Introduction
1.1 Temperature Sensing in New Technology Regime:

Sensors control machines which support man more than ever before and free him from superfluous work. The operation of today's industrialised world depends to a great extent on the ability to measure and control a variety of physical parameters. Sensors are electronic devices that gather information from the environment and act as transducers, converting the energy form associated with the information that is sought into a form in which it can be easily processed. The energy forms typically involved, in sensing processes, include chemical, electrical, magnetic, mechanical, radiant, and thermal. There is a continuous need for the development of rugged and reliable sensors capable of making measurements in harsh industrial environments found in the steel, heat treating, metal casting, glass, ceramic, pulp and paper, automotive, aerospace, utility and power industries. The application of sensor and measurement technology has resulted in many benefits including improved energy efficiency, better quality, lower scrap or off-specification products, and reduced emissions [72]. The automotive industry is an excellent example, where increased use of electronics technology in sensor and measurement has led to improvements in engine performance, higher energy efficiency and reduced pollutant emissions [76]. Environmental concerns, health and safety regulations have necessitated an increased use of sensors, from industrial plant settings to automobiles, to the workplace, and even to homes [172]. Wherever sensor technology has been applied, it has proven
to be very beneficial in improving energy efficiency, service, product quality and reducing emissions.

Temperature was one of the first physical parameters to be measured in the process field and has been sensed in just about every way imaginable over the years. At one time or another, just about every physical property that changes with respect to temperature has been used as a basis for this measurement. It is estimated that, over 50% of all measurements of important variables in industrial and related fields are measurements of temperature [73]. Discussions on precision temperature sensing and electronic acquisition have been occurring since the beginning of modern industrialisation. The amount of study, experiments, and effort that have been applied to the measurement of temperature is perhaps far greater than, that devoted to any other field of industrial instrumentation. Over the years, an enormous amount of research and development efforts have been devoted to improve temperature sensor characteristics [20,69-76119,120,123]. This is coupled with the developments in improvement of the signal conditioning circuits to reliably transform the temperature sensor output signal into a useful, electrical form [9, 23, 32, 43, 47, 48, 52, 54, 59, 67, 95]. It would make sense that this market has matured to the point where further work would just belabour the subject, seemingly, all of the concepts surrounding these sensors and electronics are all too well understood. This is far from being true. The subject of temperature sensing is kept alive with innovations in sensor manufacturing and enhancements
to sensor interfaces[71]. Over the last few years, the development of low cost, micro controllers and associated electronics circuitry has allowed the cost effective measurement and control of temperature, that was not possible before [44,89,92,96,99105]. Today's microprocessors and microcontrollers are powerful and yet affordable, and they have really revitalised the thermal instrumentation world. This impact has resulted into the fast calibration methods which has almost eliminated the huge look up tables required for error correction. So in a nutshell, to say, "Enough is enough" as regards to the research and development work of temperature sensors and circuit design may be a little premature in light of the continuing improvements, and therefore, the changing scene prompts a re-visit to the basics of temperature sensing.

1.2 Basics of Thermal Sensing Technology: A Review

As a leading sensors of ambient conditions, temperature sensors act as important sensing devices which are essential in a large variety of products. Variety of temperature sensors are available in the market, to meet specific application needs. The most common of them include thermocouple, resistive temperature detector (RTD), thermistor and silicon based sensors. The classification of temperature sensors is shown in figure 1.1. The comparison of all these sensors reveal some interesting facts. Thermocouples are the most ancient, popular, rugged; temperature sensors available in a wide temperature range. However their output is too small typically in micro-volts per change in degree centigrade and therefore
Figure 1.1: Holistic Taxonomy of Temperature Sensors by McGhee et. Al. [77]
to get adequate resolution a low noise, high gain amplification (mostly chopper based) is a must. Further for absolute temperature measurement an additional reference cold junction compensation is required. It is worth notable that for high precision linearised temperature measurement, with a K type thermocouple, a full measurement range required an 11 x 14 sized linearisation matrix [173]. Therefore, wherever accuracy is the main concern, there is nothing like using RTD as a temperature sensor. Materials for RTDs can be gold, silver, copper or platinum. Platinum, however, has become the most-used metal for RTDs. A thin film of platinum or a thin platinum wire is deposited on a flat ceramic material and sealed. Platinum has a nearly linear temperature versus resistance relationship. The Callendar-Van Dusen equation approximates the RTD curve:

\[ R_T = R_0 + R_0 \alpha [ T - \delta(T/100-1)(T/100) - \beta (T/100-1) (T^3 /100)] \]  

In the above equation \( R_T \) is the resistance of RTD at temperature \( T \), \( R_0 \) resistance at 0°C, \( \alpha \) the temperature coefficient at \( T=0°C \), \( \delta \) is a constant =1.49 for Platinum and \( \beta \) is also a constant equal to zero when the temperature is above 0°C. RTD provides high accuracy [173] between boiling point of oxygen (-82.96°C) and the boiling point of antimony (630.74°C), with a useful measurement range from -240°C to 750 °C. A typical comparison of accuracy of RTD with other sensors is as follows: thermocouple 0.5°C to 5°C; RTD 0.01°C to 0.1°C and thermistor 0.1°C to 1°C. However current excitation is the main requirement and a trade of
Figure 1.2: Non-linear thermo-emf of thermocouples. Graph shows the first derivative of this behaviour in the form of the change in temperature gradient of the thermocouple with the change in temperature.

Figure 1.2: Comparative Resistance-Temperature Characteristics of Thermistor Vs RTD
exists while deciding the value of current. With higher current levels the RTD goes into the self heating region causing measurement error, while with lower current levels yield a low output susceptible to noise. Further three / four wire connection schemes has to be implemented to avoid the measurement errors due to leads. Although IC sensors have more advantages in terms of high level linear output which almost does not require further conditioning, their range is restricted. So out of all the above mentioned temperature sensors, the discussion of thermistor looking at their wide use for temperature monitoring, control and compensation, in almost every conceivable fields like home appliances, manufacturing industries, biomedical, transportation and security. NTC thermistors offer designers, many advantages over other type of sensing technologies including the highest sensitivity to temperature changes, high signal to noise ratio, simple operation as well as low cost. Just to give an idea, have a look at these comparative figures of sensitivity viz. Thermocouple: 6 µV/°C, RTD: 0.4 Ω/°C and thermistor: 400 W/°C. Unlike RTD, lead compensation is not at all required in thermistors making them the most suitable choice for remote sensing applications. The latest comparative figures of cost, in US$, for all these sensors are, thermocouple: $1/foot, RTD $20 to $100/piece and thermistor: $10 to $100/piece (depending on configuration and other specifications). Though the thermocouple appears to be cheaper, considering the signal conditioning required, the most cost effective sensor is thermistor.
However despite of all these positive points that makes thermistor a widely used sensor, there are few misapprehensions like non-linearity, ageing, stability, cracking, batch-to-batch tolerance, time consuming manufacturing process etc. Formerly, the non-linear resistance versus temperature characteristic was problematic in analog sensing circuits. Today, however, with the advent of digital electronic controls, the translation is handled via equations in software or lookup tables. This thesis presents research work to minimise most of the drawbacks mentioned above and to improve the technical specifications of thermistors.
Table 1.1: Comparison of Widely Used Temperature Sensing Technologies:

<table>
<thead>
<tr>
<th>SENSOR TYPE</th>
<th>NTC THERMISTOR</th>
<th>RTD</th>
<th>THERMOCOUPLE</th>
<th>I.C. SENSOR</th>
</tr>
</thead>
<tbody>
<tr>
<td>PARAMETER</td>
<td>Resistance vs. Temperature</td>
<td>Resistance vs. Temperature</td>
<td>Voltage vs. Temperature</td>
<td>Voltage or Current vs. Temperature</td>
</tr>
</tbody>
</table>
1.3 Historical Note on the Thermistors:

Michael Faraday (1791-1867), the British chemist and physicist, is best known for his work in electromagnetic induction and electrochemistry. Less familiar is his 1833 report on the semiconducting behaviour of Ag₂S (silver sulfide), which can be considered as the first recorded NTC thermistor [197]. Because the early thermistors were difficult to produce and applications for the technology were limited, commercial manufacture and use of thermistors did not begin until 100 years later. Around 1930 thermistors based on CuO were developed as an immediate need of World War II. After another two years they were developed as commercial product based on Urodox (UO₂) by Osram in Germany. Philips also started making thermistors initially in the year 1936 based on silicon/ferrosilicon sintered together with inorganic binder with a trade name 'startotube' and later based on Iron Oxide with different valences. During the early 1940s, Bell Telephone Laboratories developed techniques to improve the consistency and repeatability of the manufacturing process. Some of the first commercial thermistors were the disc type, and by today's standards, their tolerances were quite broad. These devices were used primarily for regulation, protection, and temperature compensation of electronic circuits. In the 1950s and 1960s, the expanding aerospace industry's requirement for more accurate and stable devices led to several improvements in the materials used to manufacture glass bead and disc thermistors [199]. During the 1960s and 1970s, the demand for tight-tolerance devices in high
volumes at a lower cost led to the development of the chip thermistor [199]. As the reliability of these devices improved during the 1980s, the use of electronic thermometers in the health care industry increased. The rising costs of sterilisation and concerns about cross-infection among patients led to the demand for low-cost disposable temperature probes, for which chip thermistors were well suited. Throughout the 1980s and 1990s, the use of NTC thermistors has continued to grow in the automotive, food processing, medical, HVAC, and telecommunications markets [70].

1.4 NTC Thermistor Theory:

Although the word thermistor is derived from THERMally sensitive resIStOR, the NTC thermistor can be more accurately classified as a ceramic semiconductor. They are the temperature sensitive passive semiconductors exhibiting a large change in electrical resistance when subjected to a relatively minute change in body temperature. Negative Temperature Coefficient (NTC) thermistors decrease in resistance when subjected to an increase in body temperature. They are usually made of a semiconducting transition metal oxide. By controlling the chemical composition and the geometrical parameters of the NTC-thermistors, it is possible to construct devices having electrical resistance in the range of about 1 \( \Omega \) to 1 M\( \Omega \) at room temperature. Their extreme sensitivity to minute temperature changes enables them to perform many unique functions heretofore impossible with standard electronic components [75].
theoretical aspects of NTC thermistors are discussed in depth in the literature [1,12,14,20,22,26,52,53,121].

1.4.1 Thermistor Materials, From Stones to Ceramic Sensors:

Typical commercial NTC thermistors are realised using ceramic technology. These functional ceramics are stone-like materials that are made by adding various chemical raw materials, separated and purified at atomic level, to a ceramic base which is hardened by firing. By adding trace quantities of doping materials and changing firing conditions or atmospheric conditions, these "wonder stones" [135] can vary with a wide variety of electrical characteristics. Long standing involvement with these "wonder stones", or functional ceramics, has borne fruit in the form of a rich variety of innovative electronic components like soft ferrites, varistors, PZT and thermistors. These High-technology ceramics are now playing an important role in the future of electronics, processing and manufacturing systems automation, and in the automotive, utility, and fabrication industries. The ceramics technology is growing increasingly important as a key driving force in the creation of a new electronics revolution for the 21st century.

The popular NTC thermistor materials, for the temperature range from room temperature to 300°C specially useful for domestic and industrial fields consists of ceramics composed of oxides of transition metals (manganese, cobalt, copper and nickel) which can form a new crystal phase known as spinel. Although oxides of rare earth elements (e.g., Sm and Tb) have been considered for use at higher temperatures, reliable
thermistors for applications near and above 1000° C are yet to be developed. Materials like ZrO₂, Y₂O₃ and ThO₂ are also been used for making high temperature thermistors for the temperature range 300°C to 1000°C [124].

1.4.2 Raw Material Selection and Synthesis of Powder:

NTC thermistor makers have a very broad choice of chemical precursors (raw material sources). The unit processes are defined and checked for compatibility with the raw materials selection. The precursor choice is firmly established after an initial development trial and extensive processing of ground rules. The major concern during this process are consistency upon processing, cost, precursor chemistry, impurity levels, reactivity, synthesis approach, physical parameters, size, packing efficiency and mixing ease or mix homogeneity. Traditionally two synthesis approaches have been used for synthesising thermistors viz. Reactive sintering of oxide mixture compacts and sintering of synthesised powder compacts. In the former approach the oxide raw materials are usually selected for chemical purity, particle size and batch to batch consistency which are then weighed, intimately mixed, compacted into desired shape and subjected to time-temperature-atmosphere sintering cycle to form the thermistors. In the later approach, intimate powder mixtures of NTC formulations in fluid suspension are consolidated, dried, granulated and calcined typically for two to eight hours at temperature below the normal sintering conditions. This pre-sintering partially reacts the precursor mixture
to form oxide agglomerate that approximates the final NTC chemistry and crystal structure. The first method gives better chemical uniformity and good mechanical properties for the finished product. The later method allows broad range of chemical precursor as inputs and the calcination results in significant shrinkage of the precursor mix and chemical homogenisation yielding a high quality, close tolerance NTC sensors. In the present work, we have used carboxylate and oxalic methods to obtain the raw precursor and after extensive trials finalised the manufacturing schedule.

1.4.3 Thermistor Configurations:

Thermistors are available in number of configurations that includes beads, disks, wafers, SMTs, flakes, rods, and washers [197]. Non-bead thermistors are also known as surface electrode thermistors and their manufacturing process has many similarities to the construction of ceramic capacitors. First, powdered metal oxides are combined with a plastic binder and additives that enhance stability. The mixture is then formed into sheets that are cut to component size or formed into pellets and pressed into disks. The bodies are then sintered at temperatures in excess of 1,000°C that forms the final polycrystalline NTC thermistor body. The sides are then silvered, leads attached, sealed, varnished, marked and marketed.

Manufacturing of bead thermistor starts with platinum or copper alloy wires and slurry of the metal oxide with suitable binder. Drops of the slurry are dabbed onto the wires. The surface tension pulls the drops into small...
Table 1.2: Comparison of various thermistor designs:

<table>
<thead>
<tr>
<th>Thermistor Configuration</th>
<th>Prime Forming Method</th>
<th>Typical Specifications</th>
<th>Pros and Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bead</td>
<td>Slurry cast on wires</td>
<td>Dimensions: 0.01 in. to 0.06 in. (0.25 mm to 1.5 mm) in dia., Dissipation Constant 0.05-0.30 mW/K, time constant 0.2-3.0 Sec.</td>
<td>excellent long-term stability and reliability for operation at temperatures up to 300°C, quick response to temperature changes, small size devices hard to handle during assembly and have the effect of limiting their power dissipation, more difficult and more expensive to produce glass beads with close tolerances and interchangeability</td>
</tr>
<tr>
<td>Disk</td>
<td>Uniaxial Compaction</td>
<td>Dimensions: uncoated (0.05 in. to 0.10 in. (1.3 mm to 2.5 mm) in dia., coated disc 0.10 in. to 0.15 in. (2.5 mm to 3.8 mm) in dia. Dissipation Constant ≈15 mW/K, Time Constant ≈ 100 Sec.</td>
<td>Chip and Disk: tight tolerances and interchangeability at a relatively low cost compared to bead thermistors, size permits power dissipation higher than that of beads, disc thermistors normally have larger coated diameters and higher power dissipation capabilities than chip thermistors, chip thermistors typically can be produced to smaller coated diameters and are better suited for applications requiring smaller size and faster response times</td>
</tr>
<tr>
<td>Chip</td>
<td>Slurry Tape Casting</td>
<td>Dimensions: 0.04 in. by 0.04 in. (1 mm by 1 mm) to 0.10 in. by 0.10 in. (2.5 mm by 2.5 mm) in square or rectangular shapes,</td>
<td></td>
</tr>
<tr>
<td>Rod</td>
<td>Dough Extrusion</td>
<td>Dimensions: Dia.:0.5-1.5 cm, Length: 0.5-4.0 cm., A/L: 0.2-0.3 cm.</td>
<td>Uniform Temperature Profile, Good Accuracy</td>
</tr>
</tbody>
</table>
Figure 1.4: various thermistor Designs
elliptical beads. The string of beads is then allowed to dry and then sintered at high temperature. During sintering the beads shrink and form an excellent electrical connection with the wires. Later, the wires are cut to form the individual thermistors. Finally, the thermistors are coated and most often hermetically sealed with glass.

Rod extrusion employs a dough of different binder and higher oxide content than that of the slurries of bead thermistor. The stiff dough is dried and placed in an auger or plunger press. Long rods of thermistor dough are extruded through a die orifice and supported on grooved board. After slow evaporation of the solvent, rods of desired size are cut from the extrusion and processed for sintering.

Disc and washer thermistors are made by preparing the various metal oxide powders, blending them with a suitable binder, and then compressing small amounts of the mixture in a die under several tons of pressure. The discs are then fired at high temperatures to form solid ceramic bodies. A thick film electrode material, typically silver, is applied to the opposite sides of the disc to provide the contacts for the attachment of lead wires. A coating of epoxy, phenolic, or glass is applied to each device to provide protection from mechanical and environmental stresses.

Chip thermistors are manufactured by tape casting, a more recent technique borrowed from the ceramic chip capacitor and ceramic substrate industries. An oxide-binder slurry similar to that used in making bead thermistors is poured into a fixture, which allows a very tightly controlled
thickness of material, to be cast onto a belt (or movable) carrier. The cast material is allowed to dry into a flexible ceramic tape, which is cut into smaller sections and sintered at high temperatures into wafers 0.01 in. to 0.03 in. (0.25 mm to 0.80 mm) thick. After a thick film electrode material is applied, the wafers are diced into chips. The chips can be used as surface mount devices or made into discrete units by attaching leads and applying a protective coating of epoxy, phenolic, or glass. Various thermistor designs are shown in figure 1.4.

1.4.4 Thermistor Nomenclature:

a. Zero Power Condition: When current flows through the NTC thermistor it heats itself and this changes the resistance. When self-heating is negligible, it is called the zero-power condition. It is essential to know how small does the power dissipation have to be, in order to be considered as "zero-power"? Paraphrasing the MIL specification on this issue: "the power is negligible when a further decrease in power will not result in a resistance change more than 0.1%".

b. Zero Power Resistance (R₀): The zero power resistance is the dc resistance of a thermistor at a specified temperature with power dissipated by the thermistor low enough that any further decrease in power will result in no more than 0.1% (or one tenth of the specified measurement tolerance, whichever is smaller) change in resistance.

c. Resistance Ratio Characteristics: The resistance ratio is the ratio of the zero-power resistance of thermistor measured at two specified
reference temperatures. The most popular forms of specifying resistance ratio are either \( \frac{R_0}{R_{50}} \) or \( \frac{R_{25}}{R_{85}} \) or \( \frac{R_{25}}{R_{125}} \).

d. Zero Power Temperature Coefficient of Resistance \( (\alpha) \): The ratio at a specified temperature \( T \), of the rate of change of zero power resistance with temperature to the zero power resistance of the thermistor. For Negative Temperature Coefficient (NTC) Thermistors, typical values of alpha are in the range -3%/°C to -6%/°C. The temperature coefficient is a basic concept in thermistor calculations. Because the resistance of NTC thermistors is a non-linear function of temperature, the alpha value of a particular thermistor material is also non-linear across the relevant temperature range.

\[
\alpha = \frac{1}{R_T} \times \left( \frac{dR}{dT} \right) \times 100\% \quad \text{(%/°C)} \quad (1.2)
\]

Where \( R_T \) is the resistance of the component at the relevant temperature \( T \) (°C), \( dR/dT \) is the gradient of the Resistance Vs Temperature curve at that temperature point, and \( \alpha \) is expressed in units of "percentage change per degree Centigrade".

e. Maximum Operating Temperature: It is the maximum body temperature at which the thermistor will operate for an extended period of time with acceptable stability of its characteristics. This temperature can be the result of internal or external heating, or both, and should not exceed the maximum safe value specified.
f. Maximum Power Rating: It is the maximum power, which a thermistor will dissipate for an extended period of time with acceptable stability in its characteristics.

g. Dissipation Constant: It is the ratio, (expressed in milli-watts per degree C) at a specified ambient temperature, of a change in power dissipation in a thermistor due to the resultant body temperature change.

h. Thermal Time Constant: It is the time required for the thermistor to change 63.2% of the total difference between its initial and final body temperature when subjected to a step function change in temperature under zero-power conditions.

i. Resistance-Temperature Characteristics: The resistance temperature characteristics is the relationship between the zero-power resistance of a thermistor and its body temperature. The Steinhart and Hart equation is an empirical expression which best models the thermistor characteristics.

j. Temperature - Wattage Characteristics: It is the relationship at a specified ambient temperature between a thermistor temperature and the applied steady-state wattage.

k. Current-Time characteristics: It is the relationship at a specified ambient temperature between the current through a thermistor and time, upon application (or interruption) of applied voltage.
I. Stability: The stability of a thermistor is its ability to retain specified characteristics after being subjected to designated environmental or electrical test conditions.

m. Materials Constant (β): The materials constant of a thermistor β, is derived from thermistor resistance measurements obtained at 0°C and 50°C.

n. Maximum Steady State Current (I_max): For power thermistors, the maximum continuous steady state current, either DC or RMS AC, which the device is capable of passing.

1.4.5 Thermistor in the Context of Modern Instrumentation:

In the present era of inexpensive, compact microcontrollers, display modules and versatile electronic instrumentation, the scope of potential applications has grown enormously [28,32,90,114]. Inexpensive NTC thermistor elements are being utilised extensively as sensors, probes and components in complex circuits in a variety of applications. NTC Thermistor devices are extremely versatile components in electronic circuits. They offer distinct advantages in terms of matching impedance levels to available instrumentation or compensation circuit needs. The thermistor material composition, for example, can be adjusted and customised to achieve a desired resistivity-temperature response, within certain constraints, for a sensing device.

Precision NTC thermistors offer designers the greatest sensitivity to temperature of any electronic temperature sensing component. They
exhibit a negative temperature coefficient of resistance in the region of -3%/°C to -5%/°C at 25°C. This is roughly an order of magnitude higher than the sensitivity of positive temperature coefficient (PTC) metal resistors or thermocouple sensor elements. This provides some distinct advantages in system designs where sensitivity, circuit simplicity and overall system cost are important.

Drawbacks of NTC Thermistor devices include a non-linear resistance versus temperature characteristic and the fact that small bead and chip element devices have limited power handling capability. These disadvantages, however, are often overcome with innovative circuit designs. Presently, NTC thermistors are the preferred sensing element for many applications where precise measurement and control are required. Inexpensive microprocessor and display components are now being coupled with NTC thermistors and hybrid circuits. Such designs dominate industrial applications and can offer high performance temperature measurement and control capabilities for very reasonable overall system cost.

1.5 NTC Thermistor Manufacturing, A Global Scenario:

The temperature sensor market, in general, is mature but fragmented, typically characterised by moderate growth and narrow margins [134]. Individual thermistor manufacturers target their strengths at particular market segments. Numerous temperature sensor suppliers provide thermistor and RTD (resistance temperature detector) components,
as well as offer a complete temperature probe assemblies to OEMs who produce monitoring and control products that use temperature as a critical system parameter. The latest trend of thermistor manufacturing has been discussed at a good number of websites [129-174, 197]

1.5.1 State of the Art:

NTC thermistor is a such an vital sensor that its production in Asia has not been affected by the world wide economic recession. A market research report by Trade Media Holdings Ltd. UK[158] predicts that both local and overseas demand for thermistors is expected to remain steady, with a little hope to increase from last year's figure. Even this is evident from the annual report of Shibaura Electronics Co. Ltd., a manufacturer of NTC glass sealed thermistors and glass sealed thermistor sensors, head quartered at Saitama-City, Japan, a leading company not only in Japan but also in the world, in this field. Shibaura ranks one in the global thermistor market and supplies over 200 Million thermistors a year[201]. In fiscal 2000, Shibaura has posted ordinary profit 660 Million Japanese Yen on a turnover of 10,700 Million Japanese Yen. As on May 31, 2001, Shibaura had employed more than 1700 people world-wide including their affiliated companies in China, Hong Kong, and Thailand. Recently the company has signed an agreement with EPCOS, a equally strong company (In fiscal 2000, EPCOS posted net profit of Euro 240 million on sales of Euro 1.86 billion. As of September 30, 2000, the company employed more than 13 000 people world-wide), for manufacturing electronic components, for
technological co-operation in NTC glass-sealed thermistors. Using each other's sales networks, Shibaura and EPCOS plan to strengthen their market positions in Europe and Japan respectively and promote establishment of NTC glass-sealed thermistors as a world-wide standard.

As per the predictions of the Japan Electronic Materials Manufacturers Association, the production of thermistors is expected to rise to some six percent in monetary value to $388 million and 17 percent in number of units to 2.5 billion pieces in the fiscal year 2001 (April 2001 to March 2002). Japanese companies are leading in the forefront of new product releases mostly focusing on surface-mount, compact thermistors for popular applications such as mobile phones. Manufacturers also reported the prices on a downtrend in the past few years. A 10- to 20-percent drop was estimated last year. Further cuts of up to 10 percent are likely until year-end 2002. Recent reports also indicate a slight glut in thermistor supply, industry analysts however hope that the situation is likely to be a temporary one, as demand is expected to rebound in no time.

1.5.2 Growth Economics:

In order to appreciate the present market figures let us compare them with the past. In 1992, Ceramic Industry Magazine[202] reported a market of $9000 million for electronic components. At that time it was predicted the scenario to be continued for ten to fifteen more years which now seems to come true. The Indian market[68] at that time was nearly 75 million dollars which was nearly 7% of the South Korea market and 1% of
the world market. For the development period of 1986-1992, approximate cost of finished thermistors was 100 Rs/Kg for the high end products. The successful commercialisation reported in 1995, is mostly for PTC thermistors. The notable among them is the PTC thermistor developed by Bharat Electronics, Bangalore for the colour picture tube de-gaussing. They have been successful in developing know-how for doping ppm levels of dopants in the ceramics homogeneously, while maintaining the purity, reproducibly and cost effectiveness by using inexpensive sintering technology. The other two notable thermistor manufacturers in this period were Translekrtra Domestic Products, Mumbai (PTC thermistors for mosquito repellent heater), Thakarsons, Pune (NTC thermistors).

1.5.3 Revival of Thermistors and the Latest Releases:

Mobile phones are reportedly one of the biggest and most important applications of thermistors, because the market for them has grown huge over the past few years [168]. Several thermistors are usually employed in one mobile phone unit. Thus, brisk mobile phone sales have greatly contributed to the upward movement of thermistor demand. In terms of product trends, makers have been coming forth with compact models. A few years ago, 1005 NTC thermistors for TCXOs, for instance, represented a greater percentage of the total production. Smaller models have been catching on lately, and this trend is expected to continue in the near future as well. Along this line, surface-mount models have also been growing popular. In addition, some makers have begun releasing lead-free
thermistors from the standpoint of environmental protection. It has also
been reported that despite the reported lack of advanced technology in
most countries, new manufacturers are constantly entering the line and
optimistic of grabbing a share of the market. It is also observed that the
new thermistor releases are mostly targeting telecommunication
applications. Besides, booming demand for DVD players and other portable
communication appliances have also pushed up the popularity of NTC
thermistors. From the conventional device types like rod, bead, disk, new
kind of forms like SMD, lead-less are also seen to be evolving. Both DIP
and surface mount types are being heavily manufactured, although the
former are more popular due to their high flexibility in applications while
later forms the ideal solution where temperature sensing within a constraint
area is needed. Due to growing share of high precision products there is a
demand for small resistance tolerance units. Chip thermistors can be made
with tight tolerances of the order of ± 0.05°C, eliminating the costly
calibration process required by other temperature sensors like RTD,
thermocouple etc. Number of developments are also taking place for
linearising the thermistor characteristics by developing look up tables and
time efficient software routines.

In general thermistor manufacturers are seem to be busy in
extensive activities to develop customised sensors, to diminish product
sizes, improve precision, accelerate response speed, expand the range of
temperatures they cover and to establish standards to simplify mounting.
Efforts are being directed to increase of productivity by improved production technology. The main objective of present research and development is to explore further reductions in price and improvement in specifications along with the formation of thermistor based smart sensor.

1.6 Thermistor Applications:

Inexpensive NTC thermistor elements are being utilised extensively as sensors, probes and components in complex circuits in a variety of applications [70,74]. NTC Thermistor devices are extremely versatile components in electronic circuits. They offer distinct advantages in terms of matching impedance levels to available instrumentation or compensation circuit needs [54]. The thermistor material composition, for example, can be adjusted and customised to achieve a desired resistivity-temperature response, within certain constraints, for a sensing device. Precision NTC thermistors offer designers the greatest sensitivity [75] when compared to any electronic temperature sensing component. They exhibit a negative temperature coefficient of resistance in the region of $-3\%/°C$ to $-5\%/°C$ at $25°C$. This is roughly an order of magnitude higher than the sensitivity of positive temperature coefficient (PTC) metal resistors or thermocouple sensor elements. This provides some distinct advantages in system designs where sensitivity, circuit simplicity and overall system cost are important.

Drawbacks of NTC Thermistor [71] devices include a non-linear resistivity and the fact that small bead and chip element devices have
limited power handling capability. These disadvantages, however, are often overcome with innovative circuit designs. Presently, NTC thermistors are the preferred sensing elements for many applications, where precise measurement and control are required. Inexpensive microprocessor and display components are now being coupled with NTC thermistors and hybrid circuits. Such designs dominate industrial applications and can offer high performance temperature measurement and control capabilities for very reasonable overall system cost.

Thermistor applications make use of the basic thermistor features, such as Resistance versus Temperature characteristics, zero-power characteristics, self heating effects and thermal characteristics like heat capacity and dissipation constant \([44,45,49,50,51,56-59,66]\). A knowledge of these factors is important in understanding the principles of thermistor applications.

1.6.1 Domestic Applications:

It has been reported that at present 90% of all temperature sensors employed in house hold electrical products are thermistors \([76]\). One can locate them in microwave ovens, electrical cookers, refrigerators, petroleum fan heater, liquid warmers, potato chip fryer etc. One of the main reasons for such a wide usage of thermistors is their small power dissipation and low cost. They need not be too accurate but should have low price, reliability, less ageing, stability, long service life etc.
1.6.2 Applications in Consumer Electronics:

Thermistors have been used in plain paper copiers (PPC) to control the surface temperature of the image fixing rollers [73]. In this application the sensor requirements are accuracy and rapid response. Accuracy decides the quality of the copied picture and response decides the time per copy. Another application of thermistors is in maintaining the vertical linearity of the picture which changes with temperature. This is achieved either by inserting thermistor in the tube plate circuit or by embedding it into one of the coils in series to compensate the increase in resistance of the coil. Another very popular application is controlling the temperature during rapid recharging of the Ni-Cd or Ni-H₂ batteries. This greatly enhances the service life of the battery. High temperature thermistor compositions based on ZrO₂, ThO₂ and CeO₂ doped with trivalent rare earth oxides have a good potential in automobile electronics. They can be used for maintaining the optimal temperature range of catalytic exhaust converter to reduce the unburned fuel and minimise air pollution. They are also found useful for detecting various important parameters for engine performance control.

1.6.3 Thermistor for Metrology:

Since 1957, thermistor rods were used in radio sondes of the United State Weather Services for temperature measurement as well as gradient of air pressure and velocity to make weather maps. It was found that the
sluggishness and self heating of the sensors poses a bottleneck which was corrected by replacing the rod with the aluminised dot thermistor[70].

1.6.4 Other Applications:

It is not practically feasible to describe in depth each and every application of NTC thermistors in this thesis. A good amount of research papers and technical articles [3,5,9,11,28,32,37,42,43,44,45] discuss various applications of NTC thermistors. The objective of the present work is development of NTC thermistor for the temperature range from room temperature to 150°C, as this is the range required in most of the applications. Varieties of applications of thermistor are listed at 1.6.5.
1.6.5 Thermistor Applications:

[I] Consumer Electronics:
- Engine Oils Temperatures
- Sensors
- Oil Level Sensors
- Outside Air Temperature
- Sensors
- Transmission Oil Temperature
- Sensors
- Water Level Sensors

[II] Automotive
- Automatic Climate Control
- Coolant Sensors
- Electric Coolant fan
- Temperature control
- Emission Controls
- Engine Block Temperature Sensors

[III] Medical Electronics
- Blood Analysis Equipment
- Blood Dialysis Equipment
- Blood Oxygenate Equipment
- Clinical Fever Thermometers
- Oesophageal Tubes
- Infant Incubators Internal Body Temperature Monitors
- Internal Temperature Sensors
- Intravenous Injection Temperature Regulators
- Myocardial Probes
- Respiration rate Measurement Equipment
- Skin Temperature Monitor
- Thrombolysis Catheter Probes

[IV] Industrial Electronics
- Commercial
- Vending Machines

[V] Military and Aerospace
- Aircraft Temperature
- Bathythermography
- Bomb Fuses
- Fire Control Equipment
- Missiles and Spacecraft Temperatures
- Oscillator Compensation
- Psychological Monitoring

[VI] Food Handling and Processing
- Coffee Makers
- Deep Fryers
- Fast Food Processing
- Perishable Shipping Temperature
- Controlled Food Storage Systems
- Thermometers for use in food preparation

[VII] Communication and Instrumentation:
- Amplifier overtemperature Sensing
- Cellular Telephones
- Copper Coil
- Winding
- Rechargeable Battery Packs
- Transistor Gain Stabiliser
- Transistor Temperature Compensation

[VIII] Computer
- Power Supplies (Inrush Current Limiting)
- Uninterruptable Power Supplies (Over Temperature Sensing)
- CPU Temperature monitoring.
1.7 Philosophy of the Research Work:

1.7.1 Conventional Approach: trial and error

There are several factors that determine the feasibility of a sensor technology, such as the magnitude of sensitivity to the measured property, the response rate, and the cost of the final product. Sensing devices have been traditionally developed using trial-and-error techniques rather than following an insightful scientific approach. Many of the existing technologies utilise complex mixtures of several different materials, yet the functionality of each component is not known or well understood. Furthermore, the degradation mechanisms leading to the ageing behaviour of a sensor are not fully understood in most of the cases. Basic knowledge of the sensing mechanisms and their degradation behaviour is necessary for the exploitation of the full potential of existing materials and methods to obtain advanced, reliable, affordable, and novel technologies.

1.7.2 Over-specifications by Manufacturer:

One of the problems the thermistor industry has faced over the years is that some manufacturers have claimed their particular style or configuration of thermistor is better than other configurations proposed by their competitors, without regard to other, more pertinent factors. These thermistor "politics," more harmful than beneficial to the industry, can confuse engineers and purchasing agents who are looking for reliable information to help them to choose the appropriate product for their application. Although some thermistor qualities or capabilities, including
interchangeability, repeatability, size, responsiveness, and stability, can either be enhanced or limited by style or geometry, these characteristics are much more dependent on a manufacturer's ability to understand the ceramics technology being used and to maintain control of the manufacturing process.

1.7.3 Development and Optimisation of Sensor Materials:

Fundamental understanding of the materials characteristics is vital in selecting the appropriate combination of sensing elements to achieve selectivity in complex sensor array structures. Therefore, essential sensor performance parameters (e.g., stability, sensitivity, and selectivity) need to be improved, even in commercially available products. e.g. in even the thermistors available in the market, are found to lack unit-to-unit consistency which is often due to poor control over raw materials and fabrication conditions including forming, firing and electrode attachment. In this way most of the sensor specifications depend largely on the physical and chemical characteristics of the materials used to build the sensing devices. One factor having a tremendous impact on the sensor's characteristics is the processing route followed to prepare the material. Sensing devices are often bulk structures. The configuration that is most commonly employed involves either sintered powders in the form of a dense pressed pellet or porous thick films deposited on a tube or a planar substrate.
Different fabrication methods are known to result in a variety of microstructures and varying response characteristics for a particular sensor; there have been no systematic studies to identify an optimal processing technique. In large measure, this is because detailed characterisation of the materials characteristics, including the relationships between microstructure and properties, is still lacking.

The characterisation of the morphological, structural, and chemical features of sensor materials has rarely been reported in the literature. There have been several publications on the structural characteristics of very common electronic ceramic sensor materials (SnO₂, TiO₂, and perovskites), and Nickel manganite (the one which has been selected for the investigation in the present work), however these have not been directly related to sensor performance. Furthermore, in sensor-related publications, several problems that could have been analysed in a straightforward manner in a short time frame, using characterisation techniques. Instead, such problems are approached by alternative routes, typically laborious and time-consuming, often yielding ambiguous results.

1.7.4 Revolution by Materials and Evolution by Signal Processing:

Although several specifications of the sensor could be improved by materials processing, there is a limit to all this. Through study of the thermistor theory reveals that some specifications like non-linearity, lag, and even correction for ageing could be best tackled through application of mathematical modelling through software. Here the digitisation of the
sensor plays a key role. Once the digitized sensor data are ready, the rest of the signal processing is basically a question of the intelligent application of mathematical algorithms.

1.7.5 Combined Approach:

In our opinion, the improvement in thermistor specifications can not be achieved solely by materials way or by the signal processing, however a combined approach will lead in the improvement in the performance. In the course of research work, we have applied different preparation method like carboxylate precursor route to improve the unit to unit tolerance. A good number of materials characterisation tools like X-ray diffraction, TGA/DTA, have been applied to the precursor and its sintered products to confirm the completion of solid state reaction and to study the decomposition process. Efforts have been done to optimise the forming conditions like sintering temperature, which directly affects the densification, grain size distribution and dormant resistivity of the product [198-199]. Fully automated set-up have been developed to characterise the thermistors with respect to their various specifications and effect of environmental factors like moisture.

1.8 Aim and Objectives:

The present thesis reports work on development of high performance Nickel Manganite based NTC thermistors and addresses a few of their important drawbacks mentioned so far. The main objective of the research is all round performance improvement of the NTC thermistor
which requires following important parameters to be studied in detail.

- Optimisation of thermistor characteristics for domestic applications
- improving interchangeability
- improving figure of merit

While concentrating on above parameters it is also necessary to look into following aspects:

- reducing ageing effect
- better resolution
- low power dissipation
- high speed
- application of Thermistor in smart sensors

The methodology adopted and work plan undertaken is as follows.

1.9 Methodology and Work Plan:

It was decided to meet the objectives by combined approach, i.e. improved materials synthesis supported by instrumentation techniques as described at 1.7 (Philosophy of research work). Looking at the multidisciplinary nature of the work, a thorough literature survey [1-204] was undertaken in various aspects of thermistors like materials preparation methods, materials characterisation techniques, instrumentation development, smart sensors etc. The catalogues of good number of thermistor manufacturers were refereed to get the details of latest products. Several webpages were also referred to get the latest know-how on the subject.
To fulfil the first objective, i.e. sensor development for domestic applications, it was necessary to identify a stable material for the temperature range below 200°C. Several transition metal oxides having mixed metal ions, containing two or more cations have been reported to exhibit semiconducting property. The material Nickel Manganite (NiMn$_2$O$_4$) was chosen for investigation since it is stable due to less difference in valances of octahedral and tetrahedral ions and their sizes. After selection of the material, the next important thing was to finalise the synthesis route. Based on the investigator's past experience on similar materials [207-212], carboxylate precursors and oxalic precursor methods were finalised. The formation of materials was confirmed by applying characterisation techniques like XRD. The reasons behind ageing and lack of interchangeability were found to be due to poor geometry control of thermistor and their leads and less densification. In order to improve these aspects the lead attachment jig was modified. The power consumption of the thermistor is a direct function of its dormant or room temperature resistance. In order to optimise the power dissipation, the room temperature resistance was varied by changing the stoichiometry in Ni$_{1-x}$Mn$_{2+x}$O$_4$.

The need of automated instrumentation systems was felt to characterise and mark the specifications of the thermistors. Various test and characterisation set-ups were conceptualised and executed for this purpose. Finally, in order to achieve the best compatibility of the fabricated
thermistors with digital systems three architectures of smart sensors were proposed.

Thus, work plan was as follows:

- Synthesis and characterisation of materials
- Device Fabrication
- Development of Instrumentation
- Proposing smart sensor architecture

The thesis is organised in five chapters. A brief outline of each chapter is as follows.

Chapter 2 has three subparts. Part I presents the synthesis of nickel manganite required for making the device by using carboxylate precursor method. The preparation methods used are fumarate, succinate, oxalate, tartarate and malonate. Part II covers the details regarding the controlled conditions for fabricating the device with emphasis on management in the range of domestic applications. This part deals with the oxalic precursor route for synthesis of thermistor having composition Ni$_{1-x}$Mn$_{2+x}$O$_4$ with $x = 0, 0.05, 0.10, 0.20, 0.30, 0.40, 0.45, 0.50, 0.55$ and $0.60$. The details regarding the chemistry aspects of all the above mentioned techniques is given in the appendix I at the end of the thesis. The last part, presents details of a novel manufacturing set-up for fabricating disc type thermistors. The thermistors fabricated using this set-up have been found to have better interchangeability, minimal ageing, moderate materials constant and
improved resolution. This is evident from the values of resistance ratio, materials constant and its tolerance.

Chapter 3 presents the details of instrumentation for test and characterisation of the thermistors fabricated using the above mentioned techniques. A versatile computer controlled measuring system is described here, used for characterisation of the samples in terms of resistance Vs temperature and current Vs voltage. The set-up comprises of PC based ADD-ON cards having on-board analogue to digital converter and digital to analog converter. A driver software package has been developed to enable the precise acquisition of resistance Vs temperature and current Vs voltage characteristics in relatively short duration of experiments, preventing the damage to the sensor as observed in conventional characterisation set-ups. A complete software package comprising of various 'C' programs, developed for this purpose is listed at the end of the chapter. The striking feature of this set-up is accelerated testing of the thermistor in compressed test time. The chapter also presents the instrumentation set-up developed for finding the time constant of the thermistors. Thermistors are known for their immunity to moisture. In the course of characterisation some anomaly was observed which is attributed to the presence of moisture. In order to characterise the effects of moisture, a probe based on capacitive principle is developed. The probe acts as a capacitor in an oscillator wherein the frequency of the oscillator changes due to change in dielectric constant. The presence of moisture on thermistor is found to affect the dielectric
constant of the probe and hence the change in frequency of the oscillator. This chapter also includes the design of furnace, instrumentation amplifier and temperature controller.

The modest suitability of conventional thermistors is becoming a bottleneck in microprocessor-based data-acquisition systems. This problem is being overcome by the development of smart sensors that are compatible with the microprocessor. Chapter 4 presents the design of thermistor based smart sensors in accordance with one of our objective. It has three subparts. Part I presents smart sensor architecture based on modified Schmitt trigger with in which the thermistor is embedded. The built in programmable hysteresis gives a good noise immunity to the sensor, making it useful for applications like over-under temperature switches and biomedical measurements. Part II propose a non-linear ADC (NADC) for thermistor interfacing to digital systems. Presently used linear ADC technology poses various limitations in digitising the output of highly non-linear sensors like thermistors. The architecture proposed here uses a novel modified PWM technique to cancel the non-linearity of the thermistor in the process of digitisation. The last part presents an architecture of low voltage application specific integrated circuit (ASIC) for biomedical applications.

Summary, results, conclusions and scope for the future extension has been presented in Chapter 6.