

Dielectric Newsletter

Scientific newsletter for dielectric spectroscopy

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Molecular Dynamics Close to Interfaces

The physics of micro- and nano-confined systems has attracted great interest in scientific research during the past. Various types of adsorbate systems with high porosity have been investigated. In particular, the high surface to volume ratio allows a convenient investigation of gaseous and liquid phases near solid substrates [1-5]. Interaction energies, aligning properties of the surface material on the adsorbed molecules [6-8] and exchange effects [9] can be determined. The geometrical restrictions can produce interesting changes of the molecular diffusion properties [10-12]. On the other hand, the limiting pore sizes may also influence the thermodynamic properties of the confined phase. For example, one can observe the induction of thermodynamic phases [13,14], the shift of phase transition temperatures [15,16] as well as the change of the very character of phase transitions as a consequence of confinement [17,18].

The class of investigated adsorbates ranges from small inorganic molecules as hydrogen or water [6,10,19-22], organic aliphatic materials like methane [11,23,24] or simple glass forming liquids [16,25,26] to complex aromatic systems including liquid crystal mesogens [14,27,28] and polymers [12,29]. Frequently used adsorbents are for example zeolites [11,23], silica gels and aerosil [18,19,30], aluminium oxides, hydroxides or aluminosilicates [31], various types of porous

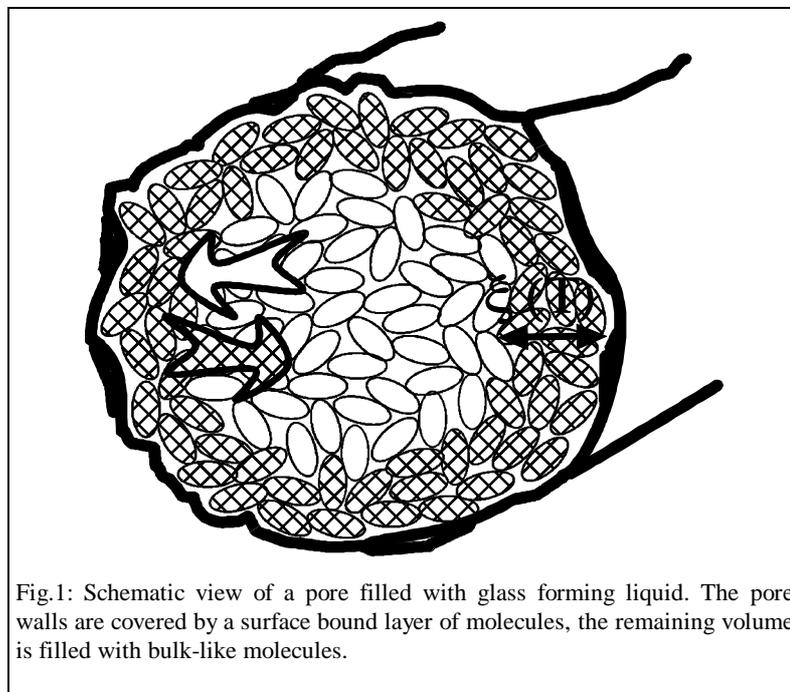


Fig.1: Schematic view of a pore filled with glass forming liquid. The pore walls are covered by a surface bound layer of molecules, the remaining volume is filled with bulk-like molecules.

glasses [7,16,26] and porous polymer membranes. Pore sizes of these systems range from few Angstrom to few tenth of micrometers. Among the experimental methods, NMR (transverse and longitudinal relaxation, Overhauser effect or line shape analysis) [6,10], DSC [15], neutron scattering [22,25], dynamic light scattering [12,29], Raman Scattering [13,24], and dielectric spectroscopy [16,21,26] have proved particularly successful.

A challenging subject of interest is the study of the dynamic glass transition in confined volumes [16,25,32]. Several theories of the dynamic glass transition predict an increase in collectivity of molecular dynamics when the glass transition temperature is approached [33]. This process should manifest in the growth of cooperatively reorienting clusters of molecules [34]. It is therefore quite natural to test such theories in porous media. When

glass forming liquids are adsorbed to sol-gel glasses with a few nanometer pore diameters, one should expect limiting influences of the cage on the increase of cooperativity and the slowing down of dynamic processes [35]. When the cluster sizes reach the pore diameters, deviations from the bulk dynamic behaviour should be observed. The temperature characteristics of molecular dynamics can provide an estimate of the cluster dimensions in the vicinity of the glass transition [36].

Broadband dielectric spectroscopy (10^{-2} Hz - 10^9 Hz) is employed to measure several glass forming liquids with different number of hydroxy groups per molecule confined to nanoporous glasses with pore sizes of 2.5 nm, 5.0 nm, and 7.5 nm. For a liquid with one hydroxy group (salol) two separated loss processes are detected in all pore sizes which are assigned to the relaxation of an

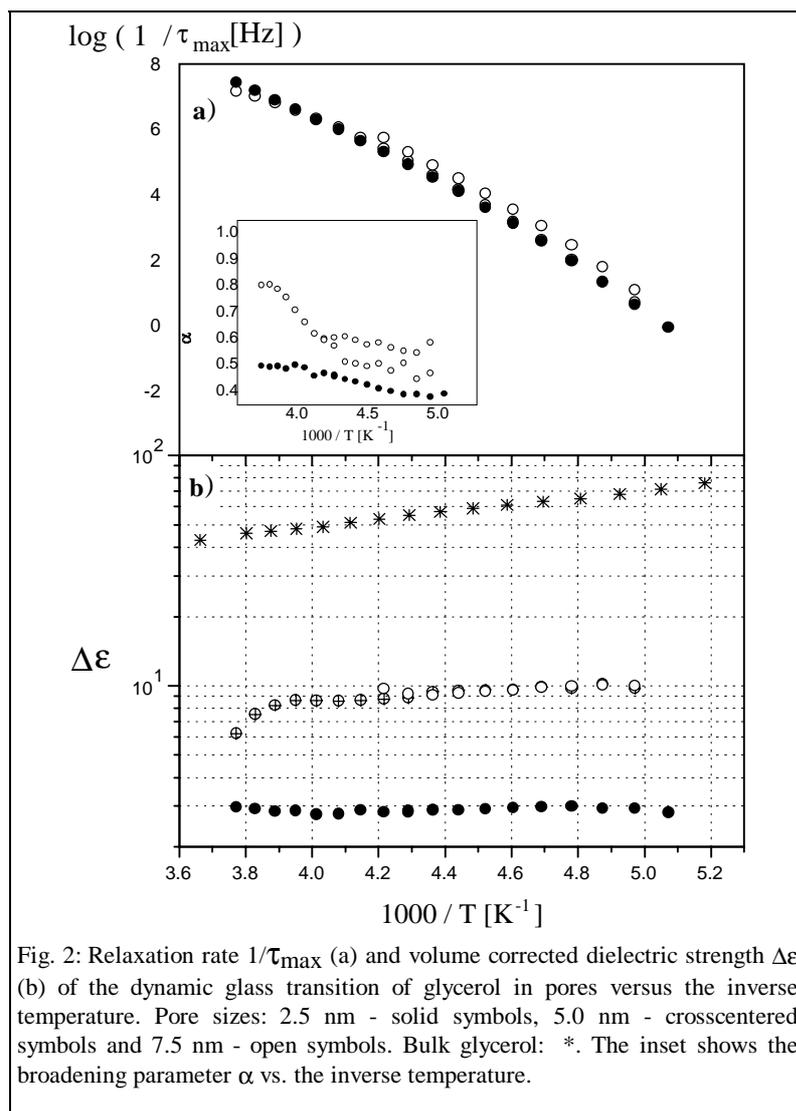


Fig. 2: Relaxation rate $1/\tau_{\max}$ (a) and volume corrected dielectric strength $\Delta\epsilon$ (b) of the dynamic glass transition of glycerol in pores versus the inverse temperature. Pore sizes: 2.5 nm - solid symbols, 5.0 nm - crosscentered symbols and 7.5 nm - open symbols. Bulk glycerol: *. The inset shows the broadening parameter α vs. the inverse temperature.

interfacial layer and the relaxation of bulk-like molecules in the center of the pores (dynamic glass transition). Liquids with two (pentylene glycol) or three (glycerol) hydroxy groups exhibit only the relaxation process connected to the dynamic glass transition. In all samples an additional loss process caused by a Maxwell-Wagner polarization is observed at low frequencies. The observed spectra can be consistently interpreted within a shell model of a bulk-like phase and an interfacial layer including molecular exchange between both subsystems (Fig.1).

The relaxation rate of the dynamic glass transition of confined glycerol (Fig.2) does not

show a pore size dependence (diameter ≥ 2.5 nm) and it is - within the experimental accuracy - identical to the bulk. The temperature dependence of its dielectric strength is comparable to the bulk. Considering the fact that the interfacial layer has a thickness of about 0.9 nm in the smallest pores one has to conclude that the dynamic glass transition takes place in a subvolume with a diameter of roughly 0.7 nm on a timescale as in the bulk. This is in pronounced contrast to theories of the dynamic glass transition which are based on the existence of so-called "cooperatively rearranging regions", of 3 nm - 5 nm size close to the calorimetric glass transition temperature.

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Book Review : Dielectric Analysis of Pharmaceutical Systems

by Duncan Q. M. Craig, Taylor & Francis, London 1995, ISBN 0-13-210279-X, 232 pp., Hardcover, £ 65.00

The characterisation of materials and tissues involved in the delivery of drugs to the body is of vital importance for the development of effective medicines. There is a need for new analytical methods in order to gain a greater insight into the structure and behaviour of drugs and medicines. While the application of dielectric spectroscopy is well established in physics and polymer research it has been only recently introduced to pharmaceutical science.

This textbook is written for newcomers in the field of dielectric spectroscopy especially for graduate students and research workers in pharmaceutical science with the aim to introduce into this field of analytical methods. The first chapter gives an introduction

to the theory of dielectric polarization starting from the fundamental physical laws so it can be easily understood without an extensive training in physics and mathematics. In Chapter two the different methods of dielectric measurement techniques which are necessary to cover the whole frequency range from 10^{-4} Hz to 10^{12} Hz are discussed. In the following chapters the author gives an overview on the dielectric properties of materials which are essential for pharmaceutical systems: starting with the dielectric properties of water aqueous and non-aqueous solutions are discussed in chapter three. In chapter four micelles, microcapsules, liposomes, and microemulsions serve as an example for heterogeneous systems in pharmaceutical science. Due to the considerable relevance of solid dosage design chapter five deals with the dielectric properties of crystalline and glass-forming solids and powder compacts. With respect to the key role of polymers in the development of pharmaceutical products they are separately discussed in chapter six, e.g. the effects of cross-linking and additives are reviewed. In the last chapter the authors attempt to demonstrate to potential for the use of dielectric spectroscopy in the analysis of biological systems.

In summary, this textbook gives an excellent introduction to the application of dielectric spectroscopy as an analytical tool for the characterisation of drugs. One can hope that this book will help to rediscover dielectric spectroscopy as a powerful experimental method in pharmaceutical science.

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High Frequency Performance for Dielectric Measurements to 1.8 GHz Improved by the NOVOCONTROL BDS 6000 System

Dielectric spectroscopy is a valuable tool for the characterization of materials properties. The complex dielectric function ϵ^* reflects the molecular relaxation and transport processes of the material. As $\epsilon^* = \epsilon' - i\epsilon''$ depends on many different physical quantities, dielectric measurements often are done as a function of frequency, temperature, time and DC bias (superimposed static electric field). The new NOVOCONTROL BDS 6000 system based on the HP 4291A RF Impedance Analyzer performs these measurements fully automatic. The HP 4291A is the successor of the

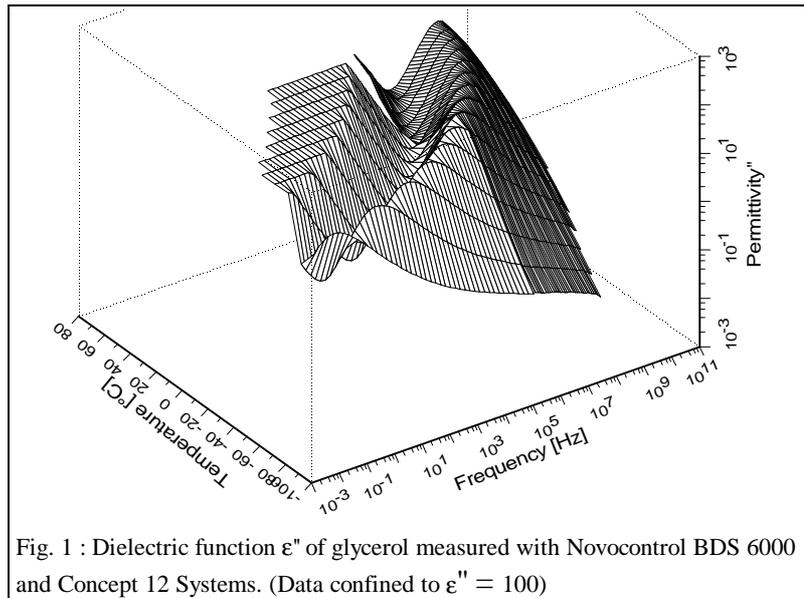


Fig. 1 : Dielectric function ϵ'' of glycerol measured with Novocontrol BDS 6000 and Concept 12 Systems. (Data confined to $\epsilon'' = 100$)

HP 4191A impedance analyzer and was developed particularly for impedance measurements. It is one of the most accurate devices in the high frequency range that is presently on the market. Compared to measurement systems based on spectrum or network analyzers, it has a much higher resolution and a broader impedance range.

In the NOVOCONTROL BDS

6000 system, the HP 4291A RF Impedance Analyzer is extended with the high performance cryogenic QUATRO temperature control system /1/ which was particularly designed for dielectric applications. The complete system is controlled by a PC with the MS-Windows software package WinDETA /2/. The system limits are: frequency 1 MHz - 1.8 GHz, temperature -160 °C to +450 °C, dc-bias -40 V to +40 V, time 2 s - 10⁷s. Moreover any multi-dimensional combination of these parameters is supported. The combination of these features make the BDS 6000 superior for top class scientific and engineering applications. Some examples for scientific applications are

- relaxation processes on the molecular dynamics of liquid crystals, polymers and liquids,
- charge transport in semiconductors, organic crystals, ceramics, etc.,
- monitoring of chemical reactions, polymerization and curing processes,
- structural material properties like phase compositions, phase transitions and crystallization processes,
- non-linear electrical and optical effects.

Industrial applications are in

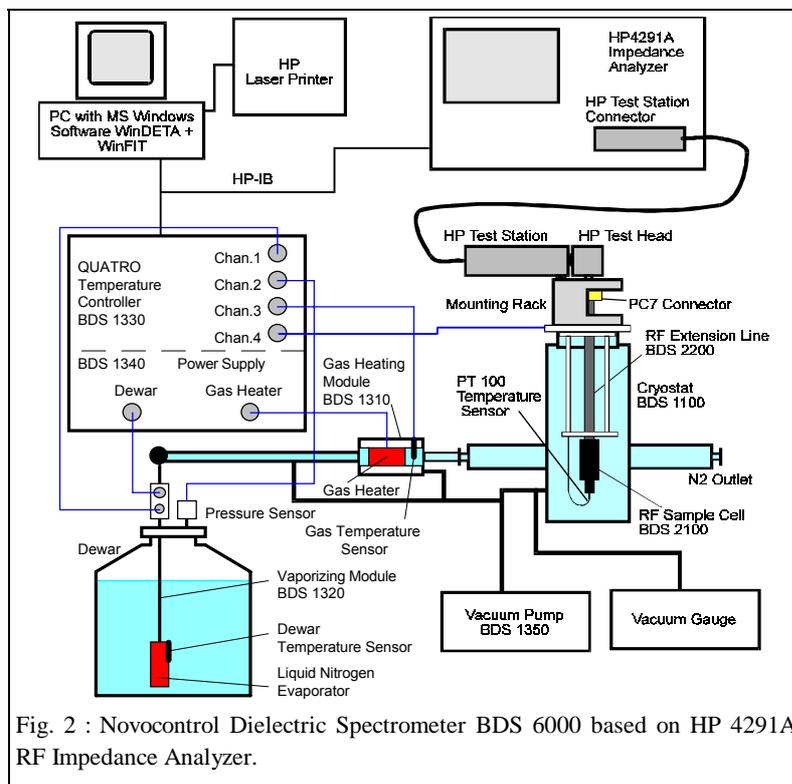


Fig. 2 : Novocontrol Dielectric Spectrometer BDS 6000 based on HP 4291A RF Impedance Analyzer.

quality control and characterization of insulating and semiconductor materials. Materials changing their dielectric function if exposed to gases or liquids are used in sensor applications.

Another interesting application is the characterization of printed circuit boards. This is necessary, as the functional behaviour of boards, operated with high speed electronics up to the GHz range, is largely influenced by the dielectric properties of the board materials.

Measurement example

The dielectric function of glycerol for temperatures between -80°C and 60°C K is shown in Fig. 1, 3 and 4. The data were measured from 1 MHz-1.8 GHz with the BDS 6000 system and below 1 MHz with the Concept 12 system based on the NOVOCONTROL Broadband Dielectric Converter BDC /3/. Fig. 3 shows the real part ϵ' , Fig. 1 shows the imaginary part ϵ'' of the dielectric function in three dimensional representation. The curves represent the main dielectric relaxation (α -relaxation) due to orientation polarization of permanent dipoles in the applied electric field. ϵ' is correlated to the

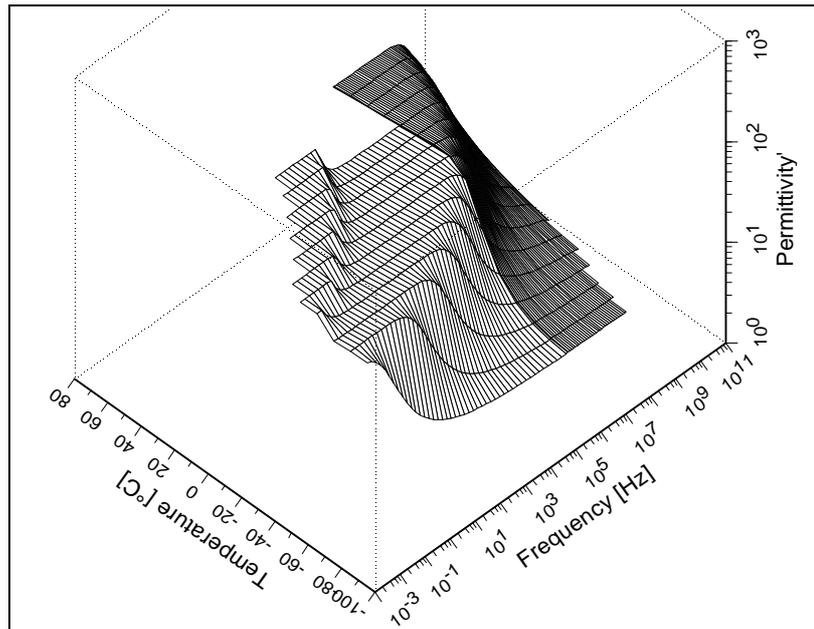


Fig. 3 : Dielectric function ϵ' of glycerol measured with Novocontrol BDS 6000 and Concept 12 Systems. (Data confined to $\epsilon' = 100$.)

polarization strength, ϵ'' measures the electric losses of the relaxation and the dc-conductivity. For a fixed temperature and low frequency, the electric dipoles follow the external field without delay. The polarization is constant at high level. If the frequency increases, the dipoles become too slow to follow the field and are only partly oriented. As can be seen from Fig. 3, the polarization decreases. The

electric losses show a maximum at the crossover frequency from high to low polarization (Fig. 1, 4).

At higher temperatures, the mobility of the molecular dipoles increases and the relaxation frequency is shifted to higher values. In addition, the dc-conductivity caused by thermal activated free charge carriers increases. This can be seen in Fig. 1 in the increase of ϵ'' on the left from the dielectric relaxation at low frequencies. In addition, the conductivity contribution can cause electrode polarization resulting also in increase of ϵ' at low frequencies shown in Fig. 3.

Fig. 4 shows ϵ'' in two dimensional representation. In contrast to Fig. 1, the conductivity contribution is subtracted, remaining the pure relaxation peaks. This was done by fitting a Havriliak-Negami function (solid lines in Fig. 4) and a conductivity function (subtracted from the data) and to each frequency spectrum. The evaluations were done with the software WinFIT /2/ which is a part of the standard BDS 6000 system. From this information about the molecular dynamics of the material like activation energy, glass

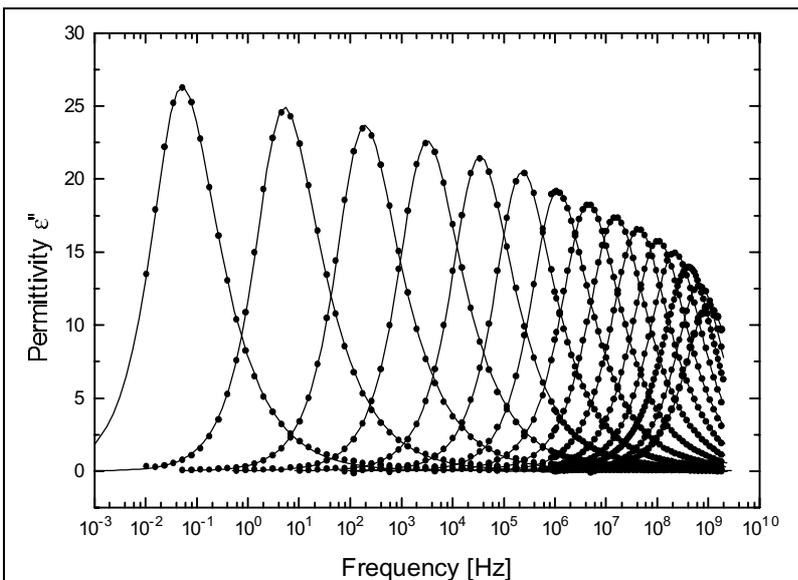


Fig. 4 : Dielectric function ϵ'' of glycerol. Conductivity contribution subtracted, solid lines : Havriliak Negami fits. Temperature from -80°C (at low frequencies) to $+60^{\circ}\text{C}$ in 10°C steps.

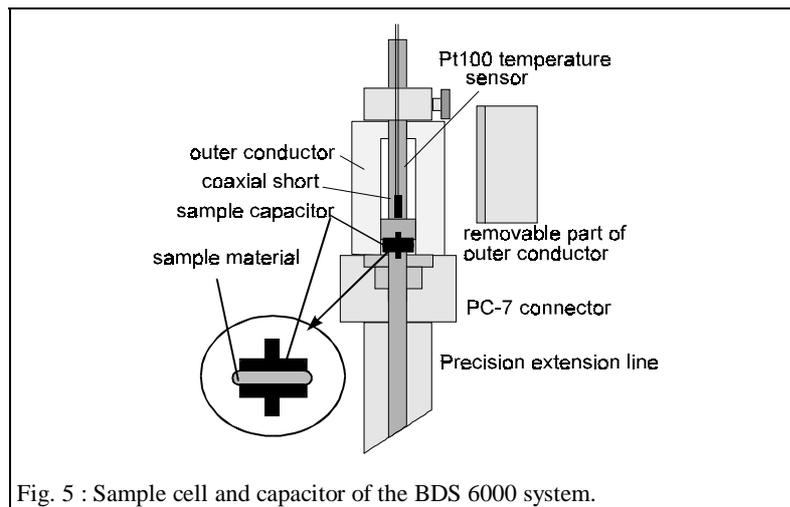


Fig. 5 : Sample cell and capacitor of the BDS 6000 system.

transition temperature, AC- and DC-conductivity, time domain behaviour and others can be obtained [2].

System Components

The BDS 6000 dielectric spectrometer consists of the following components shown in Fig. 2 :

- a special RF sample cell with the sample capacitor (Fig. 5),
- an microwave precision extension line connecting the sample cell to the impedance analyzer [4],
- the HP 4291A RF Impedance Analyzer,
- a temperature control system allowing to expose the sample capacitor to temperatures from -160°C to $+450^{\circ}\text{C}$ with 0.01°C stability and very short settling times,
- a PC with the MS-Windows software package WinDETA and WinFIT that controls the measurement flow, operates all devices and the evaluates the measured data.

Compared to the BDS 5000 system which is based on the HP 4191A analyzer and was the predecessor of the BDS 6000, it offers the following advantages :

- The frequency range is extended from 1 GHz to 1.8 GHz.
- The accuracy and resolution of the impedance measurement is improved by typically a factor 3 -

10. Especially measurements of low loss samples are improved due to an additional low loss capacitor calibration procedure.

- The NOVOCONTROL low frequency systems (10^{-5} Hz - 10^7 Hz) based on the NOVOCONTROL Broadband Dielectric Converter BDC can be easily extended to the high frequencies up to 1.8 GHz. In contrast to the BDS 5000 system for which an additional cryostat is required, the BDS 6000 system can be used with the NOVOCONTROL standard cryosystem contained in the BDC low frequency systems.

This is possible as the new HP 4291 analyzer has an active impedance measurement head which is separated from the HP 4291 main frame. In the BDS 6000 system, the NOVOCONTROL RF sample cell is mounted on the active head of the HP 4291 analyzer (see Fig. 2). This setup builds up an extended active head which can be used in the temperature range from -150°C - 450°C .

Principle of Operation

The material under test generally is placed between two electrodes creating a capacitor as sketched in Fig. 5. The capacitor plates have a diameter from 3 mm - 6 mm. The spacing between the plates may be selected between 2 mm and 10 μm . For special applications other

sample geometries may be used. The sample impedance Z_s is connected to the dielectric function by

$$\varepsilon = \varepsilon' - j\varepsilon'' = \frac{-j}{2\pi f Z_s C_0} \quad (1)$$

where f denotes frequency and C_0 is the vacuum capacity of the empty sample capacitor. The sample material is placed between two electrodes in a special high frequency sample cell shown in Fig. 5. The sample cell is mounted into a cryostat and exposed to a heated gas stream being evaporated from a liquid nitrogen dewar (Fig. 2). The test head of the HP 4291A RF Impedance Analyzer is connected to the sample cell by a microwave precision extension line.

Conclusion

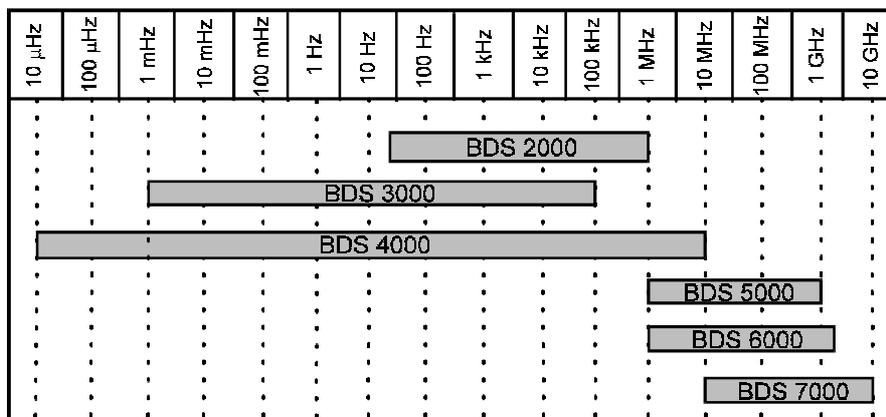
The NOVOCONTROL BDS 6000 system is a top class turnkey solution for dielectric measurements of materials in dependence of frequency, temperature, time and DC-Bias. The system is particularly suited for scientific applications in polymer, ceramic and semiconductor research, but may be also used in quality control applications. In combination with the NOVOCONTROL Concept 12 system, the system limits are: frequency 10 μHz - 1.8 GHz (14.5 decades), temperature -160°C to $+450^{\circ}\text{C}$, dc-bias -40 V to $+40$ V, time 2 s - 10^7 s. Moreover any multi-dimensional combination of these parameters is supported, which makes the BDS 6000 superior for top class scientific and engineering applications.

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- [1] , [2] , [3] , [4] , G. Schaumburg, Novcontrol Dielectrics Newsletter, Issue October 95, March 95, July 94, March 94

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