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An exceptionally large increase in electrical resistivity within a small temperature interval is termed as the Positive Temperature Coefficient of Resistivity (PTCR) while the decrease, as Negative Temperature Coefficient of Resistivity (NTCR). Both the PTCR and NTCR effects have been successfully utilized in manufacturing thermistors which are basically thermally sensitive resistors (i.e. a resistive device possessing a large temperature coefficient of resistance over an extended temperature range). These devices are made up of semiconducting materials in various shapes and sizes covering a wide range of temperature coefficient from -6.5% to 70% per ^{o}C. A comprehensive outline on the different types of thermistors has been presented in a book by Macklen[1].

The NTC thermistors generally consist of a sintered ceramic body from a mixture of oxides chosen from the elements Mn, Ni, Co, Cu and Fe. By changing the composition and geometry, their room temperature resistance can be varied from 1 to 10^6 ohm. Their temperature coefficient lies between -2 and -6.5% per ^{o}C.

On the basis of the properties of semiconducting materials used in PTC thermistors, they may be broadly divided into two categories. In the first category, a conventional elemental semiconductor, usually Si, is used with electrodes and terminals on the opposite faces. PTC region for both n- and p-type silicon extends over a temperature range from sub-zero to $150^{o}C$ or above with a temperature coefficient of the order of 0.8% per ^{o}C at room temperature. The second category contains the switching PTC thermistor,

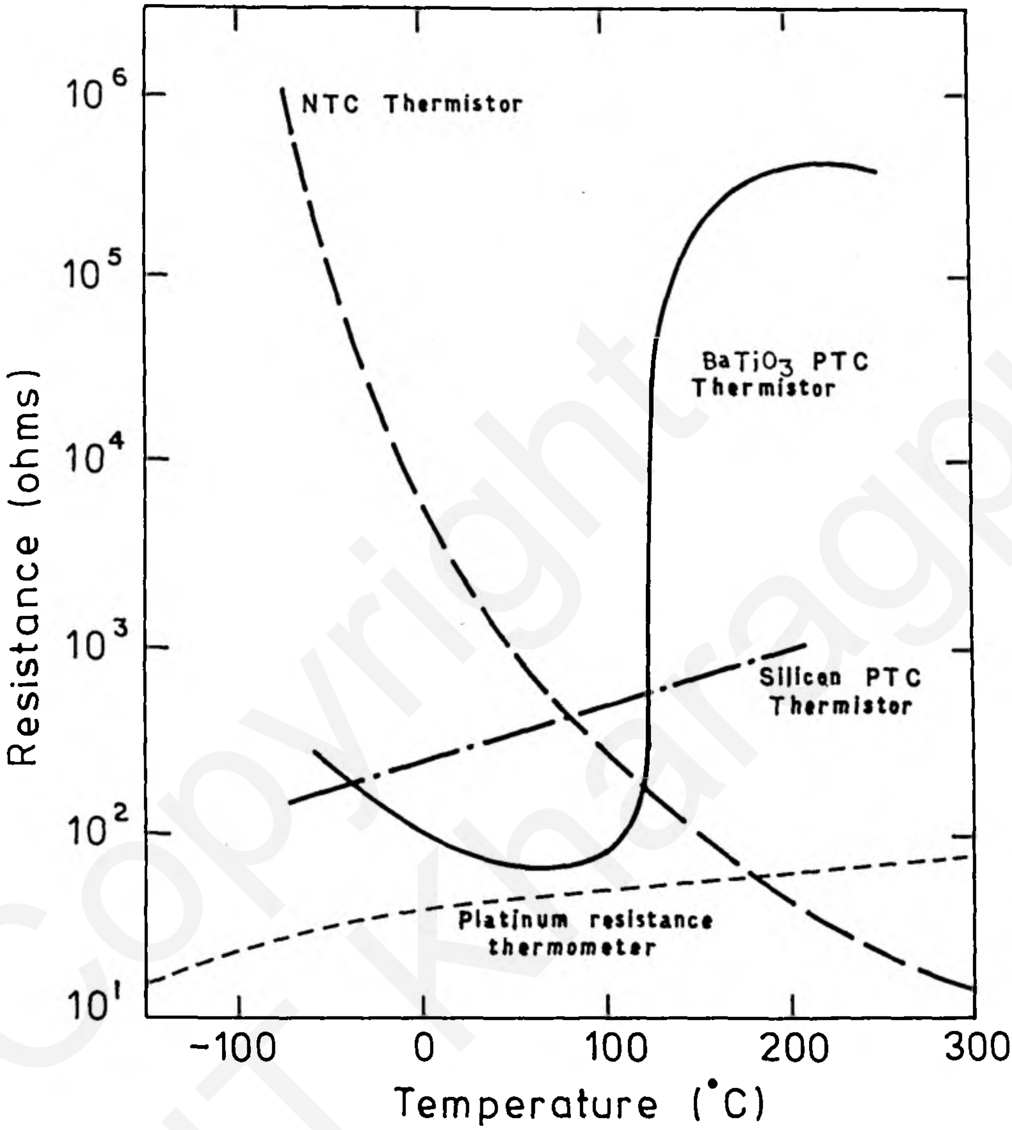

FIG. 1.1 RESISTANCE-TEMPERATURE CHARACTERISTICS OF DIFFERENT TYPES OF THERMISTOR MATERIALS AND THAT OF A PLATINUM RESISTANCE THERMOMETER (ref. 1)

for example, doped semiconducting $BaTiO_3$, which possesses a large PTCR anomaly ($\sim$70% per ^{o}C) over a restricted temperature region.

A comparison of resistance-temperature characteristics between various types of thermistors and a platinum resistance thermometer, is given in Fig. 1.1. This shows the tremendous fundamental advantages that thermistors possess over one of their major rivals, the platinum thermometer, as temperature sensor. The wide range of available physical forms from sub-pinheaded sized bead through disc, rod and flat film shapes to metal sheathed probes and plastic encapsulated assemblies add versatility to the advantages of the thermistors as a temperature sensor. Other major application, besides its use as temperature sensor, is as power sensors in electronic circuits. The world-wide production of such thermistors, at present, is $\sim$150 million pieces per year.

There are two major classification schemes of the PTC thermistors depending on whether the device is used as a sensor or as a heat-dissipator. The PTC jump, i.e. the switching, is the important device property for the former purpose, while the static I-V characteristics with its current limiting potential, for the later. Table 1.1 shows a wide varieties of applications of the thermistors. Typical properties and characteristics of commercially available $BaTiO_3$ thermistors are shown in Table 1.2.

Recently, the potential of PTC thermistor has touched a new height in engineering application as an energy saver[5] (electrocaloric flow-meters). Dostert[6] has reported simple and easily calibrated evaluation circuit for flow-meters based on the electrocaloric principle. This can lead to cost effective flowmeters for

Table 1.1 : Application of Switching PTC Thermistors (After Saburi and Wakino[2])

Mode	Application
1. Sensor (Sensing element)	Thermal indicator, regulator; temperature compensating of electronic apparatus; level meter, flowmeter, thermometer, humidity meter; voltage stabilizer; over heat protector; no-contact switch.
2. Dissipator (Heat dissipating element)	Current limitor and stabilizer; voltage stabilizer; automatic volume control; relay protection; timer; thermal chamber.

Table 1.2 : Important Properties of Commercial Barium Titanate Thermistors (After Andrich[3,4])

Specific weight	5.6 gm/cm^3
Specific resistivity (ρ_{25^oC})	20-50 ohm-cm
Specific heat	0.12 cal/g ^oC
Curie temperature, T_c	120^oC
Switching temperature, T_s	110^oC
Dissipation in still air, D (Samples with a volume of approximately 0.5 cm^3)	10 - 15 mw/ ^oC
R_{max}/R_{min} (no load)	$10^4 - 10^5$
R_{max}/R_{min} (loaded)	$10^2 - 10^3$
Inherent shunt capacitance	Approx. 1 nF
Maximum temperature coefficient	Approx. 60% / ^oC
Maximum momentary overload ($\simeq 0.15$)	Approx. 1 KW

various applications, such as the measurement of fuel consumption in motor vehicles or of the quantities of the heat consumed in central heating systems supplied with hot liquid, for example, water.

The PTCR effect is a direct consequence of the disappearance of ferroelectric polarisation near the Curie temperature of a semiconducting ferroelectric material. $BaTiO_3$, one of the most common ferroelectric ceramics, produces the strongest PTCR effect around its ferroelectric transition temperature ($\sim 120^{o}C$). The semiconductivity in $BaTiO_3$ is normally introduced by changing the valency of a part of the Ti-ions from 4+ to 3+. This valency change may be effected by two different mechanisms.

The first mechanism involves creation of oxygen vacancies in the lattice by annealing the material in a reducing atmosphere at elevated temperatures. To satisfy the electrical neutrality condition, two Ti^{4+} ions change their valency from 4+ to 3+ to compensate the loss of each O^{2-} ions as follows:

$$Ba\,Ti^{4+}O_3 - \frac{x}{2}\,O_2 \longrightarrow Ba\,Ti^{4+}_{1-2x}\,Ti^{3+}_{2x}\,O_{3-x} \qquad (1.1)$$

The second mechanism involves doping of either trivalent ion e.g. La^{3+}, Sb^{3+}, Gd^{3+} and other rare-earth ions at the Ba-site or pentavalent ions like Nb^{5+}, Ta^{5+} etc. at the Ti-site and thus forming an n-type semiconducting $BaTiO_3$ with a low room temperature dc resistivity of the order of 10 - 200 ohm-cm.

Two typical substitution reactions, one on Ba-site (La^{3+}) and the other on Ti-site (Ta^{5+}), can be illustrated as follows:

$$Ba^{2+}Ti^{4+}O_3 + xLa^{3+} - xBa^{2+} \longrightarrow Ba^{2+}_{1-x}\, La^{3+}_x Ti^{3+}_x Ti^{4+}_{1-x}\, O_3 \qquad (1.2)$$

$$Ba^{2+}Ti^{4+}O_3 + xTa^{5+} - xTi^{4+} \longrightarrow Ba^{2+}Ta^{5+}_x\, Ti^{3+}_x Ti^{4+}_{1-2x}\, O_3 \qquad (1.3)$$

In either case, the substitution results in restoration of electrical neutrality by the valency change of Ti^{4+} to Ti^{3+} and thus introducing hopping conduction between Ti^{4+} and Ti^{3+}. Normally, an optimum doping concentration ($\sim$0.2 to 0.4 atom %) corresponds to the lowest resistivity above which it increases.

After the first report of PTCR effect in semiconducting $BaTiO_3$ by Haaijman et al.[7], Sauer and Flaschen[8] have also observed the same effect in La-doped $BaTiO_3$ in the year 1956. An extensive amount of research efforts has gone into the understanding of the mechanism and other aspects of this effect. A detailed review is presented in the next chapter. Eventhen, a number of questions still remain unanswered and several controversies have been brought out in recent years.

In this investigation, an attempt has been made to distinguish between the electrical characteristics of the grainboundaries from that of the grains by complex-plane impedance analysis, adopted for the first time, to study the PTC-materials. The technique has been exploited to study the effects of various processing parameters like sintering temperature and time, cooling rate and composition. The same has also been successfully used to study the electrode effect and the extent of surface reoxidation. C-V characteristics of the specimens have been studied and explained on the basis of the physics of MIS junction. The electrical measurements have been corroborated with a detailed microstructural studies supported by electron-probe micro analysis. The investigation has led to the successful indigenous development of PTC thermistors.