CHAPTER-I

INTRODUCTION
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1.1 An Introduction to Ceramics

Ceramics are composed in large part of inorganic and non-metallic materials. The scope of the ceramics is very wide. The ceramic includes the materials as pottery, porcelain, refractories, structural clay products, abrasives, porcelain, enamels, cements, glass and non-metallic magnetic materials, ferroelectrics, manufactured single crystals and a variety of other products. These ceramic materials are of particular interest because they have either unique properties or an outstanding properties. Either they have been developed in order to fulfill a particular need in greater temperature resistance, superior mechanical properties, special electrical properties and greater chemical resistivity or they have been discovered more or less accidently and have become an important part of the industry.

It is important to realize the importance of ceramic physics and ceramic chemistry because the combined application of ceramic physics and ceramic chemistry is a powerful approach to understand the source of composition and structure and to understand the effects of changing composition and structure.
In studying the properties of ceramics it is necessary to be familiar with the manufacturing process starting with the raw materials used. Although there is a tremendous variety of raw materials used in the manufacture of ceramics, the traditional ceramic industry is largely based on various combinations of clay minerals which impart plasticity, feldspare which forms a viscous liquid at the firing temperature, and silica which is able to form glasses but is relatively infusible. In addition, there are widely used minerals fluxes, alumina and aluminum silicates, talc and related minerals, refractory raw materials and abrasive. Most of these materials are mined and subsequently prepared for use. An increasing number of raw materials are subjected to some purification process, many are manufactured as a secondary step from other primary constituents.

Various special electrical and magnetic ceramics are essential to the development of electronic control devices, computers and other apparatus. Almost every industrial production line, office and home is dependent on ceramic materials. The art of making pottery by forming and burning clay has been practiced from the earliest civilizations. Examination of pottery fragments has been one of the best tools of the archeologist. The
largest segment of the ceramic industry is the manufacture of various glass products. Lime and cement products are another largest ceramic industry. A particularly important group for their technical and industrial application are refractories.

Pure oxide ceramics have been developed to a high state of uniformity and with outstanding properties for use as special electrical and refractory components. Magnetic ceramics form the basis of the magnetic memory units in large computers. Their unique electrical properties are particularly useful in high frequency microwave electronic applications.

Enamels for aluminum have been developed and have become an important part of the architectural industry. Metal ceramic composites have been developed and are now an important part of the machine tool industry and have important uses as refractories.

Ceramic carbides are extremely important as abrasive materials. Ferroelectric ceramics have extremely high dielectric constant and are particularly important as electronic components. Non silicate glasses are useful for far infrared transmission and other special optical properties. Pyroceram has recently been
developed as a new method of fabricating ceramics by forming as a glass and then nucleating and crystallizing to form a crystalline ceramic material.

The ceramics are used as an integral part of the electronic devices. Ceramics do not creep or deformed under stress at room temperature. It has greater resistance to environmental changes and the ability to form gas tight seals with metals. The conditions in which the electrical insulating materials have to operate in electrical and radio electronic devices have become much more severe. These ceramics, used in radio electronic devices, has reduced the size of various components and accommodated in confined spaces. Thus the new materials, developed recently, have become the backbone of the electrical and electronic devices.

Some ceramics have electronic conductivities that rival those of metals, while other have ionic conductivities equivalent to those of the most highly conducting aqueous solutions. On the other hand, many ceramic materials find applications as capacitor dielectrics, circuit substrates or device package because of their extremely low conductivities.

Compared with metals, electronically conducting
ceramics have the advantages of thermal, chemical and mechanical stability. Under severe operating conditions, these features may justify the use of ceramics in spite of their brittle, non-ductile characteristics. If they are to be used, it is extremely important to understand how the conductivity of ceramic materials is affected by temperature and composition.

Ceramic materials can have ionic conductivities equal to those of aqueous solutions and fused salts. In few cases this is true even near room temperature, but more commonly the ceramics require high temperatures to achieve useful levels of conduction. The physical rigidity of a ceramic can make it useful where a liquid electrolyte would be impractical. The chemical inertness of ceramic makes them compatible with active materials as in case of batteries, e.g. the Na-S battery in which the $\beta$-$\text{Al}_2\text{O}_3$ electrolyte is not severely attacked by the electrodes. The high temperature stability can also be an advantage in electrochemical applications where electrode reactions are too slow at normal ambient temperature.

Conducting ceramics are now used in a few applications, e.g. in SrTiO$_3$ based boundary layer capacitors where the grains in the polycrystalline
ceramic must be highly conducting, and in the oxygen activity sensors in automotive exhaust gases. They are being investigated for many more applications and it can be safely predicted that their use will steadily increase as their properties are better understood and their advantages are increasingly appreciated.

In order to be useful, ceramics must be formed to a specific shape with controlled tolerances and known properties. The traditional method of forming are (a) to form clay-based ware as a suspension or a soft and stiff plastic mass and then dry and fire to a hard permanent shape (b) to form glasses at elevated temperatures as a viscous fluid and then cool to form a hard permanent shape (c) to form concrete materials by pouring the liquid mixture into forms that are removed when the chemical set has been completed.

In addition, however, the availability of automatic machinery, high pressures, and better controls have allowed an increasing variety of techniques and the development of entirely new methods. An understanding of forming methods is necessary because changes in induced porosity, grain orientation, grain size, and approach to chemical equilibrium are all related to the properties of ceramics.
Powder pressing is one of the best method of forming dense sample of ceramic materials. Powder pressing consists of compacting dry or slightly damp powder in a metal die at sufficiently high pressures that a dense and strong piece is formed. It is a forming method used extensively for refractories, tiles, special electrical and magnetic ceramics, spark plug, insulators and other technical ceramics and a variety of products for which large number of sample shapes are required. It is an inexpensive method and can form ware to close tolerances. Much electrical and technical ceramic ware is made using high speed hydraulic presses.

The demand for new and better properties has led to the development of new materials, the availability of new materials has led to new uses based on their unique properties.

Among all ceramic materials, $\text{Al}_2\text{O}_3$ has excellent oxidation resistance but its resistances to thermal shock is poor and apparently can not be much improved. Silicon nitride and Silicon carbide do possess good mechanical properties but rather poor oxidation resistance [1]. These materials are the major competitors to new phases in SiAlON and AlON systems developed since 1972.
Ceramic materials of nitride type have been extensively studied because of their promising application as components in heat engines operating at very high temperature. Metallic alloys used in such thermomechanical systems are not able to withstand the adverse operating conditions [2-4]. Ceramic materials, substituted for these alloys, must exhibit good mechanical stability at high temperatures and good chemical stability. The linear expansion coefficient, elastic moduli, toughness and good stability to creep and thermal shock are several of the key features characterising mechanical properties.

Kohn and associates [5] of the U.S. Bureau of Mines have found the aluminum nitride as a refractory material. The kinetics of densification and mechanical properties of this material have been studied [6-24] in detail. Scientists and engineers have drawn great attention to Aluminum nitride because of its promising applications as substrates for integrated circuits, crucibles for molten metal and as a heat sink or window material. Kotsch and Trontelj [24,25] found that AlN ceramic has excellent high temperature chemical stability in contact with metals and carbons. The large energy gap [26-27] of aluminum nitride is found to be suitable for
refractory. Aluminum nitride ceramics have such chemical, physical and electrical properties which are suitable for several applications in microelectronic devices. Aluminum nitride is an ideal high temperature dielectric in active and passive components [28-29].

1.2 An Introduction to AlN ceramics

Although aluminum nitride was prepared many years ago, its properties have not been well known. Early investigators considered it too unstable, especially with respect to moisture and oxidising conditions, to be useful as a refractory. However, Ray [30], Renner [31] Long and Foster [32] found aluminum nitride a relatively stable material which can be used as a refractory material.

Pure aluminum nitride is white. Blue crystals are formed when the metal is heated above 1750°C in nitrogen containing small amounts of carbon monoxide. Ray [30] states that pure aluminum nitride forms blue hexagonal crystals. Long and Foster [32] claim that pure aluminum nitride is water white and that the blue coloration results from the presence of about 7% aluminum oxycarbide (Al₂OC) in the crystals. They reported that aluminum oxycarbide is isomorphous with aluminum nitride and that the formation of
solid solution between two compounds is very likely. They suggested that $\text{Al}_2\text{O}_3$ results from the reaction between carbon monoxide, incidently formed in the graphite lined furnace, and aluminum in the sample. Chemical analysis of the crystals showed the presence of carbon and oxygen in an approximately equimolecular ratio. Ray [30] further stated that both the white and blue crystals have the hexagonal wurtzite structure. It has four atoms per unit cell. A sample of the dark blue crystals containing approximately 2% carbon and 2.7% oxygen produced an x-ray diffraction pattern with broader reflections, some of which showed three distinct peaks. Most of these were shifted from the peaks of the light material. Differences in reflections of the white and blue crystals were not detected when the usual film technique was used. Possibly, the blue samples contained enough pure AlN to overshadow the less prominent shifted reflections. Also, the general broadening would tend to produce the same geometrical centre for the reflections of both the white and blue crystals. The density of aluminum nitride, calculated from the cell dimensions $a = 3.111 \, \text{Å}$ and $c = 4.980 \, \text{Å}$, is $3.26 \, \text{g/cc}$.

The literature [31] reports melting points in the range of $2000^\circ \text{C} - 2400^\circ \text{C}$. Renner[31] observed strong vaporization of aluminum nitride at $2450^\circ \text{C}$, but no melting. The crystals were heated to $1800^\circ \text{C}$ in 2-3 min, after which the
temperature was increased at the rate of about 200°C/min. Some vaporization could be observed at 2300°C, at 2450°C vaporization was rapid and after 1 min, at 2500°C, the crystal had completely disappeared without evidence of melting.

According to Renner [31] it is found that the aluminum nitride starts to oxidize in air at between 700° and 800°C but, in case of large crystals and the dense hot pressed material, oxidation is slow up to 1400°C because of the protective oxide surface layer formed. The oxidation rate of well formed crystals, however, was slow even at much higher temperature because of the formation of a dense adherent aluminum oxide film. It is inert to hydrogen at 1700°C but is attacked by chlorine between 500°C and 700°C.

The use of hot pressing has been thoroughly developed for the production of special materials. In hot pressing, the main emphasis has been given on the saving in time as compared with the normal sintering. In contrast, the development of the method, in relation to high temperature ceramic materials, has greater technical potentialities compared with conventional sintering techniques. The ceramics made by hot-pressing are generally dense without large grain growth which frequently occurs during sintering. Hot-pressing equipment at the university of Leed described
in detail by R.J. Weston [33] is generally used. The hot-pressing apparatus, its associated control, monitoring equipment, and general procedure have been described in detail by Weston. The experimental and theoretical aspects of hot-pressing have been discussed by Kingery [34,35].

Kingery has described the hot-pressing particularly for materials that form no liquid phases or have low atomic mobility at elevated temperatures, so that densification is not obtained except at very high temperatures, it is desirable to apply pressure during the densification process. There is also the potential in this method of forming ware to high density without the large grain growth that frequently occurs during sintering. In as much as it is desirable to apply high pressure at high temperatures, it is necessary to use a die material with good high temperature strength. The material that has proved most satisfactory is graphite which has a tensile strength increasing from about 4000 psi at room temperature to 7000 psi at 2500°C. Graphite die (12.5 mm internal diameter) does not react with aluminum nitride at high temperatures. Graphite in contact with the powder was coated with high purity boron nitride suspended in an aqueous solution of methyl cellulose.

Lecompte et al [11] have reported the results of
a study of the densification behaviour of AlN during hot pressing. The AlN powder was a commercial product from Koch-light products, ref. 800 6h (d<5 μm, 99% pure) [36]. Neutron activation analysis of the powder revealed the presence of 2.7% oxygen. This oxygen is present in AlN powder in the form of oxide film of non-crystalline Al₂O₃. However the x-ray spectrum contained only the diffraction peaks corresponding to AlN.

Hot pressing was carried out at 1700°C at pressure between 5 to 30 MPa on 3 gm of powder. Rates of densification were calculated for a constant relative density of 0.8 on the relative density time plot. They found two regimes for 0.7 and 0.5 μm grain size powder, one covering the applied stress range of 5-24 MPa and the other from 24 MPa upwards where the densification rate was very fast. The threshold stress observed graphically was 6 MPa for both the powder.

They also found that, for both the powders, the stress exponents were nearly 1 in the low stress range and nearly 10 in the range of 24-30 MPa. The rate of densification also depends upon the grain size of the powder. The ratio of densification rates between the two powders in the lower stress region was found to be 2.7.
Lecompte et al [11,18] further suggested that, in the high pressure region, dislocation creep may be important for the densification mechanism, while the grain-size dependence at low pressure may be due to grain boundary diffusion controlled process. The addition of 5 wt% alumina with the AlN did not change significantly the rate of densification.

It is difficult to make high purity hot pressed aluminum nitride samples free from oxygen contamination, and it is now recognized that an oxygen content of about 2 weight % is necessary for sintering to full density [37-38]. The oxide film on the surface of the aluminum nitride powder particles reacts with the aluminum nitride to form aluminum oxy-nitride during hot pressing under pressure of 30 MPa to 40 MPa in carbon dies at temperature of 1900°C and above [39].

The porosity of the sample is found to vary with the temperature when the pressure (20 MPa) and the duration of annealing time (30 min.) are constant. When the total porosity is less than 6%, it mainly consists of closed porosity, and that when the total porosity is more than 6%, the open porosity increases rapidly whereas the closed porosity attains a maximum value and subsequently decreases [10].
Tetard and Billy [40] showed that about 25% oxidation of aluminum nitride powder takes place after heating at 900°C for 10 hours. It is observed [11,18] that the rate of densification increases with the oxide formation. Oxide contents were analysed by neutron activation and the powder contained 6.45 wt% (1 hr oxidation at 800°C) and 14.2 wt% (3 hr oxidation at 800°C) of oxygen. The threshold stress is now increased to 8 and 10 MPa for 6.45 and 14.2 wt% powder, respectively. At low pressure, a threshold stress is apparent which may be controlled by second phase particles located at grain boundaries as described by Ashby [41]. Gourdin and Tanner [42] have observed the microstructures of hot pressed AlN powder by dynamic compaction [43] and have indeed observed a dispersion of discrete particles in the grain boundaries. The observation of Gourdin et al. [42] should dispel the concerns of Lecompte et al. [11] regarding the development of a dispersion of grain boundary particles during hot-pressing.

Sakai et al. [38,44,45] have also investigated the effect of the oxygen impurity on the densification behaviour of AlN. The different amount of oxygen were synthesized from alumina in the AlN powder and hot pressed. According to the densification rate equation for the final stage of hot pressing [45], there is a linear relation between \( \ln (1-\rho) \) and \( t \) at constant temperature, where \( \rho \) and \( t \)
are the relative density of the compact and holding time. The relative density increased at the higher oxygen content. However, at the temperature higher than 1900°C, the densification rate decreased gradually during the holding period due to the libration of impurity oxygen during hot pressing. Decreasing oxygen content in AlN occurred above 1800°C and became vigorous with increasing temperature [32]. Hence the formulation adopted by Sakai and Iwata [38,45] did not prove helpful; the logarithmic plotting of the porosity \((1-\rho)\) above the initial porosity \((1-\rho_0)\) as a function of time did not yield that of the predicted straight line. This discrepancy may be associated with the libration of oxygen during the hot pressing.

Hardness value of aluminum nitride is approximately 1200 as found in the literature [32,46]. It is also found that the fully densified aluminum nitride has a microhardness of 1560 Vickers [18] which is comparable to those of silicon nitride [47] and silicon oxynitride [48]. Boch et al. [10] have measured the Vickers microhardness of AlN ceramic as a function of total porosity \((P<20\%)\) with different grain size powder. Hardness increases as the mean grain size decreases and hardness decreases as the porosity increases.
Yamada et al. [7,49] have also measured the temperature dependence of Vickers microhardness for AlN ceramic, with and without additives, hot pressed at various temperatures. According to the observations of Yamada et al. [49], the microhardness of fully dense AlN sintered body without additives is about 13 GN/m² at room temperature except in case of hot-pressed at 1573 K and it began to decrease gradually with increasing temperature. The microhardness at 1473K was about 7 GN/m². The value of microhardness of AlN body at 1573 K was lower than at temp. above 1773K due to weak bonding between grains. In case of additives of CaO(2.5 wt%) the values of microhardness degradation was observed at temperature above 1173K. They also suggested [32,46] that the drastic decrease occurred by the grain boundary sliding due to the softening of intergranular secondary phase. The sintering duration does not effect the value of microhardness.

Long and Foster [32] have reported a modulus of rupture \( \sim 11,500 \) psi for sintered aluminum nitride at room temperature. Ray [30] have reported the compressive strength of sintered aluminum nitride brick to be about 3000-4000 psi. Taylor and Lenie have reported [46] compressive strength of hot pressed material to be about 300,000 psi. The strength of hot pressed aluminum nitride
was measured by Lecompte et al. [10,18] as a function of porosity and temperature by 3-point bending method. They reported that, at room temperature, the strength of the dense AlN is rather high about 380 MPa. Boch et al. [10] have reported that the strength remains almost constant up to 10% porosity and decreases afterwards. It is well known that open porosity initiates fracture [50] and hence the strength decreases as porosity increases. Boch et al. [10] have explained such type of porosity dependence of strength on the basis of open and closed porosity. They further reported [10] that, at low percentage of total porosity (upto 6 vol%), the open porosity is almost negligible and samples have mostly closed porosity.

The temperature dependence of strength of hot pressed aluminum nitride ceramics is also studied [10,18]. The strength decreases as the temperature increases up to 700°C and remains roughly constant afterwards. The rate of decrease is low, so the strength at 1300°C is rather high. However, a value of 380 MPa has been reported by Boch et al. [10] and Glandus et al. [51] for polished specimens of almost completely dense hot pressed AlN. This relatively high value is due to the polishing of the specimens. High value (upto 500 MPa) has also been reported by Schwetz et al. [52] again for polished specimens (surface roughness, Ra < 0.5μm) of sintered materials.
The strength of AlN ceramics as a function of porosity and temperature has also been investigated by Dewith and Hattu [8]. They reported [8] that at zero porosity the strength is about 310 MPa for specimen with a centre line average roughness Ra ~ 0.2 μm. In the case of highly dense and rougher surface (Ra ~ 1.1 μm), the strength value decreases to 237 MPa. The strength value shows a strong decrease with increasing porosity up to 0 < P < 44%. They did not observe a constant strength up to a porosity of 10% as observed by Boch et al. They observed [8] that the strength at 1500K decreases to about 20% as compared to room temperature value. A decrease of about 50% is observed by Boch et al. [10] for their almost completely dense materials, while Glandus et al. [51] indicate a decrease from 380 MPa at 300K to 240 MPa at 1100 K and then constant value at temperature up to 1500 K for a fully dense material.

The fracture toughness of aluminum nitride ceramic has been investigated [7, 8, 10, 38, 49, 53] either as a function of porosity or as a function of temperature. Fracture toughness of AlN as a function of temperature for various values of porosity has also been measured by Dewith et al. [8]. At room temperature, the value of fracture toughness of the completely dense material is 2.7 MPa m^{1/2} for the planes parallel to the hot pressing axis. A sharp decrease
with porosity is observed by these workers [8]. The fracture thoughness was also reported by Dewith and Hattu[8] upto 1500K. The value of fracture thoughness decreases by about 10% upto 1500K. Boch et.al.[10] have also measured the fracture thoughness value $\sim 2.5$ to $2.7 \text{ MN m}^{-3/2}$ for most completely dense material with a grain size of about 9 $\mu$m. Hence, there is close agreement between Boch et.al. and Dewith & Hattu regarding the fracture thoughness value.

Yamada [7,49] have also reported the values of fracture thoughness as 3.0 to 4.0 $\text{ MN m}^{-3/2}$ at room temperature for fully dense AlN ceramics with and without oxide additives and were higher than those reported above. They found [7,49] little temperature dependence of fracture thoughness upto 1200$^\circ$C. The results of the temperature dependence of fracture thoughness for AlN sintered body with CaO additive indicate that fracture thoughness increased sharply at 1473K. This is interpreted in terms of softening of the secondary glassy phases which exist in the grain boundaries. The fracture thoughness increases when Vickers microhardness is large.

There are many important applications of ceramics which arise from control or manipulation of the elastic deformation under an applied stress. The elastic extension of a body corresponds to the uniform increase of the
separation between the atoms. Therefore, the elastic extension is directly related to the forces between atoms and the structural energy. Many satisfactory correlations between the lattice energy and elastic moduli have been proposed and work quite well for materials with the same structure and bond type. Taylor and Lenie [46], using the bend test, reported a value of 145 GPa for Young modulus of 98% dense hot pressed AlN. The modulus of elasticity of hot pressed aluminum nitride is about the same as that of hot pressed alumina at room temperature, but is higher than that of hot pressed alumina at 1400°C. Gogotski [54] also gave a value of 234 GPa for 97.2% sintered material using the bend test method.

The modulus, in two phase system, is intermediate between the high and low modulus components. The ultimate, in adding a low modulus material as a second phase, is to add pore space that has approximately zero bulk modulus value. In this case the overall elasticity at porosities upto about 50% has been derived by Mackenize [55]. As volume fraction of pores increases, the fractional elastic moduli decreases from 1 to 0. Boch et.al.[10] also investigated the dependence of Young's modulus, poisson's ratio and shear modulus on porosity. These measurements were made as a function of total porosity for \( P < 20\% \). According to these workers, the elastic moduli decreases as
the porosity increases in the range \(0 < P < 20\%\).

Dewith and Hattu [8] have also reported the dependence of Young's modulus on porosity. They observed a sharp increase in Young's modulus with density. The porosity dependence of Young's modulus as determined by Dewith and Hattu is non-linear up to the porosity \(P < 44\%\).

The coefficient of thermal expansion is fractional change in volume or linear dimension per degree of temperature changes. The length and volume changes associated with temperature changes are important for many applications. Taylor and Lenie [46] have measured the thermal expansion of hot pressed aluminum nitride \((4.84 \times 10^{-6} {^\circ C}^{-1} \text{ in the range } 20-600^\circ C)\) parallel to the direction of pressing. These results are very close to the results reported by Long and Foster [32] \((4.8 \times 10^{-6} {^\circ C}^{-1} \text{ in the range } 20-500^\circ C)\) for sintered aluminum nitride. The thermal expansion of hot pressed aluminum nitride is in the moderate range for a ceramic, being only slightly higher than that of silicon carbide. Lecompte et al. [18] reported a high value of thermal expansion \((5.1 \times 10^{-6} {^\circ C}^{-1} \text{ for AlN})\) for AlN. It has also been shown [10] that the thermal expansion coefficient decreases as the porosity increases.

Thermal expansion of sintered oxynitrides in the
system AlN–Al$_2$O$_3$ have been measured by Sakai and Watanabe [56]. They reported that the thermal expansion of the compact, composed with only 27 R pseudopolytype [57], was $5.91 \times 10^{-6} \text{°C}^{-1}$ and was slightly larger than that of AlN which is $5.3 \times 10^{-6} \text{°C}^{-1}$ [58]. The thermal expansion of the compact in this system increased proportionally to the amount of alumina added to AlN.

When ceramic materials are subjected to rapid change in temperature (thermal shock), substantial stress is developed. Resistance to weakening or fracture under these conditions is called thermal endurance, thermal stress resistance or thermal shock resistance. Some low loss electrical insulator applications require thermal stress resistance characteristics some where in between those for crack initiation and actual loss of weight. High fracture stress, low modulus of elasticity and low thermal expansion coefficient indicate a good resistance to thermal stress failure. However, elastic moduli as well as its coefficient of linear expansion of AlN ceramics are high and its toughness is low. Such values for these mechanical parameters lead to a rather poor thermal shock resistance. Boch et al. [10] determined the thermal shock resistance by non-destructive method to be about 250°C. This low value of thermal shock resistance agrees very well with the results of the other workers [54]. Thermoelastic analysis of
thermal shock resistance [59] may explain the rather bad results for aluminum nitride regarding its resistance to cracking by thermal shock. Thermoelastic theory enables us to predict a lower critical quenching temperature difference for the dense material than for porous samples up to $P \leq 10\%$. In this range of porosity, when the open porosity increases the strength and the coefficient of thermal expansion remain quite constant and Young's modulus decreases. The thermal shock resistance was evaluated [46] by measuring the loss in the strength of the hot pressed aluminum nitride bars after 30 cycles of heating in 2.5 min. to 1400°C and rapidly cooling to room temperature in an air blast. Taylor and Lanie [46] observed a loss of 12% of the original strength before and after thermal cycle.

The process by which heat is transferred by interaction between individual atoms, ions and molecules is called Thermal conduction. In solids, energy is transferred by interaction between the neighbouring atoms. There are two processes by which heat conduction takes place in solids. Energy is transferred by coupling between lattice vibrations or by electronic movement and collisions with atoms. For dielectric materials, e.g. in most ceramics, electrons are not free to move through the structure in appreciable concentrations and heat is mainly transferred by lattice vibrations. Thermal conductivity of AlN ceramic has
been studied by many workers [32,7,18,46,49,60-65]. Aluminum nitride has an exceptionally high thermal conductivity which is about eight times that of alumina and approaches that of Beryllia at 200°C. The thermal conductivity is about 140 W m\(^{-1}\)K\(^{-1}\) at room temperature.

The major effect of temperature on AlN ceramic, above room temperature, is rapid decrease in thermal conductivity at increasing temperatures [46,49,61-62]. Taylor and Lanie [46] have measured the thermal conductivity by a linear flow comparative method for hot pressed AlN ceramic [0.072 cal/cm/sec/°C at 200 °C and 0.048 cal/cm/sec/°C at 800°C]. A rapid decrease was observed with increasing temperature. The results indicate that aluminum nitride is a good conductor of heat, being intermediate between dense silicon carbide (0.24 cal/cm/Sec/°C) which is an excellent conductor and alumina (0.054 cal/cm/sec/°C at 200°C) which is a fair conductor. These data are in sharp contrast to those of Long and Foster [32] who reported the thermal conductivity of sintered aluminum nitride at 25°C as 0.0042 cal/cm/sec./°C for a porosity of about 40%. The thermal conductivity at zero porosity was 0.007 cal/cm/sec/°C which was same as measured by Long and Foster [32]. This difference in density is not responsible for the great dissimilarity in the thermal conductivity values [32,46]. The trouble may be caused by the oxygen impurity on the thermal conductivity of
AlN as reported by Slack [63].

The temperature dependence of thermal conductivity of AlN ceramics with and without additives of CaO and Al₂O₃ have been measured by Yamada [7, 49]. They reported that the thermal conductivity of AlN without additives decreases with increasing temperature. Yamada et al [49] indicated that the thermal resistivity was directly proportional to temperature and the gradient was same in the low temperature range. These results indicated that thermal resistivity of samples was caused by phonon-imperfection interaction. The values [7] of thermal conductivity of fully dense AlN ceramic prepared at 1700°C-3 GPa-240 min were 40 w/MK at room temperature and 26 W/MK at 700°C. Yamada et al. [49] have also shown that purity in AlN ceramic is one of the most important factors governing the thermal conductivity. The value of thermal conductivity of pure AlN ceramic, at 300 K, is estimated to about 200 W/MK by extrapolation of the relation between thermal resistivity and impurity contents.

Sakai et al. [61] have reported that the rapid decrease of thermal conductivity may be associated with heterogeneous oxygen distribution in sintered body. They measured thermal conductivity of the compacts of 27 R and 21R pseudopolytypes of AlN and aluminum oxynitride spinel...
made from mixed powder of AlN and Al₂O₃ by hot pressing as 0.015, 0.013 and 0.026 cal/cm/sec./K at 300K [61]. Decrease of the thermal conductivity of the crystal and sintered compact of AlN are remarkable with the oxygen content as observed by Slack [63]. The thermal conductivity varied not only with the amount of oxygen but also with its distribution in the hot pressed specimens. Sakai et al. [61] also reported the effect of hot pressing conditions on the thermal conductivity of AlN which was synthesized by reducing and azotizing alumina. It is reported that the conductivity of the compact (hot-pressed for 1 hr under 20 MPa at 1800°C) was about twice of the value observed for hot pressed above 1900°C. The considerable decrease of the thermal conductivity in the temperature range from 1800°C to 1900°C indicated [62] that the oxygen in spinel spread into the AlN grains and finally composes 27 R structure.

The thermal conductivity at 300K for highly pure and dense AlN ceramic to be 0.33 cal/cm/sec./K has been reported by Inomata [65]. The hot pressed AlN specimens [oxygen 1.6 wt%, density 2.54 gm/cm³, porosity 20%] shows the highest thermal conductivity value at 300K in the specimen tested [65], and the value 0.15 cal/cm/sec./K is in good agreement with 0.017-0.18 cal/cm/sec./K reported by Slack [63] for the similar hot pressed AlN specimens. At the higher concentration of oxygen (7.2 wt%), they found a
decrease in thermal conductivity value [65].

The oxidation study in air shows that aluminum nitride has good oxidation resistance [32,10,12,14,46,34,66,67]. Taylor and Lanie [46] showed that aluminum nitride starts to oxidize in air between 700°C and 800°C but in the case of large crystals and the dense hot pressed material, oxidation is shown at 1400°C because of the protective oxide surface layer formed. Long and Foster [32] also reported the difference in oxidation rate of hot pressed AlN and the sintered material. Exposure to air for 1 hour at 1200°C of 1 cm cubes of sintered material resulted in a conversion of about 11% of the sample to Al₂O₃ whereas exposure to air for 30 hr at 1400°C of dense hot pressed AlN specimens of comparable size resulted in a conversion of about 1% to Al₂O₃. The oxidation behaviour of hot pressed AlN ceramic in air has been studied [32,10,12] between 1300 to 1700°C. The results indicate that the material oxidised a little upto 1490°C (4mg/cm²) after 24 hours. Oxidation became dominant at 1600°C and its rate increased suddenly at 1680°C in isothermal reaction. The oxidation resistance of AlN at temperature 1400°C is rather high as compared with other silicon based ceramics presumably due to the different plasticity between the oxidation products (alumina, silica, silicates) [68,69]
The oxidation behaviour of AlN in static air was studied [12] in the temperature range 1200 to 1700°C on dense hot pressed specimens prepared without or by using oxides (MgO, CaO, Y₂O₃) for densification. This study of oxidation in air at high temperature [12] showed that the oxidation resistance decreases if MgO and Y₂O₃ are used as additive. However no decrease in oxidation resistance was observed in case of CaO. The above study shows that CaO can be used as an additives to get fully dense samples of AlN without having any effect on the oxidation behaviour.

Electrical conductivity of AlN samples has been investigated by many workers [70-73]. The electrical conductivity of hot pressed AlN ceramic was found to be very small (< 10⁻¹¹ Ω⁻¹ cm⁻¹) below 650 K. The conductivity (σₐc) increases exponentially as the temperature was increased and at higher temperature (950K) an appreciable conductivity (> 10⁻⁸ Ω⁻¹ cm⁻¹) was observed.

The porosity is an important parameter on which the electrical conductivity and dielectric behaviour may depend. The electrical conductivity decreases by two orders of magnitude as the porosity increases from 0.2 to 15 volume percent. The activation energy increases with the increase of porosity [79].
The measurements made on AlN show that the dissipation factor and dielectric constant practically remain constant and independent of frequency up to 550°K and increase significantly as the temperature is increased, the increase being different at different frequencies. Space charge polarization seems to be responsible for the behaviour [79].

The effect of various oxides (MgO, BeO, SrO and Y₂O₃) on the electrical conductivity and dielectric behaviour of AlN has also been studied. It is observed [74,75] that the conductivity increases and activation energy decreases as one mole percent of MgO, BeO, SrO and Y₂O₃ is added to AlN. The maximum effect is found in case of MgO additive. An increase in conductivity by one to two orders of magnitude with a corresponding decrease in the activation energy indicates a doping type behaviour similar to that of crystalline semiconductors. Concentrations of charge carriers increases and Fermi level also changes due to the presence of additives.

Dissipation factor and dielectric constant, at a particular temperature, increase on addition of oxide additives. The maximum effect is observed [74,75] in case of MgO followed by BeO and Y₂O₃. The effect of d.c. conductivity after putting these additives is responsible for the large value of dissipation factor and dielectric
constant which is consistent with space-charge polarization mechanism.

1.3 **Selection of the problem:**

As mentioned in section 1.2, the AlN ceramic has excellent mechanical, thermal and electrical properties which make it suitable for various applications in the industry. Low conductivity of this ceramic makes it suitable for substrates in integrated circuits & for other insulation purposes. A small value of loss tangent, at moderate temperatures, make AlN suitable for dielectric material in capacitors.

Ceramic materials, which are generally used outdoors, are subjected to atmospheric humidity and various exhalate vapours which come out from the part of the equipment (soldering material) or from the packaging materials (wood etc.) The effect of humidity and various exhalates (HCl, HNO₃, HCOOH, CH₃COOH vapours, NH₃, SO₂) on the electrical and dielectric behaviour have been studied in detail in some polymeric laminates [80-81] & it is found that a degradation in the insulating behaviour of these laminates occurs after exposure to these vapours. The effect of such corrosion has been studied as a function of exposure time in the above materials and a systematic changes have been observed.

In view of the above results, it is an obvious
curiosity to see the effect of such exposures on the corrosion effects in hot pressed AlN ceramic whose electrical & dielectric properties have been studied in detail in our laboratory during the last few years[80,81,82]

The effect of humidity on the dielectric behaviour indicated [74] that humidity exposure increases the electrical conductivity and dielectric loss in hot pressed AlN ceramics.

The present thesis reports the effect of various exhalate vapours (HCl, HNO3 , CH3 COOH, HCOOH ) on the electrical conductivity and dielectric behaviour of hot pressed AlN ceramics.

The effect of the porosity and various oxide additives (MgO, Y2 O3 , BeO , SrO ) on the corrosion behaviour has also been studied in detail. The results indicate that porosity as well as oxide additives, present in hot pressed AlN ceramic, play an important role in the corrosion behaviour of these materials.

Chapter 2 describes the experimental details of sample preparation and characterization of hot pressed AlN ceramics.
Chapter 3 describes the effect of exposure to some inorganic and organic acid vapours on the dielectric behaviour of hot pressed AlN ceramic without additives. The effect of porosity on the corrosion behaviour is also discussed in this chapter.

Chapter 4 describes the effect of the exposure to the some acid vapours on the electrical conductivity in these samples. The effect of additives on the corrosion behaviour of hot pressed AlN ceramic is reported in chapters 5 and 6.