Terahertz Spectroscopy Applications

(non-biological)

17 December 2009

National Physical Laboratory

THz spectroscopy has been used to study:

(amongst others, and in no particular order)

- Polymers
- Semiconductors
- Ceramics and glasses
- Organic molecules
- Gas spectroscopy
- Conductive films
- Liquid crystals
- Composites
- Oils
- Nondestructive testing

Polymers

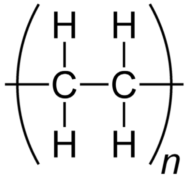
(*non-polar!*)

Non-polar, e.g.:	Polar, e.g.:
PTFE (Teflon)	Polystyrene
Polyethylene	Perspex
Polypropylene	Vinyl

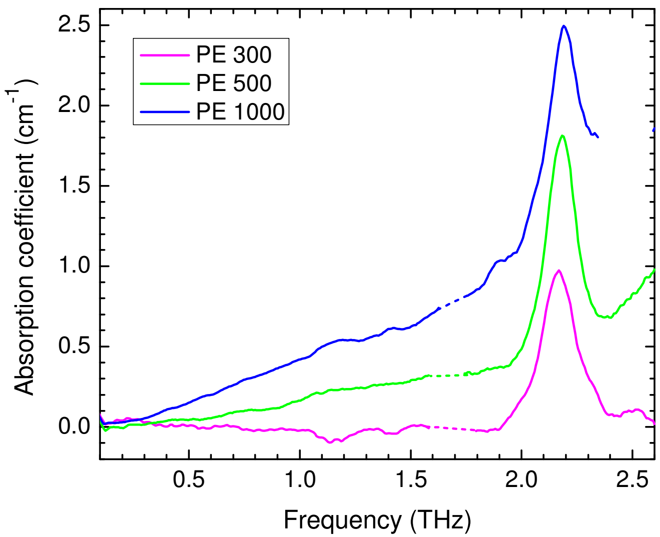
- Observing polymerisation
- Differentiating polymorphs
- Measuring electrical conductivity
- Measuring hygroscopicity

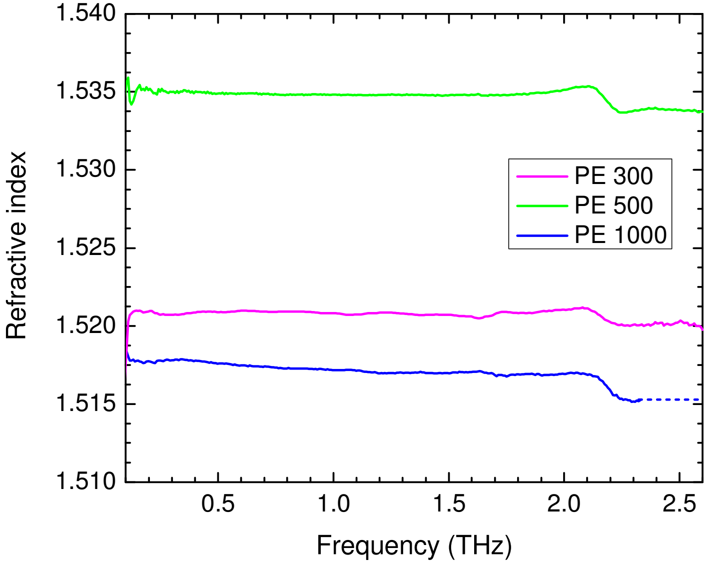
NPL
National Physical Laboratory

Effect of chain length in polyethylene



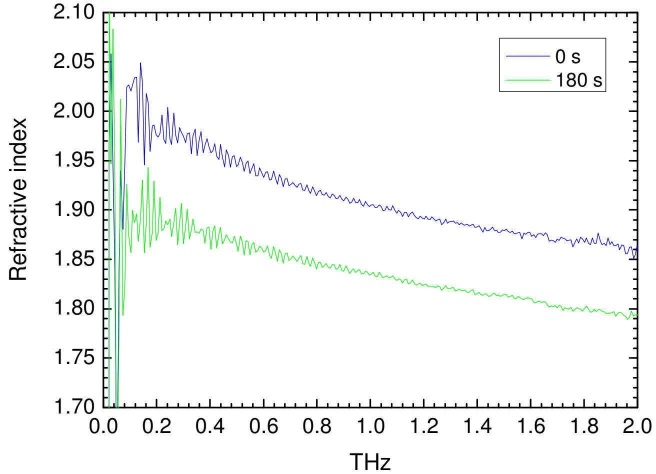
Polyethylene monomer

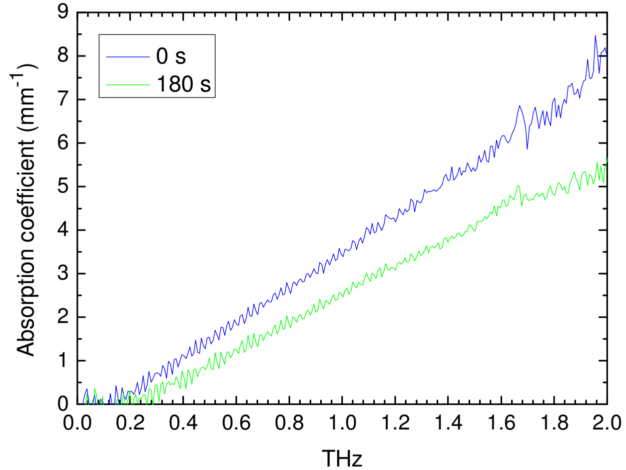


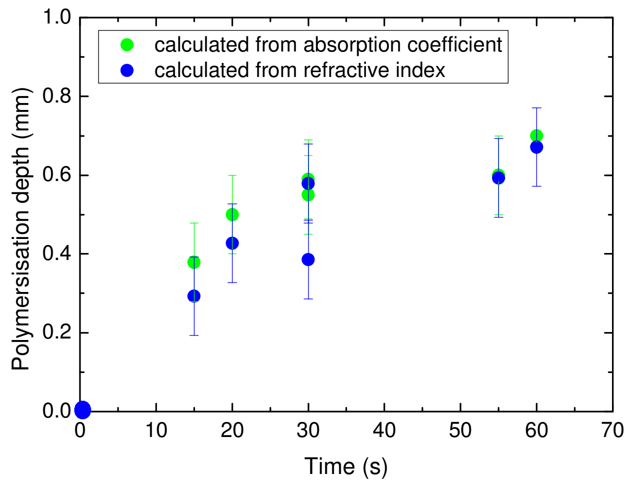


Polymerisation in SU8

SU8 is an epoxy resin used as a UV-curable photoresist





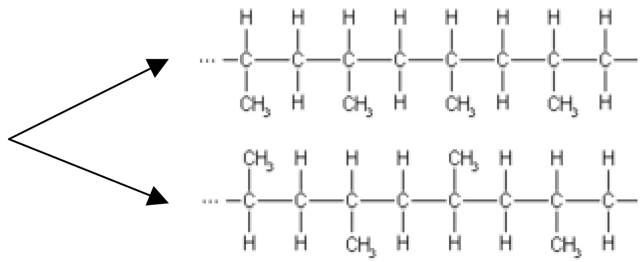


Propagation of the polymerisation front

National Physical Laboratory

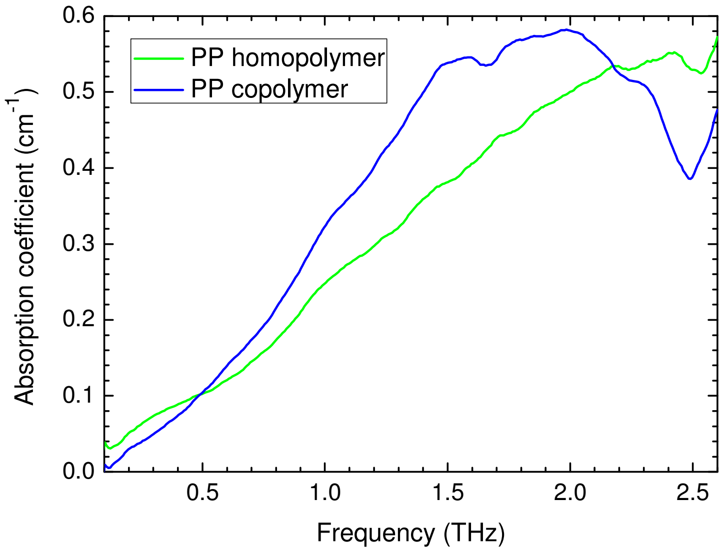
Differentiating polymorphs

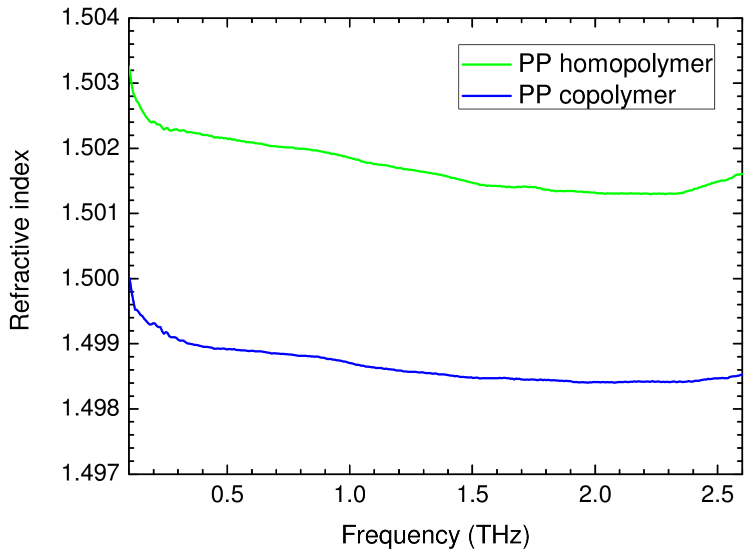
Polypropylene

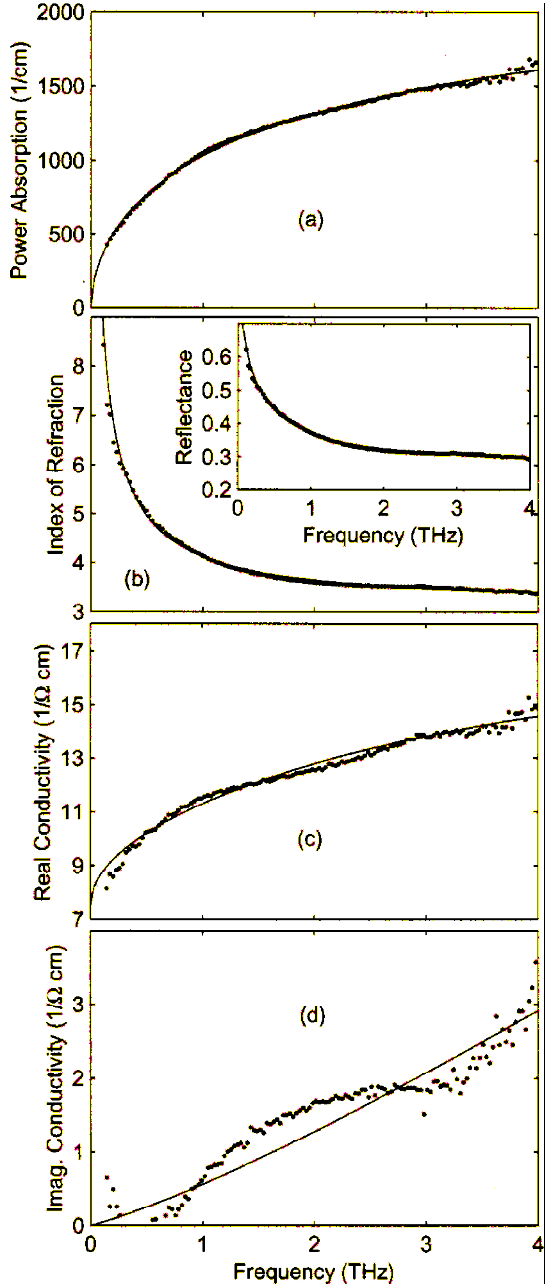


Isotactic

Syndiotactic







Characterization of conducting poly-3-methylthiophene film

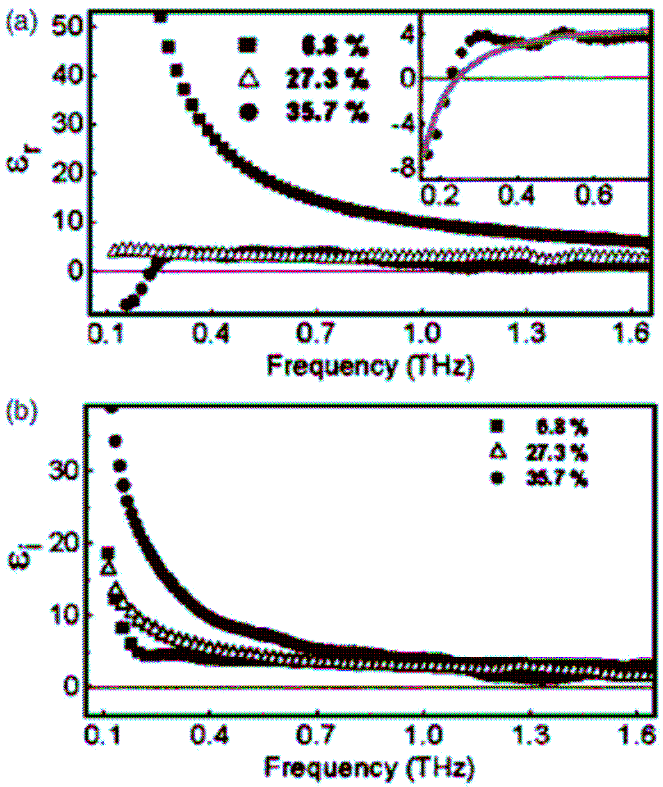
TI Jeon et al, Appl. Phys. Lett. **79/**25 (2001) 4142-4144

In this conducting polymer absorption and refractive index are mostly due to the free carriers.

(solid line: Drude model)

Observing the metal-insulator transition in PMMA-graphite composite (polymethylmethacrylate)

AM Seo et al, J. Appl. Phys,. **99**, 066103 (2006)



By varying the graphite content it is possible to engineer the dielectric constant of the material in order to manufacture absorbers with a wide range of shielding.

Measuring hygroscopicity of polymers

J. Balakrishnan et al, Appl. Opt., **48/**12 (2009) 2262-2266

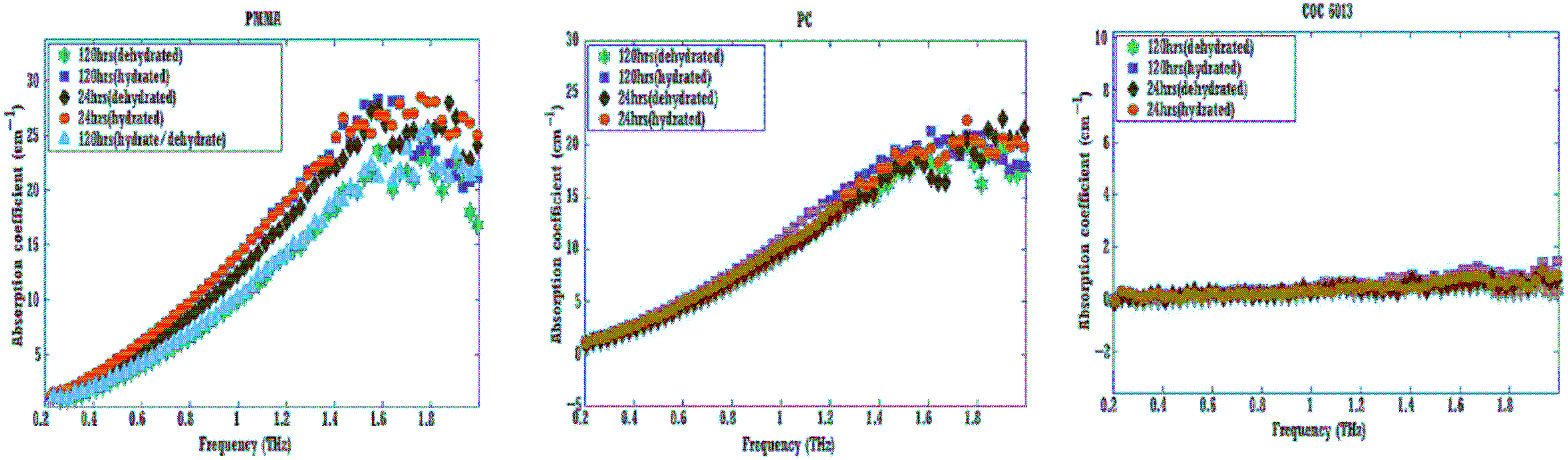


Table 1. Variation in Absorption Coefficient and Hygroscopicity of Polymer Materials for 24 h and 120 h Measurements at 1 THz[a]

		Absorption (cm^{-1})				Hygroscopicity (%)			
		24 h		120 h		Experimental		Literature	
	Polymer	Hydrated	Dehydrated	Hydrated	Dehydrated	24 h	120 h	24 h [28]	120 h
non-	COC 6013	0.269	0.240	0.361	0.160	0.01	0.09	0.01	—
polar	COC 5013	0.334	0.315	0.485	0.290	0.01	0.08	0.01	—
	HDPE	0.259	0.215	—	—	0.02	—	0.01	—
	PTFE	—	—	0.552	0.450	—	0.04	0.01	—
polar	PMMA	14.020	12.393	14.015	10.000	0.75	1.80	0.5	—
	PVC	22.218	22.087	22.263	21.998	0.06	0.11	0.06	—
	PC	10.346	9.800	10.977	9.457	0.21	0.69	0.25	—

[a]Hygroscopicity data obtained from Eq. (7) are compared with the standard test method for water absorption of polymers (ASTM D570) to verify agreement.

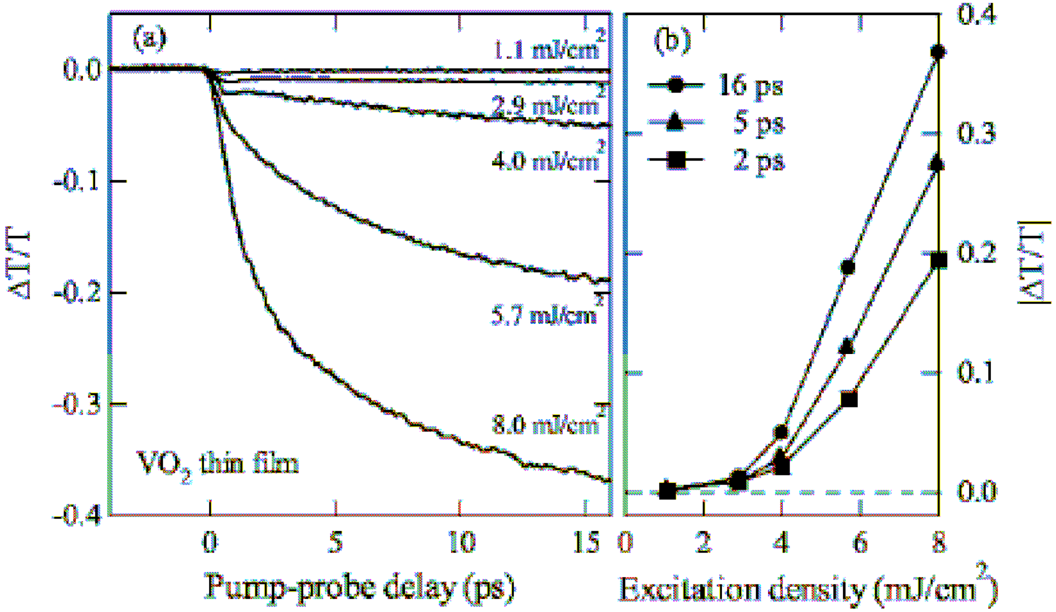
Semiconductors

- Carrier dynamics
- Electron mobilities
- Quantum dot properties
- Fault inspection

Studied by using optical pump and THz probe

Photoinduced metallic state in VO_2 using optical pump, THz probe

M. Nakajima et al., Appl. Phys. Lett. **92**, 011907 (2008)



Temporal dependence of THz transmittance

Electron mobility in GaAs alloys

DG Cooke et al, Appl. Phys. Lett. **89**, 122103 (2006)

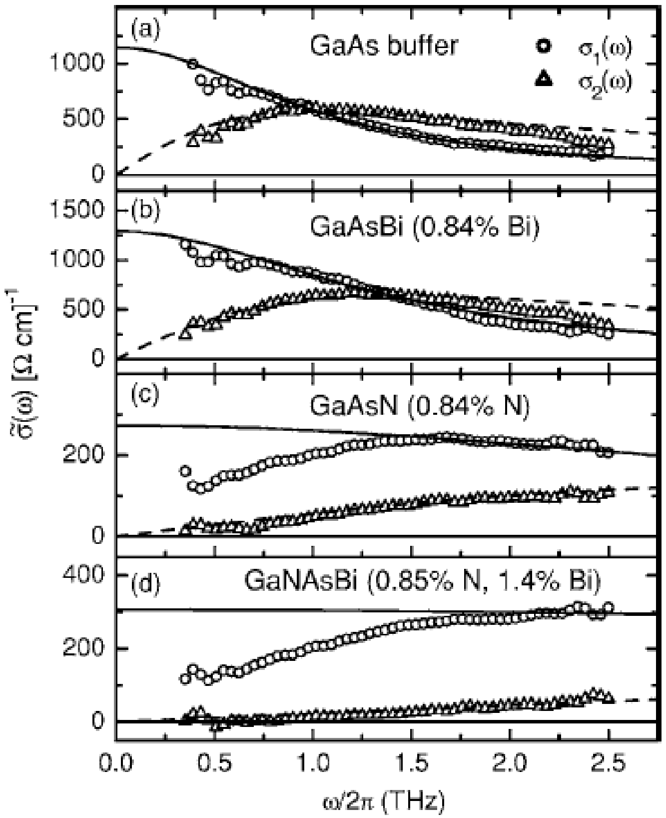


FIG. 2. Extracted complex conductivity for (a) GaAs buffer layer, (b) GaAsBi (0.84% Bi) (c) GaNAs (0.84% N), and (d) GaNAsBi (0.85% N, 1.4% Bi) 10 ps after 400 nm excitation at a fluence of 3.7 μJ/cm^2. The solid and dashed lines are fits to the real and imaginary parts of the Drude conductivity with (a) $\omega_p/2\pi=46\pm1$ THz, $\tau=157\pm7$ fs, (b) $\omega_p/2\pi=57\pm1$ THz, $\tau=115\pm4$ fs, (c) $\omega_p/2\pi=48\pm2$ THz, $\tau=35\pm3$ fs, and (d) $\omega_p/2\pi=86\pm2$ THz, $\tau=12\pm1$ fs.

TABLE I. Extracted electron mobilities from Drude fits to the complex conductivity in various samples for early delay times $\Delta t=4-10$ ps, with a 400 nm pump fluence of 3.7 μJ/cm^2 ($n\sim(2-3)\times10^{18}$ cm^{-3}).

Sample	μ_e (cm^2/V s)
GaAs buffer layer	3300 ± 100
$GaAs_{1-y}Bi_y$ ($y=0.84\%$)	2800 ± 100
$GaAs_{1-y}Bi_y$ ($y=1.0\%$, AlGaAs barrier)	2800 ± 100
$GaAs_{1-y}Bi_y$ ($y=1.4\%$)	2700 ± 100
GaN_xAs_{1-x} ($x=0.84\%$)	920 ± 80[a]
$GaN_xAs_{1-x-y}Bi_y$ ($x=0.85\%$, $y=1.4\%$)	340 ± 30[a]

[a]Derived from high frequency fits to the Drude model.

National Physical Laboratory

Electron-to-Hole Energy Transfer in CdSe Quantum Dots

E Hendry et al, Phys. Rev. Lett. PRL **96,** 057408 (2006)

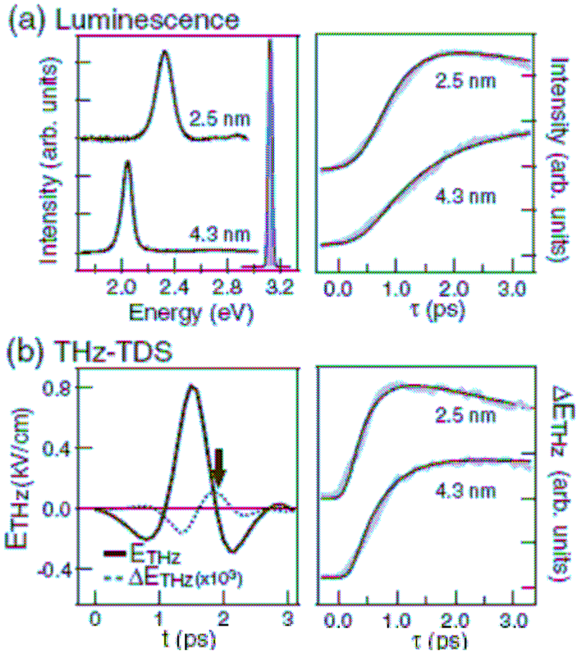
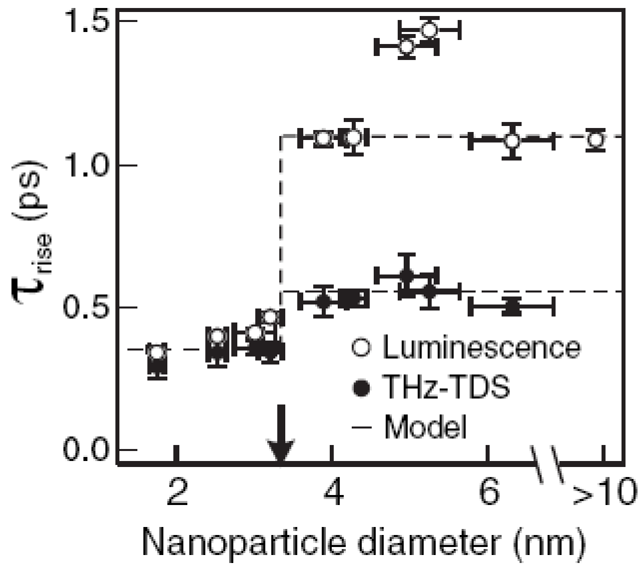


FIG. 1. (a) Left: Luminescence spectra. Also shown is the excitation pulse (shaded area). Right: We measure the increase in intensity at the peak of the luminescence spectra (gray lines) as a function of delay τ. (b) Left: The transmitted THz pulses $E_{\mathrm{THz}}(t, \tau)$ and the exciton-induced modulation thereof, $\Delta E_{\mathrm{THz}}(t, \tau)$. Right: The modulation is measured at the point marked with an arrow in the left panel ($t = 1.9$ ps), as a function of τ, giving rise to the transient hole population of the $1S_{3/2}$ level. The dynamics in both (a) and (b) are adequately described by exponential rise times determined by the carrier cooling rates (black lines in the right-hand panels).



Inspection for electrical failures in semiconductor devices

M. Yamashita et al., Appl. Phys. Lett. **93**, 041117 (2008)

Terahertz pulses are generated from nonbiased Si-MOSFETs by exciting *p-n* junctions with ultrafast laser pulses. The waveforms of terahertz pulses depend on the interconnection structure near the *p-n* junctions.Defects in the circuit wiring give rise to changes in the terahertz emission images.

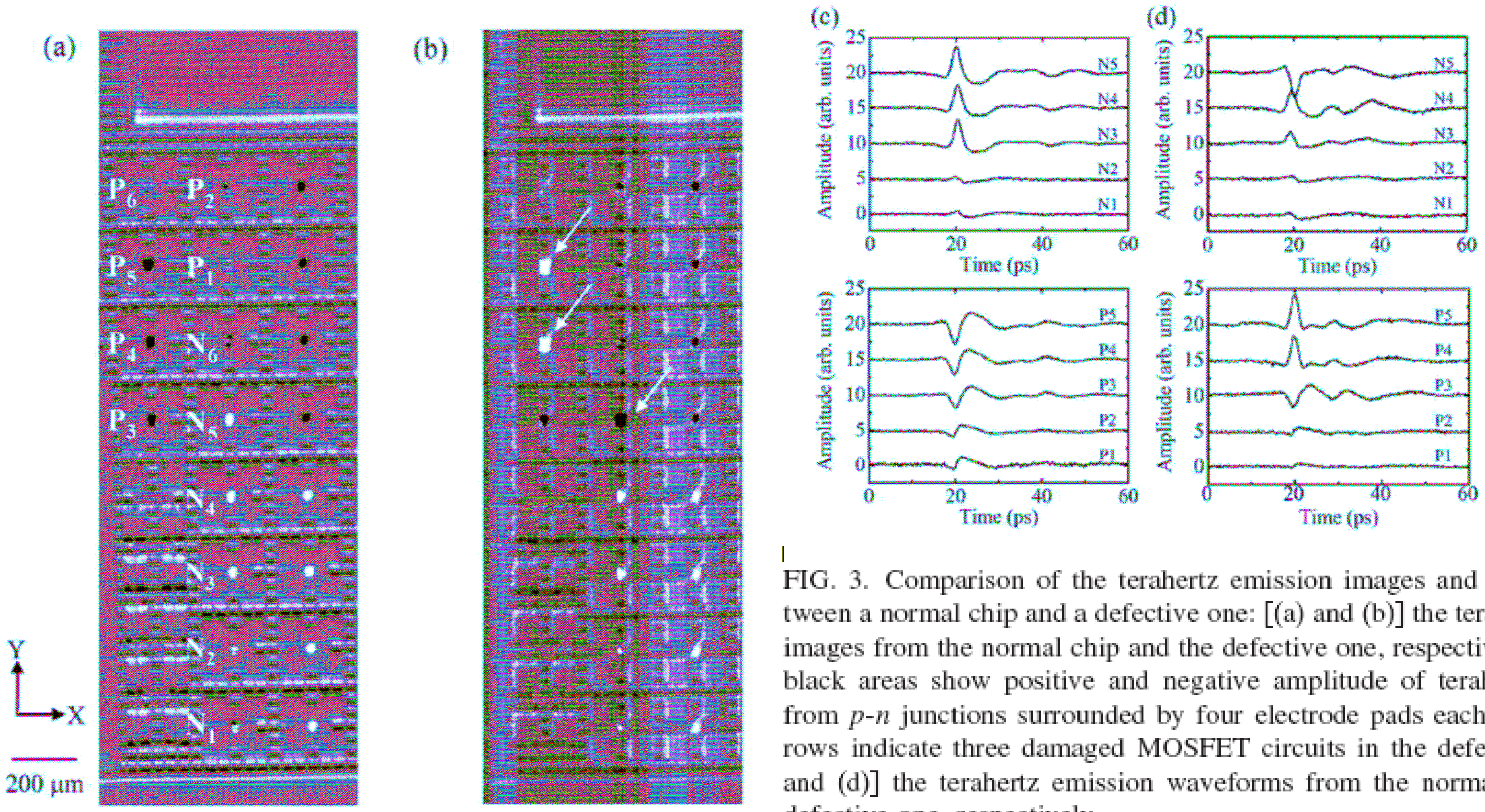


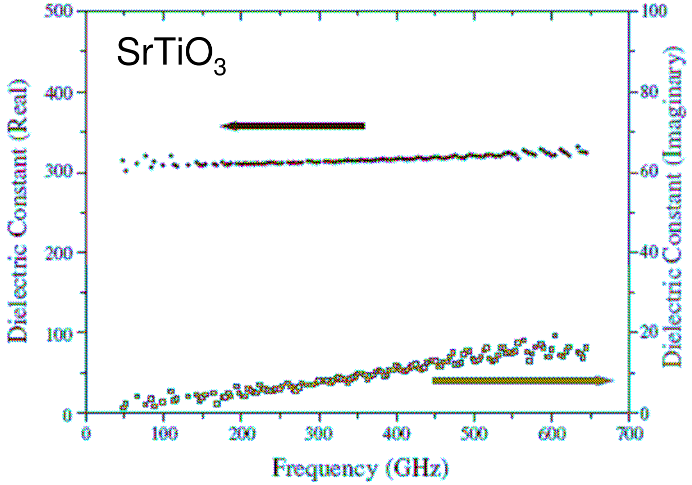
FIG. 3. Comparison of the terahertz emission images and waveforms between a normal chip and a defective one: [(a) and (b)] the terahertz emission images from the normal chip and the defective one, respectively. White and black areas show positive and negative amplitude of terahertz emissions from *p-n* junctions surrounded by four electrode pads each. The white arrows indicate three damaged MOSFET circuits in the defective chip; [(c) and (d)] the terahertz emission waveforms from the normal chip and the defective one, respectively.

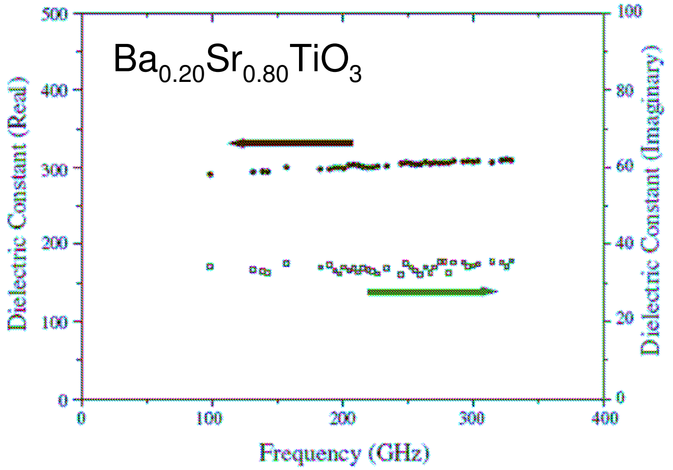
Ceramics and Glasses

- Characterisation
- Relationship with material properties

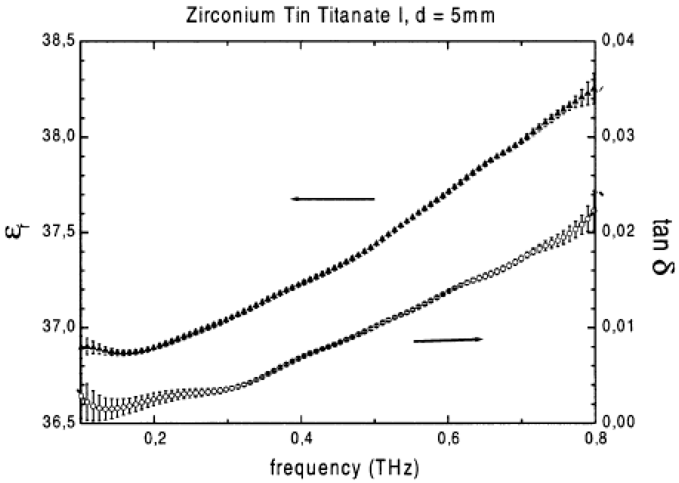
High dielectric constant ceramics

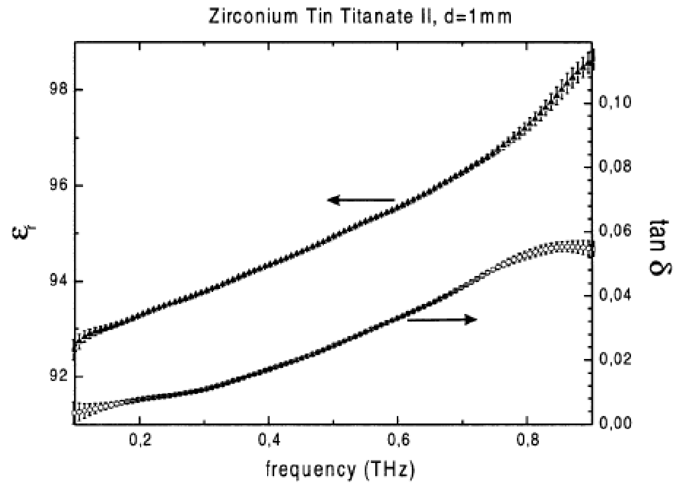
T Fuji et al, Jap. J. Appl. Phys. **43**/9B (2004) 6765–6768



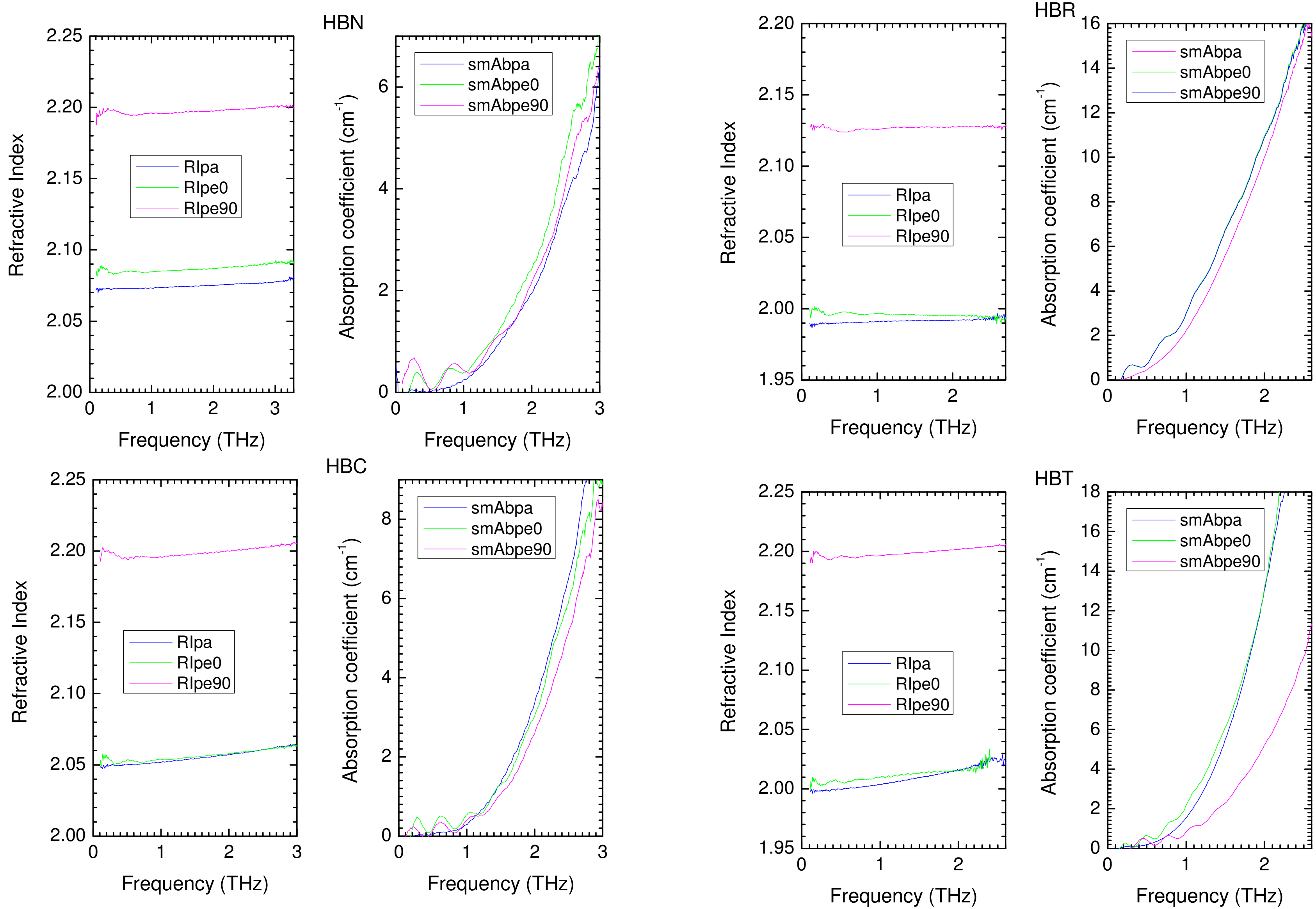


PH Bolivar, IEEE Trans. MTT **51**/4 (2003), 1062-1066

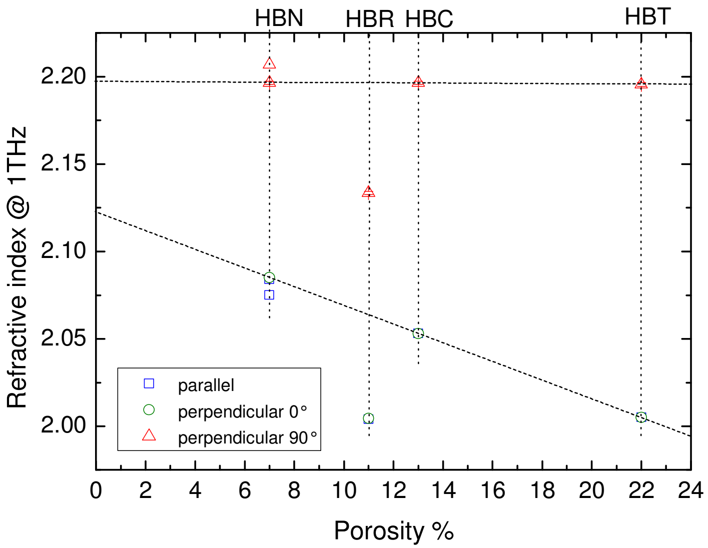




Different grades of Boron Nitride

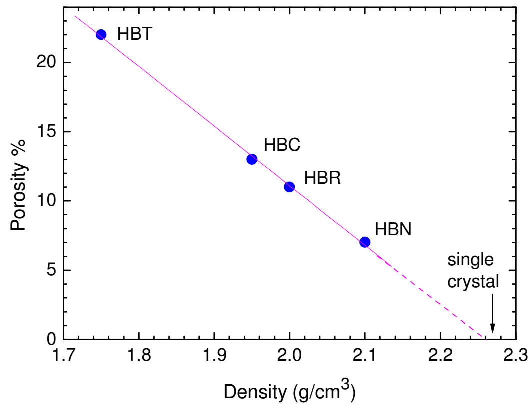


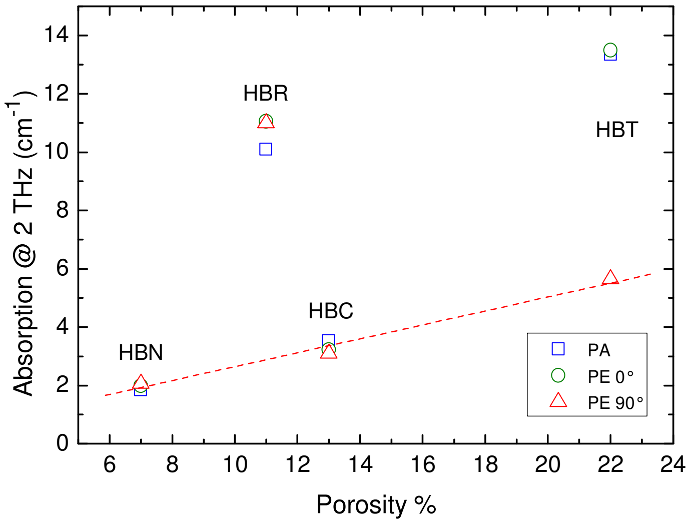
Relationship with Boron Nitride properties



Boron Nitride (BN) is birefrigent and dichroic

Crystals are oriented along the pressing axis





n_o decreases with porosity
n_e remains constant

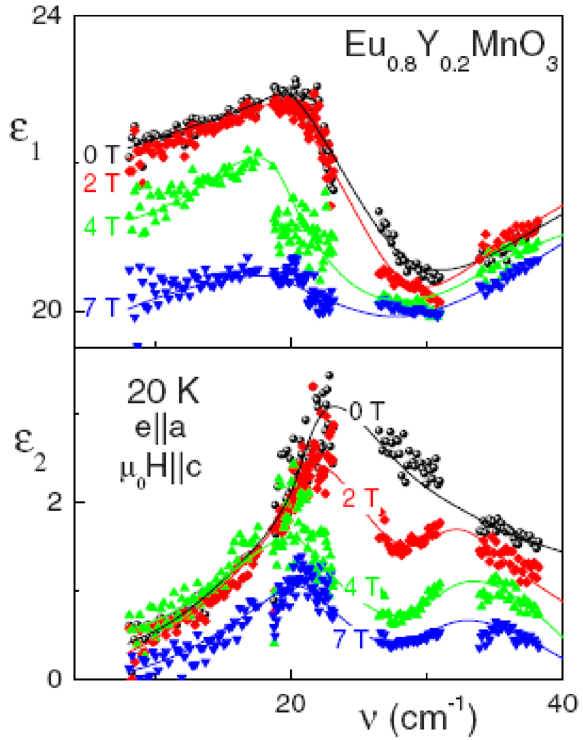
O-ray absorption increases faster than E-ray

Conclusion: porosity between platelets is anisotropic, oriented along the O-axis

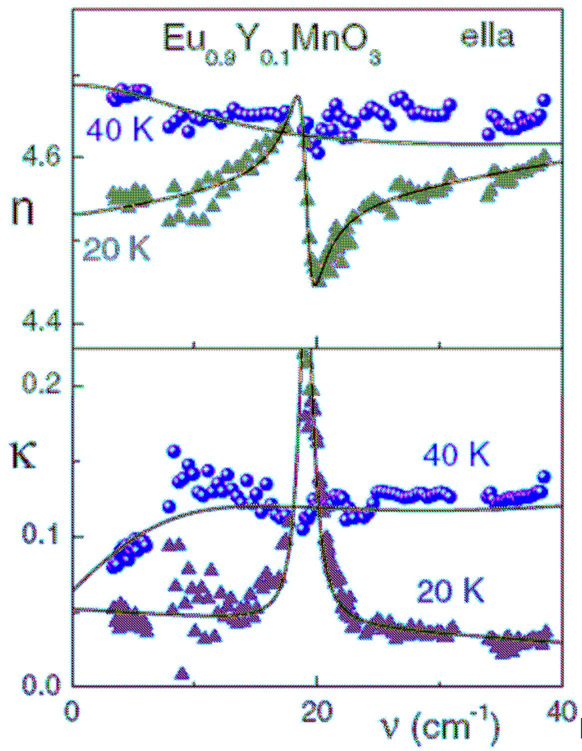
NPL National Physical Laboratory

Magnetoelectric contributions to the permittivity of $Eu_{1-x}Y_xMnO_3$

A. Pimenov et al., Phys. Rev. B **77**, 014438 2008

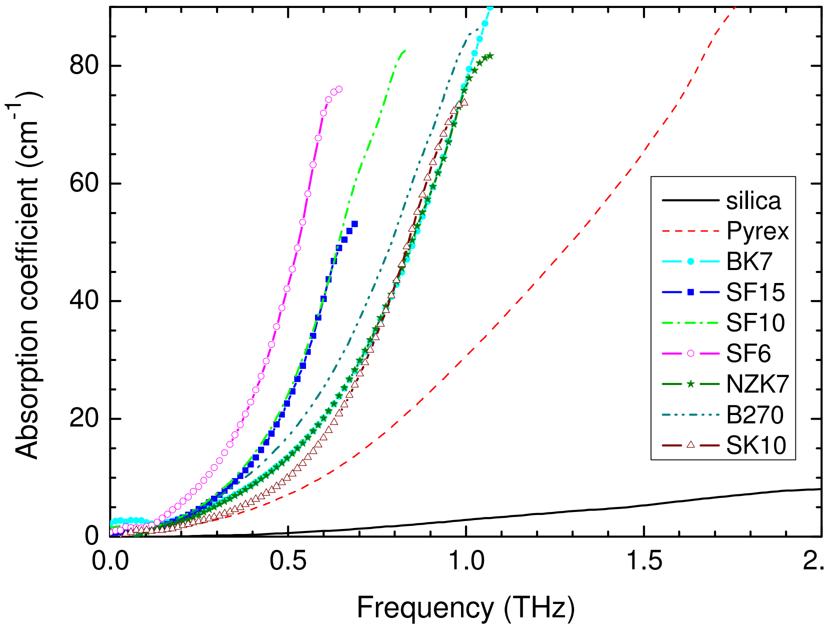


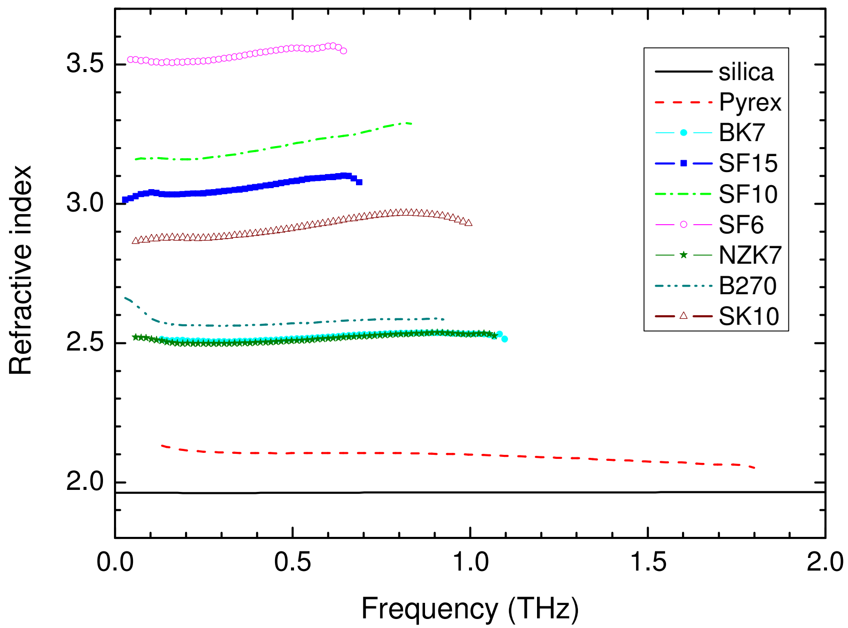
Magnetoelectric effect



Antiferromagnetic resonance

Silicate glasses (Schott)

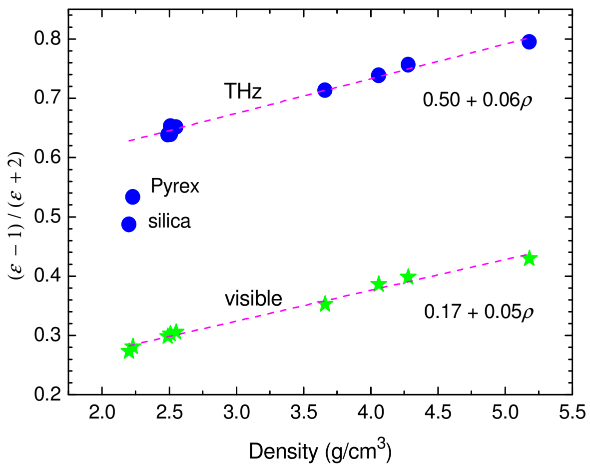


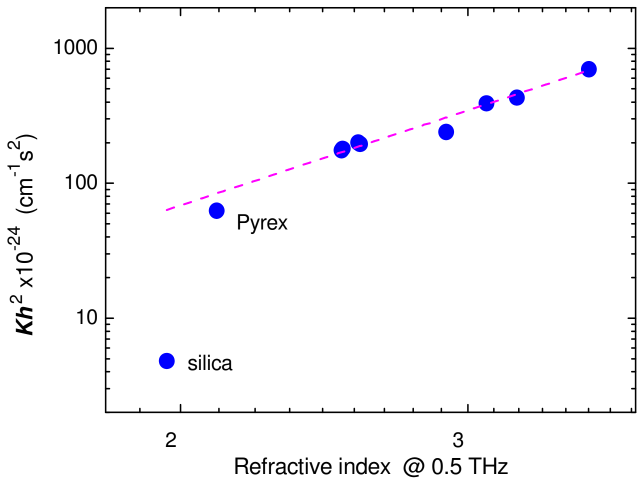


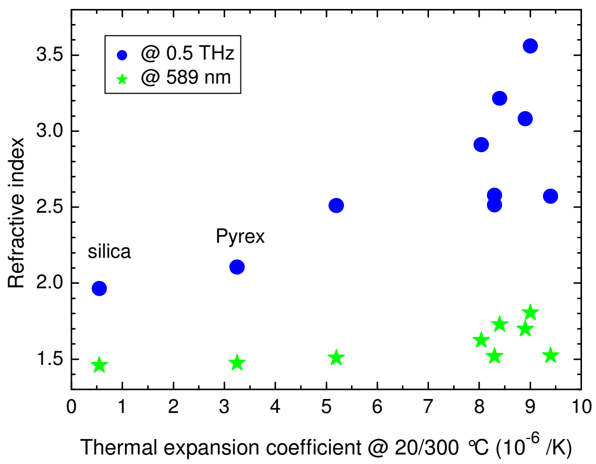
NPL National Physical Laboratory

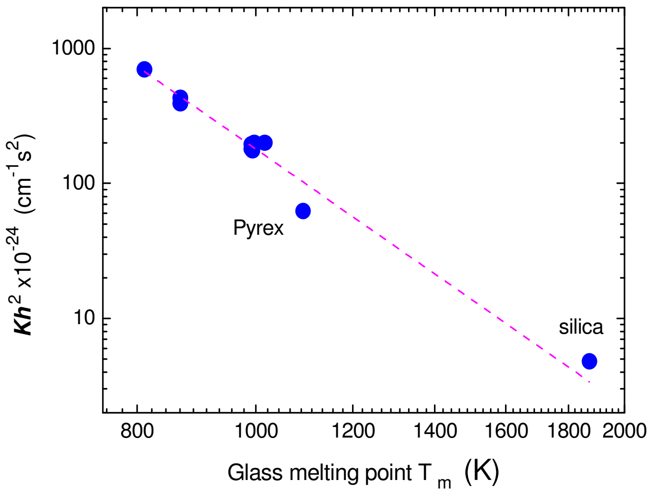
Silicate glasses

relationship with material properties









Liquid Crystals

- Dielectric properties
- Conductivity
- Mixtures and colloids

Liquid crystal colloid with SiO_2

40-n-pentyl-4-cyanobiphenyl (5CB)

M Ohe et al, Mol. Cryst. Liq. Cryst., **480**, 21–28 (2008)

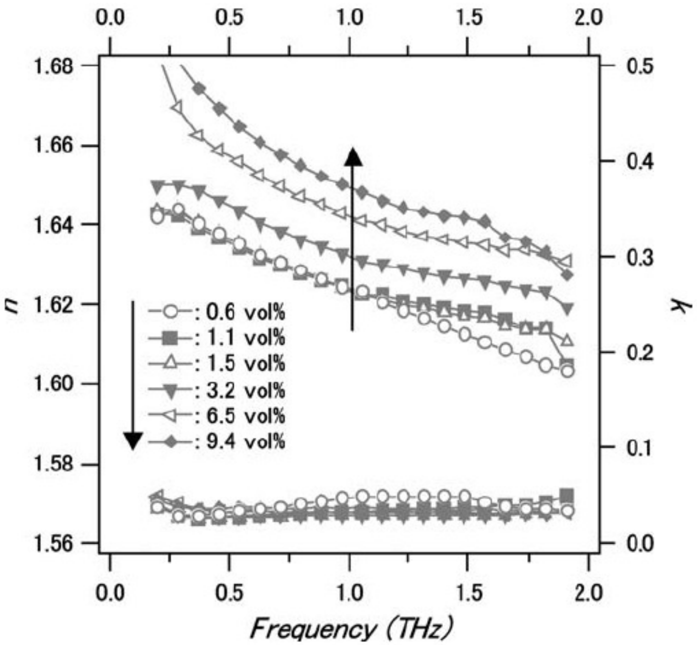


FIGURE 1 THz frequency dependence of the refractive index $n(f)$ and the absorption coefficient $k(f)$ as a function of SiO_2 particle volume fraction.

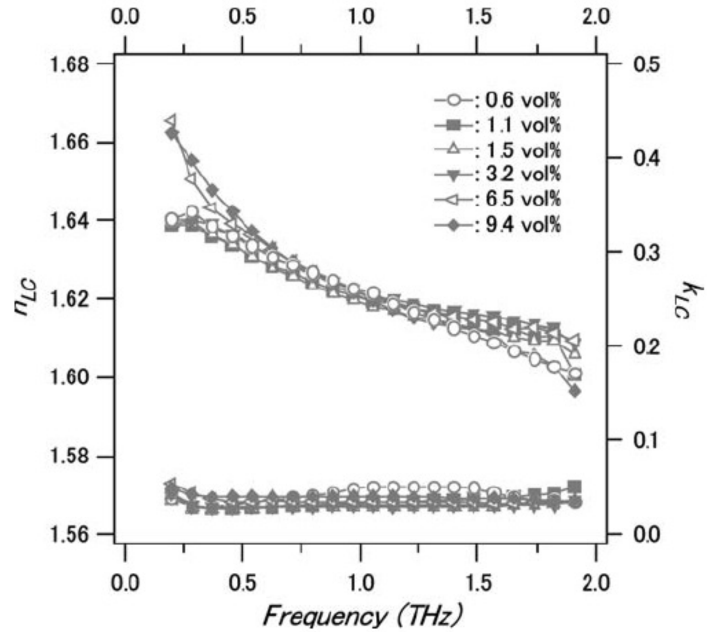


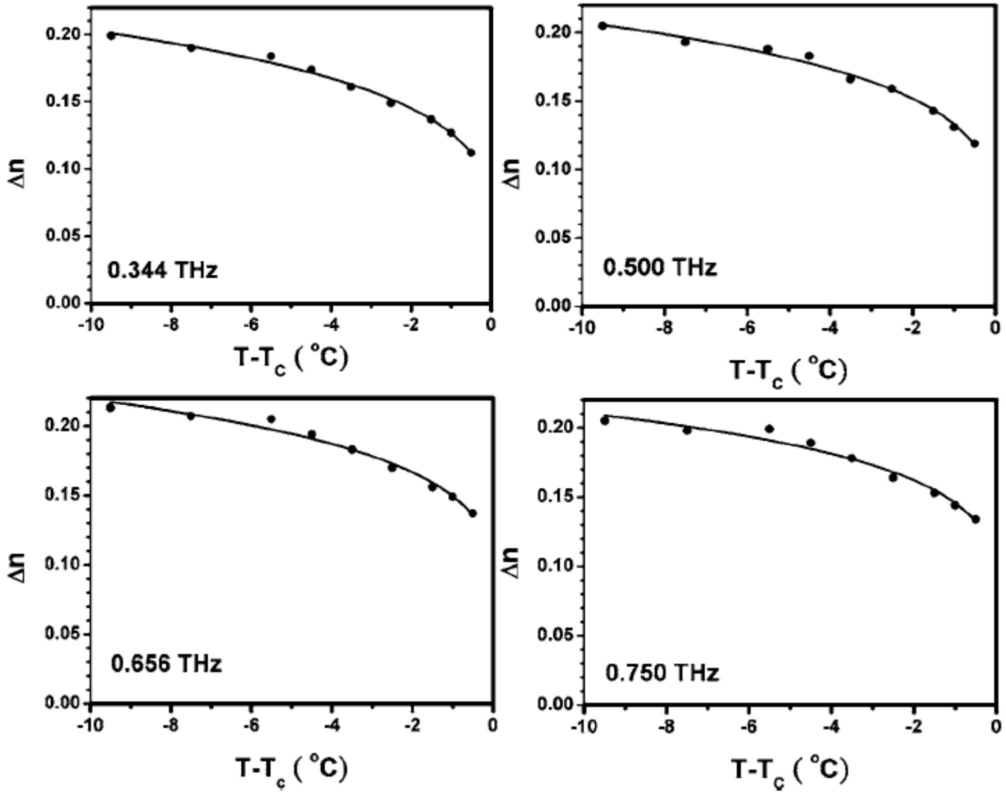
FIGURE 3 THz frequency dependence of the refractive index $n_{LC}(f)$ and the absorption coefficient $k_{LC}(f)$ extracted using effective medium theory as a function of SiO_2 particle volume fraction.

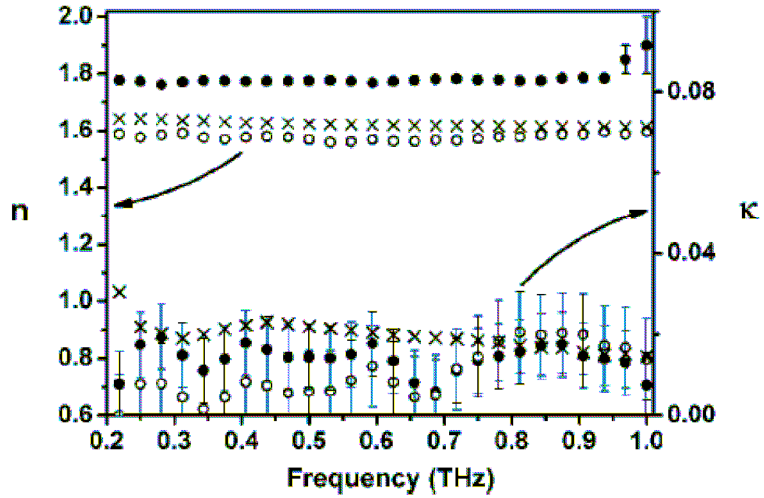
National Physical Laboratory

Temperature-dependent optical properties

40-n-pentyl-4-cyanobiphenyl (5CB)

RP Pan et al, J. Appl. Phys. **103**, 093523 (2008)

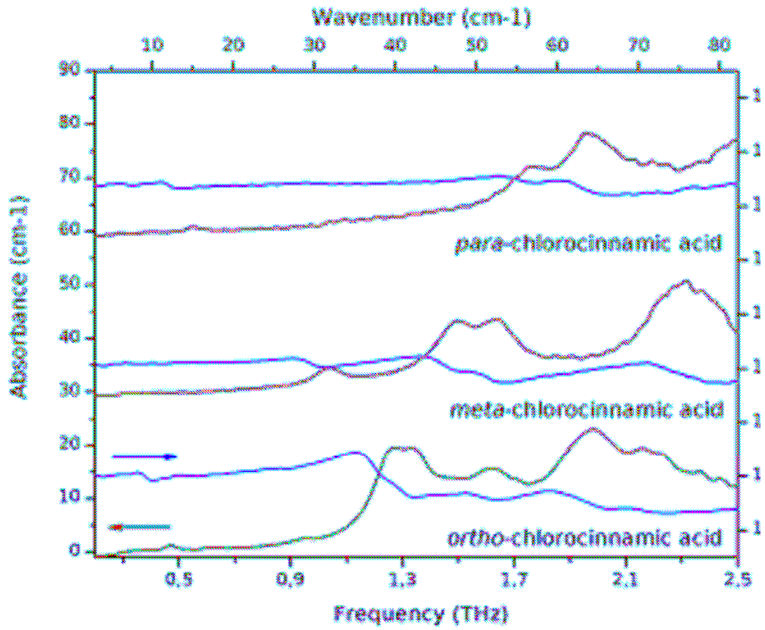


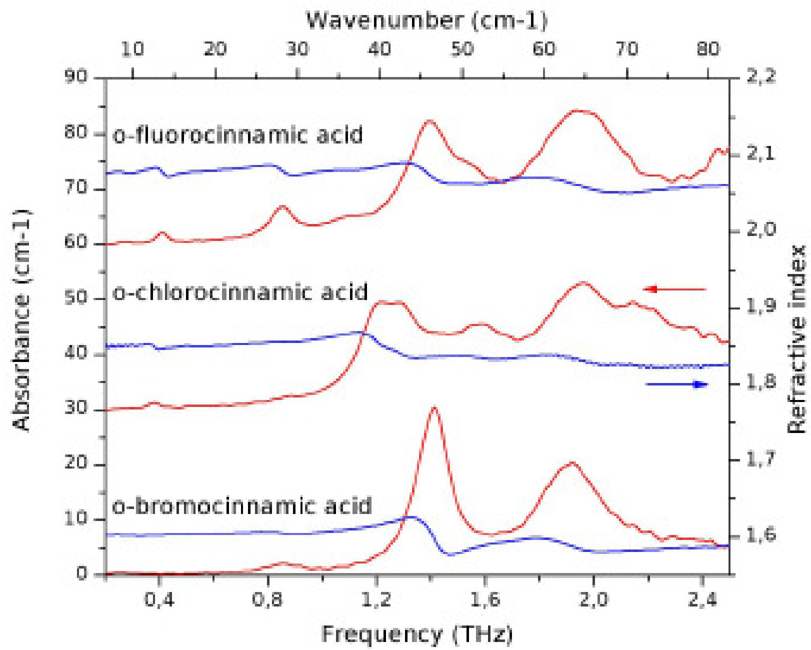


Differentiating polymorphs of organic molecules

Polymorphs of acids

P. Fromentin et al, 978-1-4244-2120-6/08/$25.00 ©IEEE.





National Physical Laboratory

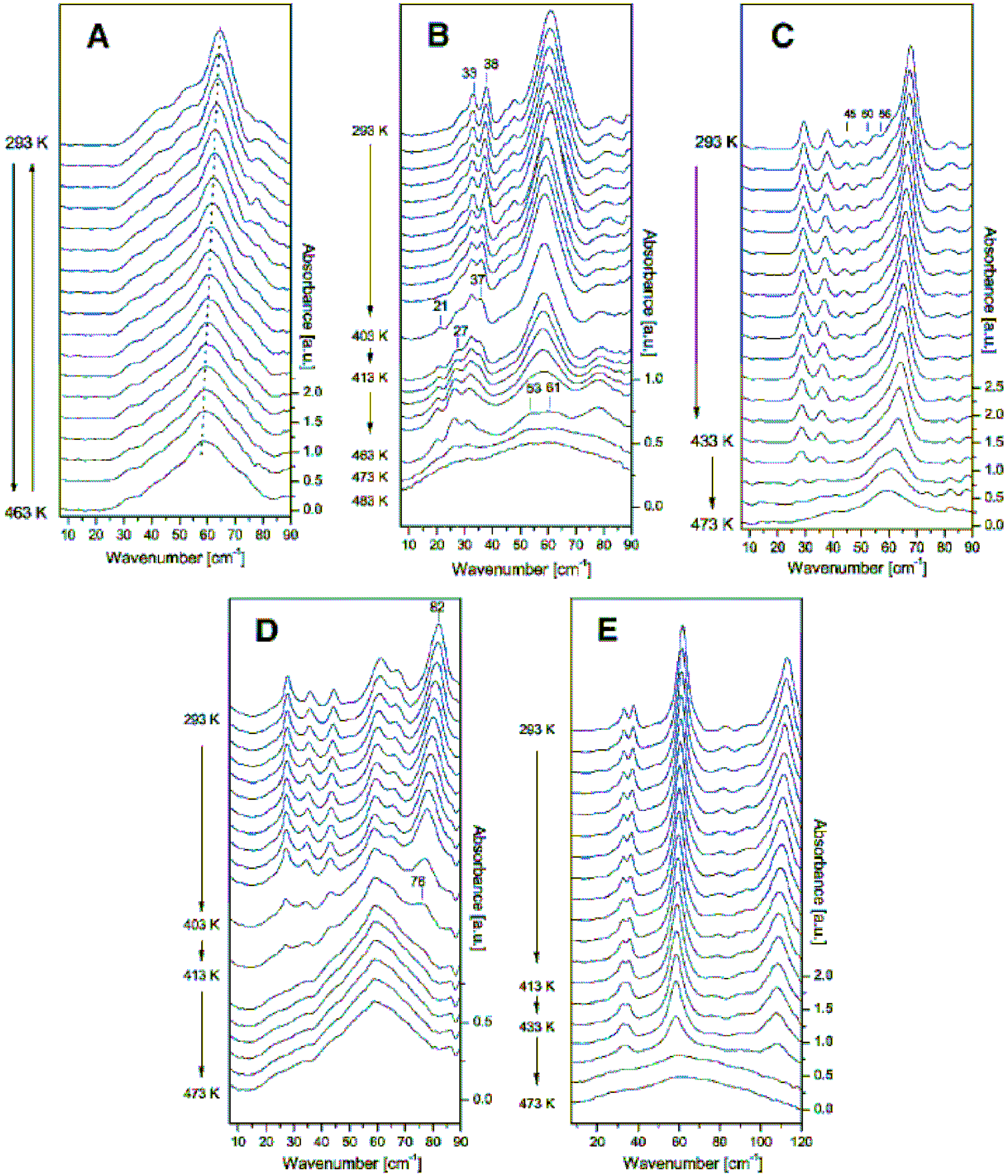


Figure 8. Sulfathiazole forms I, II, III, IV, and V. (A) Form I heating from 293 to 463 K and subsequent cooling back to room temperature. Heating from room temperature to 473 K: (B) form II; (C) form III; (D) form IV; and (E) form V.

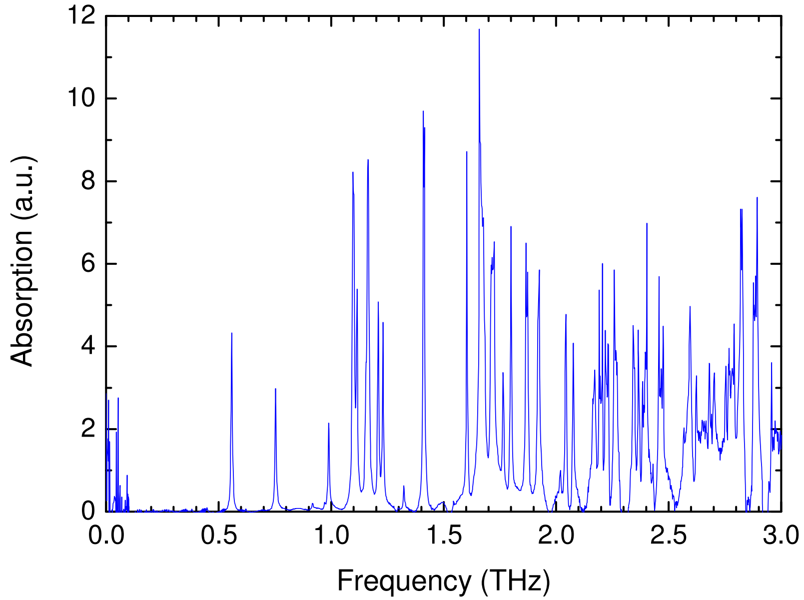
Temperature-Induced Phase Transitions in Polymorphic Forms of Sulfathiazole

JA Zeitler et al, J. Pharm.Sci. **95/**11 (2006) 2486-2498

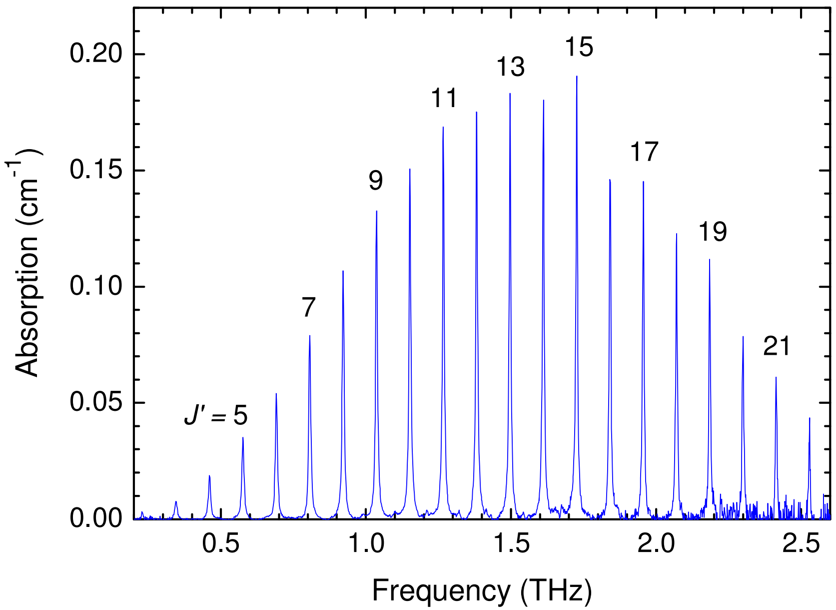
National Physical Laboratory

Gas Spectroscopy

Gas absorption spectra



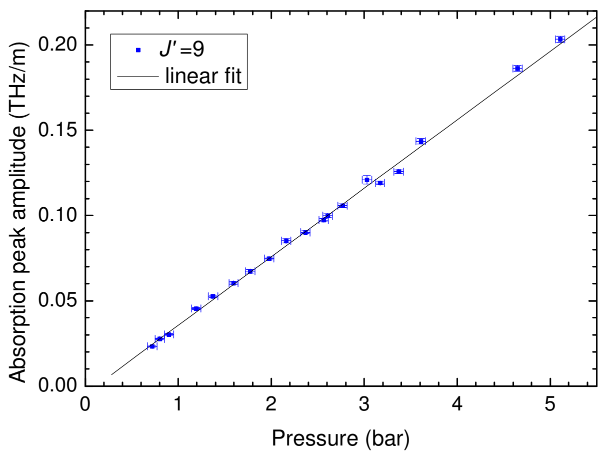
Water vapour

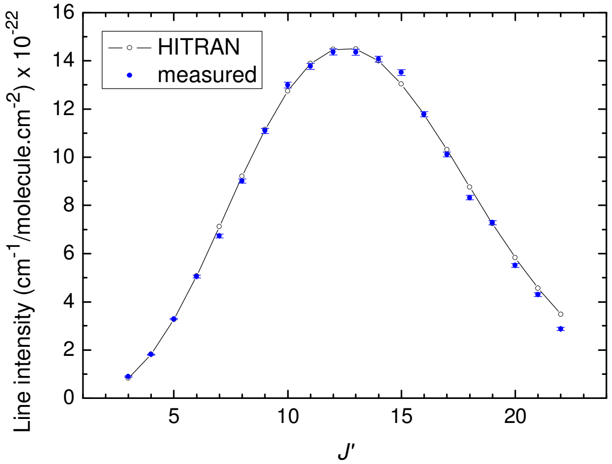


Carbon monoxide

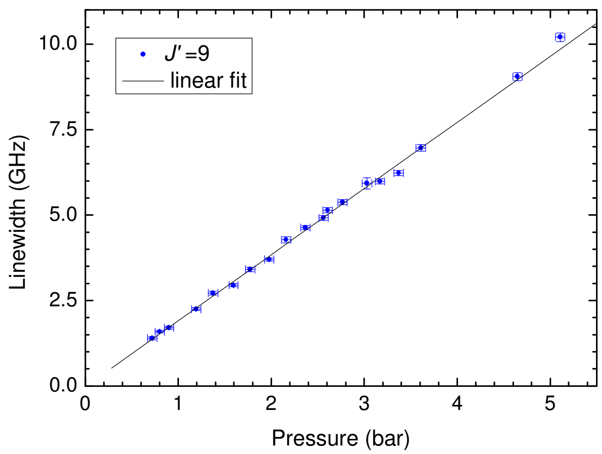
THz TDS is not suitable for high-resolution gas spectroscopy, due to its low resolution compared with other techniques.

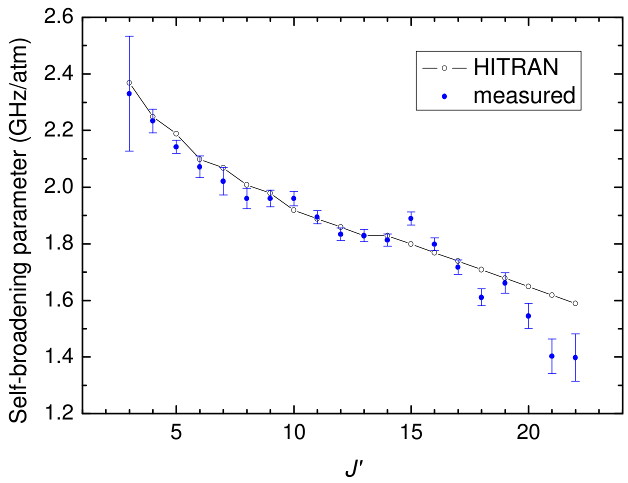
Linestrengths and self-broadening parameters of carbon monoxide





linestrengths



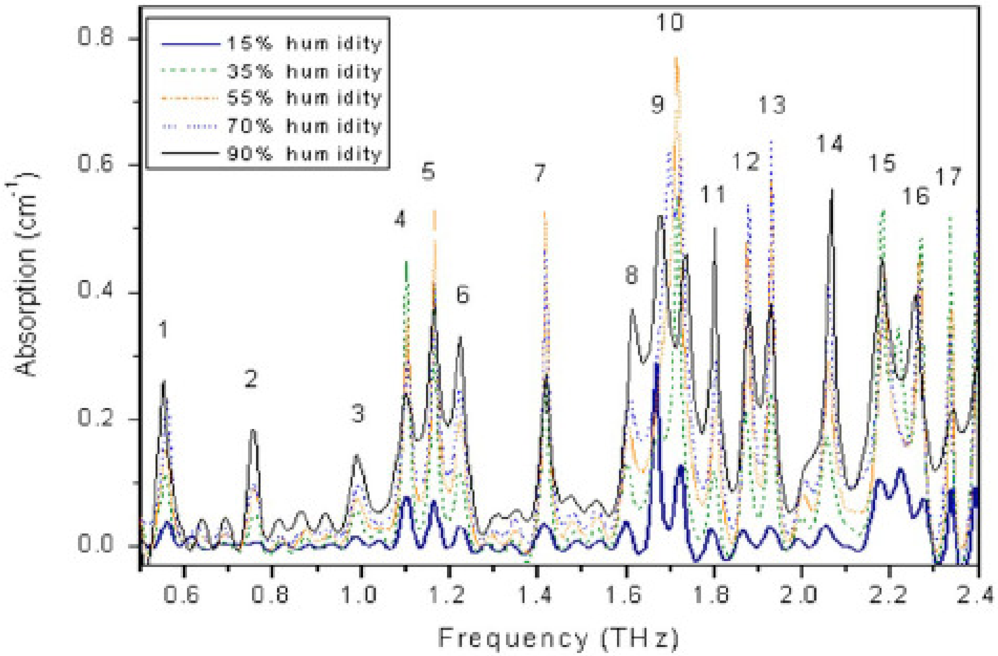


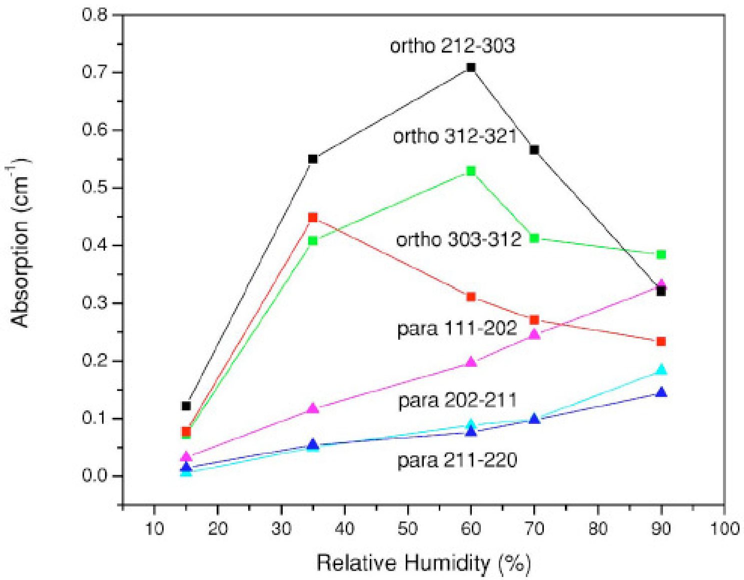
self-broadening parameters

ıal Physical Laboratory

THz absorption of *para* and *ortho* vapours at different humidities

X. Xin et al, J. Appl. Phys. **100**, 094905 (2006)



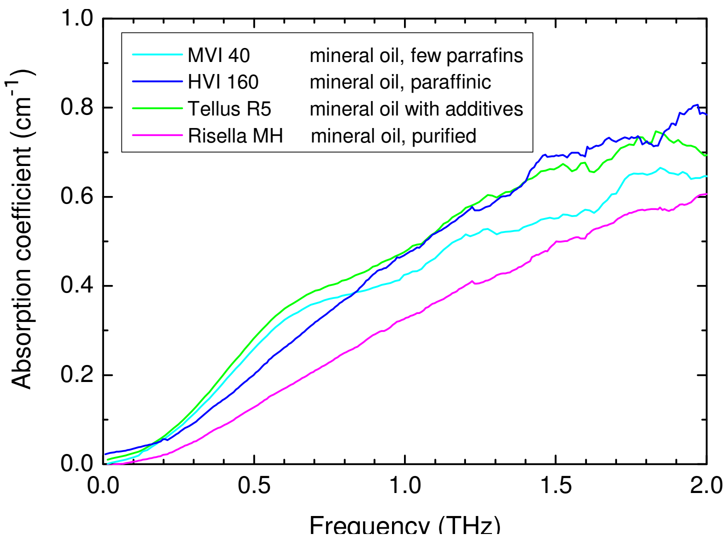


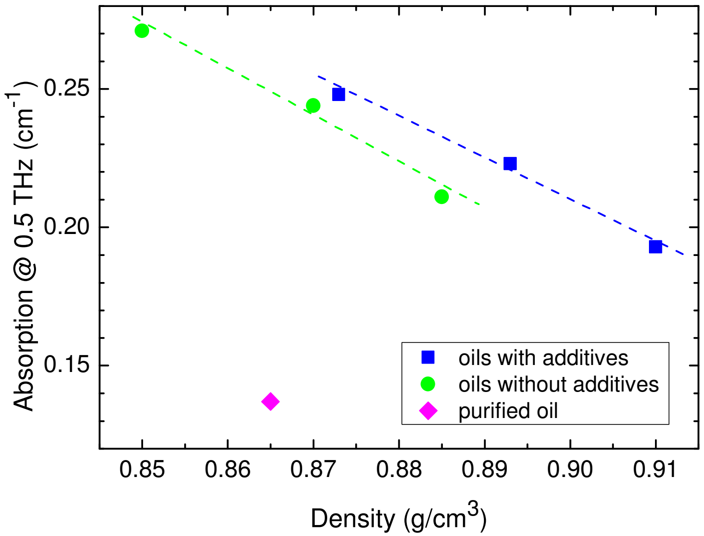
212→303: 79.496 cm^{-1}
312 →321: 173.365 cm^{-1}
303 →312: 136.76 cm^{-1}
111 →202: 37.137 cm^{-1}
202 →211: 70.091 cm^{-1}
211 →220: 95.176 cm^{-1}

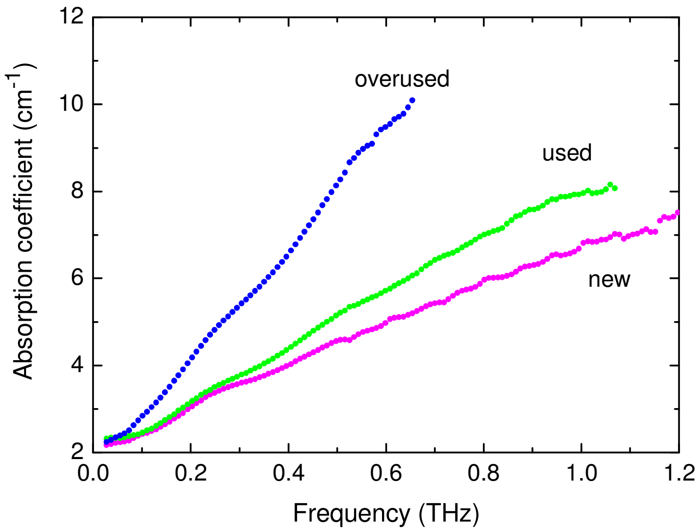
Oils

- Characterising oils
- Relationship with oil properties
- Identifying oil additives
- Observing oil degradation/contamination

Shell Oils







Degradation of engine oil

National Physical Laboratory

Oil properties

D Mittleman et al, Am. Chem. Soc. Petroleum Research 48172-AC6

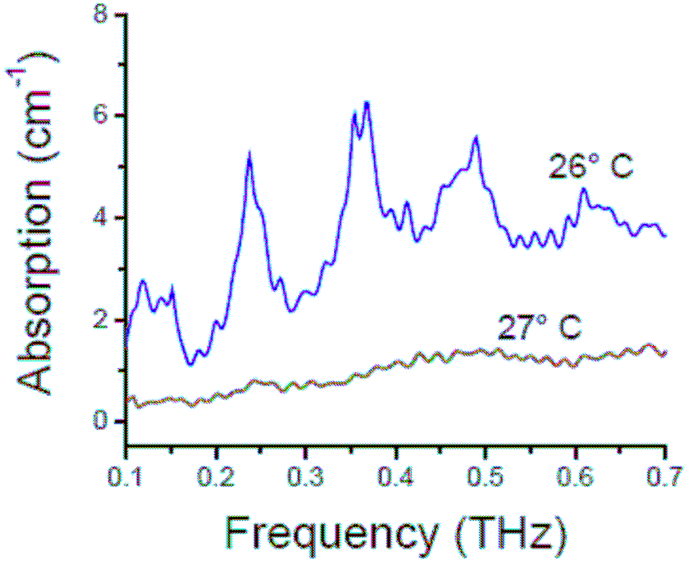


Figure 1 Absorption spectrum of liquid (red) and crystalline (blue) samples of *n*-octadecane. The spectrum of the crystal shows evidence of inter-molecular vibrational modes at 0.24 THz, 0.36 THz, and 0.48 THz. The molecular origin of these infrared-active modes is not known.

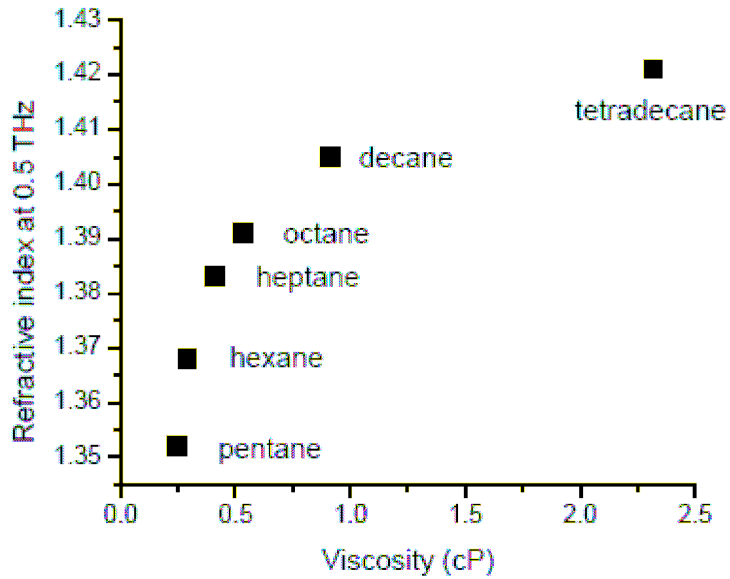


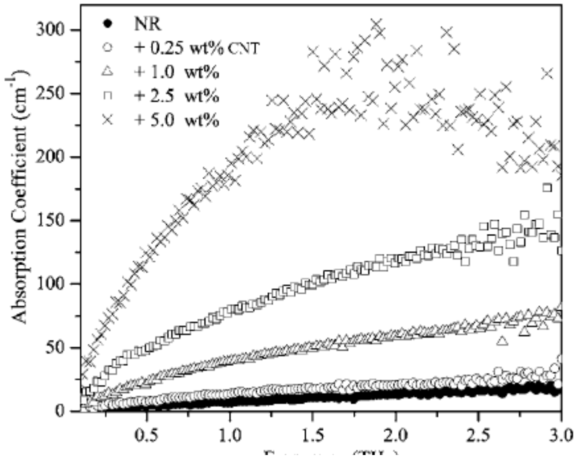
Figure 3 Refractive index of various *n*-alkanes at a frequency of 0.5 THz, as a function of viscosity at room temperature. Viscosity values taken from [46].

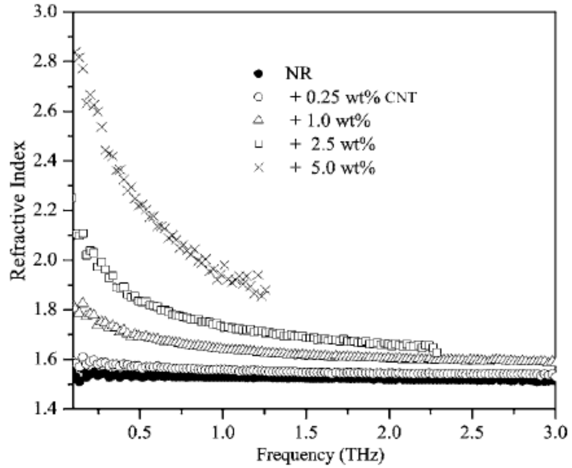
NPL National Physical Laboratory

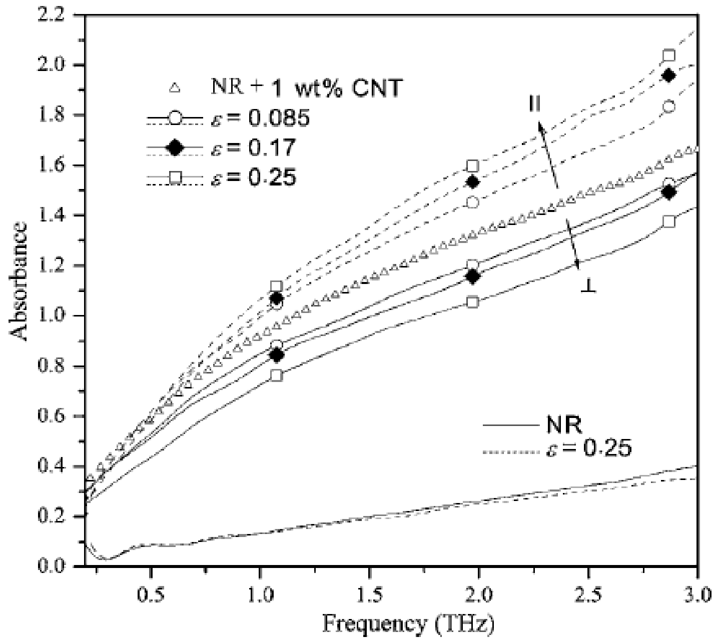
Composites

Carbon nanotubes embedded in deformable rubber

R. Rungsawang et al., J Appl. Phys. **103**, 123503 (2008)







Strain causes alignment of CNTs

National Physical Laboratory

Nondestructive testing
of fibreglass aircraft composites

CD Stoik et al, Opt. Express, **16**/21 (2008) 17039

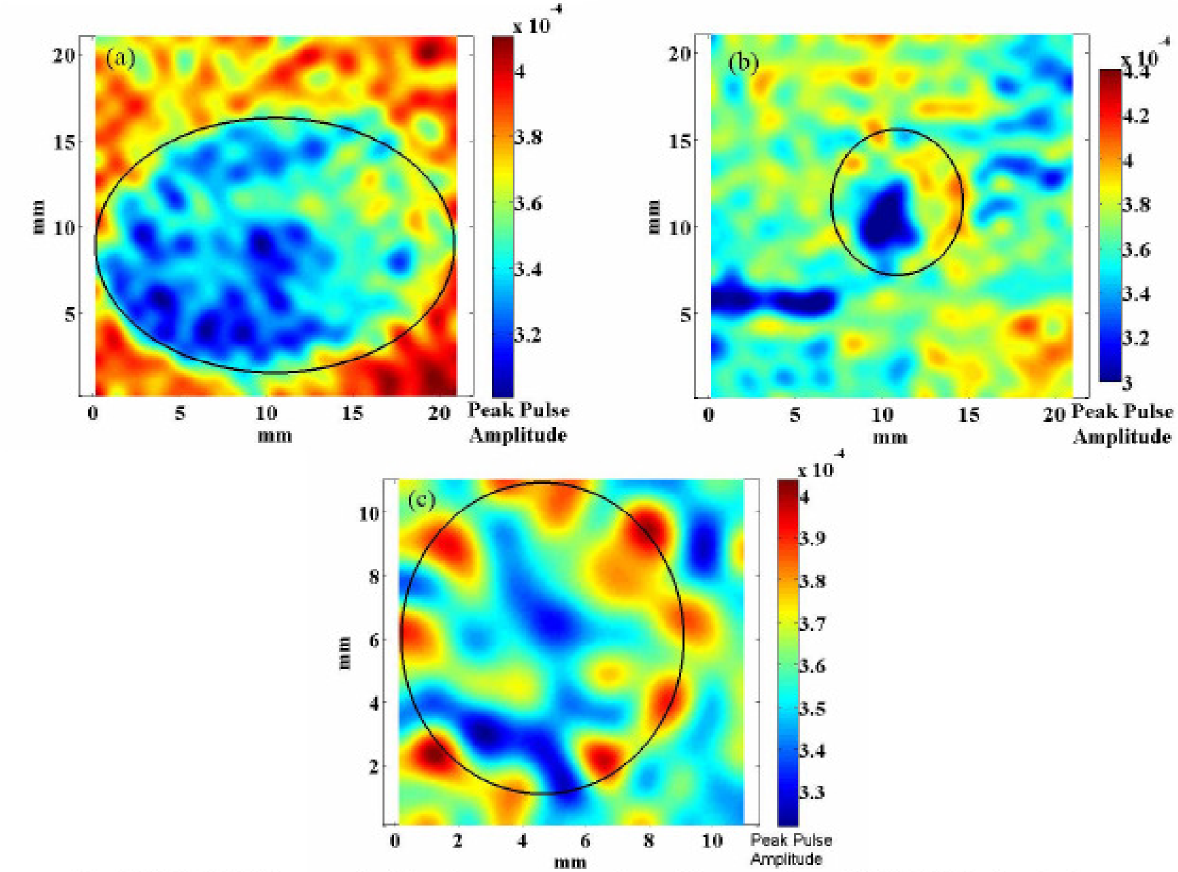


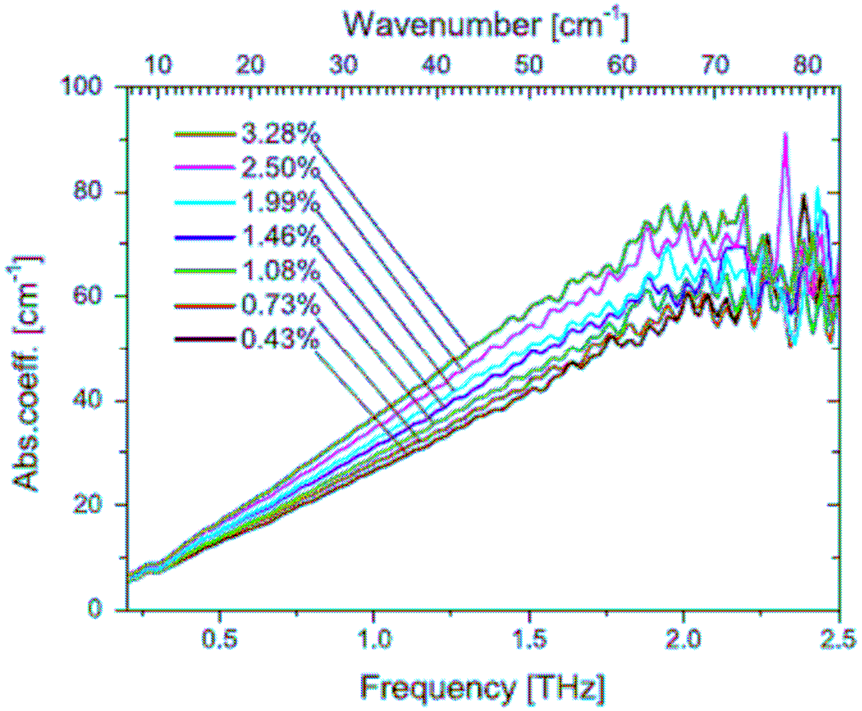
Fig. 8. THz TDS images for three burn areas on glass fiber samples: (a) 440°C for 4 minutes, (b) 430°C for 6 minutes, and (c) 425°C for 20 minutes.

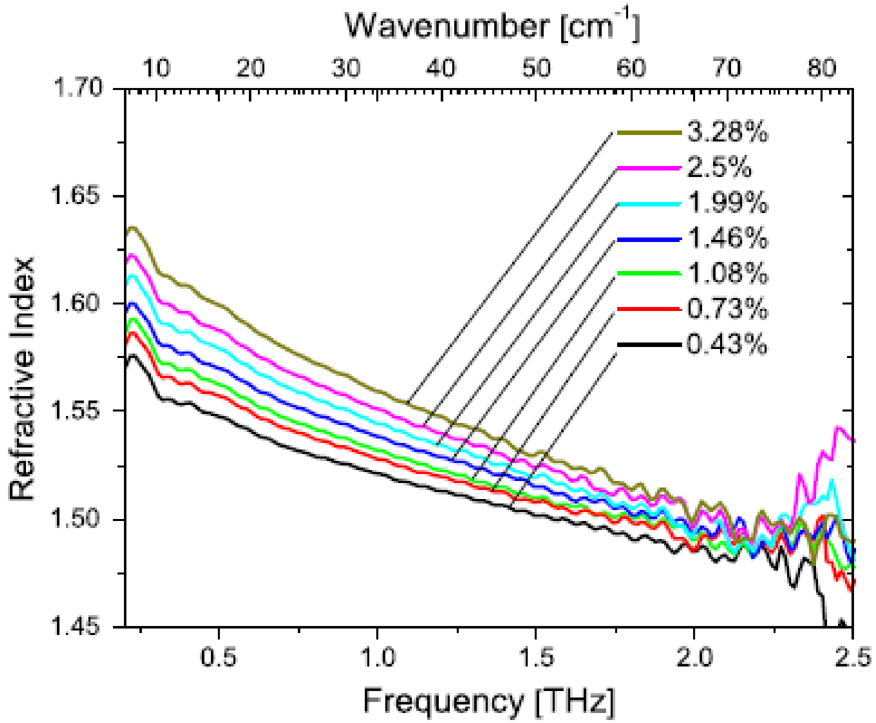
Moisture content of materials

Oil-water complexes of lubricating oils

measuring the water content

S. Gorenflo et al, Chem. Phys. Lett. **421** (2006) 494–498

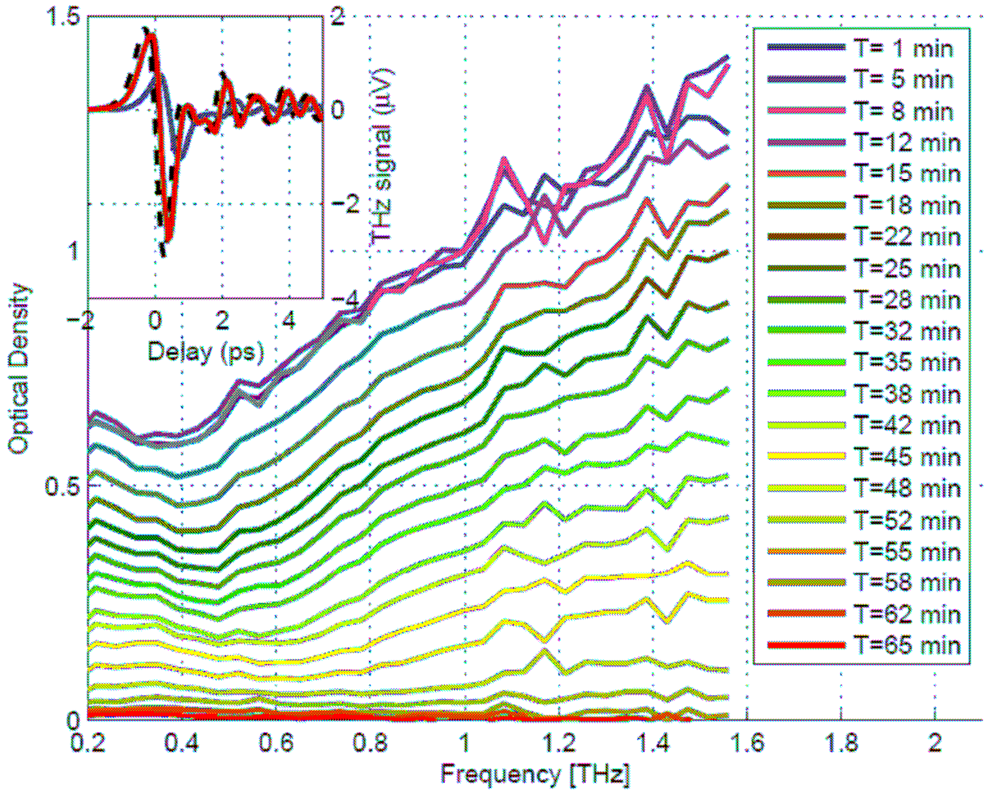


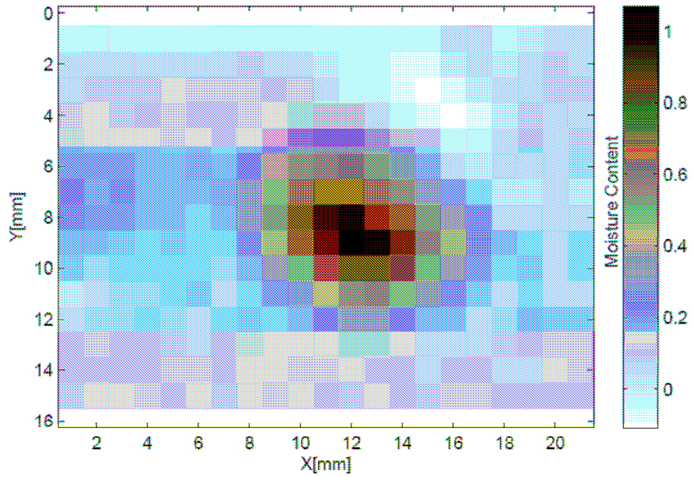


NPL National Physical Laboratory

Moisture content of paper

D. Banerjee et al, Opt. Express, **16**/12 (2008) 9060





Measuring the thickness and moisture content of paper

P. Mousavi et al, Appl. Opt. **48**/33 (2009) 6541-6546

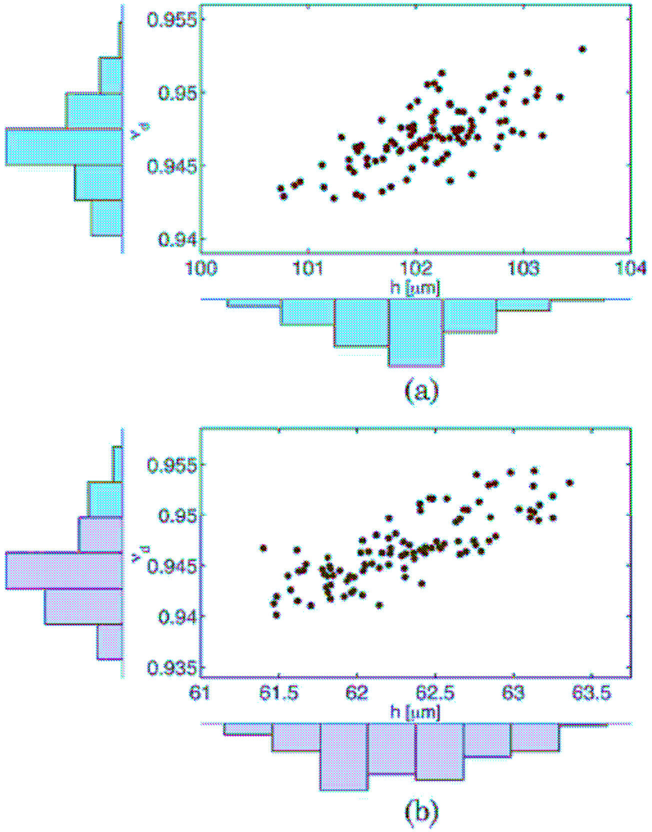


Fig. 3. (Color online) Experimental scatter plots or ν_d and h resulting from repeated THz measurements on the same spot on a sample for (a) photocopy paper and (b) fine paper.

Table 2. Paper Parameters Measured Using THz and by Independent Methods [a]

	THz		Independent	
	h (μm)	M(%)	h (μm)	M(%)
Photocopy	102.12 ± 0.58	6.04 ± 0.25	102.0	5.91
Fine	62.30 ± 0.49	5.47 ± 0.35	62.6	6.44

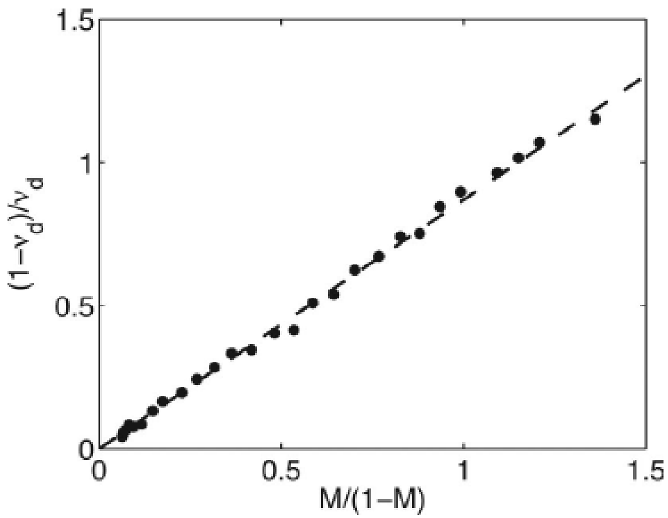
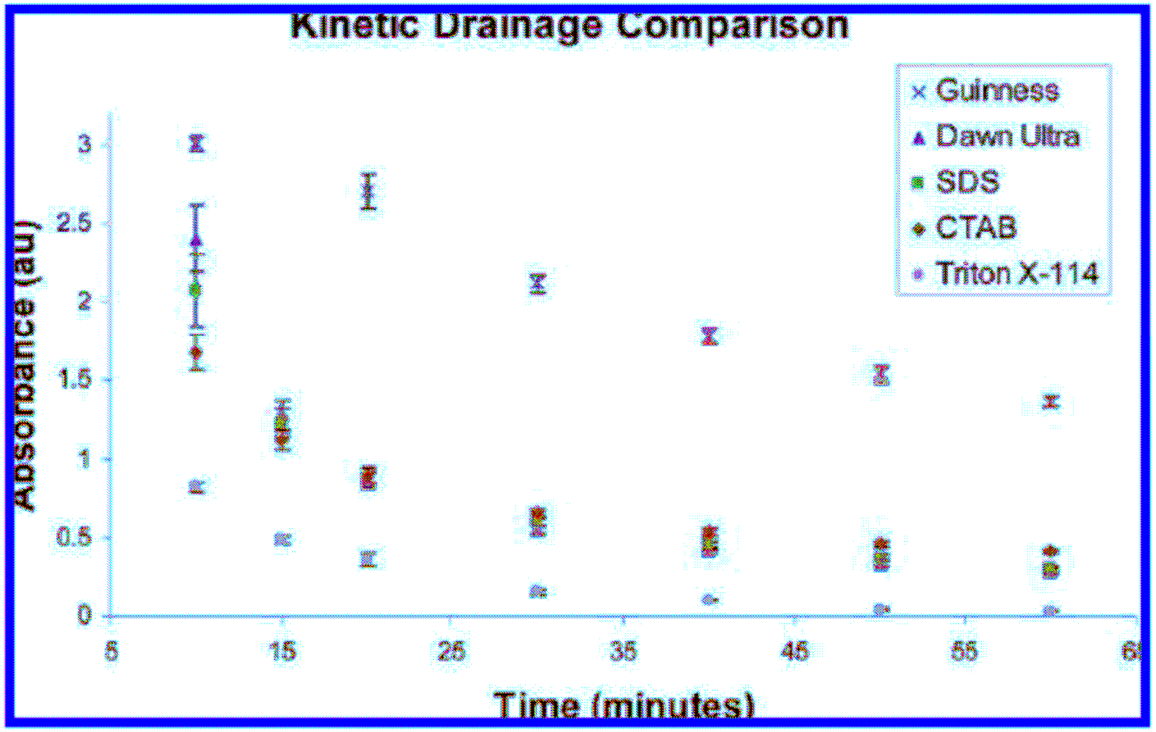


Fig. 2. Calibration of ρ_d/ρ_w. Measurements of moisture fraction M determined by weight are plotted against $\nu_d/(1-\nu_d)$ determined from THz measurements (•), together with the fit to Eq. (6) with $\rho_d/\rho_w = 0.87$ (dashed line).

Observing aqueous foam drainage

J. Heuser et al, *Langmuir* **2008,** *24,* 11414-11421



sodium dodecyl sulfate (SDS)
- anionic surfactant

(CTAB) cetyl trimethylammoniumbromide
– cationic surfactant

Triton X-114
- nonionic surfactant

Ultra Dawn dish soap
- mixed surfactants

Guinness beer
- protein surfactant solution

Conclusion

THz spectroscopy can be applied
in many and varied
areas of research

Think what it can do for you

For more information:
http://www.npl.co.uk/electromagnetics/terahertz/

☺