Automated, low-temperature dielectric relaxation apparatus for measurement of air-sensitive, corrosive, hygroscopic, powdered samples

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An automated apparatus for dielectric determinations on solid samples was designed to allow cryogenic measurements on air-sensitive, corrosive, hygroscopic, powdered samples, without determination of sample thickness, provided that it is uniform. A three-terminal design enabled measurements that were not affected by errors due to dimensional changes of the sample or the electrodes with changes in temperature. Meaningful dielectric data could be taken over the frequency range from 20 Hz to 1 MHz and the temperature range from 12 to 360 K. Tests with Teflon and with powdered NH_4Cl gave results that were accurate within a few percent when compared with literature values. © *1999 American Institute of Physics.* [S0034-6748(99)00107-0]

I. INTRODUCTION

Dielectric measurements of solids complement other solid-state techniques; changes in the dielectric constant ϵ relate to various microscopic processes. One of our interests is the characterization of low-temperature solid-state properties, including phase transitions, in alkali–metal hydroxides; these are corrosive and hygroscopic materials in which there are noticeable deuterium-induced effects.[1] Several detailed designs for dielectric measurements of solids in the appropriate frequency range (<1 MHz) have been published.[2–7] There are no published reports of apparatus fully able to meet the present requirements: cryogenic dielectric measurements of air-sensitive powder samples, where sample loading could be done quickly and easily, under inert atmosphere conditions. The present innovation can be an advantage for all granular samples, given the uncertainty in dielectric measurements that can arise from moisture absorption.[5]

II. SAMPLE CELL

The cell, shown schematically in Fig. 1, was designed to perform measurements on pressed powder samples, sandwiched between a low-potential disk electrode and a high-potential disk electrode. An annular ring electrode was located outside the low-potential electrode; this configuration enabled determination of ϵ, through measurement of the ratio of the disk capacitance (between the high-potential electrode and the disk electrode) to the ring capacitance (between the high-potential electrode and the ring electrode), without knowledge of the sample thickness.[4] All electrodes were made of brass. The low-potential ring and disk electrodes were inserted into a grounded guard block, and electrically isolated from it by varnish. The use of a three-terminal configuration incorporating a grounded guard block reduces the effects of fringing capacitance.[8,9] The ring and disk electrodes were connected to a small relay (Teledyne, model 732-12) to switch the capacitance measurement mode between the high-potential/disk electrodes and the high-potential/ring electrodes. This relay was within the vacuum chamber, and as close as possible to the conditions of the electrodes, in order to minimize lead impedance corrections. A spring-loaded brass piston, fastened to the high-potential electrode, ensured intimate contact between the sample and electrodes, the single most important limitation of precision dielectric measurements of solids.[5]

The cell was isolated from its surroundings by an indium seal and by O rings in the hermetic feedthroughs, and it was suspended in a vacuum can that could be immersed in a cryogenic fluid.

The cell was surrounded by a heater wire, and the temperature was determined using a platinum resistance thermometer (see Fig. 1).

III. MEASUREMENT

The dielectric constant and loss were determined as a function of frequency and temperature by a Hewlett–Packard 4284A precision LCR meter (20 Hz–1 MHz). The impedance measurements and the temperature measurement were set up so that they could be computer controlled. A computer interface also was used to regulate the power to the heater, the relay position (high-potential against the ring or the disk electrode), and the mode (manual or software control). The sample is the dielectric between the high-potential electrode and the low-potential disk electrode, whereas the dielectric between the high-potential electrode and the low-potential ring electrode is the surrounding atmosphere (a small amount of helium exchange gas; effectively, a vacuum as far as the dielectric constant is concerned). Residual impedance in and between the leads was handled by the LCR meter. The disk electrode/ring electrode area ratio was calibrated with mea-

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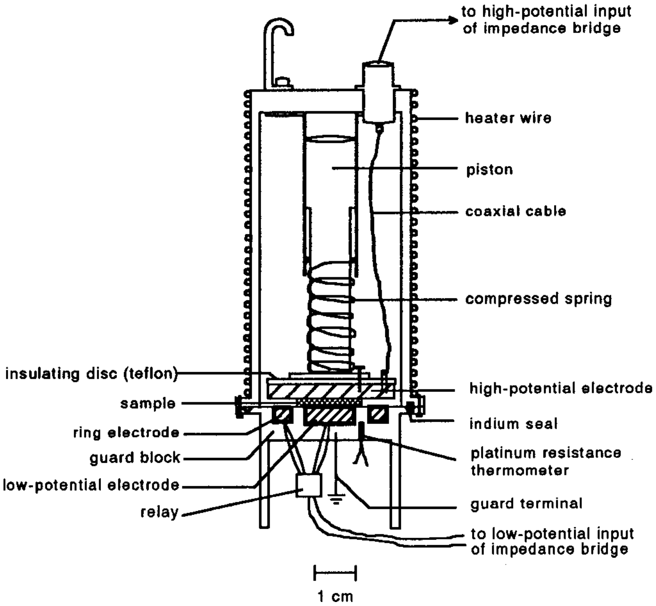

FIG. 1. Schematic of the sample cell for the dielectric apparatus used to measure air-sensitive, corrosive, hygroscopic, powdered samples at cryogenic temperatures.

surements of an annular Teflon spacer, and was determined within 0.5%, independent of frequency and temperature (80–280 K).

IV. PERFORMANCE

The dielectric apparatus has been used to take measurements in the temperature range 12–360 K. With Teflon as a test material, the results were within the published range[10,11] with estimated uncertainties (systematic and random errors) totaling 4%. To test the apparatus on a powdered solid sample, measurements were performed on a pressed pellet of NH_4Cl. A correction using Böttcher's formula[12–14] was applied to the measured powder data to obtain bulk dielectric constant values. The room-temperature bulk value obtained here from measurements of the powder is 8% lower than the single-crystal value;[15] the difference likely stems from inadequacies in Böttcher's formula and imperfect sample–electrode contact. The latter error, based on analysis of the system as three capacitors in series (air gap, sample, air gap), yields a total air gap of 1% of the sample space. More importantly for our interests, evidence for the well-studied order–disorder transition in NH_4Cl is clearly observable as an abrupt jump of $\sim$4% in ϵ near $T=250$ K. Furthermore, the apparatus has been used to successfully investigate dielectric properties of alkali–metal hydroxides.[1]

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