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PREPRINT

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Presentation

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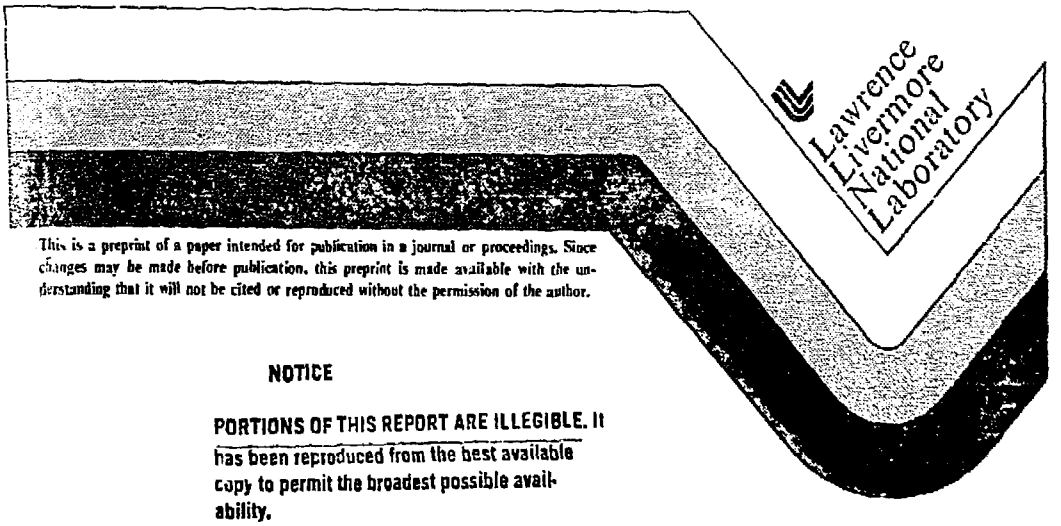

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C. F. Cline and M. J. Weber

MATERIALS PREPARATION TECHNIQUES

DISCLAIMER

Methods

Sputtering (magnetron & triode)
Electro and electroless deposition
Chemical vapor deposition
Laser and electron beam melting
Plasma and combustion synthesis
Physical vapor deposition
Inert melt spinning
Arc hammer splatting
Glass melting and casting
Czochralski growth of optical crystals
Analytical chemistry determination of composition and impurity concentrations.

States of Matter

Single crystal (metal, oxide, hydride, fluoride)
Polycrystalline
Amorphous (metallic, inorganic, organic)

MATERIALS PREPARATION CAPABILITIES

Glass melting and casting[1]--Figs. 1 and 2

Controlled environment glove boxes for mixing, melting, and casting of beryllium fluoride based glasses and similar toxic materials (Figs. 1 and 2). Resistance and induction heating of materials in platinum, graphite, and ceramic crucibles in controlled atmospheres (dry air, CO_2, N_2, etc.). Melt size ~ 500 g. Temperature limited by crucible materials.

Cutting, Grinding, and Polishing of BeF_2 Glasses--Fig. 3

Cutting, grinding, and polishing of beryllium fluoride glasses and other materials in enclosed, temperature-controlled, low-moisture environments. Disks with dimensions of 20 cm can be handled in these facilities (Fig. 3).

Czochralski Growth of Optical Crystals--Fig. 4

Induction heating of the melt in iridium, platinum, and other crucibles (50-mm diameter, 75-mm long). Maximum temperature determined by the size of the crucible and melting point of the material. Electronic balance crystal weighing technique for automatic control of boule diameter from point of seeding to completion of the run. Programmed pulling at growth rates from 0.5 to 250 g/h. Enclosed, vented growth area suitable for handling toxic materials such as beryllium compounds (Fig. 4).

Cutting and polishing facilities for sample preparation. Computerized x-ray crystallography laboratory for sample orientation.

Inert Atmosphere Melt Spinning--Figs. 5, 6, and 7

Arc Hammer Method--Figs. 8, 9, and 10

Computer Simulations of Liquids and Glasses: Programs for Calculation of Their Properties[2-5]

Molecular dynamics programs for simulating atomic structure of systems with up to 400 ions of five different species. Program to relax system to lowest energy state. Computer graphics display of simulated structures (Fig. 11).

Programs to calculate the following structural and kinetic properties: average and time-dependent radial distribution functions, average and distribution of coordination numbers, angle distributions, diffusion coefficients, velocity autocorrelation function. Options available to restrict coordination number or neighbors of ions averaged over.

Special programs to analyze coordination number of ions involved in diffusion and of ions in their neighborhood, probability of returns after "bond breaking", probability of coordination number increase before bond breaking, graph trajectories or coordination number of individual ions or pairs, probability of monodentate glass forming tetrahedra about some other ion.

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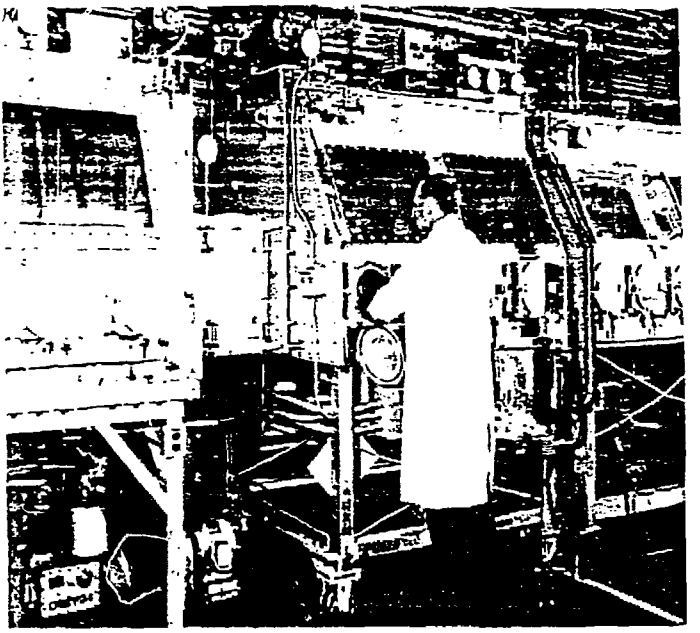

Fig. 1 Dry box line for beryllium fluoride glass preparation.

Fig. 2 Enclosed facilities for induction-melting and casting of beryllium fluoride glasses.

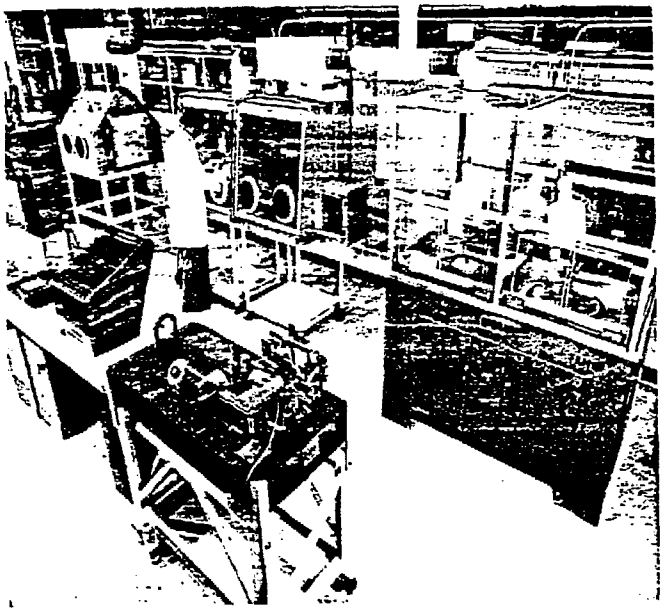

Fig. 3 Facilities for fabrication and polishing beryllium fluoride glasses.

Fig. 4 Automated Czochralski crystal growth station and electronic controls.

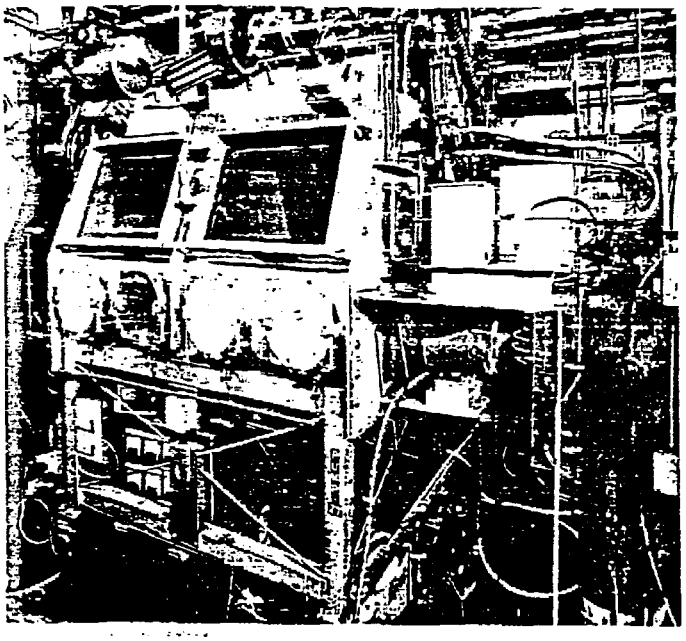

Fig. 5 Inert Atmosphere dry box with variable frequency induction generator.

Fig. 6 Inert atmosphere box with air chamber for variable speed motor to drive melt spinner.

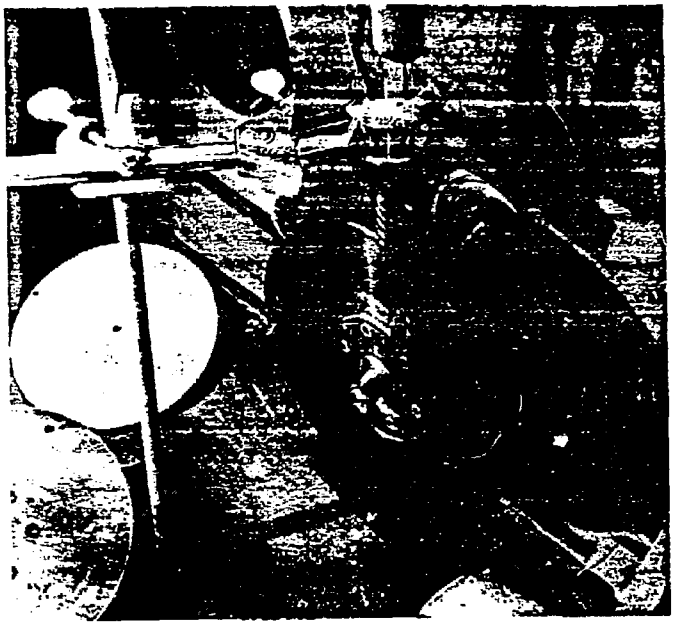

Fig. 7 Ferrofluidic feed-through for variable speed attachment to copper melt spinning wheel.

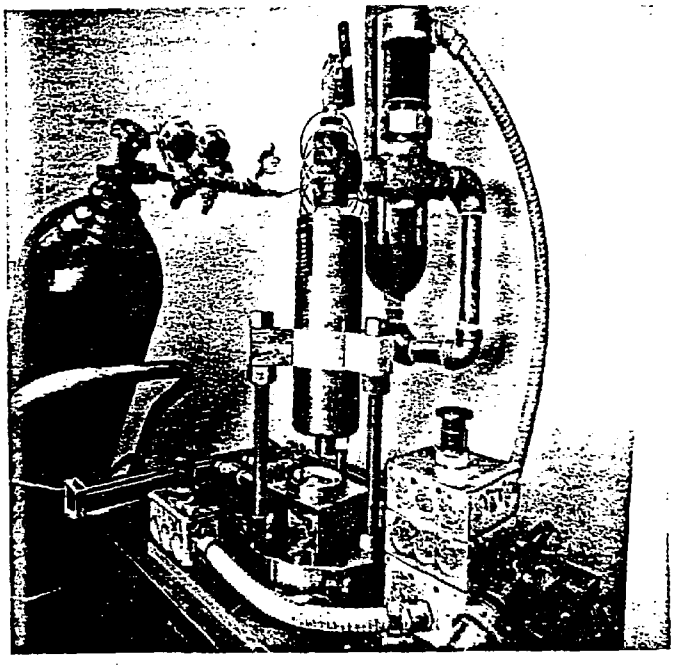

Fig. 8 Pneumatic gas driven arc hammer for glove box use.

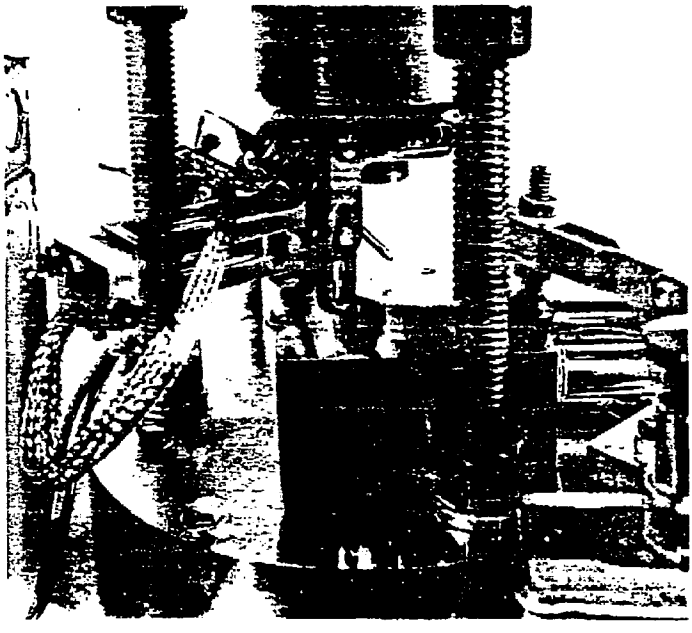

Fig. 9 Arc melt stinger for pneumatic hammer.

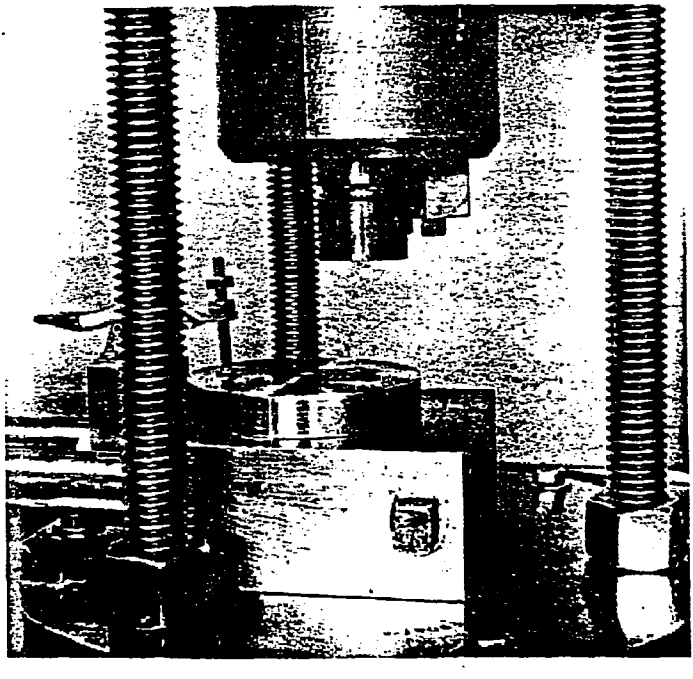

Fig. 10 Hammered foil obtained from pneumatic unit.

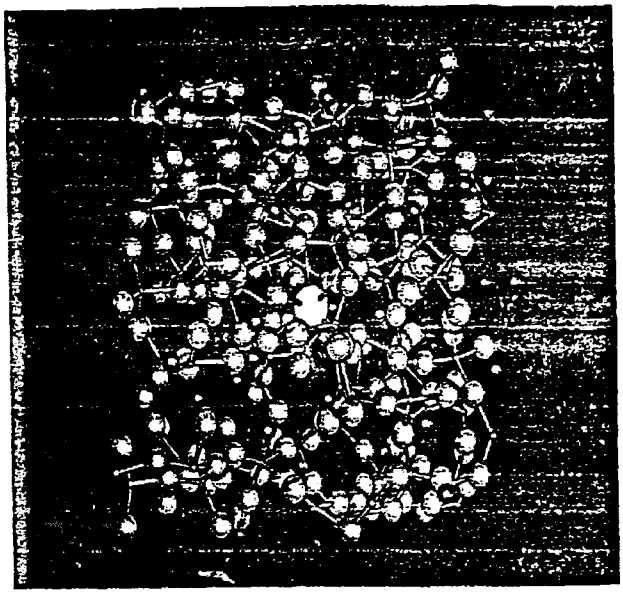

Fig. 11 Computer graphics display of one configuration of a computer-simulated beryllium fluoride glass. The large sphere in the center is a rare-earth dopant ion. The small spheres are Be ions coordinated by larger F ions. Unconnected spheres are Ca modifier ions.

Calculation of electric field gradient and asymmetry parameter and crystal field at ion sites using point charge model.

Vibrational density of states and Raman, infrared, and inelastic neutron scattering spectra calculated from diagonalization of dynamical matrix or from appropriate autocorrelation functions.

Programs written for Floating Point Systems array processor.

MATERIALS CHARACTERIZATION TECHNIQUES

Electron Beam Analyses

TEM, Transmission Electron Microscopy
STEM, Scanning Transmission Electron Microscopy
SEM, Scanning Electron Microscopy
EMP, Electron Microprobe

X-Ray Diffraction

Solid phase identification
High and low temperature "in situ" x-ray diffraction
Thermal expansion of crystal lattices
X-ray topography
Single crystal orientation

XPS (ESCA)

Bombard surfaces with x-rays, measure photoelectron energy distribution: Gives elemental analysis of top 2-5 atom layers plus chemical information of the surface (valence state, bond configuration, etc.)

AES

Bombard surface with 1-3 keV electrons, measure Auger electron energy spectrum: Gives elemental analysis of top 2-5 atom layers. An order of magnitude more sensitive than XPS. Used extensively in depth profiling.

SAM

Gives AES type information as a function of X-Y position on surface. X-Y Resolution ~0.1 micron.

RBS

Bombard surface with 1-4 MeV protons or alpha particles, measure energy distribution of back-scattered particles: Gives depth distribution of elements. Non-destructive.

PIXE

Bombard surface with keV protons, alpha particles, etc. and measure X-ray fluorescence spectrum: Gives elemental surface analysis up to 1 micron deep. More sensitive than electron probe due to absence of bremsstrahlung.

NRA

Bombard surface with selected ions, e.g. N15 at 6.3 MeV, measure γ-ray spectrum: Particularly useful for measuring depth distribution of hydrogen isotopes.

SIMS

Bombard surface with 1-32 keV O^+, O^-, Ar^+, etc. ions, determine sputter ion yield: Can be most sensitive method for depth distribution of elements (ppm-ppb, depending upon the element and the matrix).

Positron Annihilation

Bombard sample with positrons, measure lifetime and angular correlation of resulting γ-rays: Gives information concerning type and number of defects in the solid.

Cathodo-luminescence

Bombard surface with electrons, UV etc., measure lifetime and wavelength of luminescence: Gives information concerning bonding characteristics on and in surface.

LEED

Bombard single crystal surface with electrons, determine diffraction pattern: Gives information concerning surface crystal structure and structure of any adsorbed over-layer.

Laser Raman Microprobe

Bombard surface with a micron size laser beam, measure Raman scattered light: Gives information concerning chemical (molecular) entities within the beam samples area.

Nonlinear Optical Properties

Measurements of (i) intensity-dependent nonlinear refractive index of crystals and glasses using time-resolved interferometry[6,7] and (ii) multiphoton absorption coefficients and two-photon induced color centers using transmissive and photorefractive thermal lensing.

Laser Induced Damage in Optical Materials and Thin Film Coatings

Irradiation with fully characterized (spectral and temporal profiles) laser pulses; damage identified with Nomarski microscopy.[8]

Ultra-high-vacuum irradiation chamber (10^{-8} Pa) equipped with secondary ion mass spectrometer (SIMS) to measure photon-stimulated ion desorption, double-pass electron energy analyzer to measure energy distribution of laser-induced multiphoton photoelectron emission, and x-ray photoelectron spectrometer (XPS) to determine laser-induced surface compositional changes.

Facilities

Lasers available for above measurements:

Cyclops Laser Nd:YLF oscillator and five Nd phosphate glass amplifiers (Fig. 12)
- Wavelengths: 1053, 526, 351 nm
- Output Energy: ≤ 10 J at 1053 nm, ~75% at 526 nm, 50% at 351 nm
- Temporal Waveform: rectangular of selectable duration--1.4, 3.2, 6, 9, 20 ns.
- Spatial Profile: flattened Gaussian $D(e^{-2})$ ~30 mm
- Repetition Rate: 5 minutes

Intermediate Laser System (ILS) Actively mode-locked Nd:YAG oscillator, electronic switchout, high-repetition rate preamps, Nd:silicate glass amplifiers (Fig. 13)
- Wavelengths: 1064, 532, 355 nm
- Output Energy: ~3 J at 1064, 2J at 532 nm, 1 J at 355 nm
- Pulse Duration: variable, 0.1-1.0 ns
- Spatial Profile: near Gaussian $D(e^{-2})$ ~20 mm
- Repetition Rate: preamplifier--1 pps, total system--5 minutes

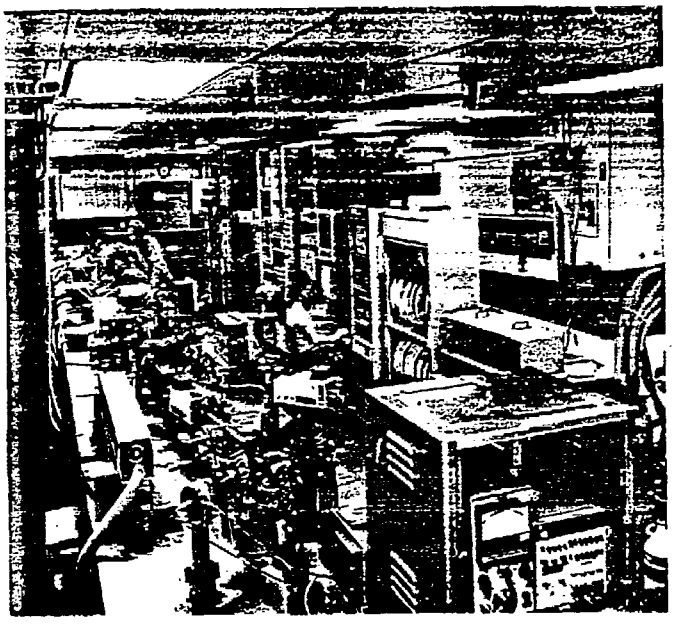

Fig. 12 Cyclops laser facility.

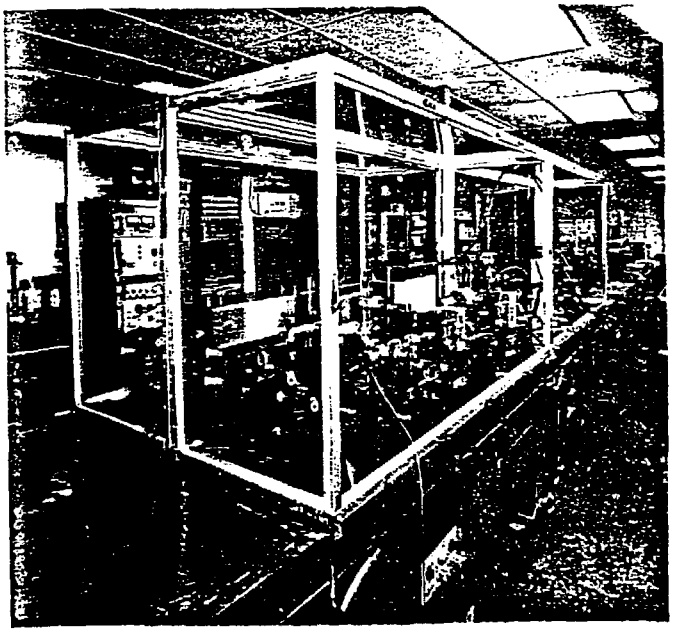

Fig. 13 ILS laser facility.

[illegible] laser (XPL): [illegible] oscillator, Pockels cell shutter, [illegible]
[illegible]
Output energy: 10 J in 1 ms
Pulse duration: rectangular 0.5 ms, near Gaussian 1 ms
Spatial Profile: Gaussian $D(r^2)$, ~ 40 mm
Repetition Rate: 10 minutes

Laser Beam Diagnostics:
Energy Per Pulse--calorimeters
Temporal Profile--fast photodiodes and/or streak camera
Spatial Profile--Vidicon, video digitizer, PDP-11 computer analysis.[9]
Probable measurement uncertainties: energy (J) ± 3%, fluence (J/cm^2) ± 5-7%, intensity (w/cm^2) ± 10-15%.

Photorefractive Spectroscopy (Fig. 14)

Photorefraction and thermal lensing are used as sensitive techniques for detecting weak linear and nonlinear absorption, nonlinear refractive index changes, and quantum efficiency of solids.[10] A typical experimental setup with excitation and probe laser beams is shown in Fig. 15. Minimum detectable absorption [illegible]
[illegible].
Available apparatus includes:

Quantronix 444-34 Nd:YAG Laser

Output per pulse of ~ 700 mJ at 1064 nm, 250 mJ at 532 nm, 125 mJ at 355 nm, and 50 mJ at 266 nm; 10-ns pulse duration; 10 Hz repetition rate; spectral width ~0.5 cm^{-1} unnarrowed, 0.05 cm^{-1} with etalon, 0.005 cm^{-1} with single frequency conversion.

Molectron DL-16 Pulsed Dye Laser

Tuning range from 360-760 nm; pulse duration ~ 10 ns; spectral width 0.3 cm^{-1} unnarrowed.

Stimulated Raman Frequency Conversion with High-Pressure H_2 Gas

Frequency shift = 4155n (cm^{-1}), where n in the order of the Stokes radiation; extends tuning range to [illegible] nm with ~15-30% energy conversion efficiency.

Tektronix R7912 Transient Digitizer for measuring temporal waveforms.

Real-time, pulsed laser-beam spatial profiles recorded and processed with vidicon, Grinnell video signal digitizer, and PDP-11/05 computer.

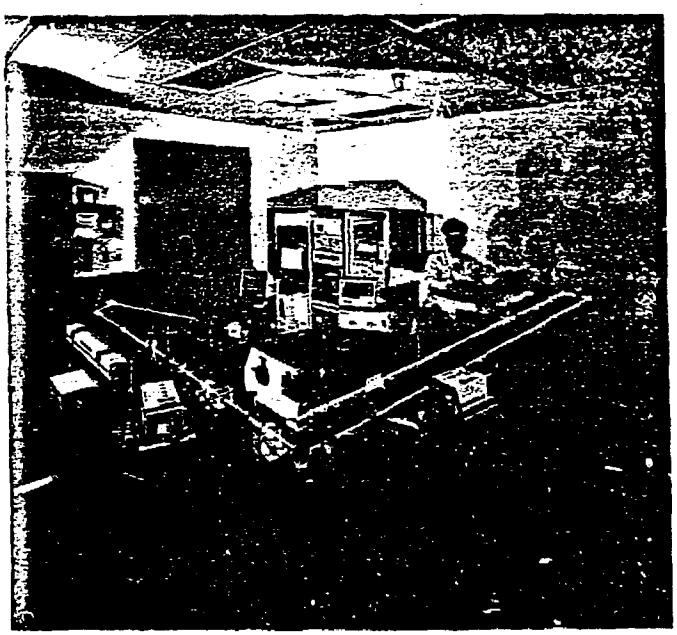

Fig. 14 Laboratory for photorefractive spectroscopy.

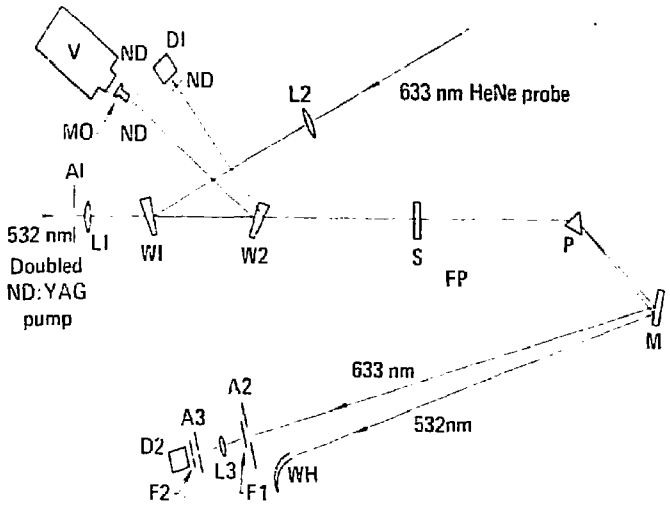

Fig. 15 Typical experimental setup for photorefractive measurement of nonlinear absorption at 532 nm. L--lens, W--beam splitting wedge, S--sample, FP--focal plane, D--detector, V--vidicon, A--aperture, F--filter, ND--neutral density filter, P--prism, M--mirror, WH--wood horn.

Laser-Excited Fluorescence Spectroscopy

Tunable pulsed laser sources and spectrometer for optical site selection spectroscopy and fluorescence line-narrowing experiments in crystals and glasses.[11] Spectral (near-UV to near-IR) and time-resolved (~10 ns lifetimes) measurement capabilities.

Apparatus and experimental configuration are shown in Fig. 16. Tunable fluorescence excitation sources include a Molectron Nd:YAG laser-pump dye laser (see above) and a Chromatix CMX-4 flashlamp-pumped dye laser with frequency-doubling capabilities: 460-680 nm in fundamental (~ 4 mJ/pulse), 1-μs pulse duration, 10 Hz repetition rate.

Sample temperature variable from ~10-300 K using Air Products He-fluid refrigerator.

Fluorescence is analyzed with a 1-m grating monochromator equipped with cooled photomultiplier tubes. PAR OMA photon-counting system; gated and delayable with 10 MHz maximum counting rate.

LSI-11 microcomputer system is interfaced for apparatus control, data manipulation and analysis, and graphics output.

Optical Spectroscopy

Computerized laboratory for optical absorption, fluorescence and excitation spectra and fluorescence decay measurements (Fig. 17). All input signals are digitized and processed in a PDP-11/40 computer system with magnetic tape storage. Programs available for determining peak wavelengths, linewidths, integrated spectral intensities, excited-state lifetimes; capabilities for baseline corrections, rescaling, and comparison of spectra.

Apparatus includes:

- Cary 17I spectrophotometer, 0.2-3.0 μm, 4-300 K sample temperatures.
- Fluorescence monochromator and detectors for spectral range 0.2-2.2 μm.
- Xenon flashlamp (5 μs) and Chromatix 1000 laser and optical parametric oscillator (100 ns) for tunable pulsed excitation for fluorescence decay studies. R7912 transient digitizer for signal averaging.

All of the above instrumentation is interfaced to and controlled by the computer system.[12]

Additional equipment available for routine optical absorption spectroscopy from the near-UV through the IR include:

- Perkin-Elmer 330 Spectrophotometer: 187-2500 nm, absorbance 0-4 A.U.
- Perkin-Elmer 983 Spectrophotometer: 5000-180 cm^{-1}, absorbance 0-3 A.U.
- Data station and software for spectral analysis.

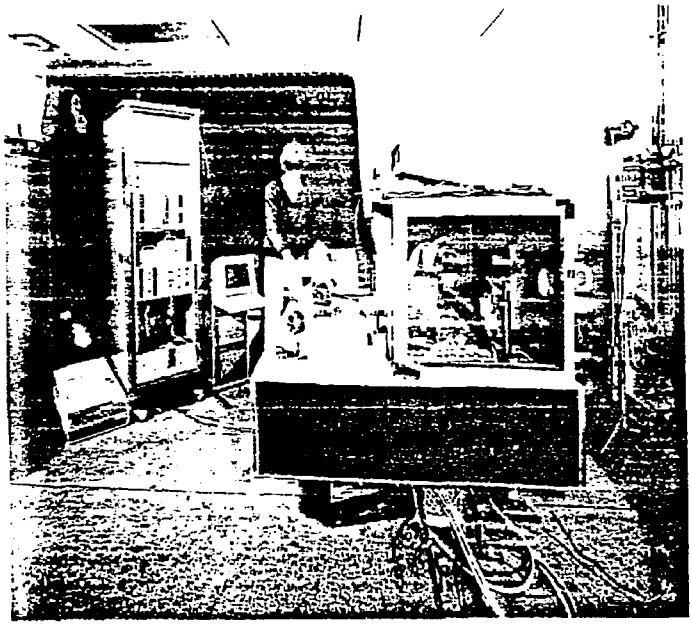

Fig. 16 Facilities for laser-excited fluorescence studies of solids.

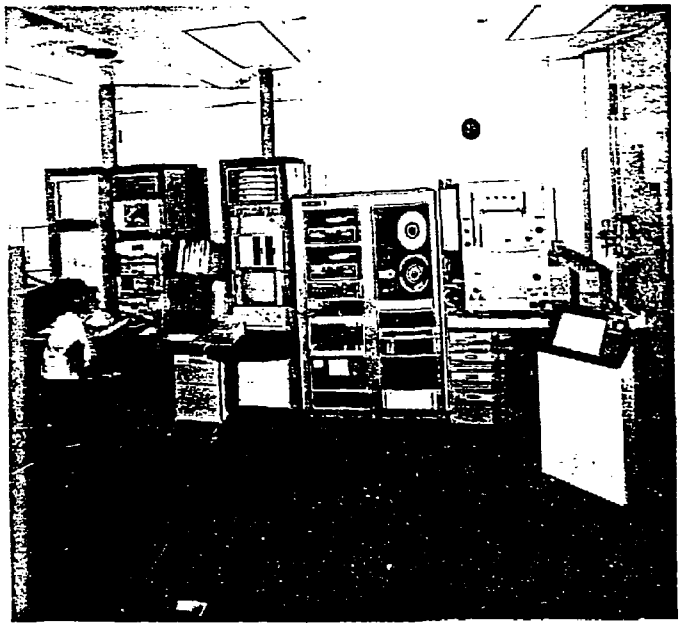

Fig. 17 Optical spectroscopy facilities. Apparatus for measurements for fluorescence spectra and fluorescence decay times is located behind the operator.

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