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Developments in ferroelectric ceramics for capacitor applications

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Abstract. A brief overview of the materials and processes for making ceramic capacitors based on $BaTiO_3$ and relaxor ferroelectric compositions is presented with special emphasis on more recent developments.

Keywords. Ferroelectric ceramics; ceramic capacitors; barium titanate; relaxor ferroelectrics.

1. Introduction

The last few decades have witnessed an ever increasing interest in ferroelectric ceramics because of their applications in a wide range of devices. Ferroelectric ceramics possess extremely high dielectric constant which makes them unenviable for making miniaturized single- and multi-layer capacitors. The excellent electromechanical response of these ceramics, on the other hand, is currently being utilized in a large number of devices such as sonars, high voltage generators, resonators, flaw detectors, lighters, actuators and micro-positioners. When doped with suitable off-valent cations, these ceramics exhibit semiconducting behaviour. In such semiconducting ferroelectric ceramics, the interaction of electrical transport with ferroelectricity near Curie point leads to nonlinear positive temperature coefficient of resistance (PTCR-effect) which is being commercially exploited in PTC-thermistors. The pyroelectric and electro-optic properties of these ceramics are no less interesting. These properties, however, have not been as much commercially exploited as the other properties mentioned earlier. Potential applications envisaged are in IR imaging and detection, goggles for avoiding flash-blindness, optical displays and optical modulations. The remanence behaviour has been shown recently to be useful for non-volatile RAM cells operating at a few volts.

As a result of intensive research activity, the topic of ferroelectric ceramics has acquired the level of a subject with an extremely large number of publications and patents coming out year after year. It is impossible to do justice to this subject in a short overview. We, therefore, restrict ourselves to a few important developments in materials and processes relevant for capacitor applications. Here again, we have not attempted to cover barrier-layer capacitors since these are based on ferroelectric and non-ferroelectric materials as well and deserve a full article of present length.

2. Barium titanate-based ceramic capacitors

As is well known, $BaTiO_3$ ceramics possess very high dielectric constant with relatively low dissipation factor. However, a severe limitation of this material in pure form for making capacitors is the high temperature coefficient of dielectric constant in the vicinity of the cubic to tetragonal phase transition. In this section, we discuss the two different strategies based on (i) grain refinement and (ii) solid solution formation which have been used to overcome this limitation.

2.1 *Grain size effect in $BaTiO_3$*

Undoped $BaTiO_3$ ceramics with grain size $\sim 10\,\mu m$ usually possess a room temperature dielectric constant (ε_{RT}) of $\sim$ 2000 and ubiquitous 90° and 180° domain structure (Jaffe *et al* 1971). ε_{RT} varies as a function of grain size. It can reach a maximum lying between 3000 and 5000 near $1\,\mu$ grain size (Egerton and Koonce 1955; Kniepkamp and Heywang 1958; Brandmayr *et al* 1965; Kinoshita and Yamaje 1976). On the other hand, the peak dielectric constant at Curie point (ε_{max}) monotonically decreases with decreasing grain size below $5\,\mu m$ (see e.g. Vivekanandan *et al* 1986) reducing the temperature coefficient of dielectric constant near Curie point drastically. The grain size effect in $BaTiO_3$ has been attributed to the near absence of 90° domains in fine grain ($\leqslant 1\,\mu m$) ceramics (Hutchins 1962) because of the significant thickness of 90° walls (0·2 to $0{\cdot}4\,\mu m$) as compared to the grain size (Little 1955; Cooke *et al* 1966). The decreasing propensity of 90° domains with grain size is believed to result in unrelieved stresses which accompany the cubic to tetragonal phase transition (Buessem *et al* 1966). These stresses are believed to suppress the spontaneous tetragonal deformation forcing the ceramic grains back towards the cubic state. However, the fact that even in loose powder form, XRD of fine $BaTiO_3$ powders does not show tetragonal deformations at room temperature goes against the internal stress model. Unlike the fine grains in a sintered ceramic, these powders have got free surfaces to relieve any transformation strains whose accumulation in ceramic samples could otherwise suppress the tetragonal deformation.

While a more satisfactory explanation for the grain size effect in $BaTiO_3$ is still awaited, the phenomenon is of great practical value. But to develop fine-grain ($\leqslant 1\,\mu m$) $BaTiO_3$ ceramics, one must start with ultrafine $BaTiO_3$ powders which cannot be prepared by the conventional solid state route. Ultrafine $BaTiO_3$ powders have been prepared by thermal decomposition of coprecipitated oxalates (Clabaugh *et al* 1956; Gallagher and Schrey 1963; Kiss *et al* 1966; Swilan and Gaddala 1973) and citrates (Mulder 1970; Kahn 1971; Hutchins *et al* 1987), thermal decomposition of metalorganic precursors (Mazdiyasni *et al* 1969; Mazdiyasni and Brown 1972; Shaikh and Vest 1986), sol–gel method (Diaz-Guemes *et al* 1989) and hydrothermal methods (Vivekanandan *et al* 1986).

The sintering of pure $BaTiO_3$ powders obtained by dry or wet routes is usually performed at temperatures between 1300° and 1400°C (Subbarao *et al* 1981). Depending on the sintering time, temperature and ambient, the average grain size is usually more than $10\,\mu m$ for highly dense ceramics because of extensive grain growth; this is irrespective of the particle size of the starting $BaTiO_3$ powder. To prepare dense $BaTiO_3$ ceramics with fine grain size, it is essential to inhibit grain growth which usually occurs above 1300°C in pure powders. Use of grain growth inhibitors such as Nb_2O_5, Ta_2O_5, La_2O_3, in excess of 0·3 at% and up to a few at%, are recommended (Payne and Anderson 1967; Kahn 1971). The same dopants, when present in concentrations less than 0·3 at%, promote grain growth and semiconductivity (Drofenik 1986). Kahn (1971) pointed out that the sintering atmosphere plays an important role. For example, reduced oxygen pressure in conjunction with moderate sintering temperatures allows the formation of small-grained $BaTiO_3$ ceramics even when $Nb \leqslant 0{\cdot}3$ at%. On the other hand, $Nb \geqslant 0{\cdot}4$ at% limits the grain size to $\leqslant 1\,\mu m$ under normal sintering in air. In principle, lowering the sintering temperature should also inhibit the grain growth and result in fine grain ceramics. However, liquid phase sintering, using LiF, $BaLiF_3$ and other similar fluxes, which can lower the sintering temperature by 400 to 500°C, does not seem to give fine grain ceramics (see e.g. Desgardin *et al* 1985; Guha and Anderson 1986) unless a grain growth inhibitor is also used. According to a recent report by Armstrong *et al* (1990), fine grain ($< 1{\cdot}0\,\mu$m) $BaTiO_3$ ceramics with near theoretical density can be prepared by sintering at temperatures $< 1175°$ for 2 h using < 2 vol% of a complex borate glass as flux and a 0·75 wt% of ZrO_2 as grain growth inhibitor. As a result of lower sintering temperature, Zr^{4+}, which usually diffuses onto Ti^{4+} sites above 1300°, resides at the grain boundary as ZrO_2 and inhibits the grain growth. Fine grain size $BaTiO_3$ ceramics have also been prepared by hot pressing of ultrafine $BaTiO_3$ powders at low temperatures (Graham *et al* 1969; Okazaki and Takahashi 1970; Carry and Mocellin 1986). Graham *et al* (1969) reported nearly flat temperature response of dielectric constant for hot-pressed $BaTiO_3$ ceramics. Application of hot pressing (HP), hot-isostatic pressing (HIP) and explosive sintering for developing fine grain $BaTiO_3$ ceramics may be preferable as the use of grain growth inhibitors as well as the sintering aids often alter the dielectric response in an undesired fashion.

2.2 *Solid solution effect in $BaTiO_3$*

A large number of cationic substitutions at Ba and Ti sites have been shown to broaden the temperature dependence of dielectric constant. Further these substitutions may also lower or raise the Curie point (T_c). Both these properties have been commercially exploited.

Isovalent substitution of Ba by Sr, Pb and Ca in the system $Ba_{1-x}A_xTiO_3$ (A = Sr, Pb and Ca) has been studied by a large number of workers (Jaffe *et al* 1971). While $SrTiO_3$ and $PbTiO_3$ show complete solid solubility with $BaTiO_3$, $CaTiO_3$ shows solid solubility to a varying extent depending on temperature up to a maximum of 21 mol% $CaTiO_3$ under normal firing conditions. While Sr is known to lower T_c at the rate of $-3{\cdot}7$°C per mol% of $SrTiO_3$ added, Pb monotonically raises T_c towards that of $PbTiO_3$ (490°C) at the same rate (for references see Jaffe *et al* 1971). Addition of Sr is known to gradually broaden the temperature dependence of dielectric constant besides raising the ε_{max} as compared to that of pure $BaTiO_3$ (Smolensky and Rozgachev 1954). Pb substitution, on the other hand, lowers ε_{RT} as well as ε_{max} and does not seem to broaden the ε vs T curve (Shirane and Suzuki 1951). The most cited work on the effect of Ba substitution by Ca is by Mitsui and Westphal (1961) according to which Ca substitution affects T_c only marginally with a shallow maximum for 8 at%. The ε_{RT} is lowered by Ca substitution but ε_{max} remains almost comparable to that of pure $BaTiO_3$.

Substitution of Ti by Sn (Smolensky and Isupov 1954; Schmidt 1990) or Zr (Kell and Hellicar 1956; Vivekanandan *et al* 1986) is also known to lower T_c as well as make the phase transition diffuse. Substitutions at Ba as well as Ti sites have also been attempted for making the phase transition diffuse (see e.g. Yoon *et al* 1988). Offvalent substitutions are also known to cause diffuse phase transition (Parkash *et al* 1991).

Recent work in our laboratory has shown that the dielectric behaviour of $Ba_{1-x}Ca_xTiO_3$ is very sensitive to the method of preparation. $Ba_{1-x}Ca_xTiO_3$ ceramics prepared by using powders obtained using dry routes either by calcining a mixture of $BaCO_3$, $CaCO_3$ and TiO_2 or by diffusion of $CaTiO_3$ into $BaTiO_3$ at high

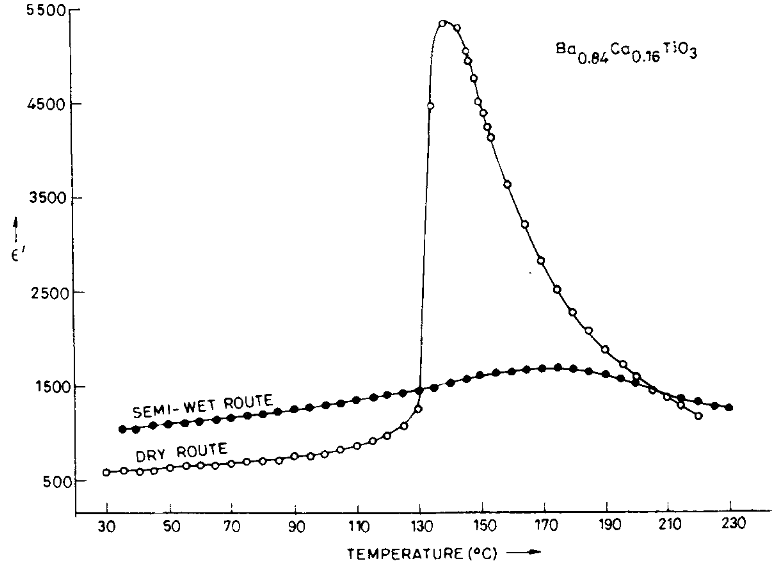

Figure 1. Temperature dependence of dielectric constant of $Ba_{0.84}Ca_{0.16}TiO_3$ ceramics prepared by (a) semi-wet (●) and (b) dry (○) routes. Note the diffuse phase transition behaviour in the semi-wet sample. (After Tiwari and Pandey 1992).

temperatures, exhibit $BaTiO_3$-like sharp transitions. The same ceramics when prepared from powders obtained by a semi-wet route involving calcination of $Ba_{1-x}Ca_xCO_3$ solid solution precursors with TiO_2 lead to a diffuse phase transition behaviour. The $Ba_{1-x}Ca_xCO_3$ precursors were prepared by chemical coprecipitation and the solid solution formation was confirmed by XRD (Pandey *et al* 1987; Tiwari *et al* 1989). Figure 1 illustrates the difference in the temperature dependence of dielectric constant for $Ba_{0.84}Ca_{0.16}TiO_3$ ceramics prepared by (i) using $Ba_{0.84}Ca_{0.16}CO_3$ solid solution precursor (semi-wet route) and (ii) by the conventional dry route using $BaCO_3$, $CaCO_3$ and TiO_2.

The diffuse phase transition (DPT) in mixed ferroelectric ceramics has been attributed by Smolensky (1970) to the presence of compositional inhomogeneities. We have compared the compositional homogeneity of $Ba_{1-x}Ca_xTiO_3$ ceramics prepared by the semi-wet and dry routes using principles of line broadening analysis (Pandey *et al* 1989). Figure 2 depicts the plot of $\beta \cos \theta$ vs $\sin \theta$, where β is the halfwidth of the pure diffraction profile and θ, the Bragg angle for $Ba_{0.88}Ca_{0.12}TiO_3$ samples. The nearly zero slope for the semi-wet sample confirms that it is compositionally homogeneous while the dry route sample is inhomogeneous. This rules out the possibility of DPT behaviour in semi-wet samples due to local compositional inhomogeneities.

On the basis of significant difference in the relative intensities of 200 and 002 reflections from the two types of powder samples, Tiwari *et al* (1989) proposed that Ca^{2+} might be going to both Ba^{2+} as well as Ti^{4+} sites because of ionic radius considerations in the conventional dry route of synthesis. This may in turn affect the nature of ferroelectric transition in these materials. It has been conjectured by several workers that Ca^{2+} can go to the Ti^{4+} site as well (Jaffe *et al* 1971; Han *et al* 1987). Recently, Tiwari *et al* (1991) determined the cation distribution in $Ba_{0.88}Ca_{0.12}TiO_3$ samples prepared by semi-wet and dry routes using Rietveld profile

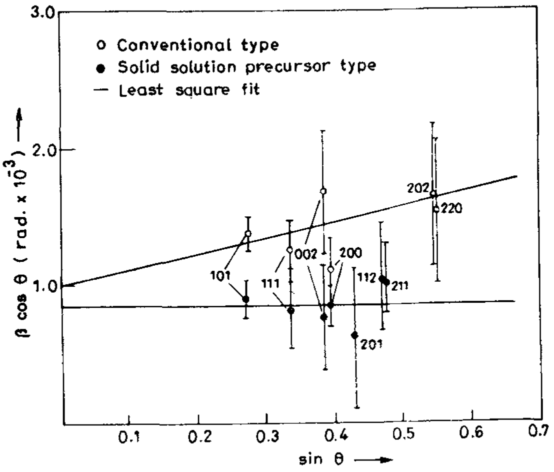

Figure 2. Comparison of compositional homogeneity of $Ba_{0.88}Ca_{0.12}TiO_3$ powders prepared by (**a**) semi-wet (●) and (**b**) dry (○) routes. Horizontal line indicates absence of compositional inhomogeneities. (After Pandey *et al* 1989).

refinement of powder neutron diffraction patterns. Neutron diffraction is eminently suited for exploring the possibility of Ti^{4+} getting substituted by Ca^{2+} since the atomic scattering factors for the two elements are of opposite signs. This study has clearly revealed that in powders obtained by the dry route, nearly half of the substituted Ca^{2+} occupies Ti^{4+} site in contrast to the semi-wet samples where all the Ca^{2+} ions exclusively occupy the Ba^{2+} site. The observed and calculated neutron diffraction patterns are in excellent agreement for both types of samples and are depicted along with the difference pattern in figure 3. This study has revealed that the ferroelectric phase transition can get diffused in barium-calcium titanate system only if Ca^{2+} does not occupy Ti^{4+} site but exclusively replaces Ba^{2+} as in samples prepared by the semi-wet route. This intrinsic effect of substitution of Ba^{2+} by Ca^{2+} on the nature of ferroelectric phase transition gets masked in the conventional dry route of synthesis as a result of mixed occupancy of Ca^{2+} at Ba^{2+} as well as Ti^{4+} sites leading to the sharp transition.

Apart from better compositional homogeneity and a control over the site-substitution, Tiwari *et al* (1989) have shown using DTA study of solid state thermochemical reaction in mixtures containing (i) $Ba_{0.9}Ca_{0.1}CO_3$ and TiO_2 (semi-wet route) and (ii) $BaCO_3$, $CaCO_3$ and TiO_2 that the reaction temperature is nearly 150°C lower for the semi-wet route (see figure 4). Further, ceramics prepared using powders obtained by the semi-wet route show very uniform microstructure with average grain size $\leqslant 1\ \mu m$ (see figure 5a), depending on the Ca^{2+} content, and density above 95% of the theoretical value for sintering at 1300° for 12 h. Ceramics sintered under identical conditions using powders obtained by the conventional route have grain size $\gtrsim 5\ \mu m$ and densities never exceeding 90% (see figure 5b).

In order to compare the effect of substitution of Ba^{2+} by Pb^{2+}, Sr^{2+} and Ca^{2+} on the dielectric behaviour, we have prepared compositionally homogeneous fine-grained ($\sim 1\ \mu m$ grain size) $Ba_{0.92}A_{0.08}TiO_3$ (A = Pb, Sr and Ca) ceramics under identical calcination and sintering conditions using our semi-wet approach. The 002 and 200 reflections for the three samples are given in figure 6 which shows that the *c*-parameter

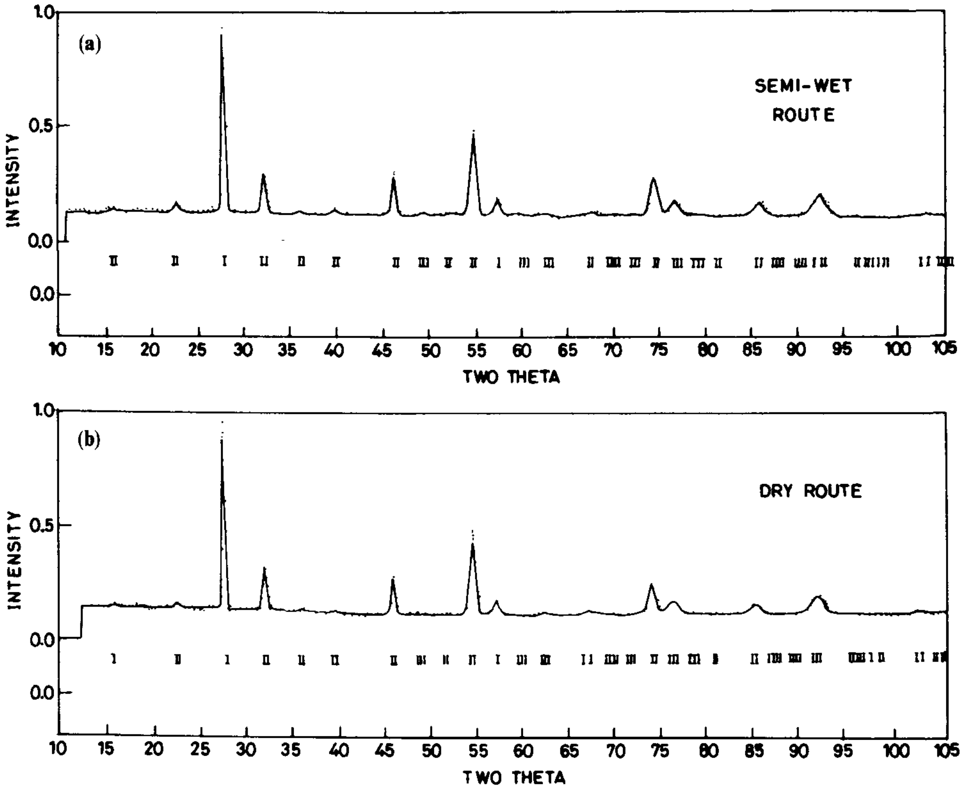

Figure 3. Results of Rietveld profile analysis of neutron diffraction data of (**a**) semi-wet and (**b**) dry route samples of barium-calcium titanate with nominal composition $Ba_{0.88}Ca_{0.12}TiO_3$. (After Tiwari *et al* 1991).

gradually increases with Ca, Sr and Pb substitutions. Figure 7 depicts the temperature dependence of dielectric constant for the three compositions. It is evident that maximum diffuseness is observed for Ca^{2+} substitution followed by Pb^{2+} and Sr^{2+}. It is important to reiterate that the diffuseness of phase transition in these samples is not due to local compositional inhomogeneities as the X-ray line broadening analysis has shown these samples to be compositionally homogeneous (Tiwari and Pandey (to be published); Singh *et al* (to be published)). Although all the three samples exhibit DPT, each one of the three systems has got its unique characteristic frequency response, the details of which will be published separately in due course.

3. Relaxor ferroelectric ceramics

The maximum dielectric constant for modified $BaTiO_3$ lies in the range 10,000 to 14,000. With continuing trend for miniaturization of single/multi-layer capacitors, the attention has shifted towards a new class of lead based complex ferroelectric ceramics, typified by $Pb(B'_{1/3}B''_{2/3})O_3$ (where $B' = Mg^{2+}, Zn^{2+}, Ni^{2+}$ etc. and $B'' = Nb^{5+}, Ta^{5+}$ etc.) and $Pb(C'_{1/2}C''_{1/2})O_3$ (where $C' = Sc^{3+}, Fe^{3+}, In^{3+}$ etc. and $C'' = Nb^{5+}, Ta^{5+}$ etc), with peak dielectric constant in the range 15,000 to 30,000 (Shrout and Halliyal 1987).

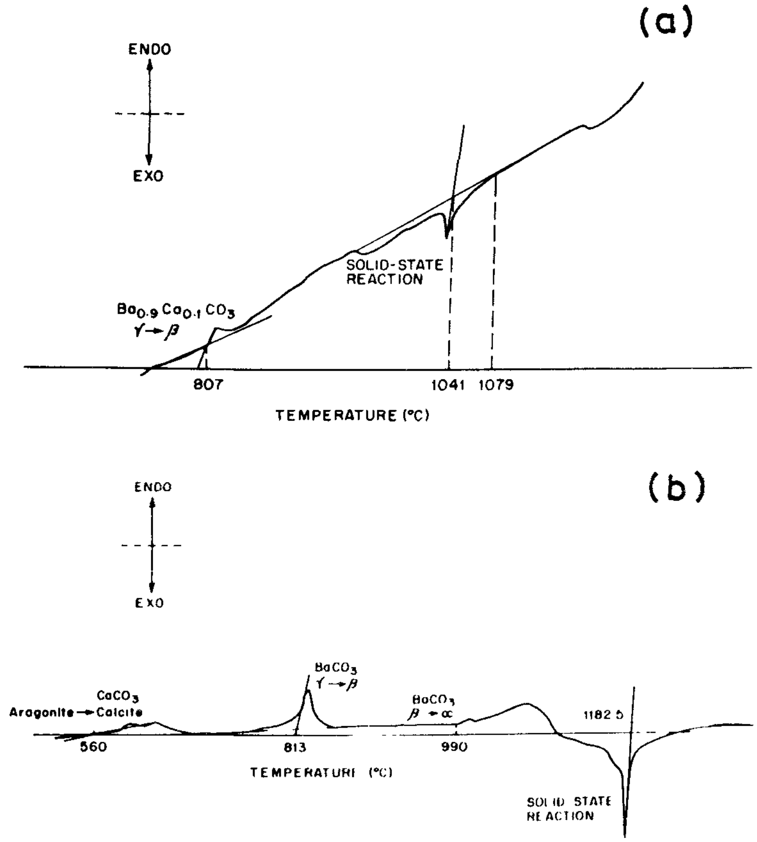

Figure 4. DTA of solid state thermochemical reaction in a mixture of (**a**) $Ba_{0.9}Ca_{0.1}CO_3 + TiO_2$ (semi-wet route) and (**b**) $0{\cdot}9\ BaCO_3 + 0{\cdot}1\ CaCO_3 + TiO_2$ (dry route). (After Tiwari *et al* 1989).

All these materials exhibit diffuse phase transition in both single crystal as well as sintered ceramic forms (Smolensky 1970) with pronounced characteristic frequency response in the audio frequency region (Cross 1987). The peaks corresponding to $\varepsilon'_{\max}$ and $\varepsilon''_{\max}$ in these materials shift to higher temperature side on increasing the measuring frequency. These materials are accordingly called relaxor ferroelectrics (Cross 1987). The DPT behaviour and the relaxor behaviour disappears if the B′, B″ or C′, C″ ions acquire ordered configuration to minimize the electrostatic and elastic energies (Setter and Cross 1980). We would like to mention that relaxor behaviour is observed in $Ba_{1-x}Sr_xTiO_3$ and $BaTi_{1-x}Sn_xO_3$ also (Schmidt 1990; Tiwari and Pandey (to be published)). Some of the lead-based complex ferroelectrics when mixed with $PbTiO_3$, $BaTiO_3$ etc. show interesting dielectric behaviour including the enhancement of ε' in the vicinity of a morphotropic phase boundary composition akin to that in PZT ceramics (Kuwata *et al* 1982; Halliyal *et al* 1987). Relaxor compositions for capacitor applications are usually solid solutions with one end member being a T_c shifter that adjusts the dielectric maximum closer to room temperature to meet the Z5U, Y5V and Y5S standard specifications.

Despite the advantages associated with high dielectric constant and low sintering temperatures, there are a few disadvantages of the relaxor materials such as (i) strong

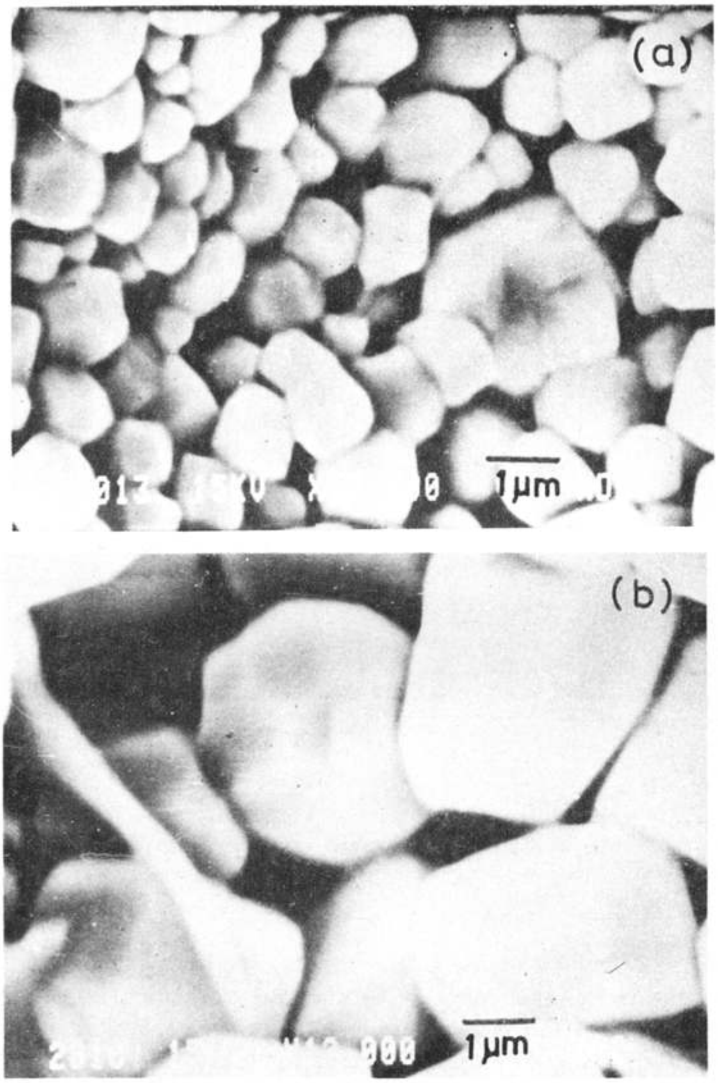

Figure 5. Microstructure of $Ba_{0.88}Ca_{0.12}TiO_3$ ceramics prepared by (**a**) semi-wet and (**b**) dry routes (After Tiwari and Pandey 1992).

frequency dependence with high dielectric losses, (ii) low mechanical strength, (*iii*) toxic nature of PbO which is the major constituent and (iv) difficult to get in single phase form free from the pyrochlore phase. Swartz and Shrout (1982) could overcome the last problem by eliminating the formation of the intermediate pyrochlore phases. This was achieved by first forming a Columbite $MgNb_2O_6$ matrix via solid state reaction between MgO and Nb_2O_5 around 1000°C. This columbite was then reacted in the solid state with PbO around 700°C to yield pure $PbMg_{1/3}Nb_{2/3}O_3$ free from pyrochlore phase. The same approach has been employed by Groves (1985) to synthesise $PbIn_{1/2}Nb_{1/2}O_3$ with limited success. For $PbZn_{1/3}Nb_{2/3}O_3$ (PZN), this approach is not at all successful. PZN by far remains the most difficult relaxor material to

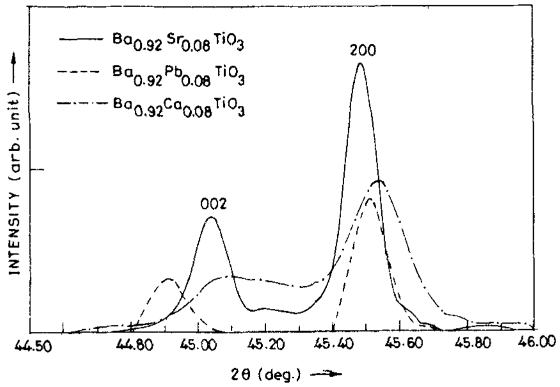

Figure 6. 002 and 200 reflections of (a) $Ba_{0.92}Sr_{0.08}TiO_3$, (b) $Ba_{0.92}Pb_{0.08}TiO_3$ and (c) $Ba_{0.92}Ca_{0.08}TiO_3$ powders prepared by semi-wet route (After Singh *et al* 1992). CuK_α radiation.

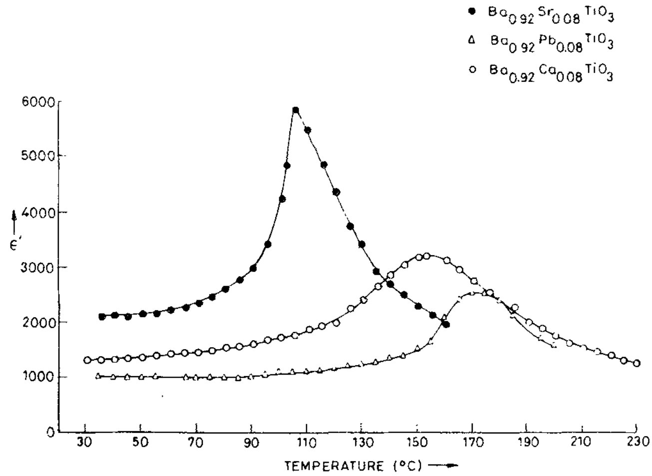

Figure 7. Temperature dependence of dielectric constant (100 kHz) of (a) $Ba_{0.92}Sr_{0.08}TiO_3$, (b) $Ba_{0.92}Pb_{0.08}TiO_3$ and (c) $Ba_{0.92}Ca_{0.08}TiO_3$ ceramics prepared by semi-wet route (After Singh *et al* 1992).

synthesize in pure form. Addition of 6 to 7 mol% of barium titanate has been shown to have resulted in single phase PZN (Furukawa *et al* 1985). There are already quite a few US patents for ceramic capacitors based on relaxor ferroelectrics.

4. Multilayer capacitors

The continuing trend towards miniaturization of electronic integrated circuits has led to considerable spurt in the multilayer ceramic capacitor (MLC) industry. Until recently, modified $BaTiO_3$ has been the main material for making these MLCs. This requires high firing temperatures in excess of 1300°C. Obviously, the materials used for inner electrodes should have higher melting points than the sintering temperature of the dielectric ceramics. To avoid oxidation of the inner electrodes during co-firing in air, it is imperative to use precious metals such as Pd and Pt. Several different strategies have accordingly been adopted to reduce the cost of these MLCs (see e.g. Goodman 1986). These include using inexpensive Ag–Pd alloy (m.p. 1220 for 70/30 composition) along with sintering fluxes to lower the firing temperature (see § 2). The second approach is the lead injection method in which molten lead is impregnated into the porous layer to form the inner electrode. The third strategy, which seems to receive maximum attention, is the use of low cost base metals, such as Cu, Ni and Fe, as internal electrode material. Use of base metals necessitates co-firing in a reducing atmosphere since these metals loose their conductivity on being oxidized at high sintering temperatures in air. Co-firing in reducing atmosphere, on the other hand, gives rise to *n*-type semiconductivity since $BaTiO_3$ based materials loose oxygen under reducing atmosphere. For dielectric applications, one needs not only high dielectric constant but also high DC blocking resistance. There has been a lot of work on the effect of doping by acceptor type ions (e.g. Co, Cr, Fe, Mn, Ga and Ni) on the dielectric behaviour and DC resistance of the ceramic MLCs co-fired with Ni electrodes in reducing atmosphere (Herbert 1965; Burn 1979; Hagemann and Iring 1979; Desu and Subbarao 1981). As a result of acceptor doping, it has been possible to co-fire the Ni-electrodes with the ceramic dielectric at low oxygen partial pressures without losing the insulating behaviour of the dielectric.

Recently, a ceramic dielectric composition for MLCs that can be co-fired with Ni electrode was reported by Sakabe (1987). The general composition is $\{(Ba_{1-x}Ca_x)O\}_m \{(Ti_{1-y}Zr_y)O_2\}$ and is effective only when $0 \leqslant x \leqslant 0{\cdot}2$ and $1{\cdot}0005 \leqslant m \leqslant 1{\cdot}030$. The role of Zr in this composition is essentially as a Curie point shifter to bring the maximum dielectric constant at the operating temperature. The most interesting aspect of this composition is the fact that (Ba + Ca) > (Ti + Zr). It was conjectured by Sakabe (1987) that for $m > 1$, Ca^{2+} can partially occupy the Ti^{4+} site because of ionic size considerations and thereby act as an acceptor impurity. This in turn facilitates the co-firing of the ceramic dielectric with Ni electrode without reducing the dielectric composition. This has indeed been confirmed by Han *et al* (1987) through equilibrium conductivity measurements. It may be recalled from § 2·2 that our recent neutron scattering work on $Ba_{1-x}Ca_xTiO_3$ ceramics prepared by the conventional dry route has revealed the presence of Ca^{2+} at Ti^{4+} site.

The capacitance per unit volume or packing density is approximately proportional to the dielectric constant and inversely proportional to the thickness of the active dielectric in a MLC. To improve the compactness of the $BaTiO_3$-based MLCs, lowest achievable thicknesses lie typically in the range of 15 to 35 μm. Any further improvement in the compactness of the MLCs has to depend on new materials with dielectric constant higher than that of modified $BaTiO_3$. Relaxor ferroelectric ceramics have opened new hopes in improving the compactness of MLCs by virtue of their extremely high dielectric constant in the range 15,000 to 30,000 as against 10,000 to 14,000 for modified $BaTiO_3$. These new materials can be sintered at low temperatures ($\sim 900°C$) and therefore obviate the necessity of expensive electrode metals. Future trend is therefore going to be in the development of MLCs based on relaxor ferroelectrics although $BaTiO_3$-based single- and multi-layer capacitors will continue to receive worldwide attention because of their better frequency response and lower loss factors.

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