Development and characterization of a high dielectric constant paste based on BaTiO₃ for use in thick-film capacitors

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Abstract. Results of measurements on a thick-film capacitor based on a paste of mixed ferroelectric phases made out of crystallization from a glassy phase are presented. This material can be used as a high dielectric constant paste for designing capacitors in hybrid circuits. The $\tan \delta$ is observed to decrease with rise in temperature.

Keywords. Dielectric constant paste; BaTiO₃; thick-film capacitors.

1. Introduction

In thick-film technology electronic components are screen printed on a substrate and the values of these components are adjusted by trimming under exact operating conditions so as to avoid effects of changed operating environment on the components. This provides very high operating reliability factor for such circuits. Capacitors are designed by laying out a layer of dielectric paste sandwiched between two parallel conducting layers on a substrate and suitably fired in a travelling furnace. For reducing the size of the capacitor layout on a substrate a paste of high dielectric constant is required. In a recent investigation, it was found that when the basic constituents of ABO₃ are heated, the dielectric constant does not increase beyond a limit due to grain boundary orientation problem and that $\tan \delta$ decreases when La₂O₃ is added in quantities more than 1 mol %. The powder reaction by our method could be used only for making low dielectric constant crossover pastes for multilayering purposes (Biur and Khan 1992).

To overcome the difficulty of increasing the effective dielectric constant caused by different orientations of the grains, each constituent was first dissolved in lead borosilicate glass and then mixed. Ferroelectric phases were crystallized out from the mixed melt of the mixture of thus prepared glassy phases. The present technique ensures that pinholes get filled up by the addition of lead borosilicate glass powder of low softening temperature. The product is observed to have a higher effective dielectric constant. This has been achieved using AR grade constituents, providing reasonably good and usable electronic functional response as a capacitor material of lower cost. This has been achieved because La content was increased in the matrix glassy regions deemed to be behaving like grain boundaries (Biur 1992). The likely presence of transition element impurities towards conduction, are also taken care of by this La in the grain boundaries. Even though dielectric properties of such materials have been reported (Harper 1974), no published information seems to be available for processing such a material into a thixotropic thick-film paste of screen-printable rheology. This paper presents results with such a pinhole-free thick film of higher dielectric constant.

2. Experimental

Each of the base materials, viz. BaCO_3 , SrCO_3 , TiO_2 , CaCO_3 , ZrO_2 , were separately dissolved in lead borosilicate glass in appropriate concentration at 1400°C . All the glasses after cooling were powdered and mixed together in a vertical ball mill. This mixed powder was reheated to form a free flowing single melt, and cooled. The process was repeated five times. During the process of heating and cooling the basic constituents react to crystallize out a mix of suitable ABO_3 phases out of glass without seriously affecting the orientation of the grain structure, thus keeping the dielectric constant at a reasonably high value. Thereafter the material was converted into a screen-printable paste by grinding in a vertical ball mill with addition of lead borosilicate glass of low softening temperature containing 2% La_2O_3 and 5% polyvinyl butyral in butyl alcohol along with emulsifying agent Spin-1 (Krishna's Chemie Olivine Laboratories) to give the whole mass the consistency of a thixotropic gel. The gel structure holds the solvent and the requisite stable distribution of the solid particles. This gel liquefies only when pressure is applied on the screen while printing and forms the gel when pressure is removed thus stopping extra flow of the paste through the screen. This gives a clear print of the paste material on the substrate. Using this paste, capacitors of $4\text{ mm} \times 4\text{ mm}$ and $\sim 70\text{ }\mu\text{m}$ dielectric thickness were prepared for measurement purposes on 96% Al_2O_3 substrate. The addition of low melting glass with La_2O_3 forms the glass matrix to hold the particles after firing in thick film and fills up the pinholes. This forms structurally diffused intragranular regions with the glass content of the precipitated ferroelectric ABO_3 particles instead of well defined grain boundaries. This region provides higher insulation standard to the thick-film because of its La content (Biur 1992). Each production batch can be standardized to a required dielectric constant by varying the glass content.

3. Results and discussion

Figure 1 shows the frequency response of dielectric constant at room temperature. The curve is a least squares polynomial fit of the data points. This is reasonably flat in the required frequency range and hence the paste can be used for thick-film capacitors. Figure 2 shows the plot of $\tan \delta$ against frequency at room temperature. The $\tan \delta (\times 10^{-3})$ varies from 1.0 to 3.5 in the range 15–100 kHz. This variation in $\tan \delta$ indicates the presence of a number of phases crystallized out of glass. The oscillatory dispersion of $\tan \delta$ is due to interaction of insulating potential barriers provided by intragranular La-rich diffused glassy regions of variable thickness and the inherent dispersion of the composite ferroelectric phases. However, the near-Debye nature of the collective performance of the material is maintained.

Figure 3 shows a plot of the imaginary part of dielectric constant against its real part with directly connected data points. This gives information on the structure of the intragranular region at the lower end of the frequency range. The plot, at the lower end of frequency, shows distributed straight lines. This indicates presence of diffused intragranular boundary-like regions in the material having diffusion of ions due partly to the crystallization process from the intragranular La content glassy phase to the grains causing extra scattering centres responding at lower frequency end. Least squares fitting of the data points of figure 3 gives the Cole-Cole plot

Figure 1. Dielectric constant vs frequency.

Figure 2. $\tan \delta$ vs frequency.

shown in figure 4. The data points are shown and a polynomial curve fit is drawn. The equation of this polynomial fit curve is found to be

$$\epsilon'' = -4.19 \times 10^{-5} \epsilon'^2 + 0.15 \epsilon' - 128.215.$$

On the real axis $\epsilon'' = 0$, and the roots of the above equation are 2169 and 1411 which correspond to the ϵ_{dc} and ϵ_{inf} (Ross Mac donald 1987).

The dielectric constant and $\tan \delta$ were also measured as a function of temperature at 100 kHz. At this frequency, the measurement response is from grain interiors. Figure 5 shows the effect of variation of temperature on dielectric constant. The solid curve is the least squares fit of the data points. The Curie peak of 120°C of BaTiO_3 is shifted to lower temperatures because of addition of Zr, Sr and Ca

Figure 3. Directly connected data points in a plot of imaginary part of dielectric constant vs its real part.

Figure 4. Cole-Cole plot.

Figure 5. Dielectric constant vs temperature.

Figure 6. $\tan \delta$ vs temperature.

(Bernard *et al* 1971). Figure 6 shows the variation of $\tan \delta$ with temperature. It is interesting to note that at around 70°C (near the Curie peak in figure 5) the $\tan \delta$ value of the material becomes extremely low. In other words, the material behaves like a near-absolute insulator after the Curie peak is reached. The implications of this observation are not yet fully clear. However, it could be pointed out that it relates to the ferroelectric paraelectric structural phase of the material when La is present in the intragranular lead borosilicate glassy material. Capacitors made out of this paste and kept on voltage stress of 1000 V DC for 36 h at room temperature showed no appreciable change in frequency response of capacitance and of $\tan \delta$.

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References

- Biur A P and Khan R U 1992 *Indian J. Technol.* **30** 322
Biur A P 1992 *Pramana-J. Phys.* **38** 167
Harper C A 1974 *Handbook of thick-film hybrid microelectronics*, (McGraw Hill Book Company) p 7–40
Ross Mac donald J 1987 *Impedance spectroscopy*, (New York: John Wiley & Sons)
Bernard J, Cook W R Jr and Hans J 1971 *Piezoelectric ceramics*, (London and New York: Academic Press) pp 69–70