherent in the Nd_2O_3/SiO_2 system, it appears that in order to prepare neodymium doped silica with Nd concentrations high enough to make it suitable for use in most laser applications, at least one other component must be added which will prevent the neodymium from clustering and give longer decay times, while causing minimal deviation from the desirable thermal and optical properties of pure silica.

Using the chemical vapor deposition process as described above the same group has been able to use aluminum or phosphorus as codopants to successfully produce materials with substantially higher decay times, but without drastically changing the macroscopic properties of the silica glass.[14] Another group successfully prepared silica-based optical fibers doped with neodymium and phosphorus with similar results.[15] Because of these results, some very preliminary investigations have been initiated at GELTECH to test the feasibility of adding aluminum or phosphorus to the silica matrix using the sol-gel process.

Summary

The objectives of the original proposal were primarily concerned with controlling concentrations of one or more dopants and then determining the effects of sensitizers such as cerium and erbium. During the course of the work it soon became evident that the densification process used for pure silica could not be adapted directly to gels doped with neodymium. This report, therefore, contains primarily a description of more basic process development work that was necessary in working toward the same goal of producing a more efficient laser glass by the sol-gel process. As a result of this six-month research program the following objectives were achieved:

1. Preparation of Nd doped sol-gel monoliths.
2. Preparation of gels of three different neodymium concentrations.
3. Preparation of gels codoped with neodymium and erbium.
4. Definition of a process to prepare Nd doped glass with a density close to the theoretical density of Nd silica glass, and higher than the density of pure silica.
5. Collection of a set of characteristics of Nd doped glass, such as texture and optical properties.
6. Fluorescence testing of the gels to determine the feasibility of using the sol-gel process to prepare Nd and Nd/Er doped materials for laser applications.

The unusually short fluorescence decay times measured for samples prepared by the sol-gel process correspond to results given in the literature for Nd doped silica glasses prepared by another process. Producing Nd doped silica laser materials with fluorescence lifetimes comparable to those in use today appears to be virtually impossible, due to an apparent clustering of neodymium ions caused by low solubility of neodymium oxide in silica. The addition of a third component is necessary to improve that solubility. This approach has been shown to result in materials with fluorescence characteristics more appropriate for laser action.

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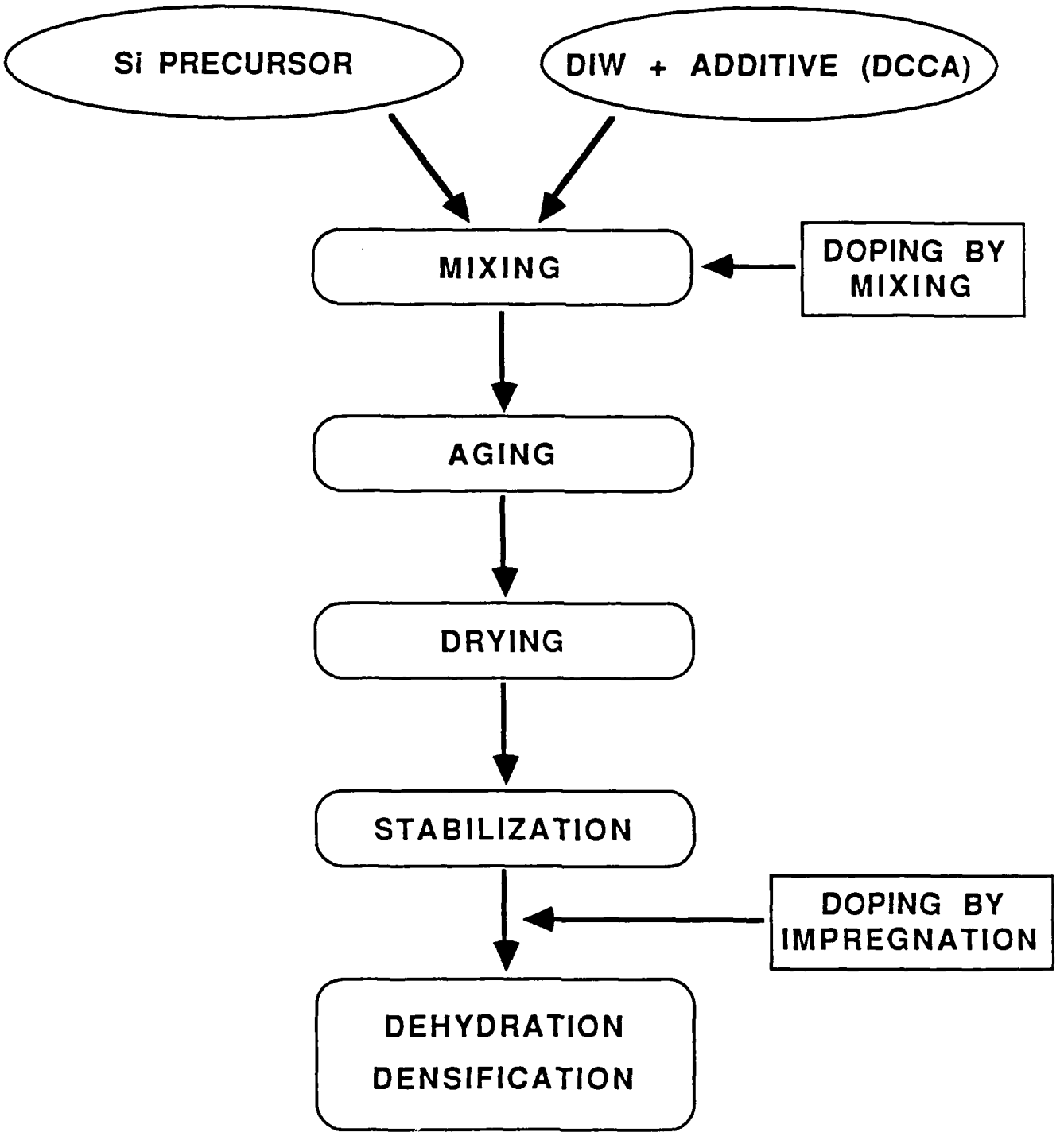


Figure 1: The Different Steps of the Sol-Gel Processing and the Two Doping Options

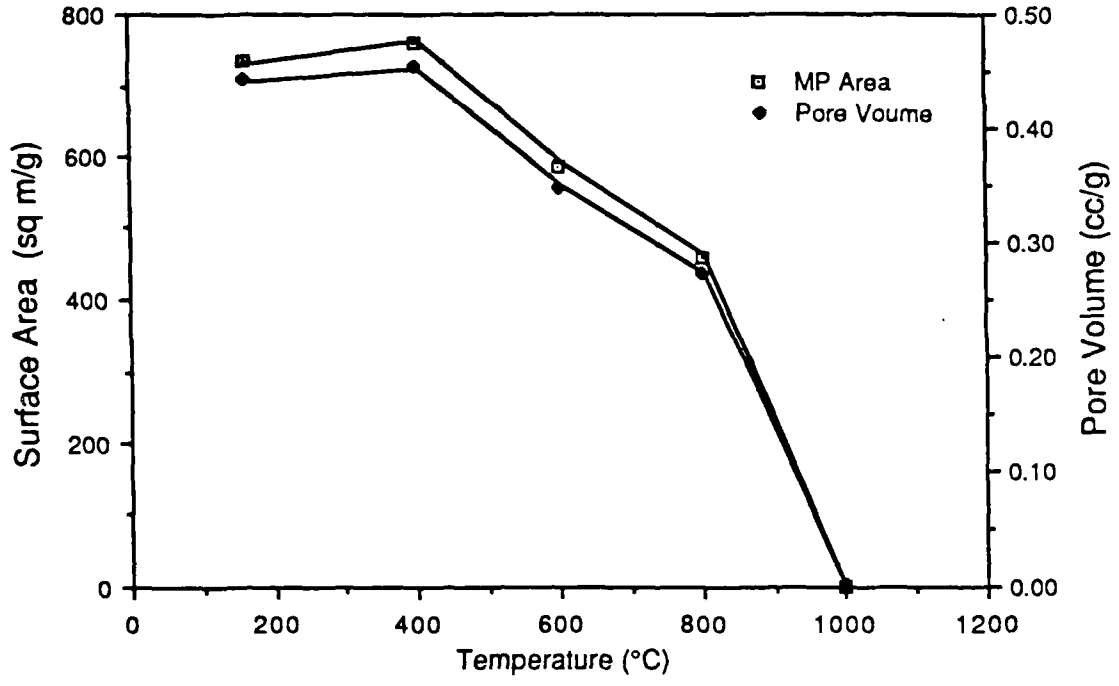


Figure 2: Pore Volume and Specific Surface Area vs. Processing Temperature for Pure Silica Gels.

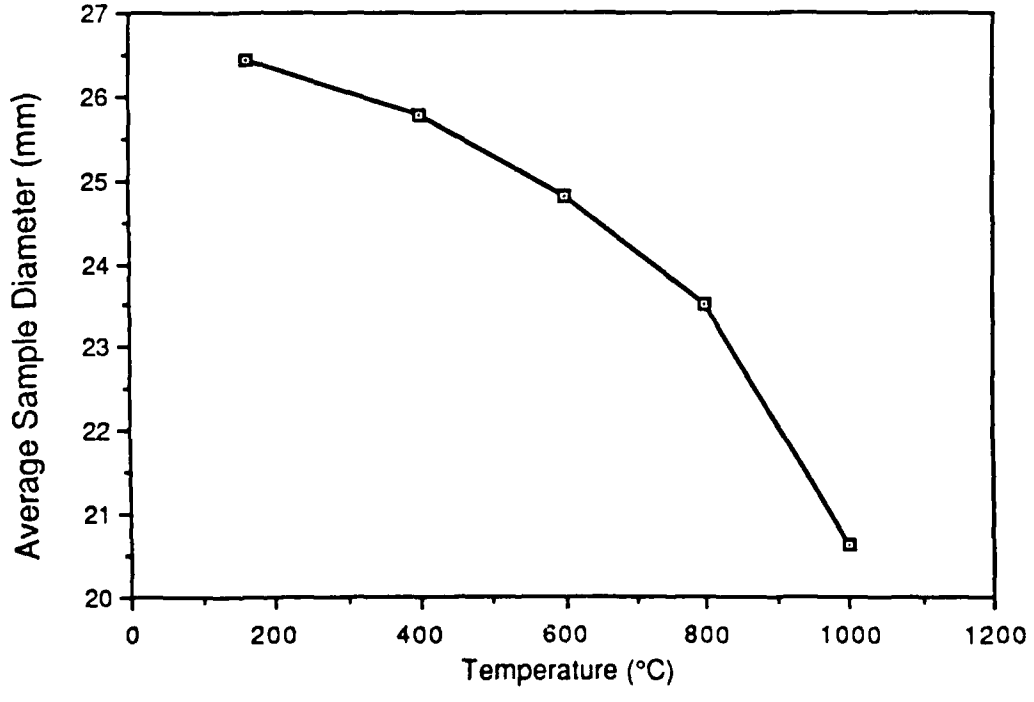


Figure 3: Shrinkage During Processing - Sample Diameter vs. Processing Temperature for Pure Silica Gels.

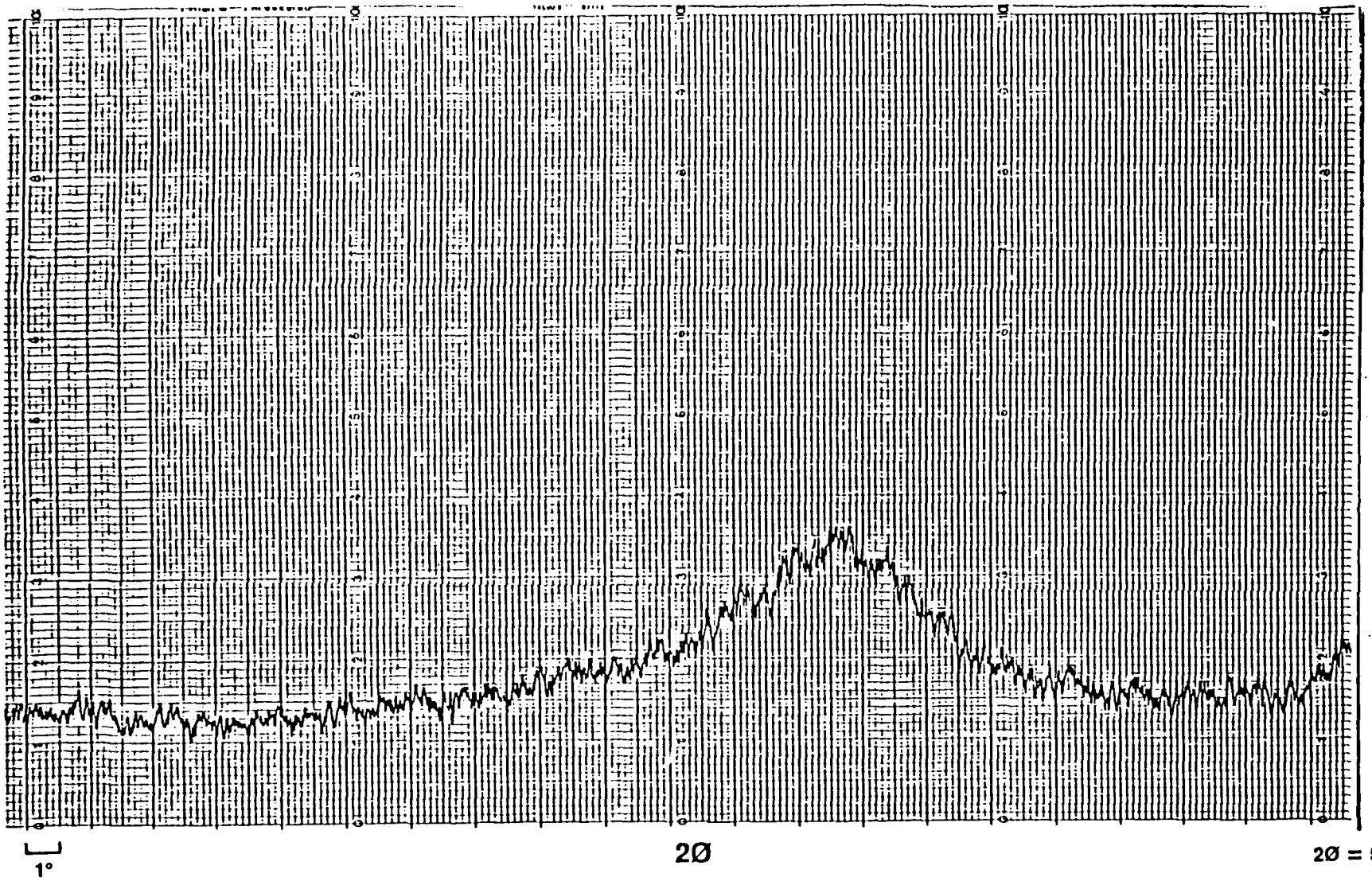


Figure 4: Results of X-Ray Diffraction of White, Opaque Neodymium Gel After Dehydration / Densification

Cu Radiation, 40KV, 20ma
500 cps 3º/min

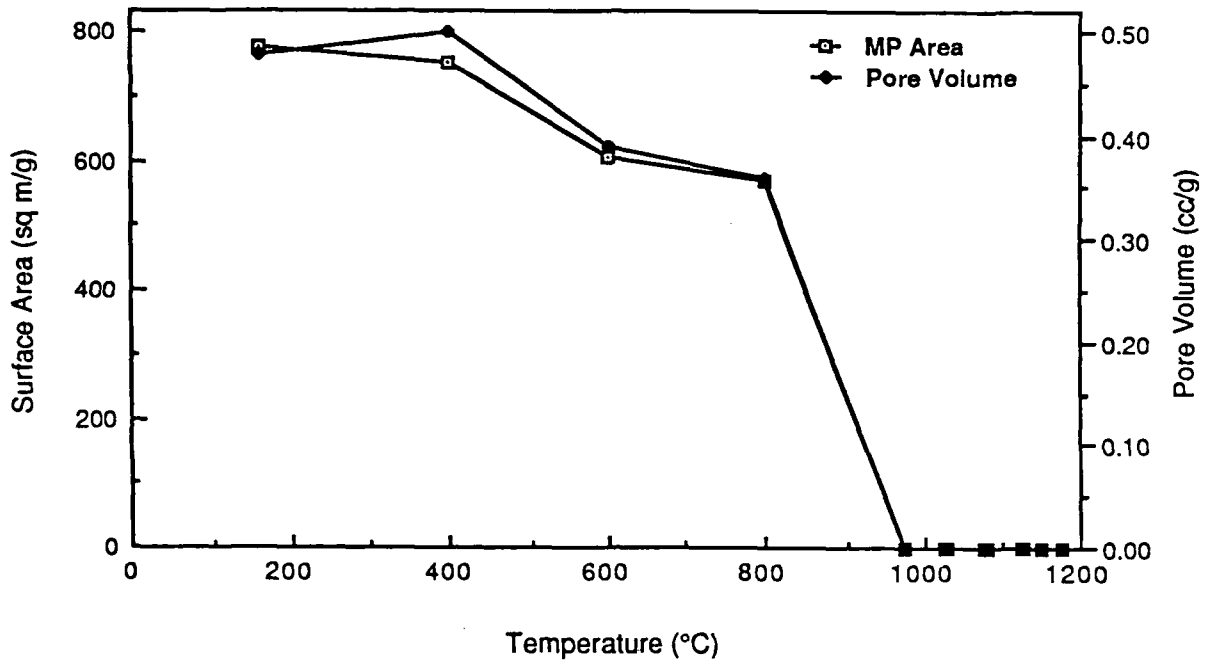


Figure 5: Pore Volume and Specific Surface Area vs. Processing Temperature for Nd Doped Silica Gels.

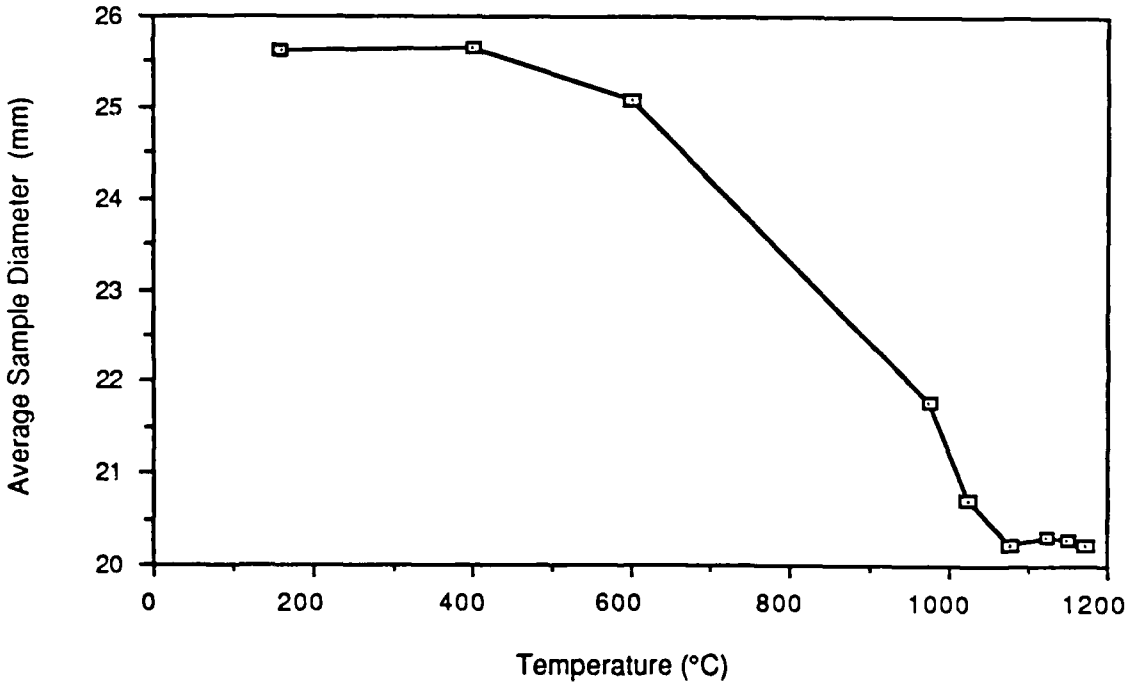


Figure 6: Shrinkage During Processing - Sample Diameter vs. Processing Temperature for Nd Doped Silica Gels.

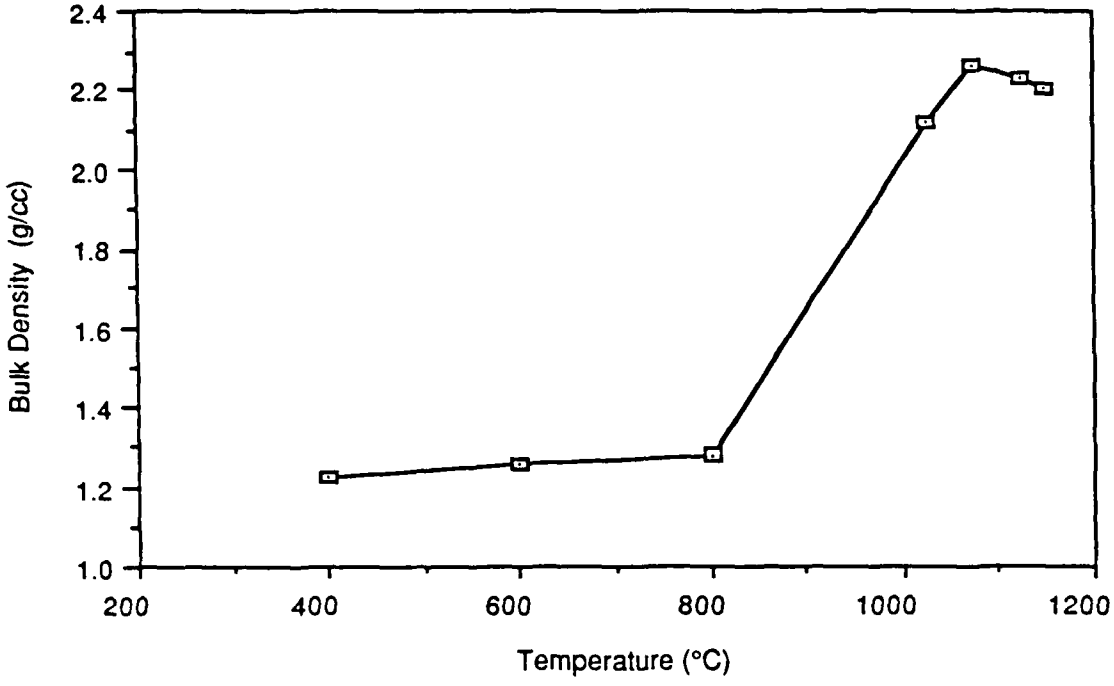


Figure 7: Bulk Density vs. Processing Temperature for Nd Doped Silica Gels

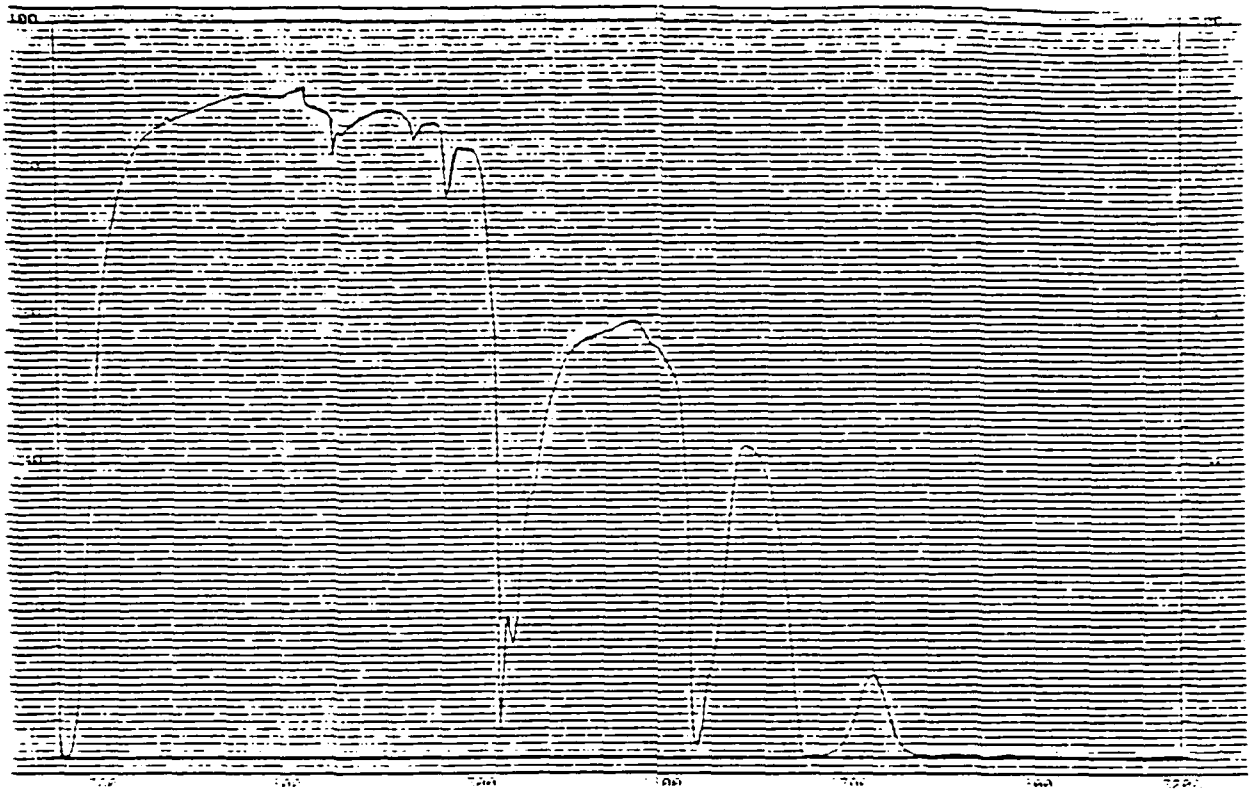


Figure 8a: uv/vis/nir Spectrum of Pure Silica Gel After Drying

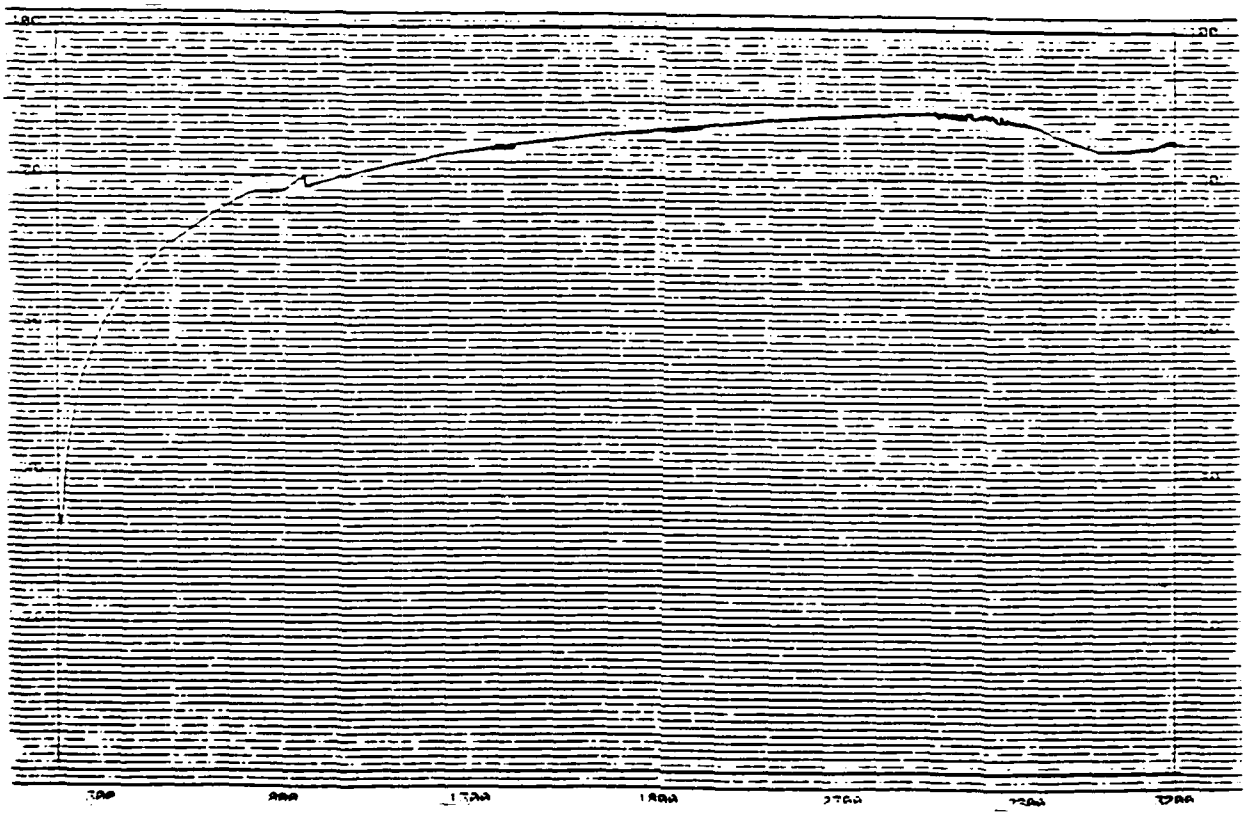


Figure 8b: uv/vis/nir Spectrum of Pure Silica Gel After Dehydration / Densification

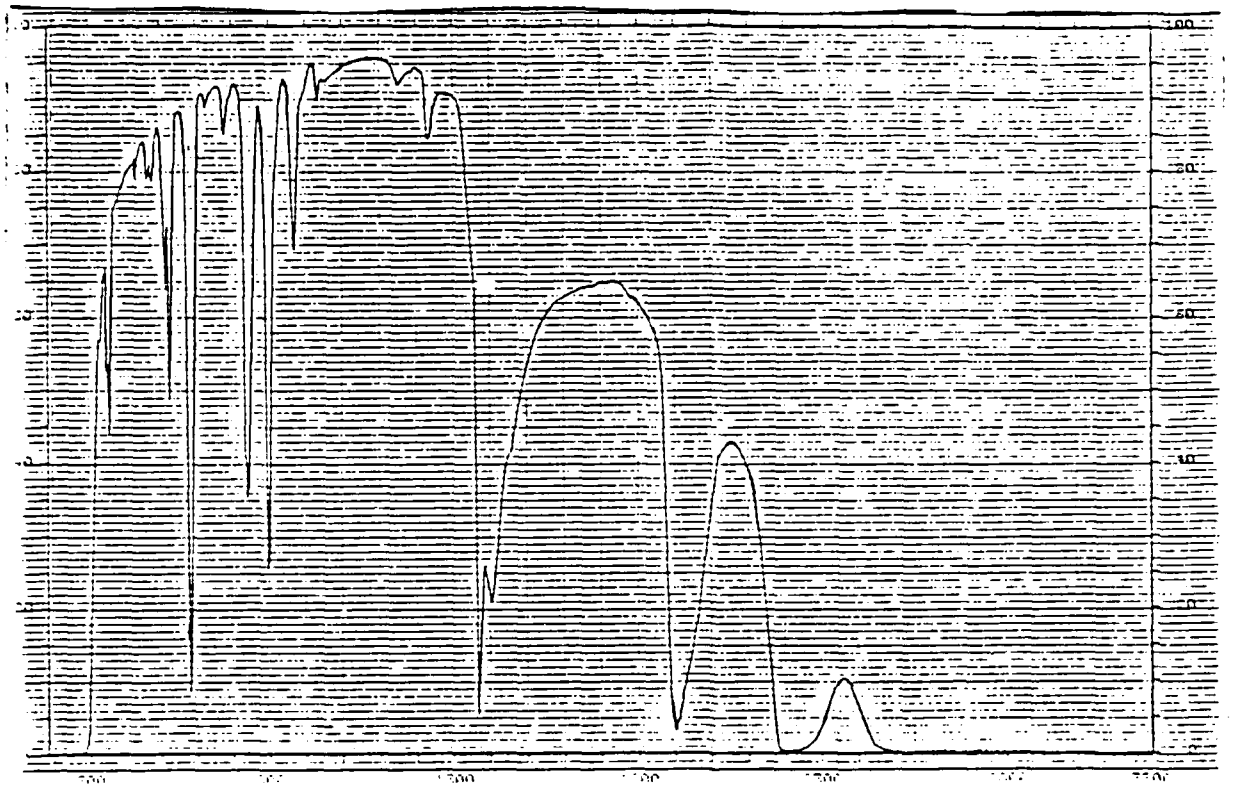


Figure 8c: uv/vis/nir Spectrum of Neodymium Gel After Drying

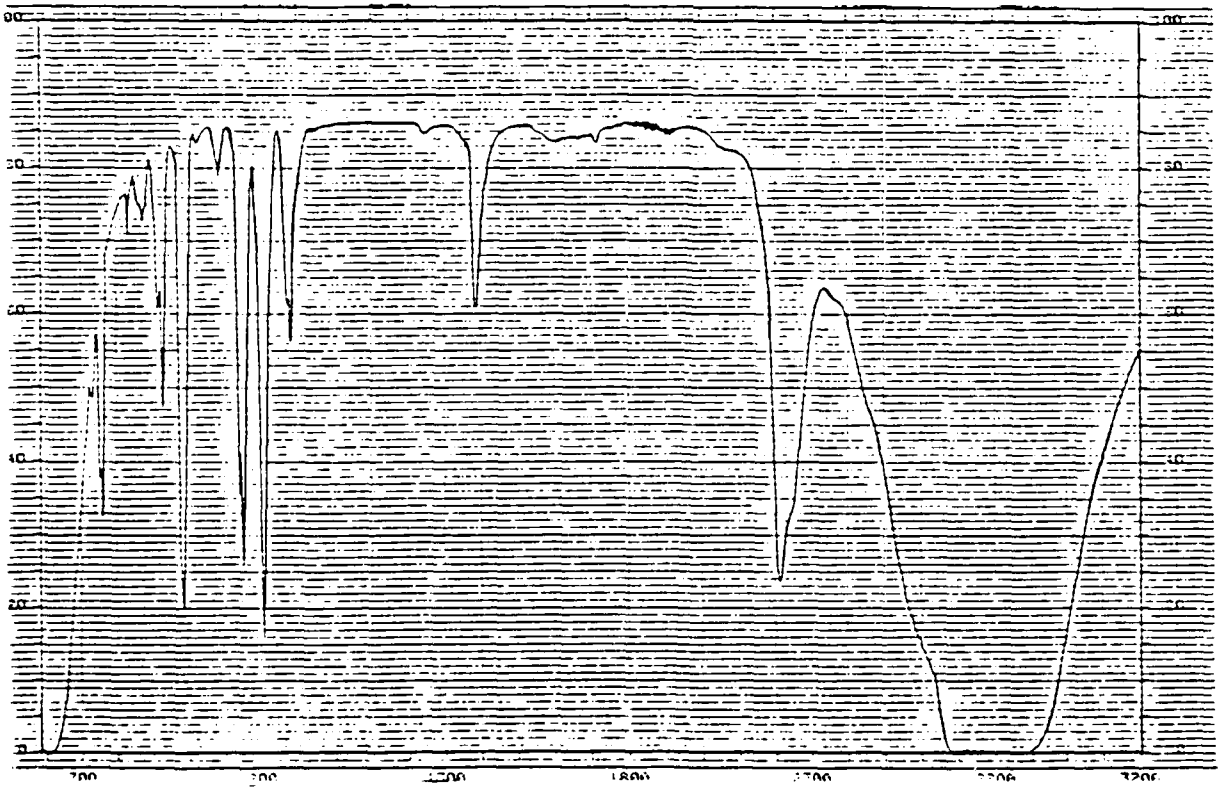


Figure 8d: uv/vis/nir Spectrum of Neodymium Gel After Processing

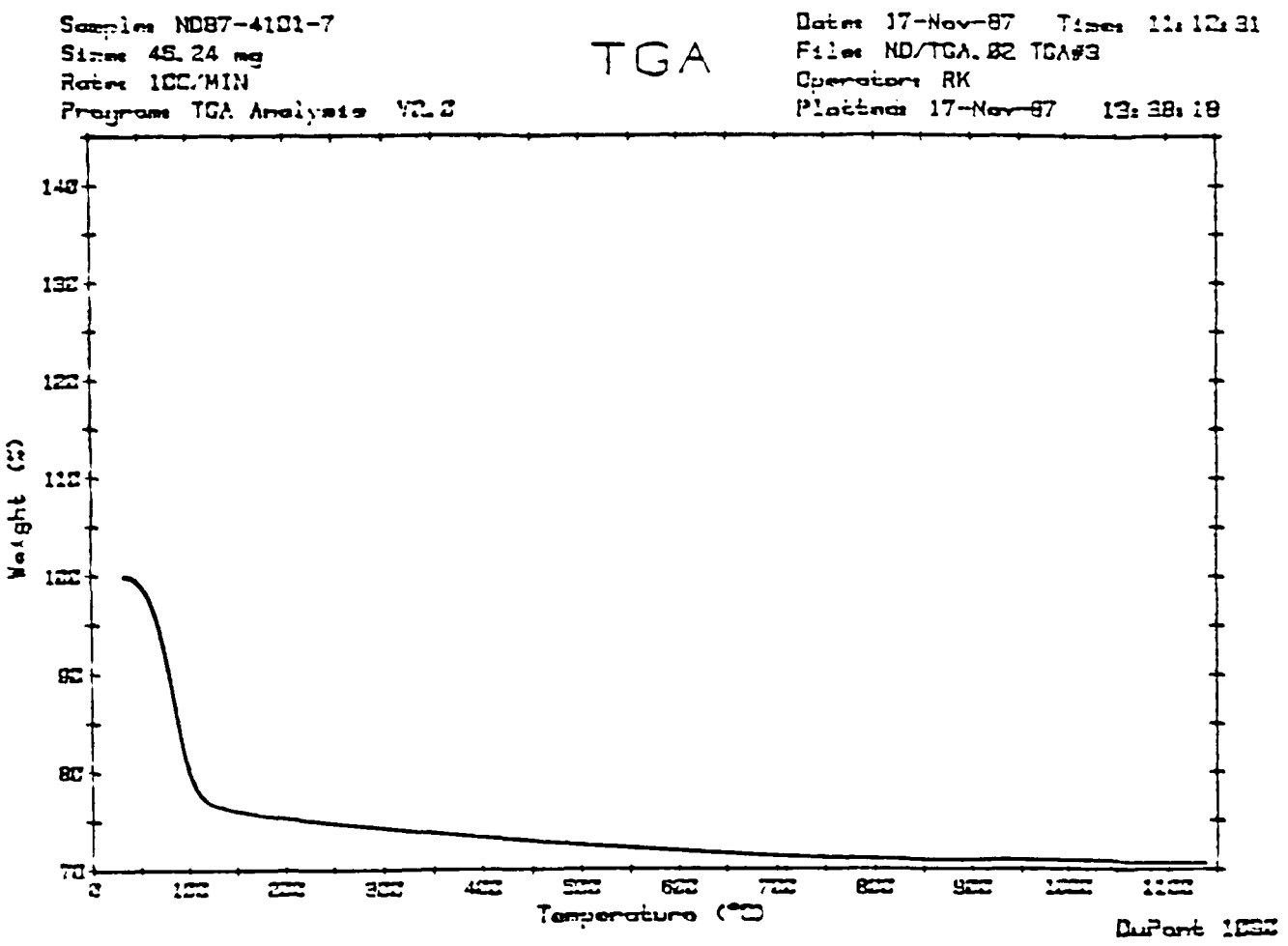


Figure 9: Thermogravimetry of Neodymium Gel

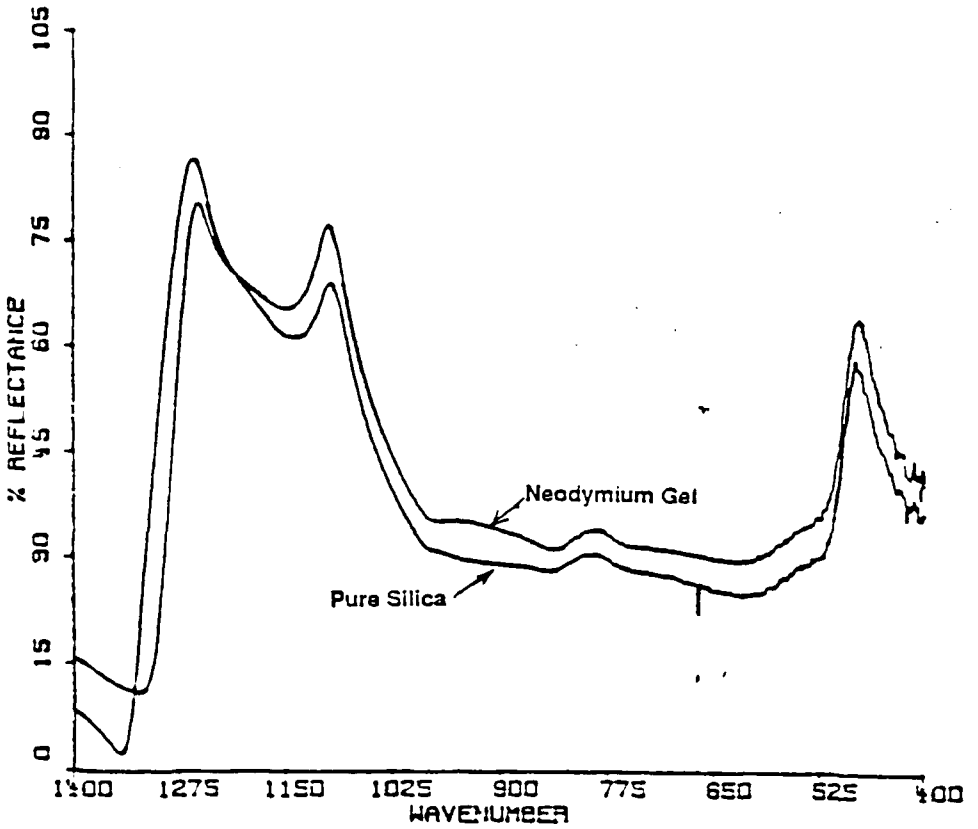


Figure 10a: FTIR Spectrum of Pure Silica and Neodymium Gels After Drying

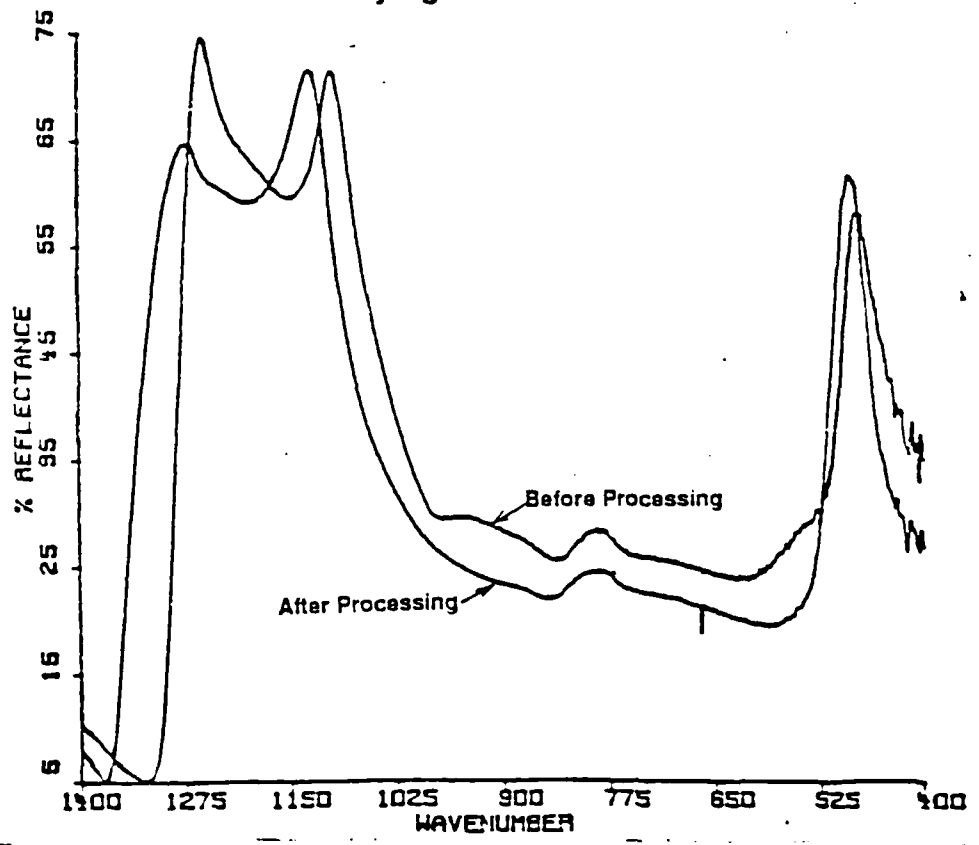


Figure 10b: FTIR Spectrum of Neodymium Gels Before and After Processing

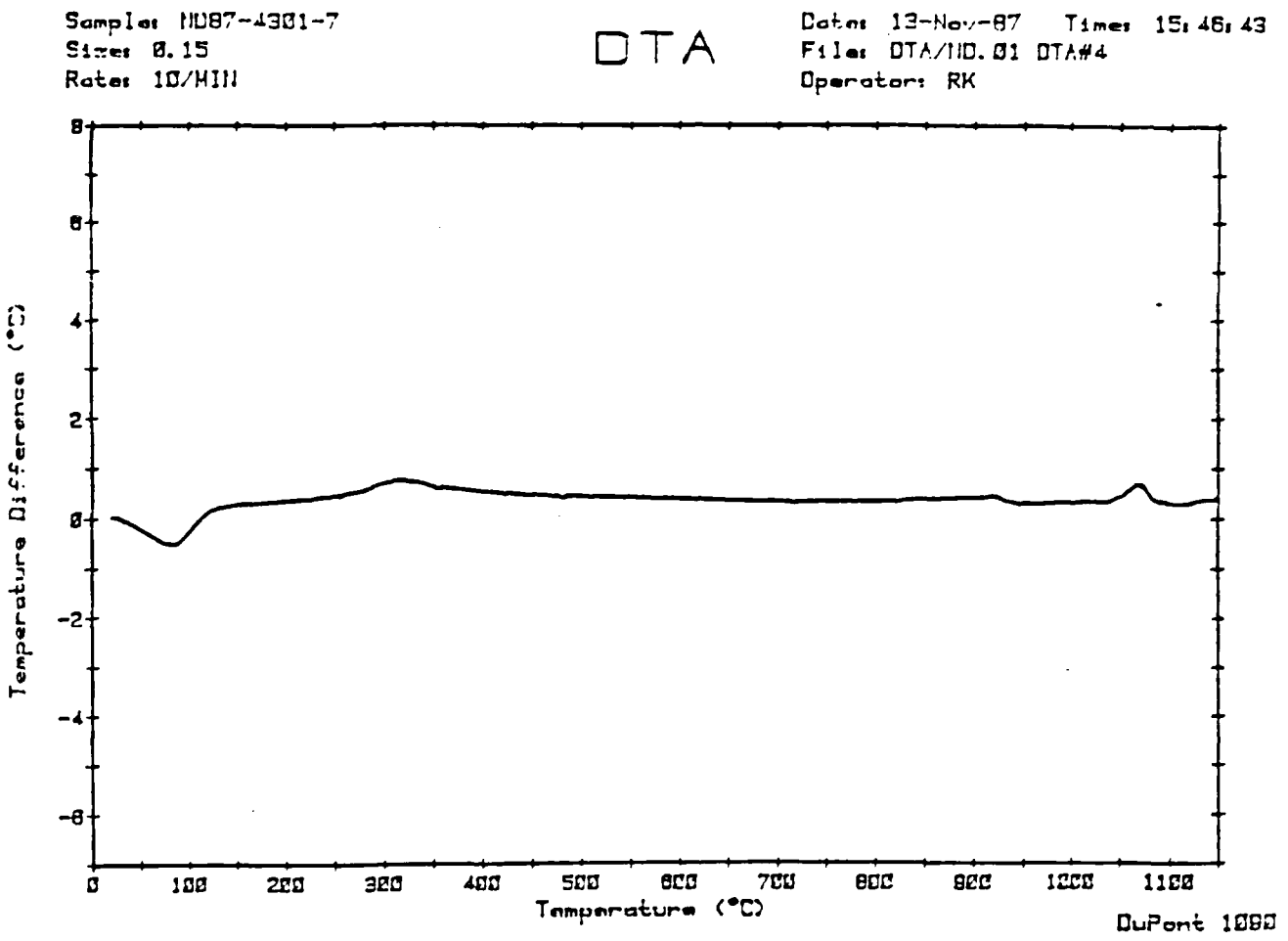
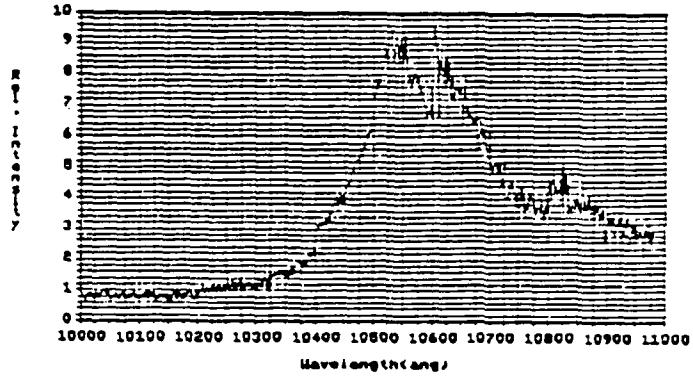
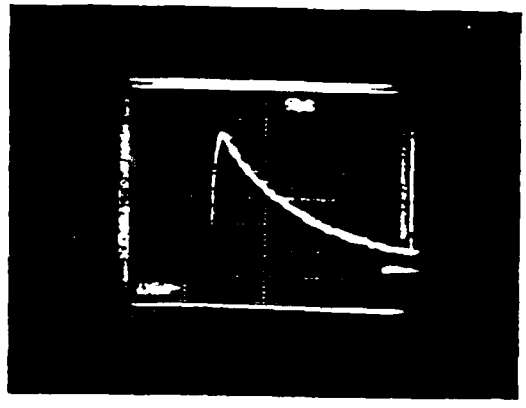


Figure 11: Differential Thermal Analysis of a Neodymium Gel



Fluorescence Spectrum

585 nm Pump

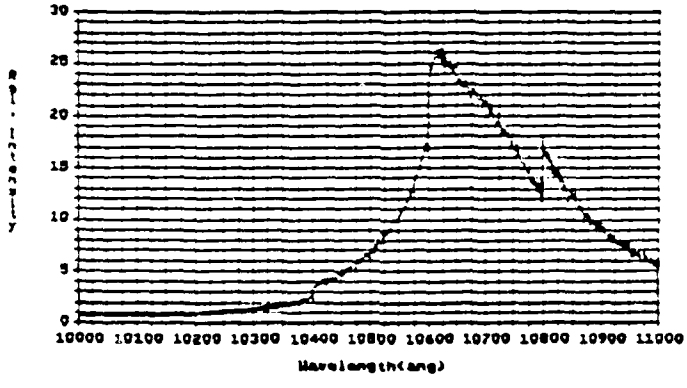


Fluorescence Lifetime

50 μsec/Large Division

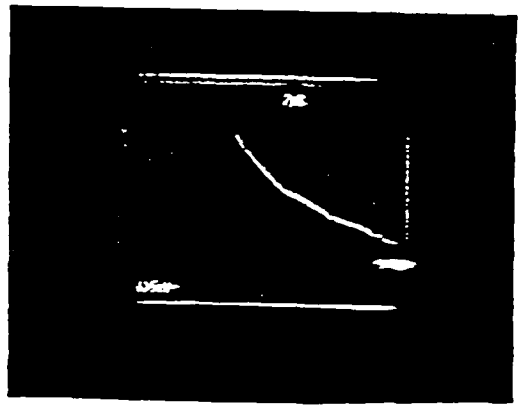
t_f = 170 μsec

Figure 12a: Fluorescence Spectrum and Fluorescence Lifetime of Nd:Phosphate Rod from Kigre, Inc., 9% Nd



Fluorescence Spectrum

585 nm Pump

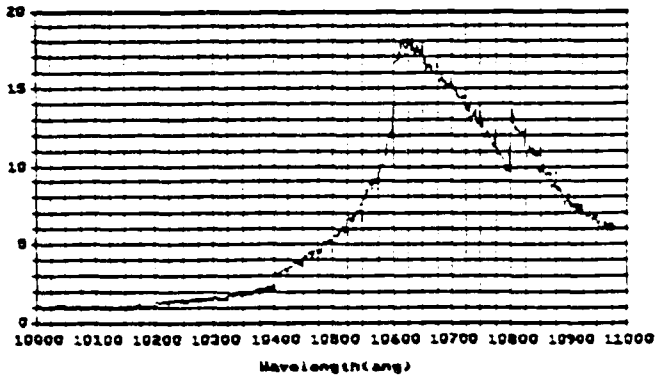


Fluorescence Lifetime

2 μsec/Large Division

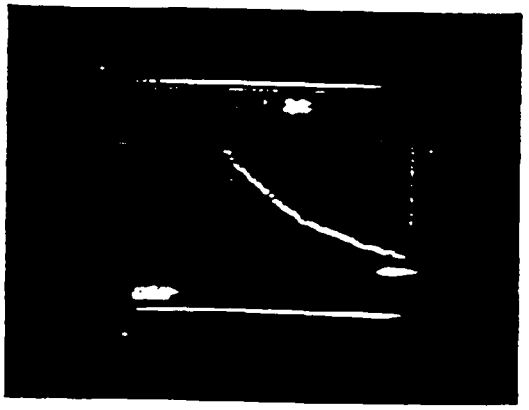
t_f = 7 μsec

Figure 12b: Fluorescence Spectrum and Fluorescence Lifetime of Nd:Silica Disc from Geltech, Inc., 5% Nd



Fluorescence Spectrum

585 nm Pump



Fluorescence Lifetime

2 μsec/Large Division

t_f = 7 μsec

Figure 12c: Fluorescence Spectrum and Fluorescence Lifetime of Nd:Silica Disc from GELTECH, Inc., 5% Nd with Alternate Treatment

Fluorescence Spectrum

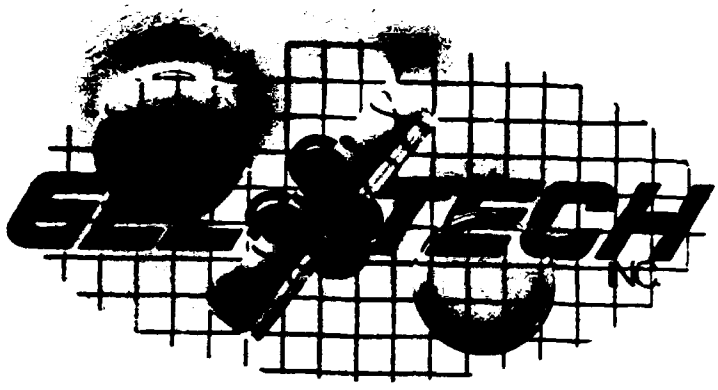
585 nm Pump

Fluorescence Lifetime

2 μsec/Large Division

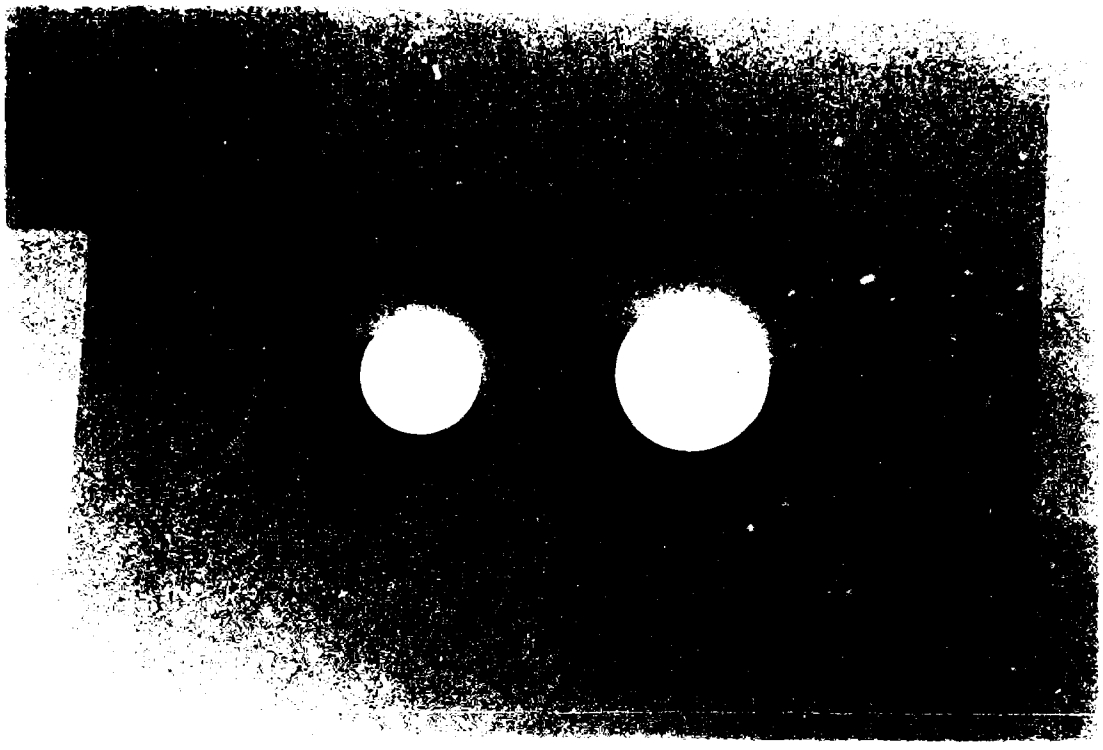
t_f = 8 μsec

Figure 12d: Fluorescence Spectrum and Fluorescence Lifetime of Nd:Silica Disc from Geltech, Inc., 4% Nd / 1% Er

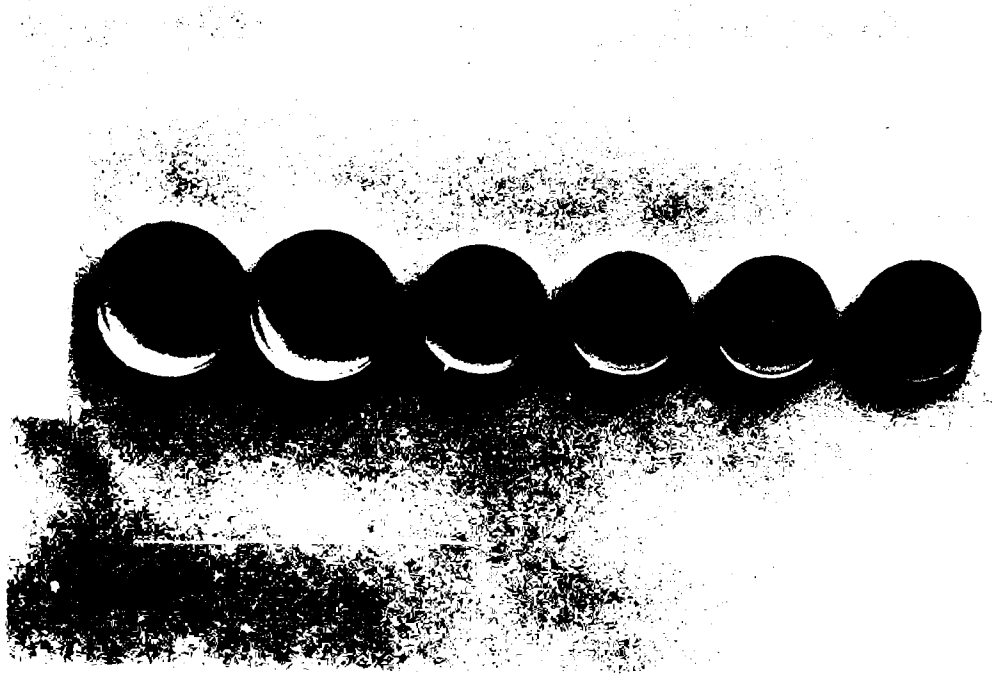


Picture 1: Monoliths Prepared by the Sol-Gel Process

Picture 2: Neodymium Doped Rods After Drying, and after Stabilization

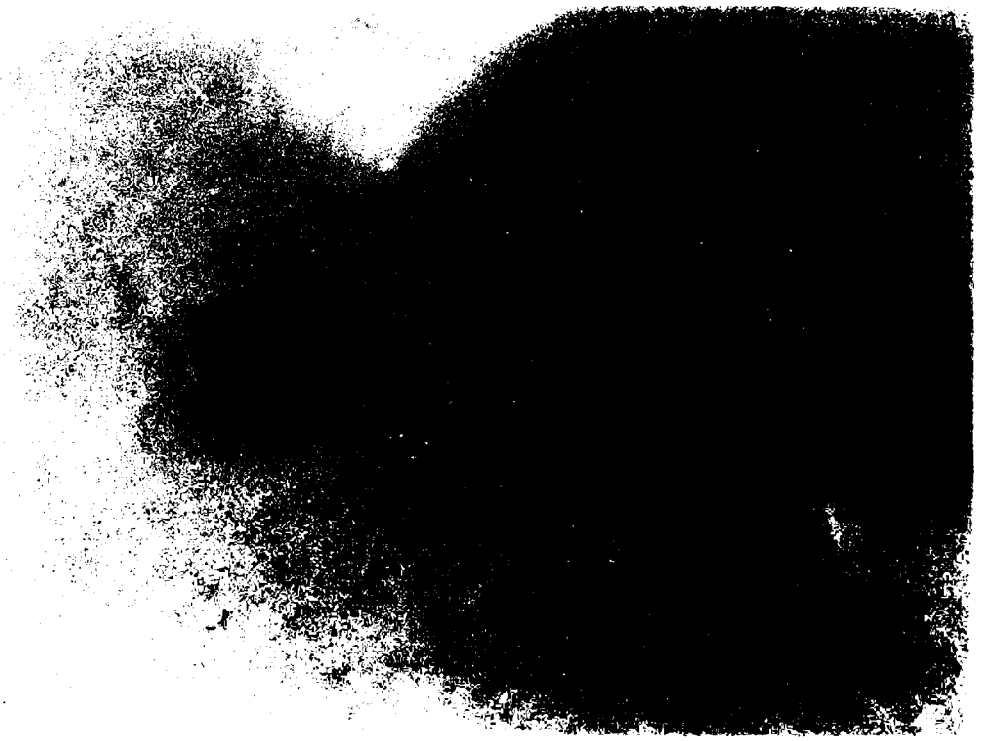


Picture 3: Neodymium Gels After Dehydration / Densification



Picture 4: Effect of Processing Temperature on Neodymium Gels

Picture 5: One, Three, and Five Percent Neodymium Gels



Picture 6: Neodymium and Neodymium / Erbium Gels

END

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