Dielectrics Newsletter
Scientific newsletter for dielectric spectroscopy
Issue september 1996

Gabby Bitton, Aharon J. Agranat and Yuri Feldman

The Dielectric Properties of a New Electrooptic Material

Introduction

Potassium Litium Tantalate Niobate ($K_{1-x}L_xT_{1-y}N_yO_3$) is a new electrooptic crystal that was found to posses very attractive properties as the storage material in volume holography memory devices [1]. In particular when operated in the paraelectric phase, slightly above the phase transition temperature, KLTN enables large storage capacity, hologram fixing, and an efficient use of the voltage controlled photorefractive effect. These unique properties are strongly related to the phase transition mechanism and relaxation processes in this crystal. It is known that in similar crystals, such as KLT[2] and KTN[3], the phase transition and relaxation processes are governed by the concentration of the impurities that form this crystals. An into insight to the mechanisms involved in the electrooptic and photorefractive effects near the phase transition can be achieved by dielectric spectroscopy.

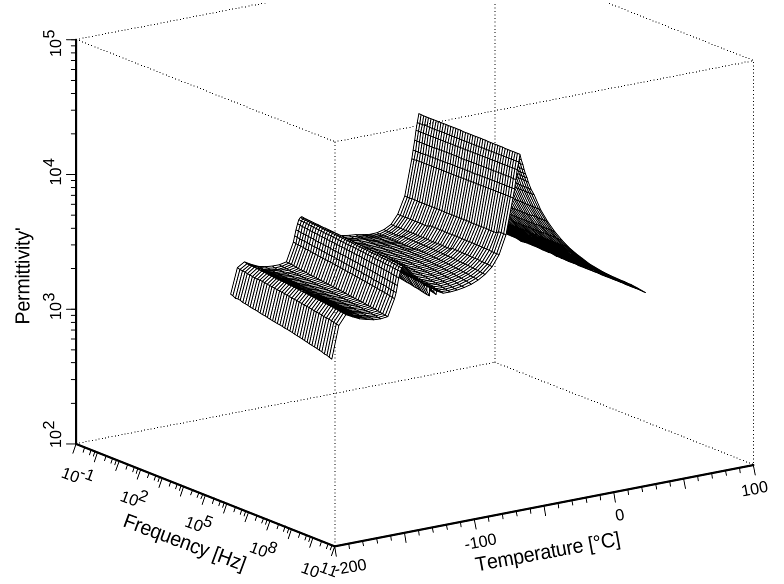


Fig. 1a The real part of the dielectric function versus temperature and frequency for low frequency.

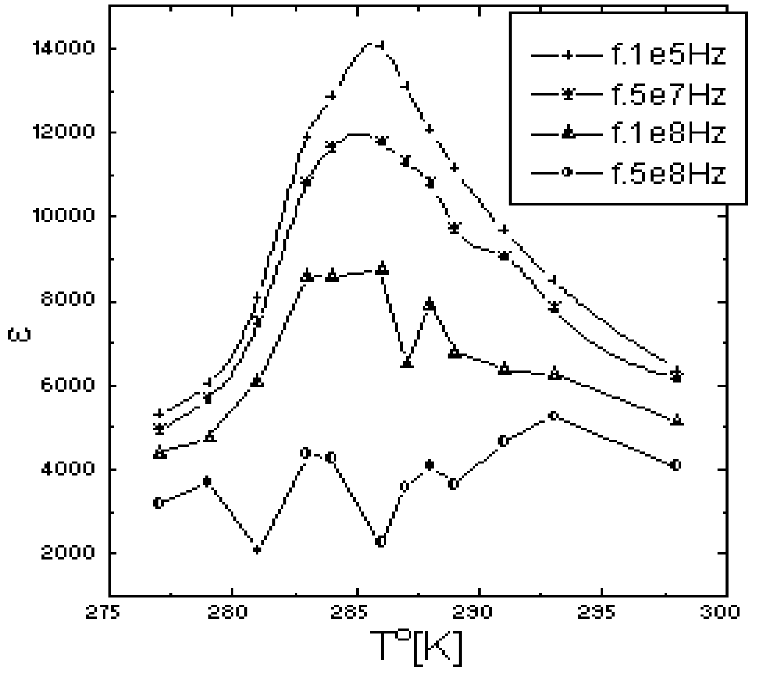


Fig. 1b The real part of the dielectric function versus temperature and frequency for high frequency.

Experimental Technique

The complex dielectric permittivity $\varepsilon^*(\omega)$ was measured in a wide frequency range (20 Hz - 10 GHz) by two different systems: 1. Broad Band Dielectric Spectrometer (BDS 4284) from NOVOCONTROL (20 Hz -1 MHz) in temperature interval 120-370 K;

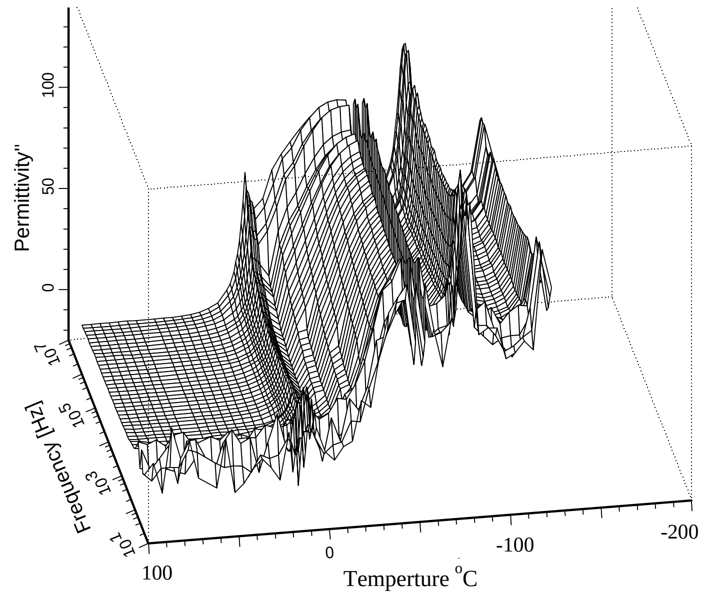


Fig. 2 The Imaginary part of the complex dielectric function Vs. Temperature and frequency.

2. Time Domain Dielectric Spectrometer (TDS-2) from Dipole TDS ltd. (100 KHz - 10 GHz) in temperature interval (273-350 K).

Results and Discussion

The real part of the complex dielectric permittivity $\varepsilon'\omega)$ versus temperature and frequency is shown in Fig.1. The three peaks in Fig.1a correspond to the three transitions: Cubic => Tetragonal => Orthorhombic => Rhombohedral, which were reported in the case of KTN [3]. The attenuation of the high frequency dielectric permittivity around the phase transition (Fig. 1b) indicates that the nature of the transition is order disorder like [Ref. 4 pp.-184].

The imaginary part of the complex dielectric permittivity is shown in Figure 2. Four processes can be seen along the temperature axis. In the case of high temperature process which is centered around the first phase transition (Cubic =>Tetragonal) one can see a an increasing of the dielectric losses curve towards high frequencies. This is correlated with the attenuation of the real part of the dielectric permittvity near phase transition as can be seen in Fig. 1b. The high frequency process is Debye type with the characteristic frequency ν_0=1.9*10^{12} Hz and the energy of activation ΔH=0.187eV. This can be compared to results of KLT, ν_0=6.31*10^{11} Hz and Δ H=0.086 eV [2]. The relaxation mechinsim can be related to Li ion hoping in an 8-fold potential well.

References

[1] A.J. Agranat, R.Hofmeister and A.Yariv Opt.Lett. 17, 713 (1992).

[2] G.A.Smolenskii, A.V.Sotnikov, P.P.Syrnikov, N.K.Yushin Bull.Acad.Sci.Ussr Phys.Ser 49 (1985) 33.

[3] C.M.Perty, R.R.Hayes and N.E.Torenberg In proceeding of the international conference on light scattering in solids, Ed.M.Balkansky (Wiely, New York, 1975) p.812.

[4] R.Blinc and B.Zaks “Soft modes in ferroelectric and Antiferroelectric” Ed. E.P.Wohlarth (North Holland, 1974)

Gabby Bitton, Dr. Aharon J. Agranat and Dr. Yuri Feldman
Department of Applied Physics,
The Hebrew University of Jerusalem.
Jerusalem 91904, Israel

Friedrich Kremer

The Dielectric Properties of Proteins

Protein molecules consist of peptide chains with amino acid residues in the side groups. Due to their partly polar character several relaxation processes are observed which are well separated in frequency and which are assigned to local fluctuations of single polar groups and the fluctuation of the protein as a whole [1-3]. While the local processes are observed on a picosecond time scale corresponding to mm-wave frequencies, the relaxation of the protein is observed at much lower frequencies in the kHz and MHz range. Proteins are often obtained as an aqueous solution. This gives rise to two additional relaxation processes being assigned to free and bound water (Fig. 1). Furthermore, due to the polar character of many protein constituents a pronounced conductivity contribution is observed [2] which is caused by a hopping conduction.

The relaxation times of globular proteins lie between 10^{-8} s and 10^{-6} s. Particularly for small proteins (myoglobin, ribonuclease, β-lacto-globulin, egg albumin, insulin, haemoglobin, γ-pseudo-globin) a linear proportionality between relaxation time and cube of molecular weights is found (Fig. 5.18 in [3]). It is noteworth that intermolecular and solvent-solute interactions do not play any significant role for the orientational relaxation. Proteins can contain considerable amounts of bound water which is adsorbed to the hydrophilic moieties inside and outside of the molecule. It causes - depending on the degree of binding

- a relaxation between 10^6 Hz and 10^9 Hz [4,5]. For proteins hydrated to more than 15 weight-% also free water is observed having its strong orientational absorption at ~10 Ghz.

Above 30 GHz (i.e. in the millimeter wave regime) one finds an absorption which increases nearly exponentially with temperature and as $\nu \ldots \nu^2$ with frequency ν (Fig. 2). This frequency and temperature dependence is described by picosecond relaxation processes in asymmetric double well potentials [5,6]. Molecularly these relaxations are assigned to fluctuations of the NH...OC hydrogen bonds of the peptide backbone. The contribution of adsorbed water can be easily distinguished from the intrinsic relaxations (relaxations 1 to 3 in Fig. 2) because of its different frequency-dependence. The intrinsic relaxation processes correspond to fluctuations between structural substrates [7] of the protein [8] and are presumably important for its flexibility.

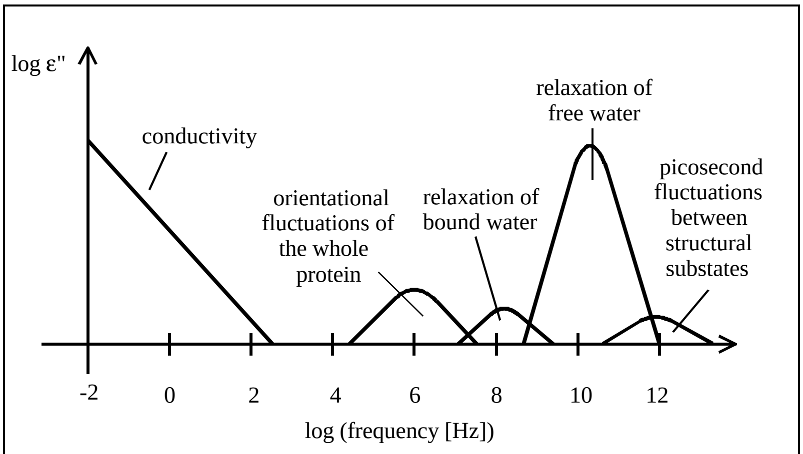


Fig.1 : Scheme of the dielectric spectrum of an aqueous solution of a protein (e.g. haemoglobin, lysozyme).

In conclusion, the dielectric properties (10^{-2} Hz - 10^{11} Hz) of (hydrated) proteins are characterized by the superposition of a conductivity contribution and four dielectric relaxation processes, which are assigned to fluctuations of the protein on a local scale and as a whole and of free and bound water. Narrow spectral features were not observed up till now.

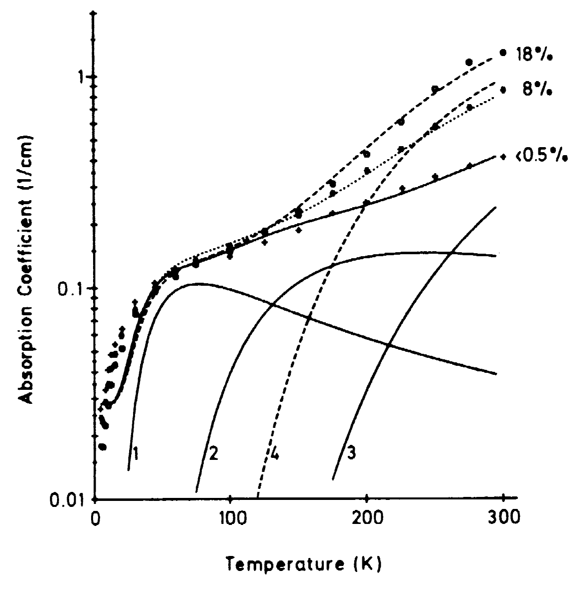


Fig. 2: Absorption coefficient of lysozyme at 50 GHz for three hydration levels. The solid lines correspond to the structural relaxations of the dry protein material (< 0.5 weight-% water content). The dashed lines describes the contribution of bound water at a degeree of 18 weight-% hydration.

References

[1] E. H. Grant, R. Sheppard and G. P. South: Dielectric behaviour of biological molecules in solution, Oxford University Press, London (1978)

[2] R. Pethig: Dielectric and electronic properties of biological materials, John Wiley&Sons, Ltd. (1979)

[3] S. Tokashima: Electrical properties of biopolymers and membranes, IOC Publishers (1989)

[4a] H. P. Schwan: Ann. N.Y. Acad. Sci. **125**, 344 (1965)

[4b] A. Poglitsch, F. Kremer and L. Genzel: J. Mol. Biol. **173**, 137 (1984)

[5] L. Genzel, F. Kremer, A. Poglitsch, and G. Bechtold: Biopolymers **22**, 1725 (1983)

[6] H. Frauenfelder, G. A. Petsko and D. Tsernoglou: Nature **280**, 558 (1979)

[7] J. A. McCammon, B. R. Gelin and M. Karplus: Nature **262**, 325 (1976)

Prof. Dr. Friedrich Kremer
Universität Leipzig, Institut für Physik, Linnéstr. 5, 04103 Leipzig, Germany

Gerhard Schaumburg

New Developments by Novocontrol

WinFIT 2.3 Supports Equivalent Circuit Calculations and Arbitrary Fit Functions

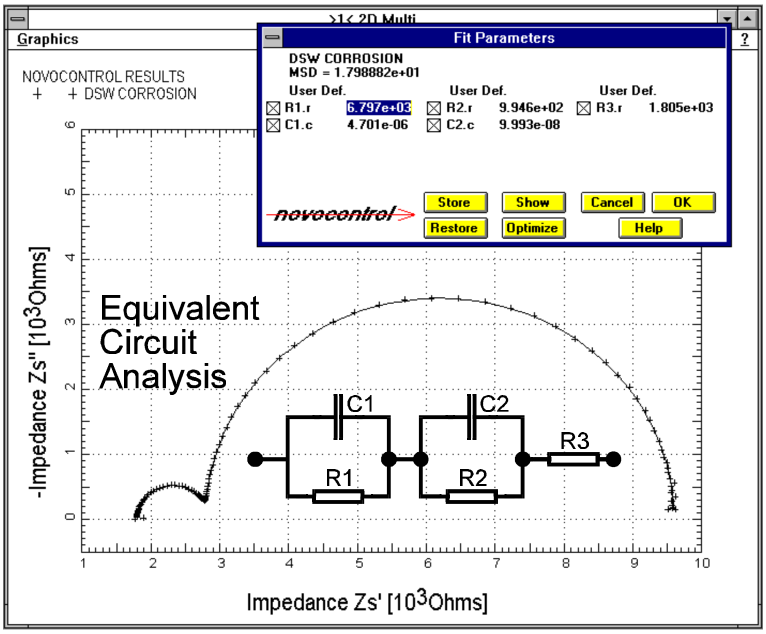
WinFIT is a scientific evaluation software program for dielectric and impedance measurements. Its main purpose is non linear curve fitting of complex analytical functions like e.g. the Havriliak Negami function to data measured in the frequency range. As WinFIT was specially developed for dielectric spectroscopy, a great number of frequency curves at different temperatures can be fitted simultaneously without interaction of the user. In a second step, the temperature dependence of relaxation times is fitted to a Vogel Fulcher or Williams Landel Ferry (WLF) function. For a more detailed information refer to /1/.

In the new version WinFIT 2.3, fit functions described by networks of electric components (equivalent circuits) were also included. Moreover, any arbitrary complex analytical fit function may be defined by simple algebraic notation. Results from equivalent circuits and analytical functions may be mixed together, allowing the user to realize nearly any desired fit function.

Fig. 1 shows an example consisting of an inductor L1, a resistor R1, two capacitors C1, C2 and an analytical defined impedance Z1. This network could be entered directly as a WinFIT fit function as

Z1= Z0*j*tanh(j/(w*t))^alpha;
Z(w)=L1+((R1+C1)|Z1|C3)

Fitting can be done for the real-, or / and imaginary part (Cole-Cole fit) and the absolute value.



DSW CORROSION
MSD = 1.798882e+01

User Def.		User Def.		User Def.	
☒ R1.r	6.797e+03	☒ R2.r	9.946e+02	☒ R3.r	1.805e+03
☒ C1.c	4.701e-06	☒ C2.c	9.993e-08		

Equivalent circuit analysis supports definition of arbitrary RLC networks in combination with any user defined complex function like sin(ω*(var1+j*var2)).

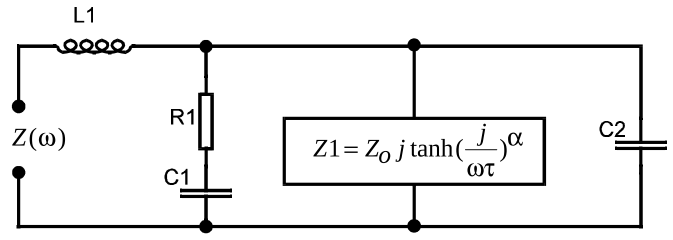


Fig. 1 : Example for an equivalent circuit containing a user defined analytical impedance.

Additional new features are multiple 3D plane (e.g. dielectric function ε'' depending on frequency f and temperature) and 3D curve diagrams (e.g. ε' and ε'' depending on f), Bode and Cole Cole plots and up to 55 dependent variables like inductance, conductivity, etc. In addition to the very precise Newton fit procedure, the faster Marquard algorithm has been included.

Economical Impedance Converter NIC

For scientists with low budget, the Novocontrol NIC is now available. This is a simplified version of the Broadband Dielectric Converter BDC described in detail in /2/. It is operated in combination with the Solartron SI 1260 or SI 1255 gain phase analyzer and especially suited for the measurement of pure dielectric samples, with a dominant capacitive response over the frequency range of interest.

The functional diagram is shown in fig. 2. The main difference to the BDC is that the NIC is not computer controlled, has no internal reference capacities and is operated at one fixed capacitive gain level. Therefore, the design could be simplified allowing a low selling price. Nevertheless, for dominant capacitive samples, the performance is quite good even in the low frequency range down to 1 mHz.

The measurement procedure is as follows : The sample capacity Cs* is connected to the input of the NIC. For each frequency of interest, the complex voltages V1s* and V2s* are phase sensitive measured by the analyzer. In a second step, the sample is manually replaced by a reference capacity Cr and the same measurement is repeated giving the results V1r* and V2r*. The results may be stored in a computer in order to use them for later measurements. For highest accuracy, the reference capacity should be selected so that |Zs*(ω)| and |Zr*(ω)| are as close as possible over the whole frequency range. (Zs*, Zr* : impedance of sample, reference capacitor, ω : circular frequency).

The evaluation of the sample impedance is in principle identical to the low frequency part of the BDC. The current to voltage conversion impedance Zx* of the NIC is determined by

$$Zx^* = -\frac{V2r^*}{V1r^*} Zr^* = -\frac{V2r^*}{V1r^*}\frac{1}{j\omega Cr} \qquad (1)$$

From this, the sample impedance is calculated by

$$Zs^* = -\frac{V1s^*}{V2s^*} Zx^* = \frac{V1s^*}{V2s^*}\frac{V2r^*}{V1r^*}\frac{1}{j\omega Cr} \qquad (2)$$

From (2) can be seen that the sample impedance in principle does not depend on the conversion impedance Zx*. Nevertheless, from the practical point of view, |Zx*| determines the amplitude of the voltages V2s* and V2r* measured by the analyzer and therefore the measurement accuracy. The phase behaviour of Zx* is not of importance, as it shifts the phase values of V2s* and V2r* simultaneously without affecting their difference.

In contrast to the BDC where Zx* is variable and automatically selected to be always in range of highest accuracy, the NIC uses a fixed impedance with one capacitor and an additional resistor for DC stabilization. The frequency dependence of |Zx*| is shown in fig. 3. At frequencies above 0.1 Hz, |Zx*| is dominated by the capacitor Cx resulting in a frequency dependence 1/(ωCr). At low frequencies, |Zx*| saturates to a constant value determined by the resistor Rx. In addition, the tan(δ) accuracy ΔE of the NIC is specified for several voltage ratios V=|V2s*|/|V1s*|. At not to low V, ΔE is between 0.01% and 1% depending on frequency and the match between |Zs*| and |Zr*|. The limits of measurement are at voltage ratios V=1 and V=10^{-4}.

For comparison, |Zs*| is shown for Glycerol and Polyvenylacetat at several temperatures. At high frequencies, the impedance is dominated by capacitive behaviour and fits well into the measurement range of the NIC. At low frequencies, Glycerol shows temperature dependent DC conductivity which partly exceeds the limits of measurement. Nevertheless, the dielectric interesting regime of relaxation is well measurable over the whole temperature and frequency range.

For PVAC, the situation is similar, but as the DC conductivity is shifted to lower values, the limits of measurement are not exceeded, but only touched.

Generally, best results are achieved for samples with |Zs*| close to the conversion impedance |Zx*|. This applies for dielectric samples with low relaxation strengths (tan(δ) << 1). For such samples |Zs*| differs rarely from |Zs*| and |Zr*| (if properly adjusted).

The device combination NIC and Solartron SI 1260 / SI 1255 is fully supported by the powerful MS-Windows software package WinIMP including measurement-, device control, data evaluation, graphical representation and data export in various ASCII formats.

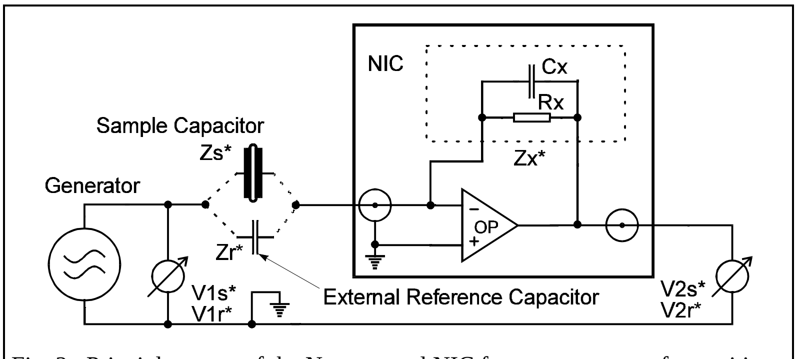


Fig. 2 : Principle set-up of the Novocontrol NIC for measurement of capacitive dominated dielectric samples over a broad frequency range.

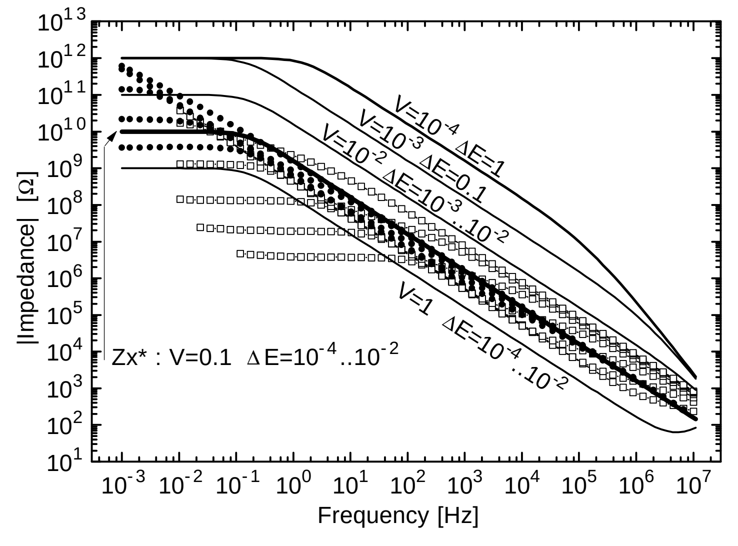
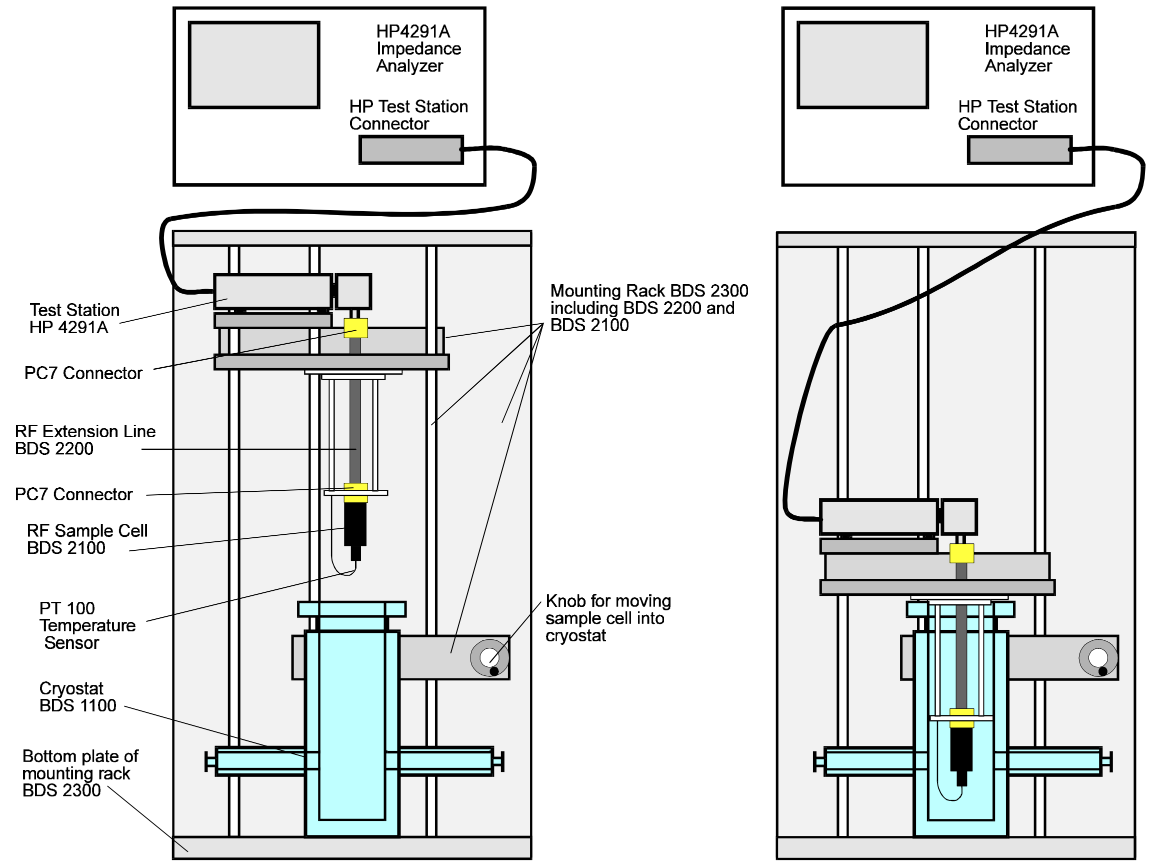


Fig. 3 : Measurement limits and tan(δ) accuracy ΔE for several output voltage ratios V=|V2s*|/|V1s*| (cable length from NIC input = 0m). For comparison : Full dots are results of PVAC for T=20°C.. 60°C, open squares for Glycerol for T = -20°C .. -80°C.



BDS 2300 and HP 4291A sample cell moved out of cryostat

BDS 2300 and HP 4291A sample cell moved inside cryostat

Fig. 4 : Novocontrol mounting rack BDS 2300 for the RF system to 1.8 GHz and temparatures from -160°C to 450°C.

BDC Operates with EG&G Lock In Amplifier from 1mHz to 1MHz

The Broadband Dielectric Converter BDC-N can now be operated also in combination with the EG&G 5302 lock in amplifier. The tan(δ) accuracy is better than 10^{-4}.

WinDETA Supports Eurotherm 818 Series Controllers

For scientists who want to use industrial environmental test chambers or an own temperature control system in combination with a Novocontrol impedance or dielectric analysis system, WinDETA supports now the low cost standard Eurotherm 818 series controllers. They can be configured to a large number of temperature sensors. The output for the heater power supply is either pulsed for solid state relais or DC-voltage for thyristors. Customized output power supplies are available by Novocontrol.

Mounting Rack BDS 2300 for 1.8 GHz RF System

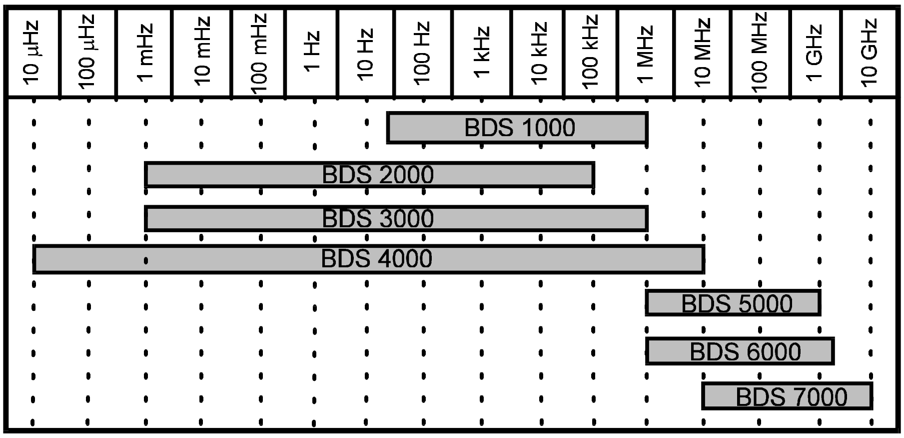
The Novocontrol BDS 6000 system measures the dielectric function and impedance of material samples in dependence of frequency, temperature, DC Bias and time /3/. The new mounting rack BDS 2300 adapts the Hewlett Packard impedance analyzer HP 4291A to the sample cell BDS 2100 and the Novocontrol Quatro Cryosystem. The impedance input of the HP4291 analyzer is mounted on a separate test station connected by a cable to the mainframe. This allows to locate the analyzer impedance input as close to the sample as possible resulting in optimal measurement precision. As the test station operates only at ambient temperature, it is thermally isolated from the sample cell by the extension line BDS 2200. The BDS 2300 mounting rack mechanically adapts the components as shown in fig. 4. In addition, the whole set-up (test station, extension line and sample call) can be moved in- and outside of the cryostat BDS 1100 by rotating a knob. This set-up guarantees a sophisticated and rugged construction in combination with straightforward handling.

References

/1/, /2/, /3/ G. Schaumburg, Novocontrol Dielectrics Newsletter, Issue March 95, July 94, April 96

Dr. Gerhard Schaumburg;
Novocontrol GmbH
Obererbacher Str. 9
56414 Hundsangen, Germany

OVERVIEW
BROADBAND DIELECTRIC SPECTROSCOPY
over 15 decades by NOVOCONTROL



Factory and Head Office

Germany:
NOVOCONTROL GmbH
Obererbacher Straße 9
D-56414 Hundsangen / GERMANY

Phone: ++(0) 64 35 - 96 23-0
Fax: ++(0) 64 35 - 96 23-33

Editor Dielectrics Newsletter
Dr. Gerhard Schaumburg

Abstracts and papers are always welcome. We can publish max. 2 pages A4 on each subject. Please send your script to the editor.

Agents

Benelux countries:
NOVOCONTROL Benelux B.V.
Postbus 231
NL-5500 AE Veldhoven / NETHERLANDS
Phone: ++(0) 40 - 2894407
Fax: ++(0) 40 - 2859209

Great Britain:
NOVOCONTROL International
PO Box 63
Worcester WR2 6YQ / GB
Phone/Fax: ++(0) 1905 - 64 09 47
contact: Mr. Jed Marson

USA/Canada:
NOVOCONTROL
611 November Lane / Autumn Woods
Willow Springs, North Carolina 27592 / USA
Phone: ++(0) 919 639 8491
Fax: ++(0) 919 639 7523
contact Mr. Joachim Vinson, PhD

KOREA:
P.S.T. Polymer Science & Technology
P.O. Box 266
Seocho, Seoul / KOREA
Phone: ++(0) 2-577-1962
Fax: ++(0) 2-577-1963
contact: Mr. Young Hong

JAPAN:
Morimura Bros. Inc.
2 nd chemical division
Morimura Bldg. 3-1, Toranomon 1-chome
Minato-Ku
Tokyo 105 / Japan
Phone: ++(0) 3-35 02-64 40
Fax: ++(0) 3-35 02-64 37
contact: Mr. Furukawa

Information request

Company ....

Division ....

Name ....

Title ....

Street ....

City ....

Postal Code ....

Country ....

Phone ....

Fax ....

I am interested in NOVOCONTROL broadband dielectric spectrometers and request you to send me the following product information:

☐ Economical dielectric spectrometers (1 mHz - 1 MHz or 100 Hz - 1 MHz)

☐ Broadband dielectric spectrometer (10 µHz - 10 MHz)

☐ RF dielectric spectrometer (1 MHz - 1.8 GHz)

☐ Temperature control systems (+20°C to +400°C or -160°C to +500°C)

☐ Accessories (liquid sample cell, electrodes, spacer rings, etc.)

Status of my request

☐ Urgent demand. Please send me also your quotation per fax.

☐ Future demand. Please contact me again when I can order your equipment.
This will be: ....

☐ General interest

Dielectrics Newsletter

☐ Please place or keep me on your mailing list

☐ Please delete me from your mailing list

t:\pinfo\dnl6\dnl6.doc