CHAPTER - I

INTRODUCTION

A dielectric is an insulating material which offers high impedance to static and low frequency potentials and also offers relatively loss-free impedance to any alternating sources. Ceramic dielectrics are produced in a wide range of compositions and shapes to cover the applications to which they are better adapted than alternative materials. A ceramic capacitor is essentially a parallel plate condenser with a ceramic material as the dielectric. The various ceramic dielectrics have wide variations in properties depending on the chemical composition of the dielectrics and the way in which they are prepared. The first ceramic capacitor was developed during World War II due to shortage of naturally occuring ruby mica with a dielectric constant of 5-7.

An ideal capacitor is one which has very high dielectric constant with very low dissipation factor, is very stable against any variation in working voltage, temperature and applied frequency and of high dielectric strength. However, an ideal capacitor really does not exist and one may reduce the size and cost of a capacitor only at the expense of stability and reliability. Multilayer capacitors are made from three main types of materials, often described as NPO, BX and Z5U materials [1]. The NPO-type materials have relatively low permittivities, which are nearly independent of temperature, the Z5U materials have very high permittivities, which vary strongly with temperature, and BX materials come somewhere between the two. Table 1.1 shows the properties of these three types of materials [2]

Ceramic capacitors have been used to a great extent in radio, television, computer and communication systems to store and release dielectric energy. In recent years the trend in electronics has been towards miniaturization, and in the case of the capacitor

TABLE 1.1 COMPARISON OF DIELECTRIC PROPERTIES OF THREE DIFFERENT TYPES OF CERAMIC CAPACITORS

	NPO	BX	Z5U
DIELECTRIC CONSTANT AT 25°C	30 - 60	1600 - 2000	5700 - 7000
DISSIPATION FACTOR AT 25°C	$< 0.2\%$	$\leqslant 2.5\%$	$\leqslant 3.0\%$
WORKING TEMPERATURE RANGE (°C)	- 55 to 125	-55 to 125	10 to 85
ΔC_{max}*	± 0.3%	± 15%	± 22%, -56%
ΔC_{max} AT RATED VOLTAGE	± 0.3%	± 15%, -25%	Very high
FREQUENCY STABILITY**	100 MHZ	1 MHZ	--------
RELATIVE DIELECTRIC STRENGTH	15	5	2
RELATIVE SIZE/COST***	1000	30	14

* C_{max} - Maximum change in capacity from 25°C value with no voltage applied over the temperature range.

** - Frequency at which properties beging to deteriorate.

*** - Relative size/cost for units of same capacitance at the same voltage rating.

as a component, this is reflected primarily in the demand for increased volumetric efficiency i.e., greater capacity per unit volume of the capacitor. The prospects and the difficulties are best discussed by starting from the well-known equation for the capacitance of a parallel-plate capacitor ;

$$C_A = \frac{\epsilon_o \epsilon_r}{d}$$

where,

C_A = Capacitance per unit area
ϵ_o = Permittivity of free space
ϵ_r = Relative permittivity of the dielectric
d = Spacing of the plates

There are two ways of increasing the capacitance per unit area : increasing ϵ_r or decreasing d .

(i) Increase of dielectric constant :

After the discovery of the ferroelectric properties in barium titanate in 1943, having ϵ_r values >1000 [3] research and development have concentrated primarily on this material as the ceramic dielectric. The room temperature dielectric constant of some well-established ceramic dielectrics, which are all modifications of $BaTiO_3$ ranges from 1000 to 15000, depending upon the exact compositions. Typical properties of a commercially available $BaTiO_3$ dielectric are shown in Table 1.2. Research on these ferroelectric materials revealed that an increase in the permittivity is generally gained at the expense of the temperature characteristics. Such an effect can be predicted from fundamental consideration on ferroelectrics, since the factors that cause the permittivity to increase also make it more sensitive to temperature changes [5,6] .

TABLE 1.2 TYPICAL PROPERTIES OF A COMMERCIAL BARIUM TITANATE CAPACITOR (Ref. 4)

Specific weight	...	5.6 gms/cm^3
Grain size	...	10 - 100 μm
Specific heat	...	0.12 Cal/g°C
Curie Temperature, T_c	...	120°C
$\epsilon_{30^\circ C}$	...	1300
$\Delta\epsilon/\epsilon$ (0-65°C)	...	19 - 12%
$\Delta\epsilon/\epsilon_0$ (0-1 KV/mm)	...	0 - 8%
Tan δ	...	1%
Resistivity ρ 25°C	...	10^{12} ohm.cm
Firing temp.	...	1400°C

(ii) Reduction of thickness :

This is mainly a problem of technology. The conventional flat (disc) capacitors are shaped by pressing, extruding or calendering a mixture of a ceramic powders mixed with binders. These techniques can reduce the thickness down to 100 μm. In addition, pieces of ceramics thinner than 200 μm are very difficult to handle during the manufacture of capacitors (e.g. during soldering the leads and encapsulation).

For greater volumetric efficiency two new types of ceramic capacitors have been developed. The first type is the 'Ceramic Barrier-layer Capacitor (CBC) which is based on the formation of a thin insulating layer at the surface or at the grain boundaries of a piece of semiconducting ceramic. The second new type of capacitor, resulting from efforts to reduce the thickness, is the 'Ceramic Multilayer Capacitor' (CMC) [7].

The cut-away view in Fig. 1.1 indicates that a multilayer capacitor consists of a ceramic body with embedded electrode layers. The electrode layers are alternately connected to the metallized end terminations on the left and right of the capacitor. With this electrode arrangement the individual capacitors formed by the ceramic layers between electrodes are all connected in parallel, so that their capacitances add upto the required total capacitance.

The multilayer capacitors are made in the following way. Powders of the ceramic materials are mixed with binders to form a suspension, and strips of thickness of about 50 μm are cast from the suspension. The strips or tapes are then cut into sheets, and a metal paste is applied by screen printing. The sheets, with the electrodes printed on them in a repetitive pattern, are stacked and

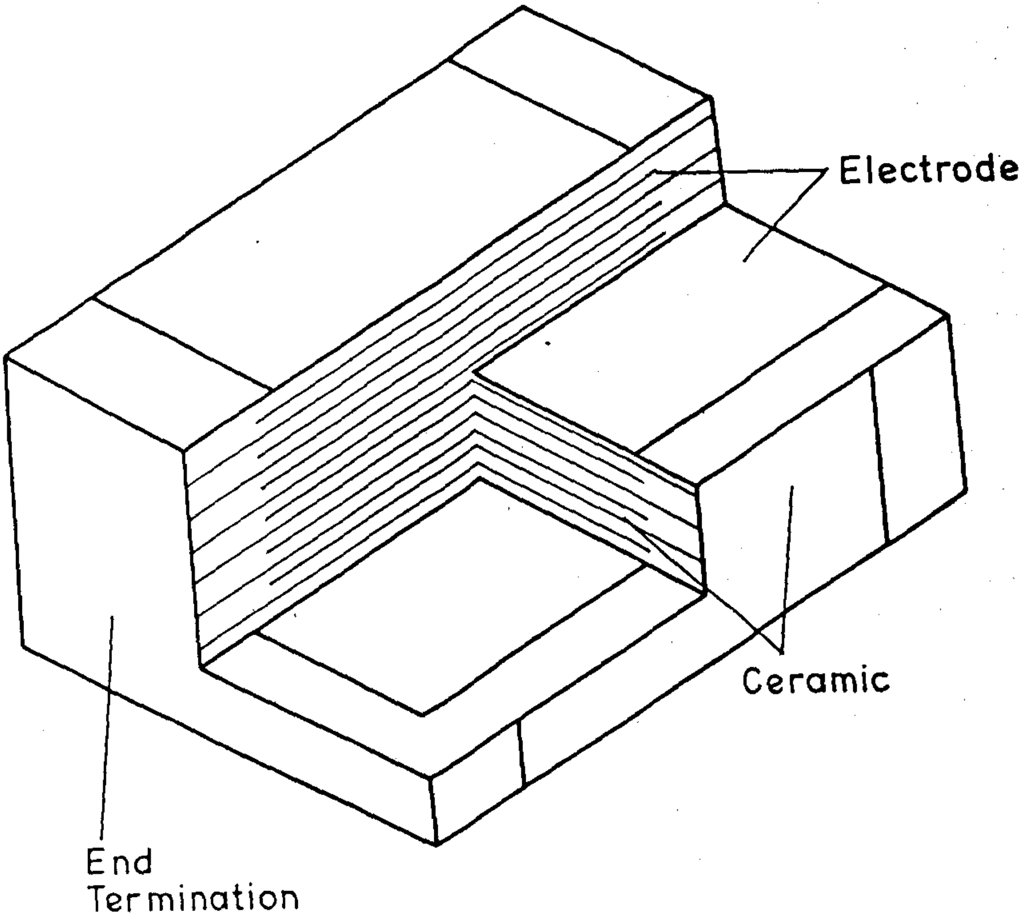

Fig. 1.1. Cut away view of a ceramic multilayers capacitors (ref. 7)

consolidated under pressure, and the individual units are then cut apart and heated to burn off binder. The complete assembly is then fired to produce a coherent, integral structure of ceramic and metal. During the screening, stacking and cutting the sheets are aligned in such a way that the electrodes on successive layers are exposed at opposite faces. These two faces are then metallized, so that the individual ceramic capacitors are all connected in parallel.

The important advantage of multilayer capacitor is that the metallized end faces of the ceramic body, making these capacitors to be 'chip components'. These are 'leadless' electronic components that can be soldered directly to the conducting paths of a printed circuit board [8]. Components of this type have become particularly important in recent years, since the introduction of automatic mounting techniques that can only handle chip components [9,10]. Except for tantalum capacitors which offer a different range of capacitances, any way, the ceramic multilayer capacitor is the only other type of chip capacitor available in quantity on the market today.

Although it has many advantages, the multilayer capacitor is expensive to manufacture. The technological processes used for making them are fairly complex compared with those used for conventional capacitors. Many manufacturers have now succeeded, however, in reducing these costs, through automation to a level at which they are no longer a major obstacle. The second problem which still exist, is that the materials used for the electrodes are very expensive.

In the manufacture of conventional multilayer capacitors the internal electrodes are fixed together with the ceramic material. Since dielectric ceramics are normally fired in air at temperatures between 1200 and 1400°C, only nonoxidizing noble metals with high melting point can be used as the electrodes of the multilayer capacitors. In practice this means that the metal must be palladium, or platinum which is even more expensive. These noble metals can in fact account for nearly half the cost of manufacture of the capacitor, depending on the capacitance value.

Work is going on in many countries to reduce the use of the expensive metals in multilayer capacitors. In one method, called 'back fill process' in which the electrode metal is not applied until after firing. In this method, instead of metal paste, a special ink which contain a ceramic powder and a large amount of binder is used. During firing the binder burns off to form volatile component, leaving behind porous ceramic layers at the electrode. After firing, this porous layers are filled with relatively inexpensive fusible alloy, e.g. of Pb and Sn, which form a more or less continuous electrode layer. However, the process has been found to be difficult to control.

The vast majority of CMC are still fabricated with $BaTiO_3$ based dielectrics, but developments are in progress towards other more versatile antiferroelectric and relaxor superparaelectric compositions. In the $BaTiO_3$ based systems, the high cost of precious metals has forced the change towards highly fluxed compositions which will densify at temperatures compatible with high siliver palladium alloy electrodes[11,12] or to heavily acceptor doped materials which can be co-fired at low oxygen partial pressure with nickel metal electrodes [13-15].

In Japan, it is evident that NEC has invested considerable efforts upon the lead based perovskite relaxors and has developed materials which densify at temperatures below 900°C suitable for use of pure silver electrodes [16]. Similarly in the U.S. there is indication from Sprague Electric Company of a PLZT based CMC dielectric compatible with silver electrode [16]. The PLZT dielectric is in an antiferroelectric phase and appears to offer significant advantage in low power factor, high dielectric linearity and lower hysteresis loss under high fields [17]. Investigation at Philips Research Laboratories in Aachen, and further developments in Eindhoven have resulted new types of CMC [7].

It would appear that both the base metal and the silver electroded units can be produced at a cost and in sizes to begin to compete with larger electrolytics and to offer lower series resistance at high frequency [18,19].

An interesting newer contender in the field of CMC in Japan offers a range of $BaTiO_3$ based compositions with controlled submicron grain size produced apparently by organic synthesis and again utilizing high silver palladium electrodes [20].

In the near future, we may surmise that with the advancing speed of VLSI on silicon circuits, self and interconnect inductance will become much more important parameters in CMCs and new sets of trade-offs may be required. Eventually one may suggest that in the very sophisticated systems, the capacitor will become an integral part of the packaging and mounting structure [21,22]

In this investigation attempts have been made to synthesise barium titanate powder at low temperatures by solution route with different starting compounds like organometallics, various halides, acetates etc. The sequence of reaction in each case has been analysed by Thermal analysis, X-ray diffraction and IR spectroscopy. Powder characteristics have been determined by surface area measurement and scanning electron microscopy. Attempts have also been made to sinter conventionally prepared barium titanate powder at relatively lower temperatures by liquid phase sintering with different low melting additives like boric oxide, bismuth germanate and lead germanate. Attempts have also been made to obtain a less temperature sensitive dielectric peak near room temperature by using mixed oxides of barium strontium titanate. The liquid phase sintering of these mixed oxide systems has also been attempted. Sintering behaviour of powders with additives has been primarily determined by density measurement and microstructure analysis. A thorough dielectric characterization has also been carried out on the sintered specimens.