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THE DEVELOPMENT OF PIEZOELECTRIC CERAMICS FOR TRANSDUCERS

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INTRODUCTION

The preparation of barium titanate [1], [2], [3] and the subsequent discovery of its ferroelectric properties by von Hippel and co-workers in 1942 [4] soon led to its realisation as the first polycrystalline ceramic transducer material as outlined in the 1949 patent by Gray [5]. Later work by Jaffe and colleagues [6], [7] in the lead zirconate titanate (PZT) system identified excellent piezoelectric properties in materials around the so-called morphotropic phase boundary near to the composition $Pb(Zr_{0.52}Ti_{0.48})O_3$. The ease with which dopants may be incorporated on cation sites in the ABO_3 perovskite structure and the large range of solid solutions that can be accommodated has led to a whole family of PZT-based ceramics many of which have properties tailored to device requirements. Whilst PZT has proved suitable for many applications, in the field of underwater sound detection and generation its poor hydrostatic response has largely constrained its use to geometries that convert hydrostatic to axial stress e.g. spheres and tubes. The material properties of interest are the hydrostatic charge coefficient, d_h and the hydrostatic voltage coefficient, g_h which are given by

$$d_h = d_{33} + 2d_{31} \quad (1)$$

$$g_h = d_h/\varepsilon^t_{33} \quad (2)$$

Typical data for PZT gives $d_{33} = 520pCN^{-1}$ and $d_{31} = -240pCN^{-1}$ leading to a low value for d_h of only $40pCN^{-1}$ [8]. In addition, the high permittivity, ε^t_{33}, results in a small value for g_h. It has been suggested [9] that composite materials formed from the stiff, high permittivity piezoelectric ceramic phase and a compliant, low permittivity non-piezoelectric polymer phase might overcome these difficulties by exploiting different forms of connectivity to modify the distribution of stresses on the ceramic (so as to minimise d_{31}) and to lower the overall permittivity. This paper reviews the progress that has been made in developing this new class of piezoelectric materials which offer properties which are attractive for other applications in addition to hydrophones.

CERAMIC - POLYMER COMPOSITES

The fabrication of composites were first reported in Japan in 1972 [10] and the USA in 1973 [11]. Piezoelectric and dielectric properties of PZT particles in a silicone rubber matrix were measured by Harrison in 1975 [9] and this led to renewed interest in the application of mixing rules for series and parallel arrangements in diphasic systems as well as for discrete dispersions of cubes and spheres in a continuous matrix [11], [12]. These were applied to the problem of predicting the effective permittivity of composites but it was not until 1978 that Newnham, Skinner and Cross [13] emphasised the importance of the connectivity of the phases and developed equations for both the dielectric and piezoelectric properties of composites from simple series and parallel models. This concept of connectivity immediately suggested the theoretical possibility of many different arrangements; thus, in a diphasic system, each phase maybe connected in 0, 1, 2 or 3 dimensions corresponding to discrete particles, rods and two and three dimensional networks. Such a system has ten connectivities, 0-0, 1-0, 2-0, 3-0, 1-1, 2-1, 3-1, 2-2, 3-2 and 3-3 in which the first number refers to the degree of connectivity of the polymer and the second to the connectivity of the ceramic. The fabrication and properties of the most important of these composites will now be examined.

3-3 Composites

3-3 composites in which both phases are continuously interconnected were first prepared by Skinner etal [14] using a replamine technique. Natural Coral was used in a lost wax process to form a ceramic skeleton which was sintered and subsequently backfilled with a high compliance silicone rubber. By lightly crushing the composite, Skinner was able to change the connectivity of the ceramic phase and reduce its relative permittivity to 40. This was explained by assuming that the network was broken into a series arrangement of air gaps and ceramic rods. Such a composite had a value for g_h 30 times higher than dense PZT with a hydrostatic figure of merit $g_h d_h$ 15 times greater.

In order to overcome the problems of uniformity of the coral and the time consuming nature of the replamime process, Shrout [15] produced 3-3 composites with similar microstructures from mixtures of PZT powder and polymethyl methacrylate spheres. These were pressed and heated slowly until the plastic had volatilised followed by sintering to produce a PZT skeleton. As before, this was backfilled with polymer. Rittenmeyer etal[17] used this so-called Burps process (burn out of plastic) to prepare composites with PZT/PMMA volume ratios from 30/70 to 70/30 which were subsequently backfilled with either a compliant silicone rubber or a stiff epoxy. They observed a linear dependency of composite density on volume fraction but found it difficult to back-fill composites with $\geqslant$ 70 volume fraction PZT because of some closed porosity. Permittivity and d_{33} increased linearly with volume fraction ceramic, the silicone specimens giving a lower permittivity and a higher charge constant. d_h showed a broad maximum between 50 and 70% PZT being some two times greater for the silicone filled material. To explain these results the authors proposed a model in which the composite is considered to be constructed of a basic repeat unit (Fig. 1) of three mutually orthogonal rectangular columns. The column in the 3-direction is assumed parallel to the poling direction and hence capable of being fully poled whilst the other two are electrically isolated from the electrodes and so remain unpoled. As the permittivity of the ceramic ${}^{1}\varepsilon \gg {}^{2}\varepsilon$, the permittivity of the polymer, the composite permittivity is dominated by ${}^{1}\varepsilon$. In addition, the columns parallel to the poling direction and so connected in series contribute far more than the perpendicular columns which are connected in parallel. This leads to the simple expression for the composite permittivity

$$\varepsilon_{33} \simeq {}^{1}\varepsilon_{33}\, L^{2} \qquad (3)$$

where L is the column width. In the silicone filled samples fracture of the ceramic phase was observed after poling in planes parallel to the electrodes and it was proposed that this might account for the lower permittivity compared with the epoxy filled samples. The charge constant d_{33} was modelled by adapting the equation of Newnham et al [13] for a perfect parallel connection subjected to uniaxial stress

$$d_{33} = \frac{{}^1V\,{}^1d_{33}\,{}^2s_{33} + {}^2V\,{}^2d_{33}\,{}^1s_{33}}{{}^1V\,{}^2s_{33} + {}^2V\,{}^1s_{33}} \qquad (4)$$

Where ${}^1V$, ${}^2V$, ${}^1s_{33}$, ${}^2s_{33}$ represent the volume fractions and elastic compliances of the ceramic and polymer phase respectively. As the polymer phase is not piezoelectric.

$$ {}^2d_{33} = 0 \qquad (5)$$

and ${}^1V$ must be replaced, by the volume fraction of poled ceramic ${}^1V*$

$$ {}^1V* = \frac{L^3 + L^2 \ell}{(L+\ell)^3} \qquad (6)$$

d_{31} was modelled assuming that the lateral stresses are transferred by the columns in the plane perpendicular to the poling direction onto the cubic blocks at their intersection. Hence

$$d_{31} = \frac{L^3\,{}^1d_{31}}{(L+\ell)^3} \qquad (7)$$

Comparison of the theoretical model with experimental results yielded good qualitative agreement.

1-3 and 2-3 Composites

These composites, in which PZT forms a continuous phase and the polymer has one or two dimensional connectivity have been extensively studied by Safari et al [16]. Square blocks with a 20 mm edge and 4 to 8 mm thick were pressed and sintered. The blocks were poled and then three or four holes drilled perpendicular to the poling direction which were filled with epoxy resin. Hole sizes of 3.2 and 4.2 mm were used with centre-to-centre separations, X, of between 3.5 and 5.75 mm. For low values of X, the composite permittivity increased linearly reaching a saturation level at higher values. Similar behaviour was observed for d_{33}. A broad maximum in d_h was noted for X between 4 and 4.5 mm and with 60-70% volume fraction of PZT. Also for a particular value of X a peak in d_h was seen. For all composites the hydrostatic charge constants were at least twice those for solid PZT, in 2-3 composites being much larger than in the 1-3 type. A minimum d_h of 372 pCN^{-1} was recorded for a 2-3 composite where the open sides were covered with a thin polymer sheet leaving the inside empty.

These authors presented a simple model in which the cylindrical holes were replaced by square section holes with an identical cross sectional area. The composite could then be considered as a combination of vertical PZT plates connected in parallel with rectangular bars of PZT and polymer in series (Fig 2).

Thus

$$\varepsilon_{33} = {}^{A}V\,{}^{1}\varepsilon_{33} + {}^{B}V\,{}^{B}\varepsilon_{33} \tag{8}$$

and

$$\frac{1}{{}^{B}\varepsilon_{33}} = \frac{{}^{1,B}V}{{}^{1}\varepsilon_{33}} + \frac{{}^{2,B}V}{{}^{2}\varepsilon_{33}} \tag{9}$$

No mathematical account for the piezoelectric coefficients was given. It is believed that the high d_h values obtained result from the rigid ceramic planes beneath the electrodes which efficiently transfer the stresses in the 33 direction to the ceramic in the centre of the composite whilst providing lateral stiffening which minimises the 31 stresses on the centre. For these reasons d_{31} is minimised and d_h values close to d_{33} for the ceramic are observed.

3-0 Composites

This class of piezoelectric composites in which a powder is dispersed in a polymer matrix was the first to be prepared [10]. As 3-0 composites are microstructurally homogeneous there is little benefit in incorporating PZT in these materials as only poor g_h and d_h values are attainable [11]. Banno [18] fabricated composites using lead titanate powder which is known to be anisotropic and in its modified form has been used to produce dense ceramic discs with virtually zero planar coupling coefficient. The powder was mixed with chloroprene rubber and rolled through a hot roller into sheets 0.5 mm thick. After electroding with conductive paste the specimens were poled at 10 kVmm^{-1} for 1 hour. Both ε_{33} and d_h were found to increase with increasing volume fraction of the ceramic. Banno developed a modified cubes theory to explain his results in which the repeat unit of the composite consists of an orthorhombic ceramic block with aspect ratio n in series with a polymer slab, this combined unit positioned in the corner of , and in parallel with, another polymer block (Fig 3). This leads to expressions for the permittivity and the hydrostatic charge coefficient of

$$\varepsilon_{33} = \frac{a^2(a + (1 - a)\,n)^2\ {}^{1}\varepsilon_{33}\,{}^{2}\varepsilon_{33}}{a^2\varepsilon_{33} + (1 - a)\,n\,{}^{1}\varepsilon_{33}} + (1 - a^2)\,(a + (1 - a)\,n)\,{}^{2}\varepsilon_{33} \tag{10}$$

$$d_h = \frac{{}^{1}d_h}{(1-2\,{}^{1}\alpha)} \cdot \frac{a^3(a + (1 - a)\,n)}{a + (1 - a)n\,({}^{1}\varepsilon_{33}/{}^{2}\varepsilon_{33})} \left\{ \frac{1}{\left[\dfrac{(1 - a)\,n}{a + (1 - a)n} + a^3\right]} - 2\,{}^{1}\alpha \right\} \tag{11}$$

Where ${}^{1}\alpha = -{}^{1}d_{31}/{}^{1}d_{33}$

This model is of particular interest because it makes predictions about the effect of particle geometry on the dielectric and piezoelectric properties. Recent advances which permit the fabrication of ceramic powders of controlled size and shape [19] could be important in this respect.

Banno was able to show that the same shape factor could be used to fit his data for ε_{33} and d_h, in support of his theory.

Turney, Whatmore and Curtis [20] fitted their results to Banno's theory obtaining values of n between 0.18 and 0.31 for composites of modified lead titanate in epoxy resin or nitrile rubber. These authors reported permittivities consistently twice those predicted by the model and this fact, together with the breakdown field of the composite being close to that of the dense ceramic, suggested to them that the powder was not fully dispersed but agglomerated to the extent that continuous ceramic chains were present between the electrodes. A similar observation was reported by Furakawa, Ishida and Fukada [21] in a PVDF-PZT system. They developed a model based upon spherical ceramic particles dispersed in a polymer matrix. Their approach was to derive the local field and stress conditions experienced by the ceramic phase due to the application of a field across the composite. Thus the apparent charge and voltage coefficients of the composite are given by.

$$d = {}^1V\, L_T\, L_E\, {}^1d \qquad (12)$$

$$g = {}^1V\, L_T L_D\, {}^1g \qquad (13)$$

where L_T, L_E and L_D are the local field coefficients with respect to stress, electric field and dielectric displacement. Derivation of these coefficients and assuming ${}^1\varepsilon \gg {}^2\varepsilon$ and ${}^2s \gg {}^1s$ leads to

$$d = \frac{15\,{}^1V}{(2 + 3\,{}^1V)\,(1 - {}^1V)}\;\frac{{}^2\varepsilon}{{}^1\varepsilon}\;{}^1d \qquad (14)$$

$$g = \frac{15\,{}^1V}{(1 + 2\,{}^1V)\,(2 + 3\,{}^1V)}\;{}^1g \qquad (15)$$

$$\varepsilon = \frac{2(1 - {}^1V)\,{}^2\varepsilon + (1 + 2\,{}^1V)\,{}^1\varepsilon\,.\,{}^2\varepsilon}{(2 + {}^1V)\,{}^2\varepsilon + (1 - {}^1V)\,{}^1\varepsilon} \qquad (16)$$

These authors considered that the discrepancy between the observed and calculated permittivities arose because of deviation from the ideal spherical shape of the powder and the possible existence of interfacial effects between the ceramic and the polymer.

The problems of poling 3-0 composites have been pointed out by several workers [22], [23], [20]. Using Maxwell's relations for spheres dispersed in a matrix Sa-Gong etal [22] have shown that the field experienced by a sphere is

$${}^1E = \frac{3\,{}^2\varepsilon}{2\,{}^2\varepsilon + {}^1\varepsilon}\,.\,{}^2E \qquad (17)$$

Where ${}^2E$ is the field in the matrix. For PZT in a polymer matrix then, the effective poling field is some two orders of magnitude less than the field applied to the matrix. That 3-0 composites can be poled at all tends to support the view of Turney etal that some higher degree of connectivity must be present. To improve upon the degree of poling that can be achieved Sa-Gong etal increased the conductivity of the polymer matrix by incorporating germanium or carbon as a third phase. This enabled composites to be poled with a field of 3.5 kV mm-1 applied for only a few minutes in marked contrast to the normal poling conditions of 10 $kVmm^{-1}$ for 1 hour.

3-1 Composites

Perhaps the most widely studied composite structure is the 3-1 type in which ceramic rods are aligned in an ordered array perpendicular to the electrodes. These were first proposed by Skinner et al [14], the philosophy being that the stiff ceramic rods would carry the mechanical stress in the poling direction whilst the high compliance polymer would effectively decouple the stresses in the perpendicular plane and thus enhance d_h by minimising d_{31}. Composites have been prepared by extruding and sintering rods which are layed in a jig prior to encapsulation [24] and by slicing sintered discs or blocks and backfilling with resin [25], [26]. Lynn et al [27] found that d_{33} increased linearly with up to 40 vol % PZT. d_h values increased with increasing composite thickness peaking at ~40 vol % PZT and also increased with decreasing rod diameter. This is of particular interest in the light of recent developments in the production of fine ceramic fibres for use in high reliability mechanical ceramic components [28].

To obtain maximum piezoelectric response from a 3-1 composite it is clear that most of the stress normal to the electrodes should be borne by the ceramic rods. However Klicker et al [29] only obtained $d_h = 40pCN^{-1}$ for a composite prepared with a low modulus polyurethane matrix as compared to $80pCN^{-1}$ for a much stiffer epoxy. This was explained by the high Poisson's ratio of polyurethane (~0.5) which makes it virtually incompressible. Under hydrostatic stress, the polyurethane transfers stress in the 31 direction onto the ceramic rods which enhances d_{31} and leads to a low d_h. This was overcome by foaming the polyurethane which provided an easily compressed gaseous third phase. This increased d_h to $225pCN^{-1}$. However, the main disadvantage of this system was that there was a non-linear dependency of d_h above pressures of 0.7MPa which was ascribed to collapse of the pores. Under these conditions the composite containing epoxy (Poisson's ratio 0.35) performed much better. Shorrocks, Brown, Whatmore and Ainger have developed an expression for d_h which accounts for the Poissons ratio of the polymer

$$d_h = \left[\frac{{}^1V\,{}^2s_{33} - 2\,{}^2V\,{}^1V\,({}^1s_{13} - {}^2s_{13})}{{}^1V\,{}^2s_{33} + {}^2V\,{}^1s_{33}}\right] \cdot {}^1d_{33} + 2\,{}^1d_{31}\,{}^1V \tag{18}$$

which for an epoxy with Poisson's ratio 0.35 predicts a peak in d_h for 25 vol % ceramic. This however was not observed and it was suggested that the assumption of uniform strain in the ceramic and polymer in the direction parallel to the rods was not achieved. Greater strain in the polymer would result in coupling of the stresses to d_{31} so reducing d_h. This was supported by lower d_h values for the lower modulus resins. Two approaches to this problem were suggested in order to stiffen the composite laterally, one being to use thick copper plates which would act as stiff electrodes in much the same way as 1-3 and 2-3 composites utilise solid PZT layers and the second to incorporate a mat of self bonded glass fibres between the rods [31] which could be bonded to the resin. Addition of fibres alone doubled the g_hd_h figure of merit from 1.61 to 3.221 TPa^{-1} while use of fibres and the stiff electrodes completely removed the dependency of the composite behaviour on the epoxy resin. A low modulus silicone rubber showed the best response with a g_hd_h of 5.471 TPa^{-1} using both these stiffeners. Subsequent work [32] has shown that fibre reinforced composites with silver paste electrodes exhibit less hysteresis and a much flatter response to pressure than do those with rigid electrodes.

CONCLUDING REMARKS

Some of the important experimental and theoretical developments of piezoelectric ceramic-polymer composites have been discussed. It is clear that these composites offer a quantum leap in property improvements over conventional PZT compositions , the principal benefits being:-

1) Improved hydrostatic charge and voltage coefficients.
2) Low density resulting in good acoustic impedance matching to materials such as water (underwater detection applications), concrete and aluminium (NDT applications) and human tissue (medical ultrasonic applications) and the possibility of mutually buoyant systems.
3) High compliance giving good damping, conformability and improved mechanical shock resistance over dense ceramics.
4) The potential to be fabricated into large area devices.

Future areas of work important for the wide spread exploitation of these materials must include more representative mathematical models to accurately describe the properties of these materials, better understanding of the interfacial properties which are fundamental to the performance of composite devices and most importantly the development of reliable and reproducible fabrication techniques.

Table 1. Properties of Ceramic Polymer Composites

Property (Units)	$^T\varepsilon_{33}/\varepsilon_o$	d_{33} (pCN^{-1})	g_{33} (mVmN^{-1})	d_h (pCN^{-1})	g_h (mVmN^{-1})	d_hg_h (TPa^{-1})	Ref
PZT	3200	520	18.3	40	1.4	0.06	8
3-3 replamine Silicone rubber	50			36	104	1.14	14
3-3 Burps Silicone rubber	300	250		260	100	26.0	15
3-3 Burps Epoxy resin	500	175		120	27	3.2	15
3-1 Epoxy resin	450	290	73	222	56	12.3	16
3-2 Epoxy resin	290	290	114	329	128	42.0	16
3-2 Sealed edges	340	340	112	372	123	45.7	16
3-0 Nitrile rubber Modified lead Titanate	51			18	40	0.73	20
3-0 Silicone rubber + Carbon filler	120	50		30	30	0.9	22
3-1 Epoxy resin			97	39.7	69	6.1	27
3-1 Epoxy resin + Stiff electrodes + Glass fibre				145	25.3	3.69	32
3-1 Silicone rubber + Stiff electrodes + Glass fibre				116	32.8	5.47	32

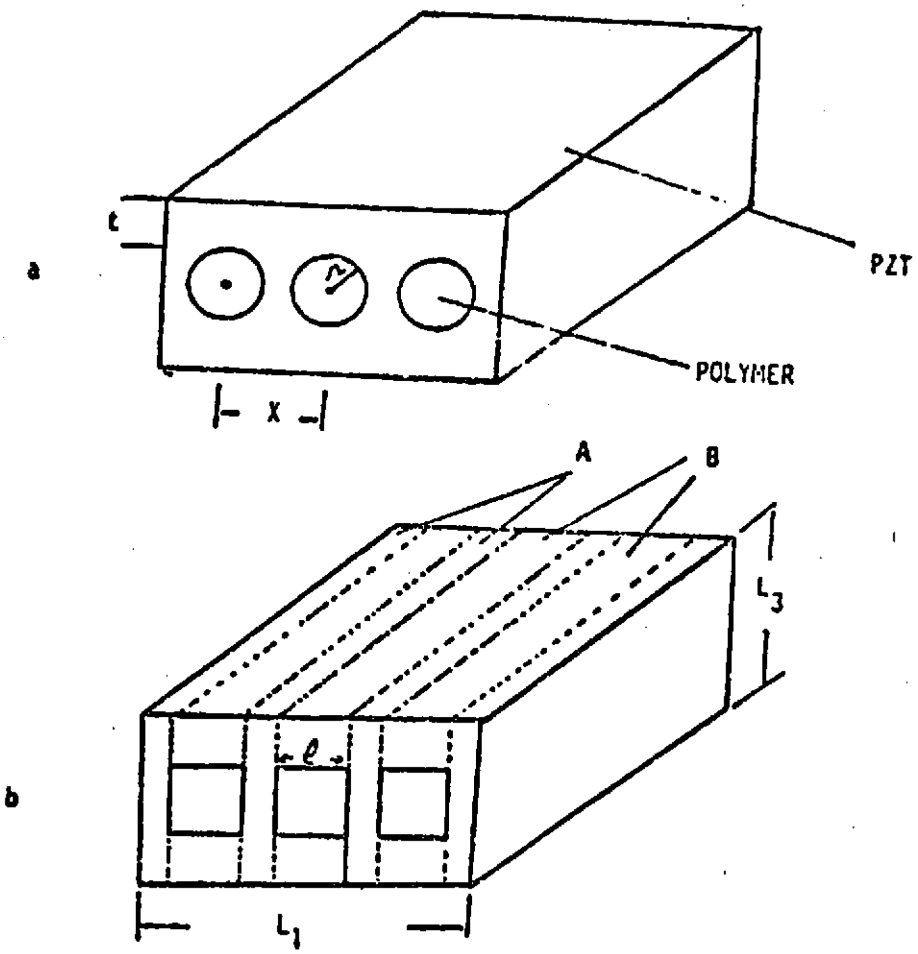

Fig 2: Model Structure for 1-3 Composite [16]

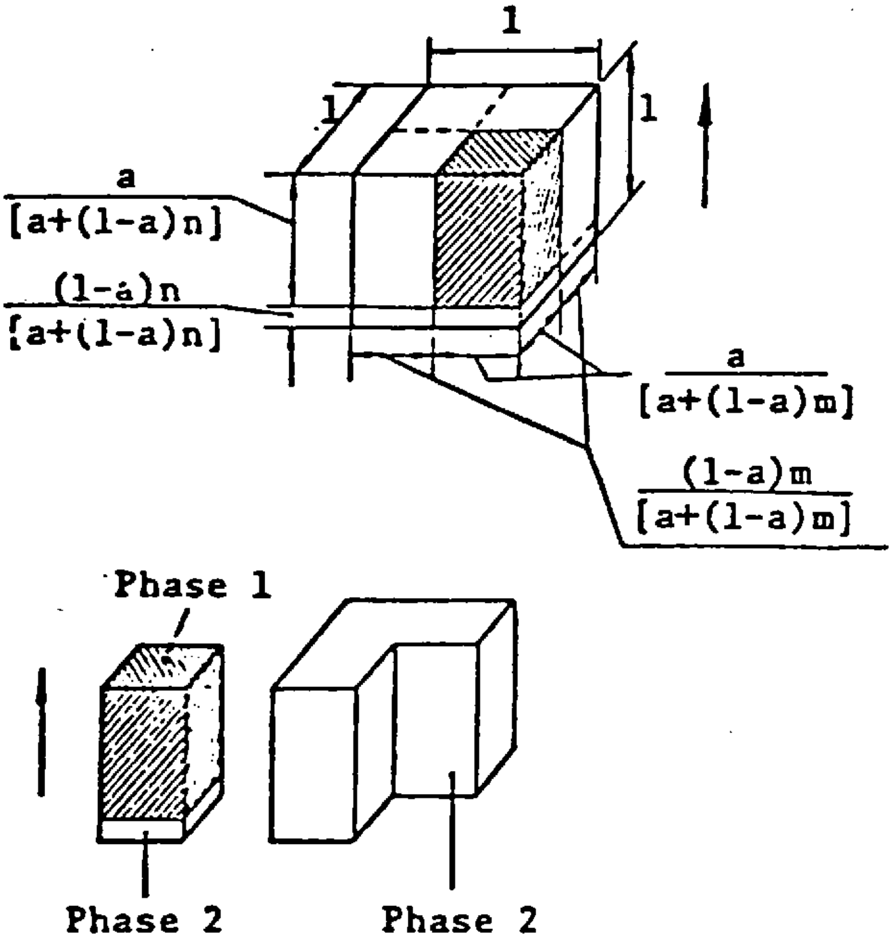

Fig 3 : Model Structure for 3-0 Composite [18]

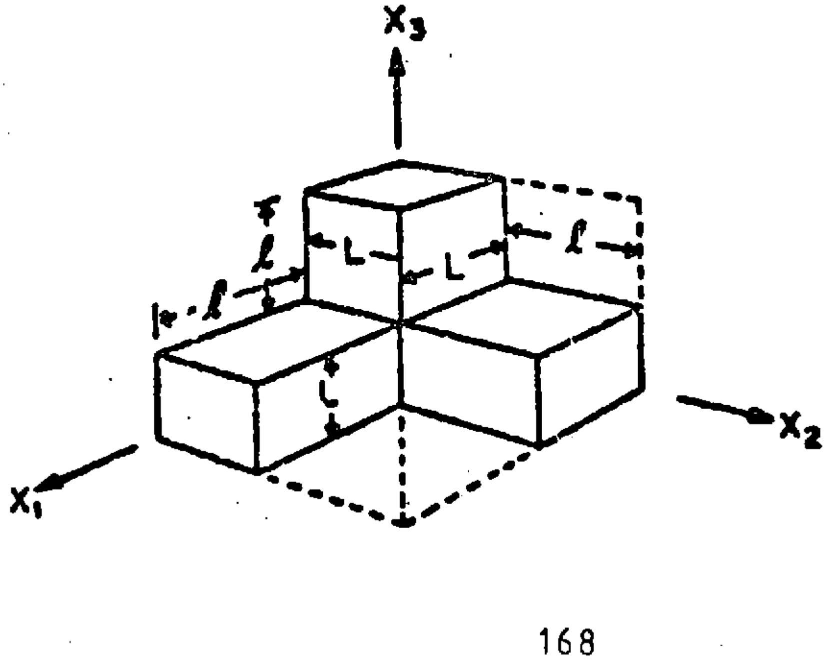

Fig 1: Model Structure for 3-3 Composite [15]

REFERENCES

[1] E. Warner and A.N. Salomon, Titanium Alloy Manufacturing Company, Elect. Rep. 9 (1942)

[2] T. Ogawa, Presented at the Meeting of the Research Institute of High Dielectric Constant Materials (1944)

[3] B. Wul, Nature 156 480 (19450

[4] A. von Hippel etal N.D.R.C. Rep. No. 300 (August 1944)

[5] R.B. Gray, 'Transducer and Method of Making the Same', U.S. Patent No. 2,486,560 (Nov. 1, 1949)

[6] B. Jaffe, R.S. Roth and S. Marzullo, J. Res, Nat. Bur. Stds., 55,239-54 (1955)

[7] B. Jaffe, W.R. Cook Jr and H. Jaffe, 'Piezoelectric Ceramics', Academic Press (London) (1971)

[8] Data for PC-5H, Unilator Technical Ceramics, Piezoelectric Ceramics Catalogue

[9] W.B. Harrison, Proc. Workshop on Sonar Transducer Materials, Naval Research Laboratory 257 (Nov 1975)

[10] T. Kitayama and S. Sugawara, Rept. Prof. Gr. Inst. Elec. Comm. Eng. Japan CPM 72-17 (1972)

[11] L.A. Pauer, I.E.E.E. Inter. Conv. Res. 1-5 (1973)

[12] W.R. Tinga, W.A.G. Voss and D.F. Blossey, 'Generalised approach to multi-phase dielectric mixture theory', J. Appl. Phys. vol 44(3)897-902 (1973)

[13] R.E. Newnham, D.P. Skinner and L.E. Cross, 'Connectivity and Piezo-electric-Pyroelectric Composites', Mat. Res. Bull. 13 (5) 525-36 (1978)

[14] D.P. Skinner, R.E. Newnham and L.E. Cross, 'Flexible Composite Transducers', Mat. Res. Bull 13 (6) 599-607(1978)

[15] T.R. Shrout, L.J. Bowen and W.A. Schulze, 'Simplified Fabrication of PZT-Polymer Composites', Mat. Res. Bull 14 1553 (1979)

[16] A. Safari, R.E. Newnham, L.E. Cross and W.A. Schulze, 'Perforated PZT-Polymer Composites for Piezoelectric Transducer Applications'

[17] K. Rittenmeyer, T. Shrout, W.A. Schulze and R.E. Newnham, 'Piezoelectric 3-3 Composites'

[18] H. Banno, 'Recent Developments of Piezoelectric Ceramic Products and Composites of Synthetic Rubber and Piezoelectric Ceramic Particles' 1983 I.E.E.E. Int. Symp. on Applications of Ferroelectrics NBS, Maryland, 1983

[19] B. Fegley, E.A. Barringer and H.K. Bowen, 'Synthesis and Characterisation of Monosized Doped TiO_2 powders', Comm. Am. Ceram. Soc C-113-6 (June 1984)

[20] R.C. Twiney, R.W. Whatmore and A.C. Curtis, 'Piezoelectric Materials Exhibiting 3-0 Connectivity'

[21] T. Furukawa, K. Ishida and E. Fukada, 'Piezoelectric properties in the composite system of polymers and PZT ceramics', J. Appl. Phys. 50 (7)4904-12 (July 1979)

[22] G. Sa-Gong, A. Safari, S.J. Jang and R.E. Newnham, 'Poling Flexible Piezoelectric Composites', Ferroelectrics Letters vol 5 131-142 1986

[23] W.A. Schulze and J.V. Biggers, 'Piezoelectric Properties of $Pb_5Ge_3O_{11}$ bonded PZT Composites', Mats. Res. Bull 14 721-30(1979)

[24] R.E. Newnham, D.P. Skinner, K.A. Klicker, A.S. Bhalla, B. Hardiman and T.R. Gururaja, 'Ferroelectric Ceramic - Plastic Composites for Piezo-electric and Piezoelectric Applications', Ferroelectrics Vol 27 49-55 (1980)

[25] W.A. Smith, A.A. Shaulov and B.M. Singer, 'Properties of Composite Piezoelectric Materials for Ultrasonic Transducers'

[26] G. Hayward and J. Hossock, 'The Measurement, Construction and Evaluation of Piezoceramic - Epoxy composites for High Frequency Sonar Arrays'

[27] S.Y. Lynn, R.E. Newnham, K.A. Klicker, K. Rittenmeyer, A. Safari and W.A. Schulze, 'Ferroelectric Composites for Hydrophones', Ferroelectrics Vol 38 995-8 (1981)

[28] N. Claussen, K.L. Weisskopf and M. Ruhle, 'Tetragonal Zirconia Polycrystals Reinforced with SiC Whiskers', J. Am. Ceram. Soc. Vol 69 No. 3 288-91 (March 1986)

[29] K.A. Klicker, W. A. Schulze and J.V. Biggers, 'Piezoelectric Composites with 3-1 Connectivity and a foamed Polyurethane Matrix', Comm. Am. Ceram. Soc C208-210 (Dec 1982)

[30] N.M. Shorrocks, M.E. Brown, R.W. Whatmore and F.W. Ainger, 'Piezoelectric Composites for Underwater Transducers', Ferroelectrics Vol 54 215-8 (1984)

[31] M.J. Haun, P. Moses, T.R. Gururaja, W.A. Schulze and R.E. Newnham, 'Transversely Reinforced 1-3 and 1-3-0 Piezoelectric Composites' Ferroelectrics Vol 49 259-264 (1983)

[32] A.G. Munns, R.C. Twiney and R.W. Whatmore, 'Piezoelectric Composites with 3-1-1 Connectivity'