

Electrical Properties of Barium Titanate Ceramics.

SAFED S. BABKAIR, FARAG S. AL-HAZMI, ALI M. AL-SANOOSI and AZHAR A. ANSARI
Department of Physics, Faculty of Science, King Abdulaziz University.

ABSTRACT. Barium titanate ceramics, both in the pure and the doped forms, have been prepared by the thermo-chemical method. The ceramic powder thus obtained was compressed into pellets on which AC and DC measurements were made.

The relative permittivity of the samples has been studied over a frequency range of 50Hz. to 100KHz. and temperatures varying between 300K and 500K. The resistivity of the doped samples has also been studied at different temperatures.

The result exhibited a sharp decrease in relative permittivity with increasing temperature around the Curie point. It also exhibited a sharp increase in resistivity of the doped samples with increasing temperature around the Curie point, which is commonly referred to as the PTCR (Positive Temperature Coefficient of Resistance). The behavior is explained on the basis of Heywang's model as modified by Jonker (1981).

Introduction

Barium titanate (BT) exhibits a number of interesting properties that make it suitable for applications in electronic and electrical industries. BT undergoes a dramatic PTCR effect (Positive Temperature Coefficient of Resistance) beyond a certain temperature when the resistivity increases by several orders of magnitude. This phenomenon is made use of in heat sensors and thermally operated switches. Also BT has an extremely high dielectric constant, this makes it an ideal material for use as dielectric in large value and small size capacitors. These are called Barrier Layer Capacitors. BT also exhibits a large Piezoelectricity near the Curie point making it a potential candidate as a detector in stress sensing applications. (Capurso 1998).

Barium Titanate

Barium titanate is a semiconducting oxide ceramic with a band gap of 3.1 eV. In the undoped form it has a resistivity of the order of 10^{10} Ω cm. (Heywang, 1971). It has a perovskite structure as shown in figure 1. Perovskites are a subgroup of the Oxygen-

Octahedra-Group and have a general chemical formula ABO_3 . Here A is a di- or monovalent metal and B is a tetra- or pentavalent metal. Barium titanate is a ferroelectric material which exhibits a spontaneous polarization below the Curic point which occurs at 120°C . The transition from ferroelectric to non ferroelectric (paraelectric) phase is accompanied by anomalies in physical properties. The anomalous PTCR effect at the phase transition and an extremely large value of the dielectric constant in the ferroelectric phase are the peculiarities that are exploited in devices. The Curie temperature T_c of suitably doped Barium titanate varies with the lattice constant of the mixed crystal. This makes it possible to "tune" the Curie temperature from 83°C to 393°C . (Dekker 1970, Al-Allak *et al.*, 1989).

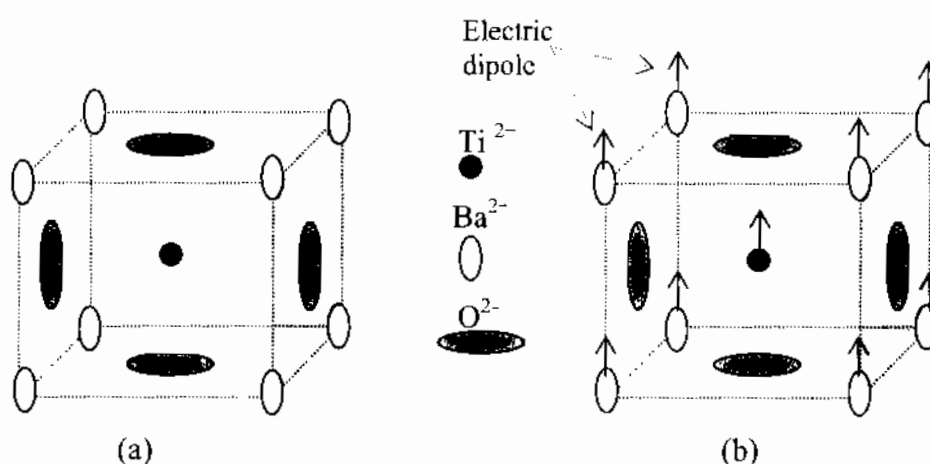


Fig. 1. The crystal structure of $BaTiO_3$. (a) Above T_c , the structure is cubic. (b) Below T_c , the structure is slightly tetragonal, developing electric dipoles
For clarity reason, the oxygen ions of the back and front faces are not shown.

Ferroelectric barium titanate consists of electric domains each having uniform homogenous polarization as shown in figure 2. A domain is defined as a region in the material where all the dipole moments of adjacent unit cells have a common direction. The material can have zero polarization under zero electric field due to the random orientation of the electric domains. If the electric field is applied as the material is cooled, the polarization can be measured as a function of temperature. Barium titanate has three ferroelectric phases as shown schematically in figure 3.

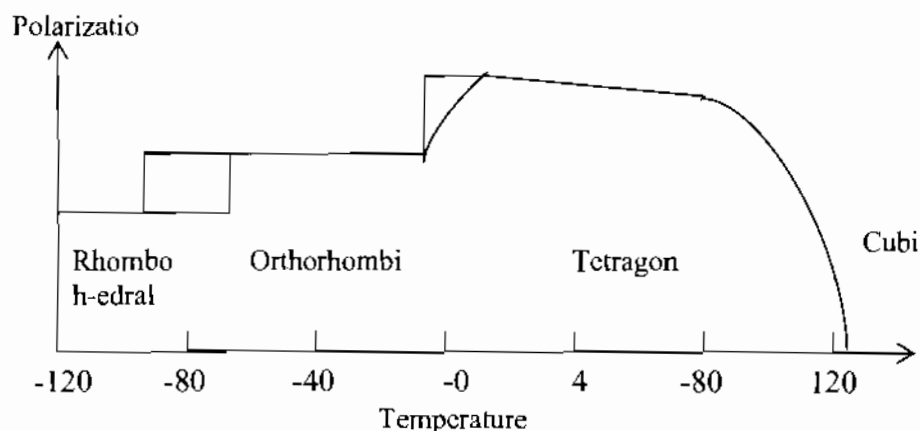


Fig. 2. The polarization in the various phases of $BaTiO_3$ as a function of temperature.

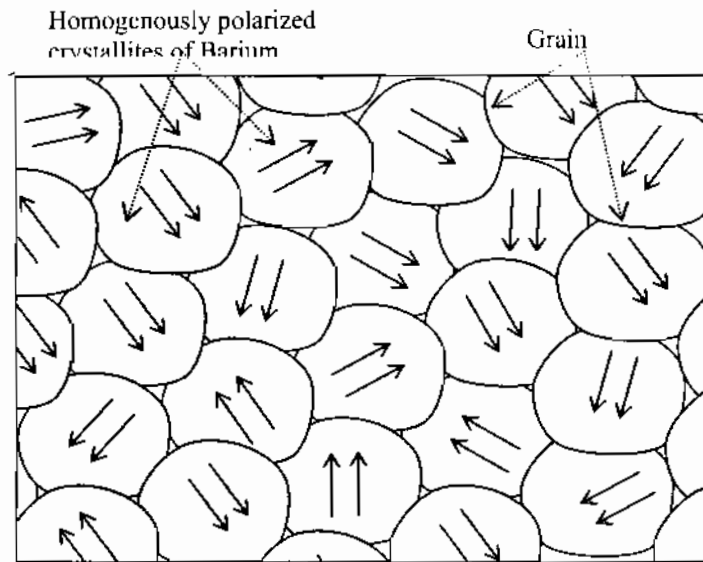


Fig. 3. Domain structure of polycrystalline Barium Titanate.

PTCR effect and anomalous permittivity behavior in BaTiO₃:

The many interesting electrical properties, of barium titanate ceramics owe their existence to its ferro-electric nature. The permittivity of a ferroelectric material is anisotropic, and therefore dependent on the direction of the field for crystalline materials. This is a consequence of the non linear relationship between the field and the polarization vectors. The permittivity is large in the vicinity on the transition temperatures being of the order of 10^4 to 10^5 . Crystalline Barium titanate does not exhibit the PTCR effect. (Heywang 1964, Jonker 1964). On the other hand, polycrystalline Barium titanate exhibits a pronounced PTCR at the ferroelectric-paraelectric transition temperature T_c also called the Curie point.

The two most technically useful properties of barium titanate are the PTCR effect where the resistance suddenly increases by several orders of magnitude at the Curie point (Osak & Tkacz 1989), and a parallel phenomenon of anomalous behavior of permittivity which registers a large decrease beyond the Curie point (Karasawa & Fukami 1994). The former finds applications in heat sensors and thermal switches, whereas the later property is used in the barrier capacitor capacitors.

Both these effects have their genesis in the physical features of the polycrystalline material; the interfacial grain boundaries existing between crystallites of Barium titanate and the existence of spontaneous polarization in the ferro electric phase. (Heywang 1971)

The fact that only n-type conductivity has been observed in polycrystalline barium titanate implies that the high temperature region observed experimentally cannot be due to the bulk of the crystallites. The bulk grains generally have a resistivity of $5 \Omega\text{-cm}$ which can be ignored. [Illingsworth 1990]. Heywang (1971) has postulated that interfacial layers, existing between crystallites, contain an effective blocking mechanism – a potential barrier – and play a critical role by impeding the free flow of carries. The presence of acceptor states in the grain boundaries has been invoked to explain the existence of the barriers. Acceptor states trap electrons from the bulk of the crystallites and create a depletion region adjacent to the layers. Figure 4 shows the creation of such a barrier at the grain boundary.

The depletion regions exist in both the adjoining grains creating a back-to-back Schottky type barrier.

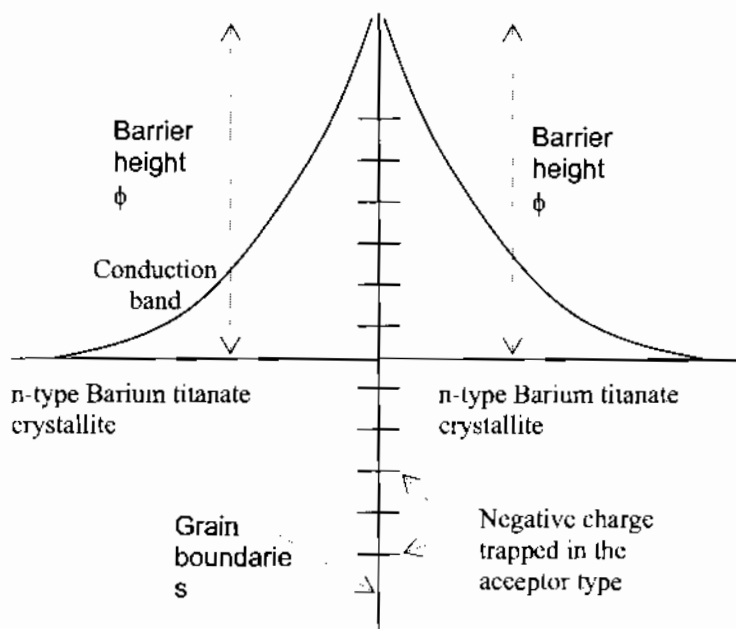


Fig. 4. Potential barriers at the grain boundaries.

Sample Preparation

Thermo-chemical method was chosen for the fabrication of BaTiO_3 powder from which pellets were made for measurements.

The procedure for fabricating BaTiO_3 powder both, in the pure and the doped forms, is as follows. Undoped Barium titanate was prepared by reacting an equimolar mixture of Barium carbonate BaCO_3 and Titanium-di-oxide (TiO_2) by the thermo-chemical method. To make the doped semiconducting Barium titanate, 0.3 mol.% of Ho_2O_3 was mixed with BaCO_3 and TiO_2 in the correct atomic ratios. The same calcinations, sintering and annealing cycle was used for both types of Barium titanate. The samples reported here, had a diameter of 10mm and thicknesses between 1.5 to 2 mm.

The constituents were thoroughly mixed in ethanol and later dried in an oven at 500°C . The mixture was calcined at 1200°C in a programmable Thermocline 300 furnace for six hours. Calcination temperature of 1200°C was reached at a constant heating rate of $5^\circ\text{C}/\text{min}$. The powder was removed, thoroughly grounded and mixed with a small quantity of a binder PVA (Poly-Vinyl-Acetate). This hinder helps in the formation of mechanically rugged pellets. Some of this mixture was loaded into a die and was compressed to a pressure of 200MPa. The pressure was maintained for 10 seconds. The pellets had a diameter of 10mm and a thickness of nearly 2 to 2.5mm. Several pellets were made by this method.

The pellets were placed in a ceramic crucible and loaded in a Thermocline 300 programmable furnace. The properties of the BaTiO_3 powder are strongly dependent upon the heat treatment especially the sintering and annealing temperatures and the cooling rates, (Brian *et al.*, 1999). Figure 5 shows the firing schedule adopted for sintering and annealing BaTiO_3 pellets. The sequence begins with the binder burn out stage at 600°C . The pellets are held at this temperature for one hour to drive out all the PVA. This is

followed by a quick heat of the pellets at a constant rate of $5^{\circ}\text{C}/\text{min}$. up to 1400°C at which the sample is sintered for 2 hours. During sintering the sample undergoes grain growth and densification. In this stage Oxygen is chemisorbed in the grain boundary regions and act as acceptor states, (Sinclair & West 1994). It is these traps at the grain boundaries which create potential barriers and resistivity anomalies at the Curie Temperature. After annealing the pellets were allowed to cool to room temperature at a fixed rate of $5^{\circ}\text{C}/\text{min}$.

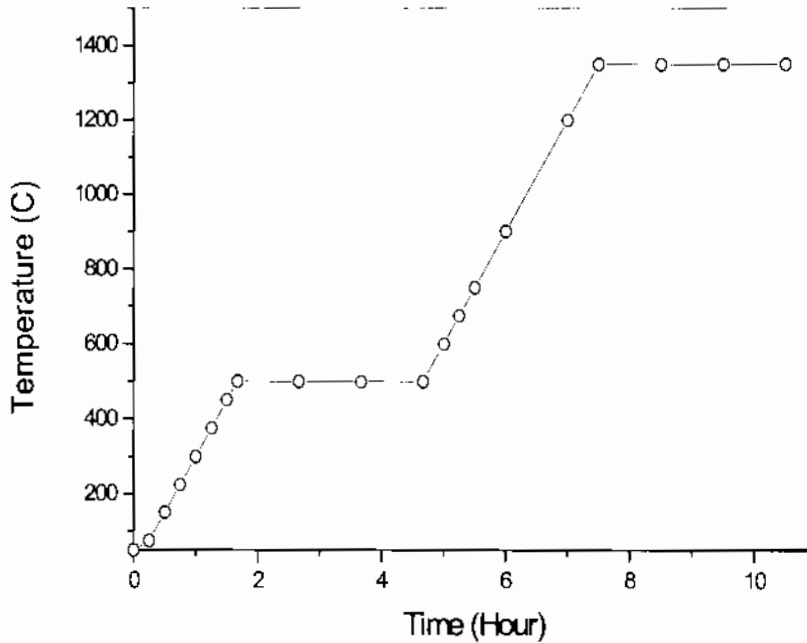


Fig. 5. The firing schedule for sintering and annealing

The pellets obtained had a rough surface and were polished by rubbing the pellets successively on increasingly finer grades of diamond pastes which reduced their thickness. Finally, electrical contacts were obtained by rubbing the polished surfaces of the pellets with Indium-Gallium alloy (Indium and Gallium in the ratio of 2:1).

Experimental Setup

Figure 6 shows the schematic diagram for measuring the I-V-T and C-f-T characteristics of the specimens.

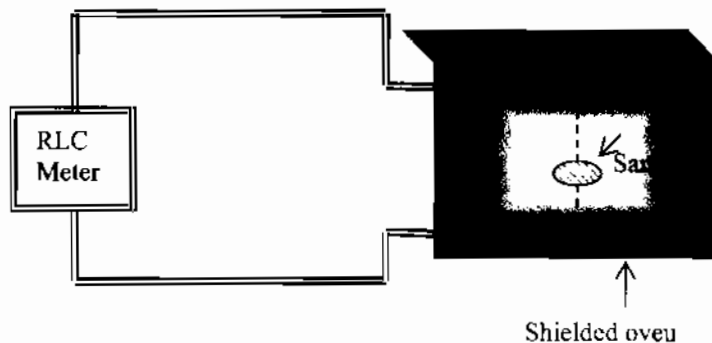


Fig. 6. Measurement circuit

A Fluke 3606 automatic programmable RCL meter was used to measure the capacitance of the sample as a function of frequency. The amplitude of the applied signal could be varied from 50mV to 2V pk-pk. The frequency range was 50Hz to 1MHz. The sample mounted on the sample holder was placed in an oven capable of achieving temperatures up to 350°C. Shielded co-axial cables were used to connect the sample inside the oven to the RCL meter.

The stray capacitance of the system was determined for all temperature over the full frequency range and was later subtracted from the actual readings to obtain the capacitance of the BaTiO₃ pellets. This data was used to determine the dielectric constant of the material as a function of frequency and temperature.

Experimental Results and Interpretation

i) Measurements of permittivity on undoped samples

The relative permittivity was calculated for samples of undoped Barium titanate from the capacitance-frequency data obtained at various temperatures. The temperature range covered both, the ferroelectric and the paraelectric, phases. Permittivity ϵ was calculated using the simple relation;

$$\epsilon = C_0 d / \epsilon_0 A \quad (1)$$

Here, A is the area of the contact, C₀ is the Capacitance, d the thickness of the sample and $\epsilon_0 = 8.85 \times 10^{-12}$ F/m is the permittivity of free space.

Figure 7 shows the typical behavior of the permittivity-temperature characteristics at three measuring frequencies of 100Hz, 1.2KHz and 50KHz. It can be seen that at the Curie temperature 120°C (~393K) the value of permittivity ϵ increases sharply and approaches infinity. Above the Curie temperature (in the paraelectric phase) the value of permittivity depends upon the Curie Weiss law, (Issa 1992);

$$\epsilon = C / (T - T_c) \quad (2)$$

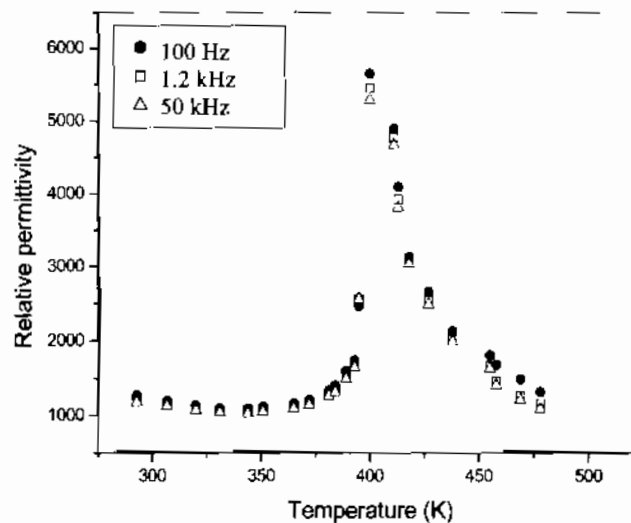


Fig. 7. Permittivity versus temperature for three different frequencies.

Thus plotting $1/\epsilon$ against temperature should result in a straight line with a reciprocal of the slope equal to the Curie constant. Figure 8 shows such a plot. It can be seen from the graph that the relationship is linear and the linear part extrapolates to $T_c = 393\text{K}$ (120°C). The Curie constant determined from the slope has a value of $1.1 \times 10^5 \text{ }^\circ\text{C}$ and compares favorably with the value of $1.2 \times 10^5 \text{ }^\circ\text{C}$ reported in literature, (Dekker 1970).

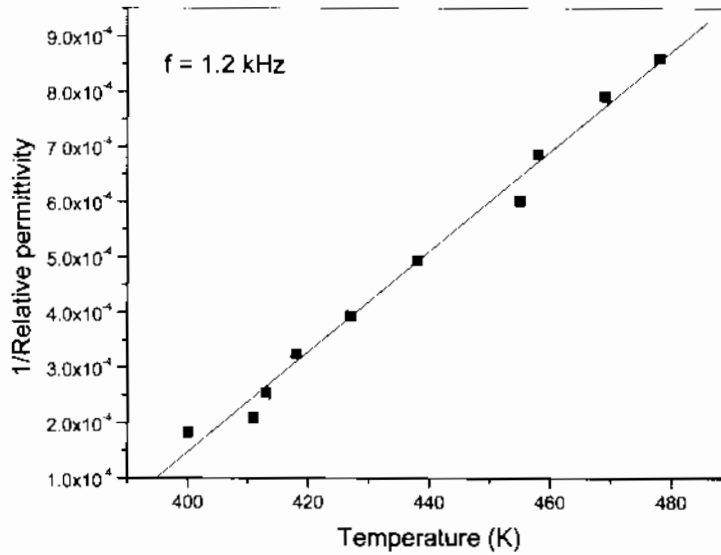


Fig. 8. Reciprocal of relative permittivity versus temperature at $T > T_c$.

ii) Measurements of permittivity and resistivity on doped samples:

The resistivity of the Ho-doped samples was measured over a temperature range of 300K to 570K. The results are shown in figure 9. It can be observed that the resistivity exhibits a sharp increase at about 120°C which is the often quoted characteristic value for Barium titanate, (Dekker 1970).

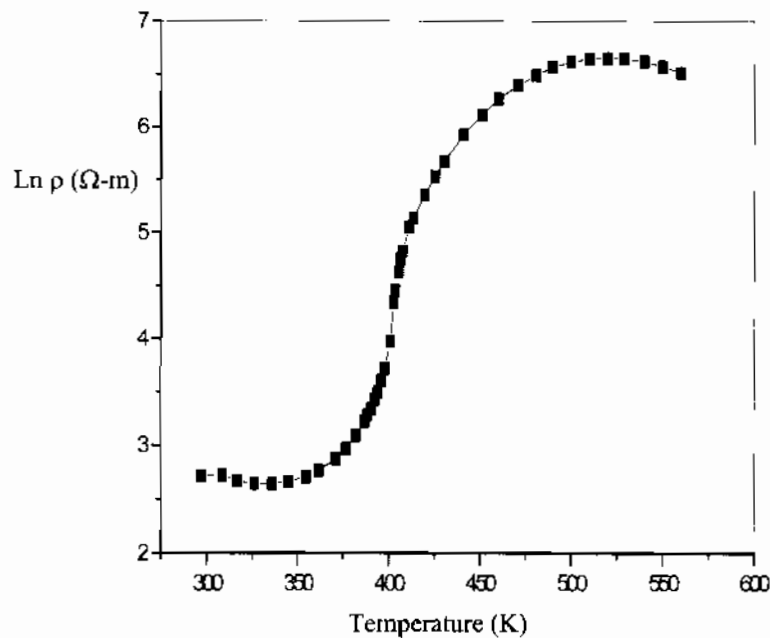


Fig. 9. Resistivity-temperature characteristics of BaTiO_3 .

Fig. 10 gives the permittivity ϵ_m as a function of temperature. All these measurements were taken at a fixed frequency of 1.2 KHz. The temperature range employed (300K to 570K) covered both the ferro and para electric domains. The regions were separated by the Curie point T_c . It can be seen from the plots that the permittivity under-goes a sharp increase at about 400K, corresponding to the Curie temperature and then decreases. In the region beyond T_c permittivity for doped BaTiO₃ usually follows the modified Curie-Weiss law (Issa 1992);

$$\epsilon = \epsilon_{\text{const}} + C / (T - T_c) \quad (3)$$

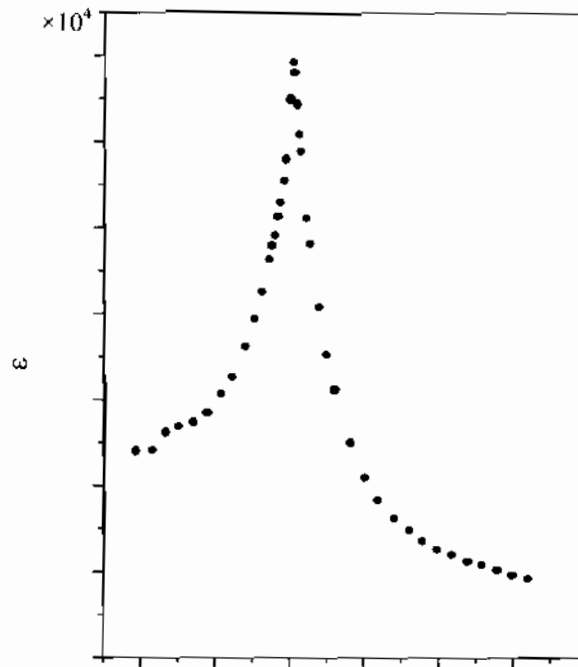


Fig. 10. Temperature dependence of permittivity for Ho-doped samples.

Where ϵ_{const} is the value of permittivity independent of temperature. The Curie constant of the sample and T_c were calculated from a plot of ϵ^{-1} Vs. temperature in the linear region of data where equation (3) is obeyed. They were found to be

$$C = 5.6 \times 10^6 \text{ K} \quad T_c = 393\text{K}$$

Substituting this value of T_c (393) into equation (3) and calculating $(T - T_c)$ for different experimental temperatures the ϵ versus $1/(T - T_c)$ was obtained. This is demonstrated in figure 11 and the value of ϵ_{const} has been determined from the intercept of the straight line with the permittivity axis. It was found to be

$$\epsilon_{\text{const}} = 3.2 \times 10^4$$

Discussion

Resistivity R is exponentially dependent on the height of the interfacial barrier. Additionally, the theory of Schottky barrier states that the height of the barrier Φ is inversely proportional to the permittivity of the medium. R and Φ are related by the relation; (Wang and Umeya 1990),

$$R = R_0 \exp (e\Phi/kT) \quad (4)$$

Above T_c , in the paraelectric phase, there is no spontaneous polarization of barium titanate and the dielectric constant is low. This increases the barrier height and results in a region of high resistivity. Conversely, below T_c , the charge in the barriers is partially compensated by the surface charge due to the abrupt terminations of the normal polarization components of the ferroelectric domains at the grain boundaries. This results in an increased dielectric constant which lowers the barrier and increases conductivity, (Capurso 1998).

The addition of a suitable ion results in the formation of acceptor levels at different energies giving rise to a temperature dependent PTCR effect. It is known that the Curie point can be raised or lowered by the substitution of Ba^{2+} ions with Pb^{2+} or Sr^{2+} ions. (Chun. & Tseng, 1994). External influence and material properties also affect the barrier heights. The two of the more important influences are:

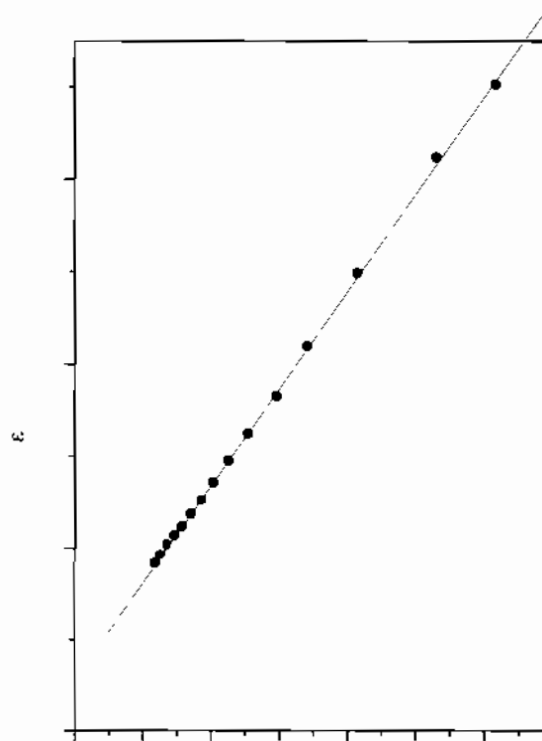


Fig. 11. Plot of permittivity ϵ_m vs. $(T-T_c)^{-1}$ for Ho-dope Barium titanate sample. The Curie-Weiss law.

i). In the ferroelectric state the material polarizes and at least partially compensates the trapped charge and reduces the dielectric constant which results in a lowering of the barrier and increasing conductivity.

ii). Increasing the temperature (beyond Curie point) results in two competing processes.

(a). As the spontaneous polarization disappears and the permittivity of the medium is reduced which results in an increased barrier and a reduced conductivity.

(b). The increased temperature will tend to increase conductivity through enhanced thermal activation of electrons over the barriers.

The contribution to conductivity due to the thermal activation of carriers is very small due to the increased barrier height. Consequently, the net result is a reduced conductivity beyond Curie point.

In view of the foregoing the permittivity decreases dramatically with increasing temperature which is elegantly summarized in the Curie-Weiss law.

Conclusions

1. Permittivity measurements performed on pure barium titanate samples give a value of Curie constant as $1.1 \times 10^5 \text{ }^\circ\text{C}$ which compares favourably with the reported value in literature.
2. Curie temperature determined from ϵ_m Vs. $(T)^{-1}$ gives a value of 120°C while agrees very well with the accepted value for barium titanate.
3. In the para-electric region where the spontaneous polarization vanishes the Curie-Weiss law is obeyed as predicted by theory.
4. Samples of undoped barium titanate show a high resistivity region over the full temperature range employed which is characteristic of the material.
5. For the doped samples the relative permittivity has been shown to obey the modified Curie-Weiss law.
6. A significant difference between the resistivity behavior of the doped and the un-doped material was the high resistivity of the undoped barium titanate. Un-doped barium titanate did not exhibit a PTCR effect although it underwent the permittivity anomaly.

References

- Al-Allak, H.M. et.al.**, (1989) Permittivity temperature behaviour of donor doped positive temperature coefficient of resistance BaTiO₃ ceramics. *J. Phys. D. Appl. Phys.*, **22**, 1920-1923. 1989.
- Brian C. LaCourse and Vasantha R.W. Amarakoon**, (1999) Characterization of the Firing Schedule for Positive Temperature Coefficient of Resistance BaTiO₃. *J. Am. Ceram. Soc.*, **78**(12), 3352-56. 1999.
- Capurso, J.S.** (1998) Piezoresistivity in PTCR Barium Titanate Ceramics: I, Experimental Findings. *J. Am. Ceram. Soc.*, **81**(2), 337-46. 1998.
- Chun, H.L. and Tseng, Y.T.** (1994) Investigation of Resistivity and Permittivity for (Ba,Pb)TiO₃ PTCR Ceramics. *J. Am. Ceram. Soc.*, **77**(9), 2419-2424. 1994.
- Dekker., A.J.** (1970) Solid State Physics. Chapter 8. *Ferroelectrics*. p.190. Macmillan and Company. London. 1970.
- Heywang., W.** (1964) Resistivity Anomaly in Doped Barium Titanate. *J. Am. Ceram. Soc.*, **47**(10), 484-490. 1964.

- Heywang., W.** (1971) Semiconducting Barium Titanate. *Journal of Material Science*, **6**, 1214-26. 1971.
- Illingsworth., J. et.al.** (1990) Dependence of grain boundry potential height of BaTiO₃ ceramics on donor dopant concentration. *J. Phys. D. Appl. Phys.*, **23**, 971-975. 1990.
- Issa., M.A.A.** (1992) Electrical properties of polycrystalline PTCR barium titanate. *Journal of Material Science*, **27**, 3685-3692. 1992.
- Jonker., G.H.** (1964) Some aspects of semiconducting Barium titanate. *Solid State Electronics*, **7**, pp 895-903. 1964.
- Jonker., G.H.** (1981) Equilibrium barriers in PTC thermistors. *Advances in ceramics*, **1**, p155-166. 1981. Editor L.M.Levinson.
- Karasawa, J. and Fukami, T.** (1994) Anomalous dielectric relaxation in Ni-doped barium strontium titanate ceramics. *Jpn. J. Appl. Phys. Part I*, **33**, p4936-4939. 1994.
- Osak.,W. and Tkacz., Katarzyna.,** (1989) Investigation of I-V characteristics in polycrystalline BaTiO₃. *J. Phys. D. Appl. Phys.*, **22**, 1746-1750. 1989.
- Sinclair., D.C. and West., A.R.** (1994) Effect of atmosphere on the PTCR properties of BaTiO₃ ceramics. *Journal of Material Science*, **29**, 6061-6068. 1994.
- Wang., Da Ya and Umeya, Kazumasa** (1990) Depletion Dielectric Properties of Positive Temperature Coefficient of Resistance of Barium Titanate. *J. Am. Ceram. Soc.*, **73**, 1574-81. 1990.

الخواص الكهربائية لتيتانات الباريوم الخزفية

سعيد سالم بابكير، فرج سعيد الحازمي، علي محمد السنوسي، و أظهر أحمد أنصاري

جامعة الملك عبد العزيز - كلية العلوم - قسم الفيزياء

مستخلص. لقد تم تحضير مادة تيتانات الباريوم الخزفية في حالتها النقية و الشائبة بالطريقة الكيميائية الحرارية. في هذا البحث تم ضغط بودرة من هذه المادة و تحويلها إلى أقراص لدراسة خواصها الكهربائية في حالة التيار المتردد (AC) و حالة التيار المباشر (DC).

لقد تم دراسة السماحية النسبية للعينات باستخدام ترددات مختلفة تتراوح بين 50Hz إلى 100kHz تحت درجات حرارة مختلفة ابتداء من درجة حرارة الغرفة 300K إلى درجة حرارة 500K. كما تم أيضا دراسة المقاومة النوعية للعينات تحت درجات حرارة مختلفة.

لقد أثبتت الدراسة هبوطا سريعا للسماحية النسبية بازدياد درجة الحرارة عند درجة حرارة كوري. كما أثبتت الدراسة أيضا ازديادا سريعا للمقاومة النوعية بازدياد درجة الحرارة عند درجة حرارة كوري وهو ما يعرف بمعامل المقاومة الحراري الموجب (PTCR). لقد فسرت هذه الظاهرة على أساس نموذج Haywang الذي تم تطويره من قبل Jonker.