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Wide-Temperature-Range Dielectric Permittivity Measurement under High Pressure *

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Two measurement systems are developed for in-situ dielectric property measurement under high pressure in a wide-temperature range from 77 K to 1273 K. The high-temperature system ranging from room temperature up to 1273 K is equipped with a hexahedron anvils press, while the low-temperature system ranging from liquid nitrogen temperature to normal condition is equipped using the piston cylinder setup with a specially designed sample chamber. Using these configurations, the dielectric property measurement of ferroelectric $BaTiO_3$ and multiferroic $Tm_{0.5}Gd_{0.5}MnO_3$ compounds are demonstrated, which proves the validity of the systems through the tuning of the polarization and phase transition boundary by high pressure. These two systems will be equally applicable to a wide variety of electronic and transport property measurements of insulators, semiconductors, as well as battery materials.

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Dielectric measurement techniques have developed from a tool for the mere low-frequency 'quasi-static' characterization of samples to methods for the extremely broadband spectroscopy as well as high-frequency imaging of materials in the past 95 years.[1] Recently, there has been increasing interest in using high-pressure techniques to measure the dielectric properties of materials with technological advances.[2,3] Dielectric measurement techniques have been notably promoted by the application of high pressure, which is an effective way to modify the interatomic distance and tune the local electronic structure, thereby exploring the physical and chemical properties of solid materials without introducing any impurities and defects.[4−7] There are several systems that have been developed for measuring the dielectric properties of materials under high pressure over the past few years. For instance, Xu *et al.* have made great progress on the high-pressure dielectric property measurement of solid materials.[2,8] They have succeeded in measuring the hydrostatic pressure and temperature dependence of the dielectric response for the ferroelectric samples such as PZT95/5-Nb ceramics,[8] La-doped Pb(Zr, Sn, Ti)O_3 antiferroelectric ceramics,[9] and PMN-PT68/32 single crystal.[2] Due to the potential explosion of oil pressure medium at high pressure and high temperature, the maximum pressure was limited to below ∼1 GPa and temperature lower than ∼523 K. At higher pressure, Peng *et al.*[10] have developed a two-electrode configuration for high-pressure dielectric measurement based on *in situ* impedance measurement in a diamond anvil cell. With a regularly shaped microcircuit, dielectric constant can be measured up to the pressure of 30 GPa at room temperature. However, taking dielectric measurement under both high-pressure and wide-temperature range is still a challenging work due to experimental difficulties.

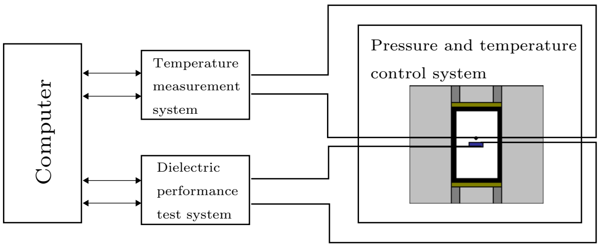

Fig. 1. The schematic diagram of the high temperature system. The temperature can be varied between room temperature to 1273 K and the pressure range can go up to 6 GPa, depending on the pressure generation as shown in Fig. 2.

In this work, we present two recently developed systems which can be used to measure the dielectric properties of solid materials under high pressure up to 3–6 GPa with a wide-temperature-range from liquid nitrogen temperature zone to 1273 K. The two systems, namely high-temperature and low-temperature systems, consist of four main components: the temperature measurement unit, the dielectric permittivity test unit, the software control unit and the pressure/temperature control unit, as shown in Figs. 1–4. The main differences between these two systems are the pressure generation unit and the temperature control unit. The hexahedron anvils press (Fig. 2) and the piston cylinder pressure cell (Fig. 4) are used depending on the measurement temperature range. Application of these different control systems results in a

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great improvement of the experimental accuracy and provides the possibility to introduce precise dielectric measurement under both static high-pressure and wide-temperature-range conditions.

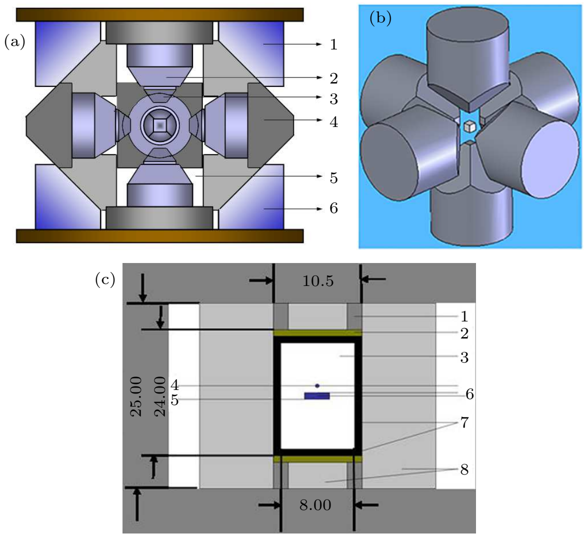

Fig. 2. (a) The schematic diagram of the pressure cell chamber: 1, the up container; 2, the sheath; 3, top anvils; 4, the slider; 5, the chute; and 6, bottom anvils. (b) The sketch map of 6-anvil. (c) The schematic diagram of the pressure cell: 1, steel ring; 2, molybdenum sheets; 3, hexagonal boron nitride; 4, thermocouple sensor; 5, electrodes (coaxial wire); 6, sample; 7, graphite furnace and the circuit formed by the top/down hammer; and 8, pyrophyllite (the molecular formula is $Al_2(Si_4O_{10})(OH)_2$, chemical composition is $Al_2O_34SiO_2H_2O$).

Figure 2 shows the schematic diagram of the hexahedron anvils press, including the schematic diagram of the pressure cell chamber (Fig. 2(a)), where the assembled cell in Fig. 1 can be fitted in, and the schematic diagram of the pressure cell (Fig. 2(c)). The length units are mm in the shown figure. The sample pellet should have diameter smaller than 3 mm, and the upper and lower surfaces are coated with silver paste, which form a parallel capacity. The electrodes will directly contact with the two surfaces (Fig. 2(c)). The hexahedron anvils press has larger pressure cavity for larger bulk samples and uniform pressure can be applied, even solid pressure medium has to be used, with the multiple anvils centripetal compress method (Fig. 2(b)). The shape of the pressure surface of the anvil is square ($28\times28\,\mathrm{mm}^2$ in area). To acquire more precise result and eliminate the error from the contact between the sample and the electrodes inside, we have developed a unique assembly method of the pressure cell, as shown in Fig. 2(c). The heating parts include steel ring, molybdenum sheets, graphite furnace, and the circuit formed by the top and bottom anvils. The pressure transmission part contains hexagonal boron nitride and pyrophyllite. There are several unique techniques for the cell parts. First, all the electrode wires and thermocouple wires are shielded by high-temperature resistant and high-ductile materials in the purpose of survival at high pressure and high temperature, as well as the insulating layer between the wires and the heat furnace. Secondly, the samples are in small diameter (<3 mm) and relatively larger thickness to avoid the deformation of the sample and maintain quasi-hydrostatic condition as the pressure medium is solid. Finally, a buffering layer of hexagonal BN powders was placed around the sample to avoid the sample deformation and also functioned as the insulator layer, as the thermocouple is mounted very close to the sample to obtain accurate temperature readings. The advantage of this uniquely designed pressure cell is that they are light in weight, small in volume, simple and compact in design, which can be installed perfectly with various types of hexahedron anvils press.

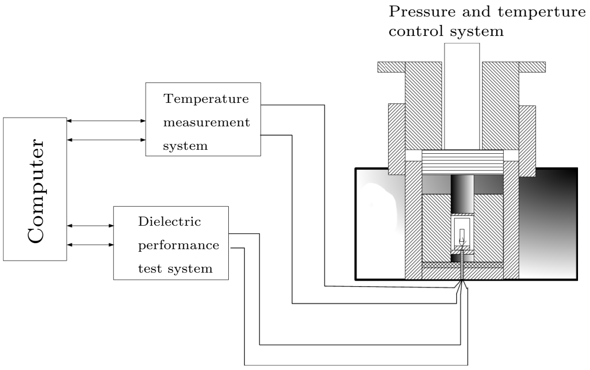

Fig. 3. The schematic diagram of the low temperature system. The temperature can go down to about 78 K from room temperature and the pressure can go up to maximum of 3 GPa, depending on the piston-cylinder cell.

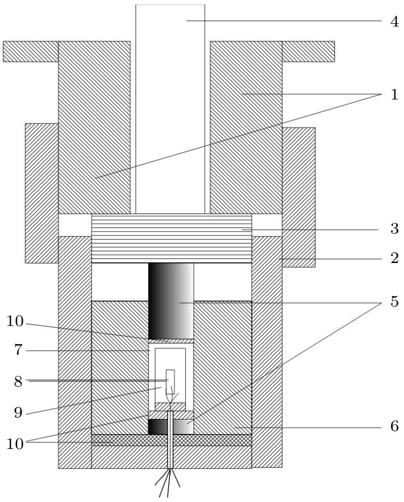

Fig. 4. Schematic diagram of the piston cylinder pressure cell: 1, lock nut; 2, Cu-Be outside the cylinder; 3, Cu-Be gasket; 4, steel column; 5, tungsten carbide cylinder; 6, Cu-Be inside the cylinder; 7, teflon material cylinder; 8, sample; 9, liquid pressure medium; and 10, Cu-Be gasket.

Figure 4 shows the schematic diagram of the piston cylinder pressure cell, which was used in our experiment to measure the dielectric properties under pressure, while varying temperatures between room temperature down to liquid nitrogen temperature zone. The sample chamber was carefully designed to carry out the dielectric measurement precisely under application of pressure. The WC was used to transmit pressure similar to hexahedron anvils press, while teflon was used for the sample chamber, as they are good insulating materials and they can seal the pressure medium well. Applied pressure was transmitted via copper between the WC and the sample chamber. To keep good hydrostatic pressure, we chose a 1:1 mixture of silicon oil and coal oil as the pressure transmitting medium and the sample was immersed in the transmitting medium. The resistance of the medium was large enough, which can be ignored during measurement. The size of the sample was less than 4 mm in diameter and sample surface was coated with insulation glue in the experiment to acquire a more precise result and to eliminate the error brought by the contact loss between the sample and inside wall of the cylinder. The electrodes on the sample were prepared by applying a thin coating of Ag paint on the two parallel planes of the sample, and a coaxial enameled wire was used in the measurement. The piston cylinder pressure cell was pressurized at room temperature after sample loading and the lock nut at the top was tightened to maintain the pressure. The gap between the thermistor and the sample should be kept to be about 1 mm to make sure that they would not contact with each other.

The dielectric permittivity was measured using an electrical impedance analyzer (HP 4192 A), which was grounded during the capacity measurement. Dielectric constant can be deducted from the equation of parallel-plate capacitor $\varepsilon = c \cdot d/S$, where c is the capacity, d is the thickness of the sample, and S is the coated surface area. The temperature and dielectric constant values were recorded by a personal computer with an automated measurement software package programmed by our group. It should be noticed that limited by the pressure cells, there were about 10 mm length electrode leads that were not coaxial or twisted pair wire. Thus we tested every sample outside the pressure cell by using the standard ambient method as well as inside under the ambient condition. The results were consistent, which indicated that the inside lead will not affect the results. The temperature sensors of the measurement system, installed in the high-pressure device, can be chosen according to the needs of the experiment, which can be a thermistor or a thermocouple. The temperature signal, obtained from the temperature measurement sensors, was transmitted to the data acquisition system in the computer through a temperature measurement system. The dielectric permittivity constant of solid materials can be deducted with the parameters of surface area and thickness of the sample pellet.

$BaTiO_3$ (BTO), a classical ferroelectric material, has been studied for more than half a century and been widely used since its discovery in the early 1940s.[11,12] At ambient pressure, BTO undergoes several structural phase transitions with decreasing the temperature, from cubic ($Pm3m$) (C) to tetragonal ($P4mm$) (T), and then to orthorhombic ($Amm2$) (O), and stabilizes as rhombohedral ($R3m$) (R) structure at low temperature.[13,14] These phase transitions are associated with changes in the dielectric constant. $Tm_{0.5}Gd_{0.5}MnO_3$ (TGMO) compound is one of the rare earth manganates and known as an important multiferroic material. Up until now, only a few of the physical and electronic properties of TGMO have been found.[15] The magnetoelectric effect caused by the coexistence of ferroelectric and magnetic ordering brings out rich and fascinating physics of multiferroics. In addition, the ability to couple with either electric or magnetic polarization offers an extra degree of freedom in design of new apparatus.[16–19] These facts make both BTO and TGMO good candidates to study the dielectric properties by using newly developed measurement systems.

The dielectric property of BTO/TGMO ceramics under high temperature and high pressure up to 6 GPa was measured in the hexahedron anvils press. The electrodes were prepared by applying a thin coating of Ag paint and they were placed at the center of a pyrophyllite cube ($25 \times 25 \times 25\,\mathrm{mm}^3$ in size). The samples were surrounded by a pressure transmitting medium (hex-boron nitride). This was then loaded into a graphite tube with two metal pellets attached to the top and bottom anvils, serving as contacts for the electric circuit. A Cu wire of 0.1 mm in diameter encapsulated by a teflon tube was used to make a flexible contact with the BTO ceramic at the diagonal corners of the pyrophyllite cube and the external leads were screened by a woven metallic shield. The temperature was monitored by a NiCr-NiSi thermocouple mounted very closely to the samples. The pyrophyllite cube was placed in the central cavity of the cubic anvil apparatus, which could generate high pressure up to 6 GPa, as shown in Fig. 2. Figure 5 shows the dielectric constant of BTO ceramic with grain size of 100 nm measured at 100 kHz (Fig. 5(a)) and TGMO ceramic measured at 1000 kHz (Fig. 5(b)) as functions of temperature and pressure. When the applied pressure was increased, $T_{\rm C}$ of ferroelectric phase to paraelectric phase transition in BTO will shift to lower temperature and the peak values of dielectric constant will be significantly suppressed. This can be explained by considering that a positive volume strain is produced at the cubic paraelectric to tetragonal ferroelectric phase transition.[5] Similarly, the phase transition temperature of TGMO compound will shift to lower temperature with pressure change at a rate of 13.2 K/GPa. However, the dielectric constant almost keeps the beginning value with the increase of the pressure, indicating that the polarization mechanism is different from that of BTO.[19,20]

The dielectric property measurement for BTO under low temperature and high pressure up to 2 GPa was carried out in a piston cylinder pressure cell. The electrodes on the BTO ceramic were prepared by applying a thin coating of Ag paint on the two parallel planes of BTO. To conduct the dielectric measurement precisely under high pressure, the size of BTO ceramic was about 3–4 mm in diameter and a coaxial enameled wire was used in the measurement. The gap between the thermistor and the BTO ceramic should be kept to be about 1 mm to make sure that they will not contact with each other. The pressure transmitting medium is a 1:1 mixture of silicon oil and coal oil and the BTO ceramic was immersed in the transmitting medium. Figure 6 shows the results obtained from the dielectric constants measurements on BTO ceramics with grain sizes of 5 μm, 800 nm, 500 nm and 200 nm as a function of pressure at low temperature. The two broad peaks observed upon lowering temperatures are the indications for phase transitions from T phase to O phase (T_1) and O phase to R phase (T_2). It was found that the peak value of the dielectric constant is strongly suppressed by increasing the compressive pressure and the permittivity of BTO ceramic changes nonlinearly with the reduction of the grain size. More specifically, at ambient pressure, the reported phase transition temperatures for 800 nm BTO from T to O and O to R phases were 290.3 K (T_1) and 200.8 K (T_2) for 800 nm BTO at ambient pressure, respectively. Our results showed that the increasing compressive pressure resulted in the shifts of T_1 and T_2 to lower temperature and also significantly suppressed the peak dielectric constant value. This is the case similar to that observed in the nanosize grain ceramics, where the internal stresses are mainly compressive and isotropic, and the application of hydrostatic pressure resulting in low-temperature shifting of T_1 and T_2.[5,21]

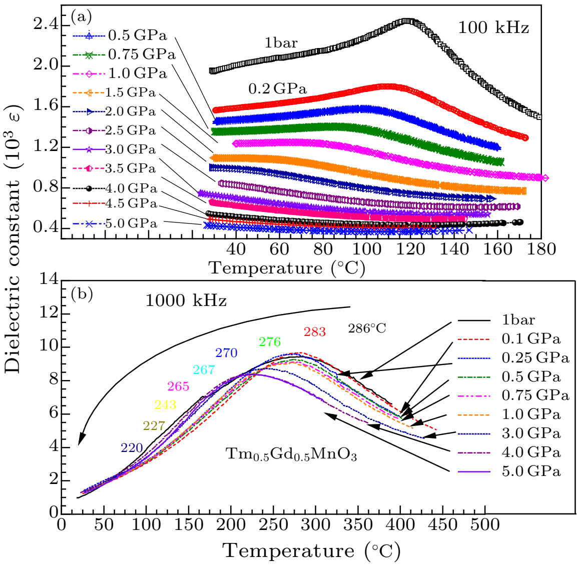

Fig. 5. (a) Dielectric constant of $BaTiO_3$ ceramic with 100 nm grain size measured at 100 kHz under high temperature and high pressure, and more detailed information can be found in Ref. [5]. (b) Dielectric constant of $Tm_{0.5}Gd_{0.5}MnO_3$ multiferroic ceramic as function of temperature and pressure. The phase transition located at ∼286°C under the ambient condition and shifted to 220°C under pressure of 5 GPa.

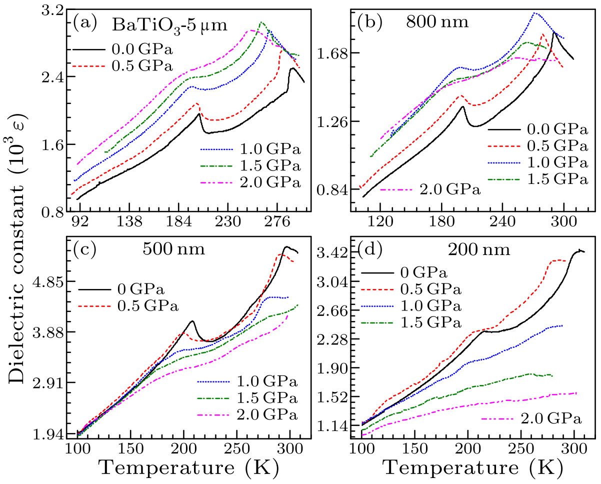

Fig. 6. Dielectric constant of $BaTiO_3$ ceramics with grain sizes of 5 μm, 800 nm, 500 nm and 200 nm measured as a function of pressure upon lowering temperature.

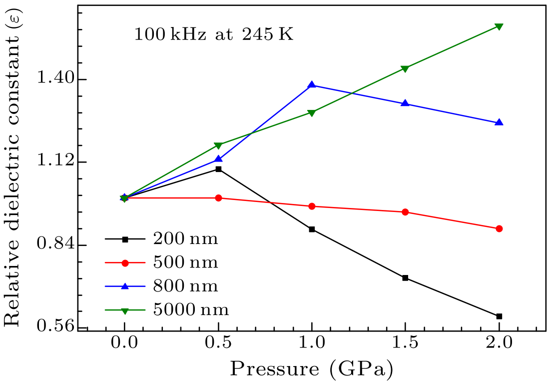

Fig. 7. Evolution of normalized dielectric constant at 245 K in the orthorhombic phase region as a function of pressure for different grain-sized samples.

For the nanosize grain ceramics, the internal stresses are mainly compressive and isotropic, like an applied hydrostatic pressure, resulting in low-temperature shifting of T_1 and T_2.[5,21] Figure 7 gives the evolution of normalized relative dielectric constant at 245 K in the O phase region as a function of pressure for different grain-sized samples. The change of the relative dielectric constant with pressure is a result of the competition between the increased relative dielectric constant caused by the downward T_1 shift and the permittivity suppression caused by the external pressure. In coarse-grain BTO ceramic, the increase of permittivity due to T_1 shift caused by pressure is larger than the permittivity suppression. Hence, the total dielectric constant increases, as shown in Fig. 7. In contrast, for the three nanograin BTO ceramic samples, the dielectric peak becomes more diffusing under high pressure. The pressure suppression and the coexistence of T and O phases result in the decrease of the dielectric constant in nanograin BTO ceramics with the increase of pressure.[22]

From the above two examples, we can clearly see that the two measurement systems can be used to accurately measure the dielectric properties of solid materials under high pressure. This will provide equipment support for the research of ferroelectric phase transition mechanism of solid materials. Moreover, these two systems can be extended to all kinds of electronic and transport property measurement by replacing the data test system. The error of measurement may come from two aspects. The error origin from the circuit can be treated as a fixed system shift. It can be eliminated by system calibration. The other source of error may come from the shape change of the sample under high pressure. However, fortunately the surface area S and the thickness d shrink at the same time, which result in the fact that most of the errors cancel out against each other.

In summary, we have presented two new dielectric property measurement systems, which can be successfully used to measure dielectric constant from liquid nitrogen temperature zone up to 1273 K under high pressure. The dielectric measurement techniques under high pressure are becoming easier to use and compatible with modern standard analysis equipment. Thus we can expect that more and more electronic-related properties, such as dielectric, resistance and impedence, could be measured under high pressure for the purpose of understanding the fundamental functional mechanisms of solid materials.

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