Development of an experimental tool for measuring electrical properties of materials from liquid nitrogen temperature up to 1000°C

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Abstract

An equipment for thermally stimulated current (TSC) analysis has been developed. The system can be operated at temperatures from 90 up to 1273 K. The cryogenic system developed for measuring the electrical properties of materials below room temperature is described. The reactor containing the sample is hermetically closed and can be operated from high vacuum ($<10^{-5}$ mbar) up to 1 bar over the temperature range. Moreover, the reactor is equipped with a very simple tool for measuring the influence of the pressure on the electrical properties of the analysed samples, which is of interest if piezoelectric materials are involved. The force to be exerted on the pellet's surface can be selected by the user. The determination of the dielectric permittivity of $BaTiO_3$ as a function of the temperature has been used for checking the equipment. It has been shown that the peak temperatures for the rhombohedral $\Leftrightarrow$ orthorhombic $\Leftrightarrow$ tetragonal $\Leftrightarrow$ cubic transitions are clearly detected.
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1. Introduction

Knowing the glass transition (T_g), melting temperature (T_m) and temperature of phase transition (T_t) are of great interest for the application of many materials like epoxy resins, liophylised products or ferroelectric ceramics used for manufacturing multilayer capacitors. Knowing the T_g is also important for understanding the interaction between water and the solutes in order to model the freeze-drying process [1].

The differential thermal analysis (DTA) or differential scanning calorimetry (DSC) can be proper methods for determining the above parameters. However, the sensitivity of DTA or DSC instruments would be a handicap in the case of transitions characterised by a very small transition enthalpy. The thermally stimulated current (TSC) methods are an alternative procedure for determining T_g, T_m or T_t. It has been shown that glass transition temperatures measured by TSC are similar to those measured by DSC [2,3]. However, as Galop [1] has pointed out, there is no way to enhance the DSC signal of weak transitions while the TSC signal can be enhanced by increasing the electrical field applied to the sample. Thus, this

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method is much more sensitive than DSC and permits detection of transition temperatures in many cases in which DSC fails.

Lavergne and Lacabanne [4] have reviewed the applications of TSC. One of the most widely used TSC methods is the so-called thermally stimulated depolarisation current (TSDC) [5–10]. This method measures the mobility of dipoles present in the sample after being previously activated. An electrical field (E_0) applied at a temperature higher than the transition temperature to be measured (T_g or T_m) orients all the mobile dipoles. The orientation of the dipoles or polarization (P_0) is frozen after cooling the material at a temperature T_0 where dipole mobility is low enough to achieving equilibrium after removing the electrical field [1]. Once the applied voltage has been removed the depolarisation current is measured as a function of temperature by submitting the sample to a linear heating rate from the starting temperature T_0 until the final temperature (T_f) selected.

The use of TSDC assumes the stability of the sample above the transition temperature. However if the sample were thermally unstable, it would be necessary to apply the thermally stimulated polarization current (TSPC) method [11,12]. In such a case the excitation field is applied at low temperature, where molecular mobility is low, and maintained during the whole experiment. It is noteworthy to point out that neither polarisation nor measurement of polarization or depolarization currents [1] requires direct electrode contact with the sample that is required for ohmic current. Thus, it would be wise to insert an insulating film between the sample and the electrodes in order to block the ohmic current thereby avoiding any ionic conductivity overlapping and hiding the dipole current.

A direct contact sample-electrodes would be required if TSC is used for determining the ferroelectric transition of a ceramic capacitor (like in the dielectric analysers (DEA) available in the market) or the transition temperature of a superconductor. In such a case the electrical resistance, the surface charge of the capacitor or its capacity would be measured using either an electrometer, or LCR bridge.

The scope of this work is to design and develop a sensitive and relatively inexpensive TSC (DEA) system that allows determination of the transition temperature and dielectric constants for ferroelectric materials from very low temperatures up to $1000°C$.

2. Experimental

The $BaTiO_3$ has been prepared following the Clabaugh method [13] using $BaCl_2·2H_2O$, $TiCl_4$ and $C_2O_4H_2·2H_2O$ as starting materials. We have shown in previous papers [14,15] that the above method leads to the single compound $BaTiO(C_2O_4)_2·4.5H_2O$ that crystallises in the monoclinic system with the following lattice parameters: $a=13.382(2)$ Å; $b=13.812(2)$ Å; $c=14.044(2)$ Å, and $\beta=91.48(1)°$. The thermal decomposition of the above precursor has been carried out by constant rate thermal analysis (CRTA).

The DSC experiments were carried out with a Setaram DSC 111 equipment with a sensitivity of 1 μW/s. A flow of helium of 20 cm^3/min and a heating rate of 3 K/min were used.

3. Development of a TSC equipment

Fig. 1 shows a detail of the vertical reactor developed by us for measuring the electrical properties of materials. It has been manufactured in stainless steel 410 in order to work at temperatures up to $1000°C$. A square window has been cut open at the bottom of the reactor for handling the temperature sensor, the electrodes, the sample pellet and the ceramic support used for isolating the sample from the metallic body of the reactor. The wires to the electrodes and the temperature sensor (either a type K thermocouple or a Pt-100 thermoresistance) were isolated with ceramic insulating beads and were connected to the proper measuring devices through a special high vacuum feedthrough attached to the reactor. The pressure of a ceramic bar supporting a stainless steel weight assures good contact between the sample and the electrodes. The weight is placed far from the heated zone of the tubular reactor and, therefore, is maintained at room temperature. The user can select the mass of the counterweight from 200 up to 4000 g, in order to study the influence of the pressure on the electrical properties of piezoelectric materials. The whole reactor is hermetically sealed into an outer jacket that allows work from high vacuum or controlled
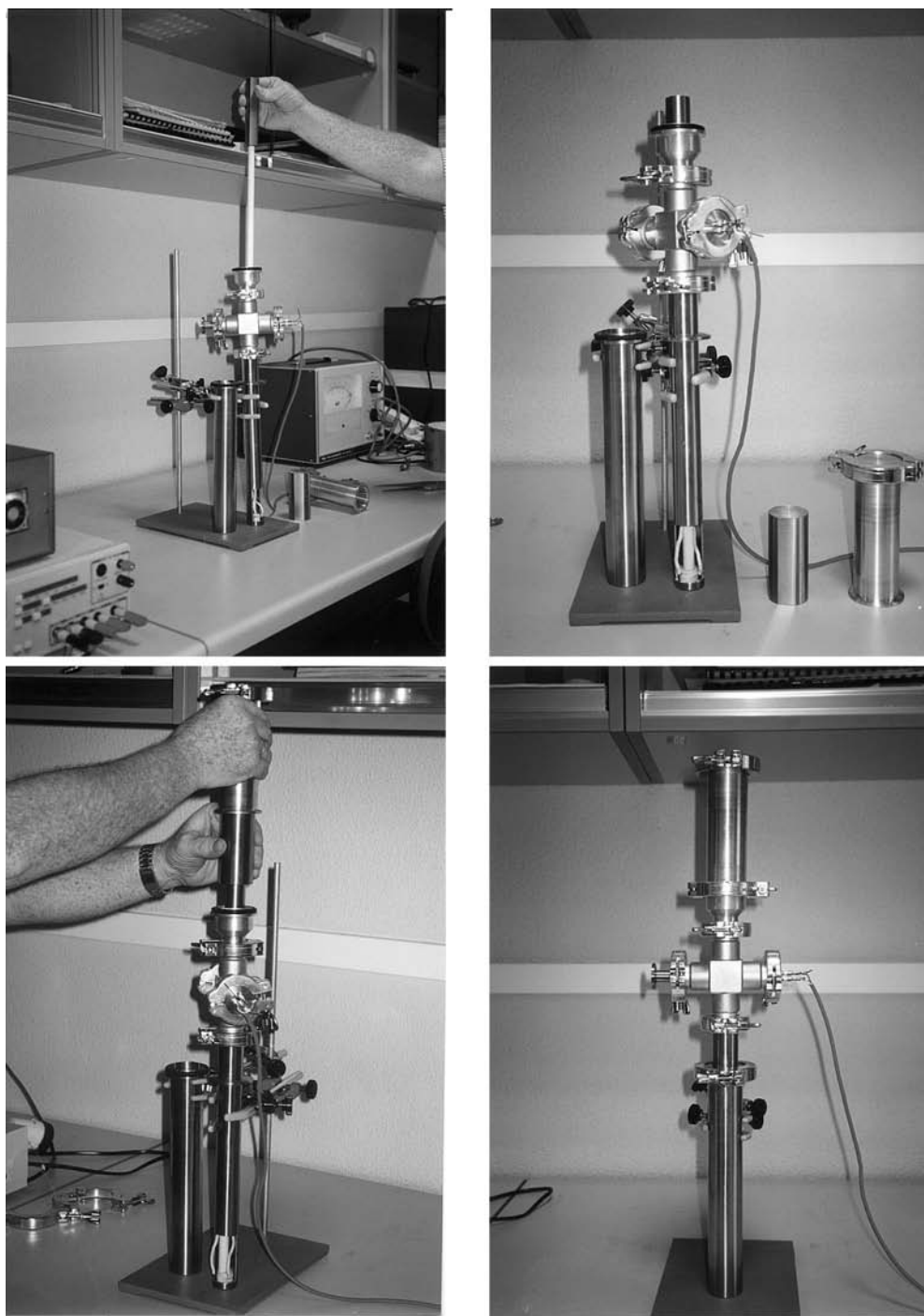
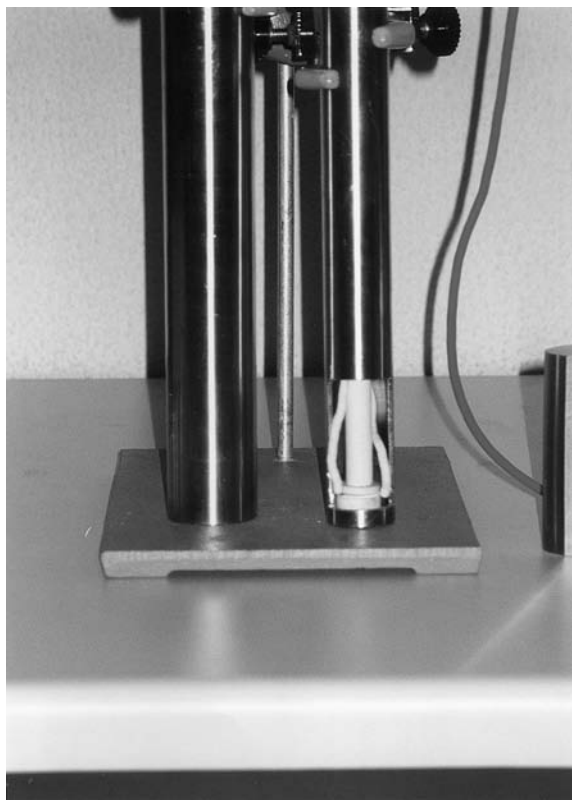Fig. 1. Stainless steel reactor developed for measuring electrical properties.

Fig. 2. Details of the way of placing the ceramic rod, the weight and the jacket of the reactor.

atmosphere. Fig. 2 shows the way of placing the ceramic bar, weight and closing jacket.

A conventional thermostatic bath filled with silicone oil was used for heating the sample from room temperature to 250°C. A tubular vertical furnace was employed for controlling the temperature from 250 to 1000°C. The temperature of both devices was controlled by using the same PID programmer after selecting the proper values of the proportional (P), integral (I) and differential (D) parameters for each heating device through the keyboard of the programmer.

A cryogenic system developed by us was employed for measuring the electrical properties of selected samples from 90 K to room temperature. It is basically constituted, as shown in Fig. 3 of a Dewar having a capacity of 7 l filled with liquid nitrogen and equipped with a coiled pipe coupled through an isolated pipe to another coiled pipe. The latter surrounds the reactor

and is submerged into a 1 l capacity Dewar vessel filled with ethanol. A volume of 350 ml of ethanol is required for filling the Dewar after connecting both the coil and the reactor. The sample was cooled by flowing the previously cooled nitrogen gas through the coil surrounding the reactor. A continuous flow rate of nitrogen, close to 5 l/min, was required for cooling the sample to 90 K in approximately 1 h. This temperature is the lowest that can be achieved with this device. Control of the temperature was performed by controlling the flow of nitrogen using a normally open electrovalve controlled by an on/off programmer as shown in Fig. 3. The same programmer used for heating the sample from room temperature to 1000°C was used, but selecting through its keyboard a value equal to zero for the three parameters P, I and D in order that the device behave like and on/off programmer. Thus, the flow of nitrogen was allowed if the temperature of the sample was higher than the programmed one and was stopped in the opposite case. An accuracy of 0.1 K was achieved using a Pt-100 temperature sensor. The natural heating rate of the reactor after stopping the nitrogen flow was never higher than 2 K/min. Therefore, this value is the maximum heating rate that can be programmed with this system. It is noteworthy that the good thermal conductivity of solid ethanol provides very good control of the temperature, even below its melting point (155.7 K). Moreover, the fact that there is no volume change during the solidification of this chemical minimizes the risk of breaking the Dewar.

4. Results and discussion

The above experimental system has been checked by studying the variation of the dielectric permittivity, ε, of $BaTiO_3$ as a function of temperature. A pellet, 13 mm in diameter and a thickness close to 1 mm was prepared by uniaxial pressing at room temperature in a rigid stainless steel die by applying during 5 min a stationary load of 10^4 kg on the top punch. This pellet was sintered at 1200°C in air. XRD analysis showed that after sintering the tetragonal phase of $BaTiO_3$ was stabilised at room temperature because during this thermal treatment the crystallite size was grown above the critical size for the stabilisation of the metastable cubic phase. This critical size is about 25 nm [16–18].
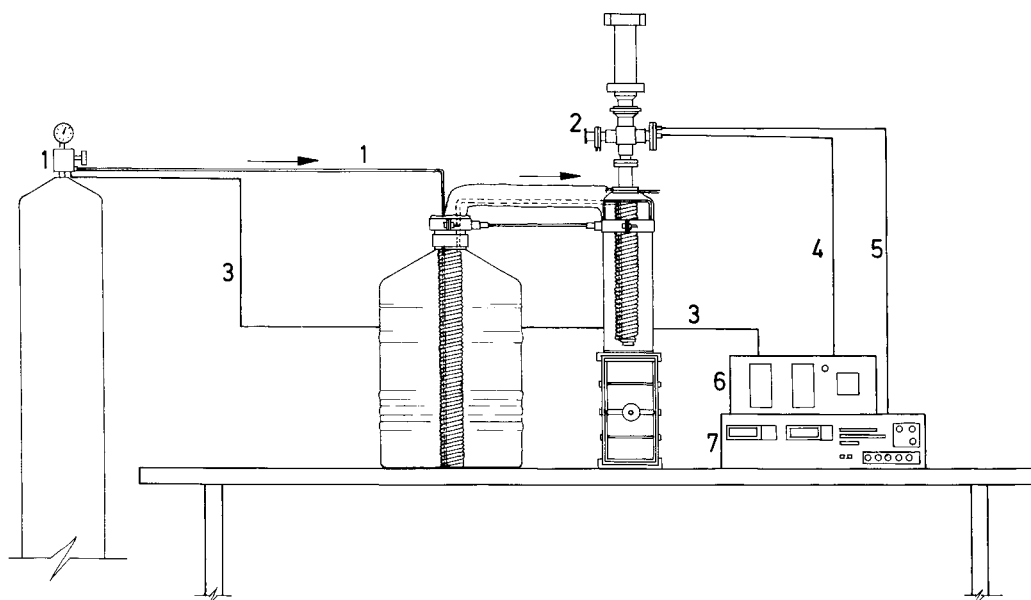
Fig. 3. Scheme of the device developed for performing electrical measurements. (1) Nitrogen container with manometer and electromagnetic valve. (2) Reactor with flange for vacuum connection. (3) Connection wires of the electrovalve to the temperature programmer. (4) Connection of the temperature sensor to the temperature programmer. (5) Connection of the electrodes to the LCR bridge. (6) Temperature programmer. (7) LCR bridge.

A thin layer of gold was deposited by vapour deposition on the two parallel surfaces of the pellets for improved electrical contact with the electrodes. The capacitance of the pellet was measured under isothermal conditions at different temperatures ranging from 120 to 450 K under an applied voltage of 2 V and a frequency of 1 kHz. The dielectric permittivity was calculated from the capacitance, C, by means of the expression.

$$C = \varepsilon \frac{S}{d} \tag{1}$$

where S is the surface of the pellet and d is the thickness.

The capacitance was measured under a vacuum of 2×10^{-5} mbar to avoid condensation of moisture. The values of ε calculated for $BaTiO_3$ are shown as a function of the temperature in Fig. 4. The recorded peak temperatures agree with the values reported in the literature [17,19] for rhombohedral (a=4.001 Å; α=89.8°) $\Leftrightarrow$ orthorhombic (a=3.990 Å, b=5.669 Å, c=5.682 Å) $\Leftrightarrow$ tetragonal (a=3.994 Å, c=4.034 Å) $\Leftrightarrow$ cubic (a=4.034 Å) transitions. The lattice parameters reported have been taken from Ref. [20]. It

must be remarked that the tetragonal $\rightarrow$ cubic transition was the only one observed by DSC as shown in Fig. 5. A comparison of Figs. 4 and 5 shows excellent agreement between the peak temperatures obtained from TSC and DSC.
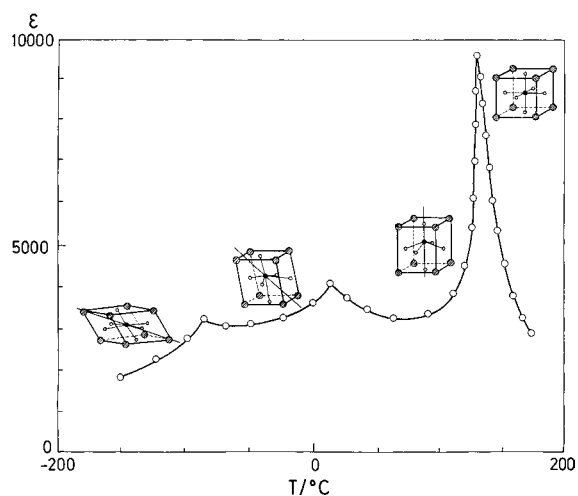

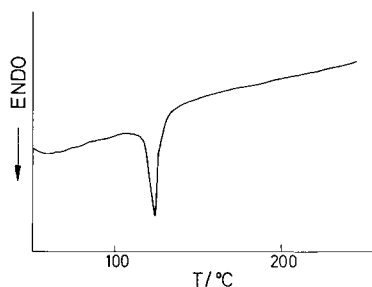Fig. 4. Plot of the $BaTiO_3$ permittivity as a function of the temperature.

Fig. 5. DSC curve for BaTiO$_3$.

In summary, we can conclude that TSC can be an alternative to DSC for analysing phase transitions processes whose transition enthalpy is very low.

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