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Temperature Coefficients of Capacitance of Solids

P. J. HARROP
The Plessey Company Limited, TCC Capacitor Division, Bathgate, West Lothian, UK

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An earlier treatment of temperature coefficient of capacitance, γ_c [1] has been extended to include most solids. Materials are divided into those with given ranges of permittivity, ϵ, and temperature coefficient of polarisability. It appears that, for low dielectric loss, high permittivity glasses, like simple ionic compounds, always have a positive γ_c, whereas paraelectrics and polymers have negative γ_c. Ferroelectrics can have any value of γ_c. Limitations in γ_c and ϵ for given classes of solid are discussed.

1. Introduction

In a previous paper [1] some attempt was made to analyse the temperature coefficient of capacitance of materials of low permittivity such as plastics, alkali halides and simple inorganic compounds.

The purpose of the present paper is to extend this treatment to solids in general, in particular including paraelectrics, ferroelectrics and high permittivity glasses. An attempt is made to identify the limitations in the range of temperature coefficient (γ_c) of given groups of materials. For instance, we attempt to answer such questions as, "Can the value of γ_c of a high permittivity glass be negative?"

2. Theory

It was shown previously that the intrinsic polarising species in solids could be considered as mutually interacting, infinitely small dipoles. They obey the Lorentz approximation and hence the Clausius-Mosotti equation, which in its differentiated form gives [1, 2]

$$\gamma_c = \frac{1}{C}\left(\frac{\partial C}{\partial T}\right)_p = \frac{(\epsilon - 1)(\epsilon + 2)}{\epsilon}\left(\frac{1}{3\alpha}\left(\frac{\partial \alpha}{\partial T}\right)_p - \alpha_l\right) + \alpha_l \quad (1)$$

where C is capacitance, ϵ permittivity, α the polarisability of a macroscopic volume V, and α_l the linear expansion coefficient of the solid. Equation 1 is therefore an expression for the intrinsic γ_c of a solid. (Note that in earlier work [1, 2] the term $1/3\alpha(\partial\alpha/\partial T)_p$ was split into two further terms. This is unnecessary for present purposes.) When a material has appreciable extrinsic loss mechanisms (e.g. dissipation factor greater than 0.001) then another term for the extrinsic contribution to γ_c must be added [1]. Gevers [3] showed that this term usually approximated to 0.05 $\tan\delta$.

The following discussion will be concerned with the intrinsic contribution. Where data can only be obtained for materials with appreciable loss the extrinsic term will be subtracted. The classification of compounds requires them to be grouped in terms of those having given ranges of permittivity (ϵ) but also given ranges of the temperature coefficient of polarisability $1/3\alpha$ $(\partial\alpha/\partial T)_p$.

3. General Discussion

3.1. Glasses

Recently a variety of data has become available for glasses of high permittivity [10-12] (e.g. between 10 and 40) and it emerges from this data that values of $1/3\alpha$ $(\partial\alpha/\partial T)_p$ are not only always positive but are in the region of 15 ppm/° C. This can be seen from fig. 1. Such permittivities owe little to electronic polarisabilities: this contribution, being equal to the refractive index squared, is around 4. Similarly the simple counter-vibration of non-deformable ions, as analysed by Born [4] and appropriate to alkali halides [1-5] would make a small contribution to the permittivity of high permittivity glasses, since these consist of heavy ions.

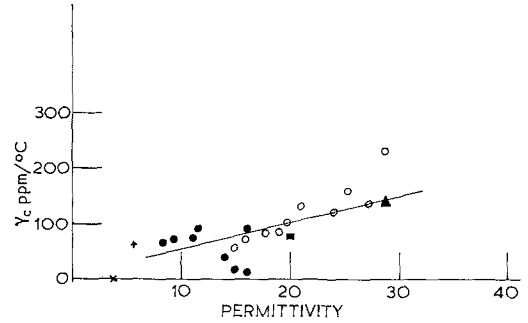

Figure 1 $\gamma_c - 0.05\tan\delta$ versus ϵ for glasses. × SiO_2; ▲ Bi/Cd/Si glasses [10]; ■ $PbTiO_3$ [11]; ● B/Al/Pb glasses [12]; ○ B/Bi/Pb glasses [12]; + SiO [13]. The line is given by

$$\gamma_c - 0.05\tan\delta = \epsilon\left(\frac{1}{\alpha}\left(\frac{\partial\alpha}{\partial T}\right)_p - \alpha_l\right) + \alpha_l$$

where $\alpha_l = 10$ ppm/°C (a typical value for these substances) and $\frac{1}{\alpha}\left(\frac{\partial\alpha}{\partial T}\right)_p = 15$ ppm/°C.

(This is a simplification of equation 1 for high ϵ.)

In the absence of structural effects, such as paraelectricity and ferroelectricity, this probably leaves the deformation of the ions as the major factor. Indeed, if one visualises large deformable ions counter-vibrating this should give an amplification of the (small) Born polarisability. Now the alkali halides, having small, rigid ions, have primarily Born polarisability and this leads to large positive values of γ_c [2]. Qualitatively, one might therefore expect high permittivity glasses to have positive temperature coefficients of polarisability and therefore γ_c.

Fig. 1 appears to indicate that this is indeed usually the case.

3.2. Paraelectrics

Bosman and Havinga [2] determined γ_c for a wide variety of paraelectrics and calculated the relative volume and temperature-dependent contributions to γ_c. However, a simpler approach is possible.

If $1/3\alpha\ (\partial\alpha/\partial T)_p$ is negligibly small (an unproven assumption) equation 1 gives, for high ϵ,

$$\gamma_c = -\alpha_l\epsilon\ . \qquad (2)$$

Fig. 2 shows that this equation is closely obeyed by the data of Bosman and Havinga [2].

Fig. 3 gives more detail for the lower permittivity region, whence it is seen that the same simple behaviour seems to be obeyed (γ_c values for fig. 3 are taken from references [1-3, 6, 7]). The "conventional" behaviour of TlCl and TlBr in fig. 3 is, however, fortuitous, as they probably have appreciable ionic bonding, giving a positive value of $1/3\alpha\ (\partial\alpha/\partial T)_p$ that is counter-balanced by a large α_l.

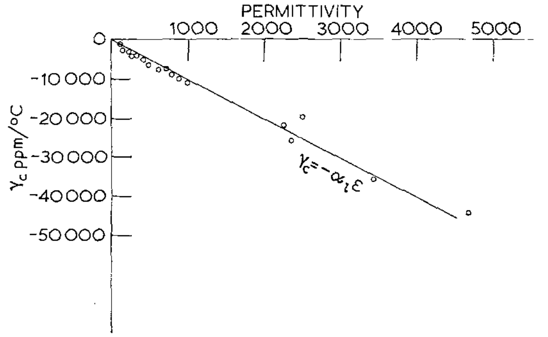

Figure 2 γ_c versus ϵ for paraelectrics. Data from [2]. $\alpha_l \sim 10$ ppm/°C for these materials.

3.3. Ferroelectrics

The capacitance of a simple ferroelectric varies with temperature in the manner shown in fig. 4. Clearly then, as shown in this figure, γ_c for a ferroelectric may be zero, positive or negative. The permittivity of a ferroelectric can be very high or very low, and zero γ_c can even occur for high permittivities when two transition temperatures occur.

3.4. Summary

One can now generalise the above simplification by plotting γ_c versus ϵ for low loss as in fig. 5. In this figure the alkali halides, ionic inorganic materials, covalent inorganic materials, and polymers are in the general areas discussed in the earlier paper [1]. To these are added the high permittivity glasses (i.e. those containing ions from Period 6 – see later), paraelectrics and ferroelectrics.

The limitations of the regions have been delineated in fig. 5. These limitations are justified in the next section. However, one general observation is worth making. It emerges from fig. 5 that for materials with permittivity less than 10, the value of γ_c is little more than a function of the type of chemical bond they exhibit. This can be seen more clearly if, as in fig. 6, we plot γ_c versus per cent ionic bond for low permittivity materials.

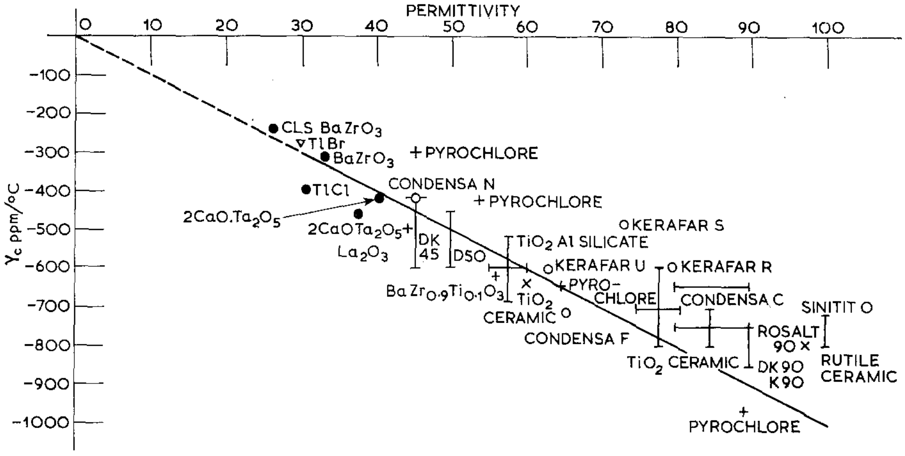

Figure 3 γ_c versus ϵ for paraelectrics.

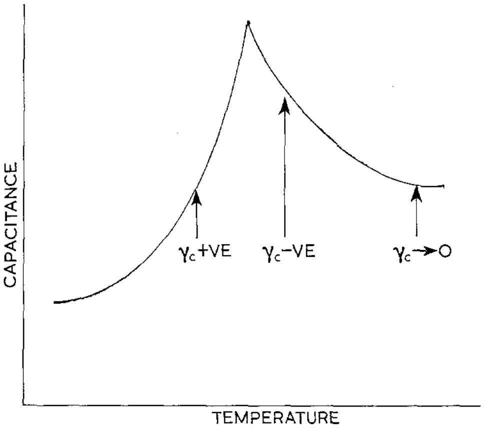

Figure 4 Possible variation of capacitance, C, with temperature, *T*, for a ferroelectric.

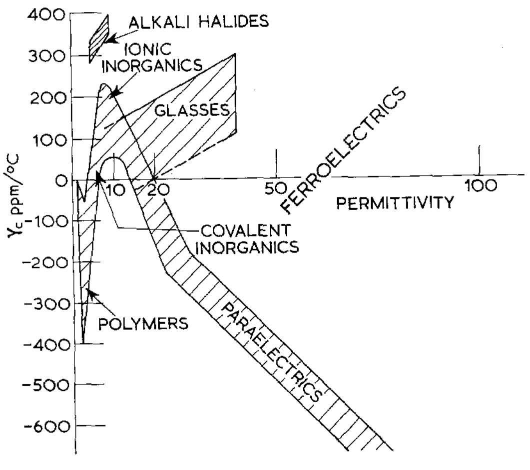

Figure 5 General ranges of γ_c versus permittivity for various types of solid.

From fig. 6 it is seen that the most ionic substances, epitomised by lithium fluoride, have the highest positive values whereas, at the other extreme, covalent compounds have near-zero and negative values.

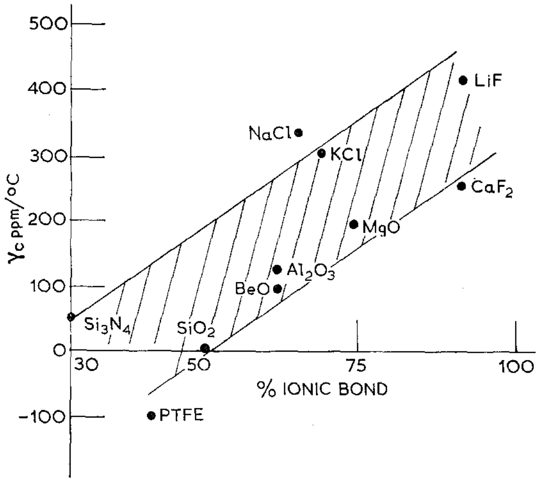

Figure 6 γ_c versus % ionic bond for various materials having a permittivity less than 10. Data from [1] and [6].

4. Limitations

4.1. Polymers

As noted in the earlier paper [1], since low loss polymers typically have permittivity near to 2, their values of γ_c approximate to $-\alpha_l$. Indeed, experiments have proved that the limits in range of γ_c are the limits in range $-\alpha_l$ [14]. The extremes are probably represented by silicones (e.g. $\alpha_l \sim 400$ ppm/° C) and, polyphenylene oxide, having $\alpha_l \sim 50$ ppm/° C.

4.2. Alkali Halides

The lower limit for alkali halides is difficult to define but the upper limit must be represented by lithium fluoride since this contains the lightest and hence most (Born) ionically polarisable ions of all [4]. Thus (recalling fig. 6) there can be no low permittivity, low loss compounds with γ_c greater than 400 ppm/° C.

4.3. Glasses

Low permittivity glasses usually have small positive or zero values of γ_c [1]. High permittivity glasses are less well understood. However, it appears that their polarisability is due to the presence of heavy deformable ions [5], this mechanism giving positive values of γ_c, as already discussed and illustrated in fig. 1.

It remains to determine the highest permittivity possible with glasses (and hence the upper limit of γ_c). One would expect that as one progressed down the Periodic Table of Elements one would find elements with larger, and hence, more deformable electron clouds. However, if one made glasses of the very largest ions, their size (number per unit volume) would outweigh their deformability and their permittivity would be lowered again. This is illustrated by fig. 7, where the data are for anodic and sputtered thin film glasses, since traditional bulk glass-forming techniques are limited to too few compounds. Simple oxides are chosen since these maximise the proportion of heavy ion and hence the permittivity [5, 8]. In fig. 7, the packing consideration is conveniently represented by plotting mean atomic number per molecule/cation radius.

It is seen that the high permittivity glasses should be those containing the maximum amount of Period 6 ions and that these glasses are unlikely to have a permittivity much above 40. This therefore represents the upper limit of permittivity of high permittivity glasses, and, extrapolating fig. 1, the highest γ_c for high permittivity glasses is probably in the region of 300 ppm/° C as shown in fig. 5.

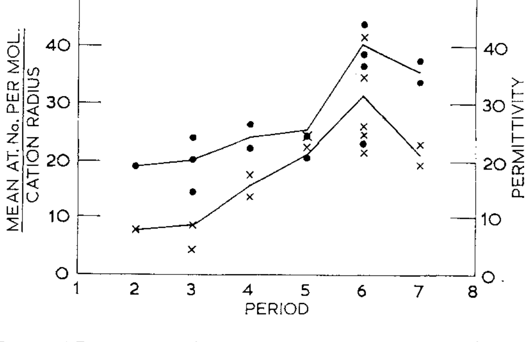

Figure 7 Permittivity (x) and mean atomic number/cation radius (●) versus cation period for oxides glasses.

4.4. Paraelectrics

It has been noted that these materials have values of γ_c approximating to $-\alpha_l\epsilon$ and since their value of ϵ ranges from 20 to 10 000 or more [2] (α_l being near 10 ppm/° C [2]) their values of γ_c must range between -200 ppm/° C to $-100\,000$ ppm/° C, or more.

4.5. Ferroelectrics

We have seen that ferroelectrics can have any value of γ_c, and any value of permittivity.

4.6. Intermediate Compounds

Having now established the basis for fig. 5, which only refers to extreme cases, one must note that there can be many intermediate compounds having intermediate values of γ_c. In particular, many complex compounds exist which have zero γ_c allied with a permittivity near 40. We can now see that these may be either two-phase mixtures of Period 6 glasses and paraelectrics (the latter are of their nature crystalline) or single-phase paraelectrics which contains a large proportion of a Period 6 element (barium metatitanate may be a case in point); or such compounds may be ferroelectric with one transition temperature above the temperature of measurement and one below. By contrast, if a complex compound has near zero γ_c and a permittivity significantly above 40, then it probably exhibits some form of ferroelectricity. Since ferroelectricity usually causes somewhat inflated dielectric loss, zero temperature coefficient materials with high permittivity but very low loss may be difficult to produce.

5. Conclusions

The temperature coefficients of capacitance of all solids having low loss can be rationalised by placing them in given regions of a plot of temperature coefficient versus permittivity. There is a phenomenological basis for establishing these regions.

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Letter

A Minimum Value for the Density of Random Close-Packing of Equal Spheres

The density of random close-packing of equal spheres has been the subject of empirical study for a considerable period, and a value of about 0.61 is generally accepted. Scott [1] has distinguished between "loose random packing" with a density of 0.60 and "dense random packing" with a density of 0.64. A computer model of random packing yielded a density of 0.609 [2]. The theoretical upper limit for the density of packing corresponds to that of four touching spheres at the vertices of a regular tetrahedron, and has the value 0.780 [3], which is somewhat greater than the densest regular packing. It is known that tetrahedra cannot be stacked together to fill space, so that this value is unlikely to be realised in practice.

No theoretical value for the density of a random packing appears to exist, but it will be shown that a minimum value can be calculated by considering the similarity between the random packing of spheres and the shape of grains in a single-phase polycrystalline material. Various authors have compressed random packings of spheres until all porosity was removed, and have shown that the resulting cell shapes are closely similar to those of grains in a polycrystalline material [4]. The reason for the similarity is that in both cases space is divided in the most economical fashion. No unique cell shape exists, but the average cell can be shown to have 5.10 edges per face, 13.4 faces, and 22.8 vertices [5]. The derivation of these values assumes that the edges of the cells are straight.

The geometry of the cells may thus be taken as defining the positions of the centres of the spheres in random packing, and the density of such a packing will then be given by the ratio of the volume of the sphere inscribed in the average cell to the volume of the average cell. The metric properties of the average cell can be calculated [6] by applying the standard formulae which apply to the regular polyhedra, yielding the value $9.87\,l^3$ for the volume of the average cell, and $l\sqrt{3/2}$ for the radius of the inscribed sphere, where l is the length of the (equal) cell edges. It follows that the density of the packing is 0.780, in agreement with the value for a single tetrahedral arrangement, as might be expected from the fact that the cells meet four to a point. The arrangement described is thus an extended one consisting of packed tetrahedra of spheres, and the derivation shows at once that the co-ordination number of the average sphere is 13.4. It is known that the co-ordination of a real packing cannot exceed 12, so that the packing considered above must dilate further in practice. A sufficient dilation, keeping the spheres in the same relative positions, will be obtained by increasing the sphere-to-sphere distance from twice the inradius of the average cell to the diameter of the sphere of volume equal to the cell. This dilation is 1/0.780 in volume terms, and gives a minimum density for the random packing. The value of this minimum density is obviously $(0.780)^2$, which is 0.608, a value in excellent agreement with experiment.

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* Now at Doulton Research Ltd, Basil Green Labs, Hanworth Lane, Chertsey, Surrey.