NPL REPORT CMMT (A)78

MATERIALS AND TEST CONDITIONS FOR PROJECT CAM 7

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July 1997

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Summary

Representative samples of piezoceramic materials have been examined in the Scanning Electron Microscope. The microstructures have been compared and contrasted in terms of porosity, grain sizes and grain size distributions, homogeneity and pore size. Samples with typically hard and soft piezoelectric responses, manufactured by conventional powder processing and atmospheric sintering have been analysed and compared to a soft piezoceramic that has been hot pressed. Generally, all the samples showed some porosity, were homogeneous in phase identity, and were readily etched to delineate the grain boundaries.

ISSN 1361-4061

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INTRODUCTION

As part of the DTI programme on the development of test methods for characterisation of advanced materials, project CAM 7 *Electroactive materials properties under conditions of high stress or stress rate*, has the overall aim of defining and improving the measuring framework for electroactive materials which will enable them to be used with greater confidence by UK industry. The objectives are to define test methods and models for the degradation of the functional properties of electroactive ceramic materials. Electrical and mechanical stressing will be applied to the chosen materials and functional properties such as dielectric response, strain field performance and polarisation field hysteresis behaviour will be measured.

To ensure that the measurement methods that are employed will meet the needs of UK industry, a survey of firms was conducted by mail and by direct visits. The results from this survey are discussed with respect to the overall objectives of the project. The materials that will be examined are described, and an outline given of the test conditions that will be employed in the test method development.

Finally, this report characterises the microstructures of the chosen ceramic materials using conventional Scanning Electron Microscopy techniques of polished cross sections and samples which have been etched to reveal their grain structure.

SUMMARY OF PROJECT CAM 7

Piezoelectric materials

This project is concerned mainly with the development of measurement methods for the characterisation of piezoelectric ceramics which are increasingly being used in actuator and sensor applications. As the performance of these materials is known to degrade with exposure for extended periods to high mechanical and electrical stresses, this work is focussed on the production of procedures for the evaluation of this long term behaviour. This overall aim is dependent on the availability of methods for the measurement of the functional and electronic properties, which are also being developed where necessary in the project. It is intended that as many measurements as possible of the materials properties (and their degradation) will be made while the samples are still in place in the exposure systems.

Measurement of functional properties

The key functional property that will be evaluated is the strain that is obtained when a piezoelectric material is subjected to an electrical stress. Fibre-optic probes (which have been shown to provide a reliable and easy to use measurement method) will be incorporated into sample holders for the stress exposure system, so that measurements of the strain performance of piezoelectric materials can be made during stressing.

Ways of making measurements of other parameters such as the mechanical strength and electrical strength of samples will be explored. Results from these experiments will be used to define the outer envelope of experimental conditions that will be used during the degradation experiments.

Measurement of electronic properties

The dielectric constant and loss factor for piezoelectric materials are important materials parameters which are currently very difficult to measure at the high driving fields that are increasingly being demanded. New measurement methods are being developed for high field measurement which can be used to monitor the changes in these parameters during stress exposure experiments.

The utility of measurements of polarisation-electric field hysteresis behaviour (which underlies the functional behaviour of piezoelectric materials), is also being explored by Manchester University.

Measurement of degradation behaviour

Measurements of the changes in electronic and functional properties of samples of piezoelectric ceramic will be made as the samples are being exposed to static and cyclic mechanical and electrical stressing for extended periods. The requirement for a high frequency of mechanical stressing will necessitate the development of novel high frequency mechanical actuators.

Development of modelling procedures

The Structural Materials Centre, DERA, will develop procedures for the numerical modelling of the performance of model devices constructed from piezoelectric materials will be developed, and the predictions will be compared with the actual performance of constructed devices. The modelling of time dependent behaviour will also be considered.

Guidance for industry

The results of the project will be collated into a guide for industry on the measurement and characterisation of piezoelectric materials. Guidance notes on specific aspects will be also be published.

INDUSTRIAL SURVEY

AM4 Industrial survey

The industrial survey carried out in project CAM 7 was designed to complement and update the similar survey undertaken in project AM4 [1]. In this earlier survey, clear support was given by the returns from industry for the development of new and improved test methods for the characterisation of electroactive materials such as piezoelectric and electrostrictive ceramics, with the measurements that received the most support being, (Figure 1):

- the development of improved methods of strain measurement with better strain resolution,

- measurement of the degradation of properties with time,
- measurement of the mechanical behaviour under high electrical loading.

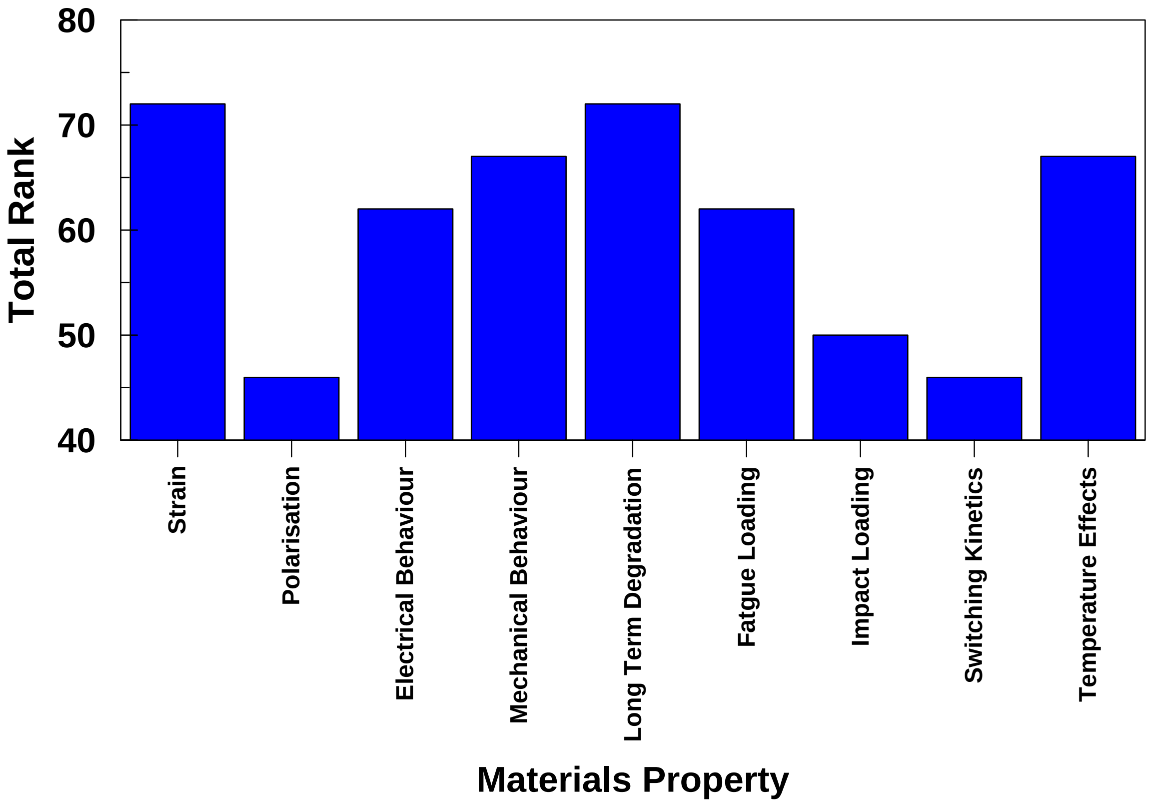


Figure 1, Relative ranking of importance of different properties determined by AM4 industrial survey

The other significant point was that although there was considerable interest in test methods for the measurement of properties of frequencies above 1MHz, there was clear need for measurement methods at much lower frequency levels (Figure 2).

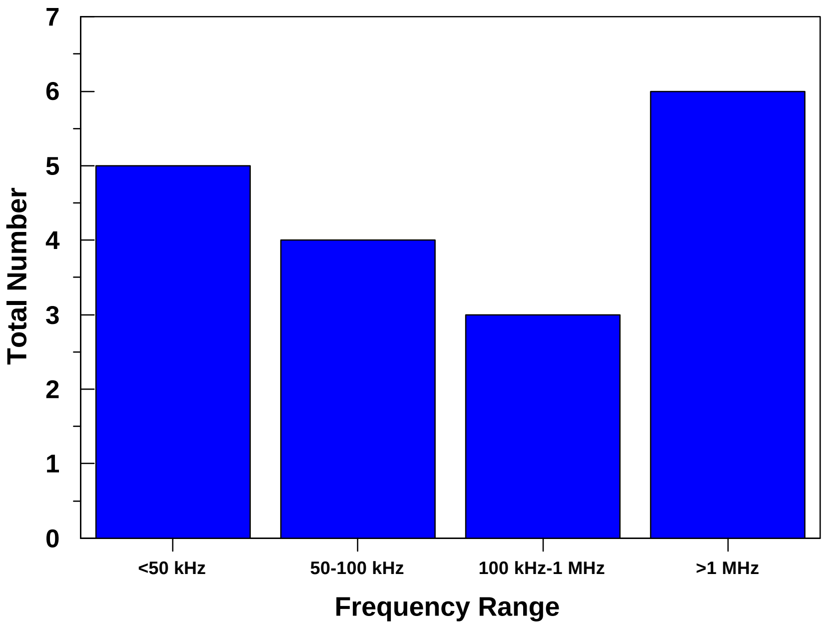


Figure 2, Frequency range of interest from AM4 industrials survey.

CAM 7 Industrial survey

The CAM 7 industrial survey was carried out with a postal survey followed up by selected direct industrial visits. A simple questionnaire (Annex 1) was sent out to 94 organisations. The annex was simplified in an attempt to encourage answers. The two questions on the questionnaire were to ask which materials were considered to be a priority for test measurement development, and to ask what test conditions were thought to be important.
In the event, only a relatively small response was achieved, with only 10 returns. To ensure that adequate representation from UK industry was achieved, some effort was put into following up the postal survey by telephone with eleven firms contacted.

Another important element of the survey was direct industrial visits. This gives the opportunity of understanding the measurement problems that are faced by industry on a first hand basis. Seven firms have been visited as part of the industrial survey, but it is planned that visits will continue throughout project CAM 7 as a primary mechanism for dissemination and also for ensuring the project remains in touch with industry.

The contacts that have been made in the survey are:

- Advanced Ceramics
- Extech Hybrids
- Filtronic Comtek
- Morgan Matroc (Unilator)
- Morgan Matroc (Transducer Products)
- Sonardyne
- Sensor Technology Ltd
- Domino
- QMW
- Bath University
- BAeSEMA
- DERA
- Xaar
- Oxley Developments
- GEC-Marconi
- Queensgate Instruments
- Intravascular Research
- Ford
- Lucas-Varity
- Pafec
- ABB Kent Taylor
- Ferroperm

Industrial Concerns

A full listing of all the responses is not given, but some of the major themes that were made by firms are quoted. Only overall comments are made here, the implications of the survey in terms of materials to be examined, and test conditions used will be discussed in the relevant sections.

- A major concern which was expressed with piezoelectric materials is the variability in properties that is experienced both from batch to batch of a material, and also (of perhaps rather more concern) very high variations from one sample to another, and also variations from one position within a sample to another. One firm quoted variations of up to about 30 % in dielectric properties from one position of a sample to another position in material that came from what was said to be a very high quality source. This factor was stated to be a major problem which was holding back the development and production of new products.
- A related issue was the poor quality of some of the materials on the market which often exhibit major defects such as porosity and other damage. However, although this is true in some cases, many of these materials are used very successfully in applications where the highest quality of material is not required, often in mass market, relatively low technology products.
- The machinability of piezoelectric materials was a concern, particularly for high technology products where very precise machining is required, and the very act of machining may cause damage to the materials properties and severe degradation in performance.
- The need for improved methods for the measurement of dielectric constant ε, tan δ, and hysteresis behaviour under different stress conditions, particularly at high stresses.
- The need to define test methods which would be able to give information on the survivability of piezoelectric materials under long term duration exposure to mechanical and electrical stressing.

The response was encouraging in that many of the issues of concern are being addressed in project CAM 7, showing the industrial relevance of the work.

MATERIALS

In 1992 Don Berlincourt's review [2] on piezoelectric compositional development claimed that along with quartz, modified PZT compositions shared almost 90% of the market for piezoelectric applications. Near stoichiometric mixtures of $PbTiO_3$ and $PbZrO_3$ (PZT) show the highest level of piezoelectric activity of this pseudobinary system. There is a temperature independent phase change near this composition from tetragonal on the titanium rich side to rhombohedral on the zirconium rich side. Most of these PZT materials lie on the tetragonal side of this boundary, with small amounts of various additives to fine tune the piezoelectric properties. Depending on the valency of these additives the properties of the PZT can be tuned for specific applications.

These additives give rise to two broad classes of PZT, 'hard' and 'soft'. Acceptor type dopants such as potassium and iron tend to make the material electrically 'hard', lowering the permittivity and piezoelectric properties but reducing the mechanical and electrical losses. For this reason the hard materials are suitable for high electrical and mechanical drive applications such as sonar transducers. In contrast donor additives such as lanthanum, niobium and antimony make the material electrically 'soft', increasing piezoelectric behaviour at the expense of increased mechanical and electrical losses. These materials are used where sensitivity is the main concern such as hydrophones.

The terms 'hard' and 'soft' come from a similarity of the ferroelectric hysteresis loops with the magnetic hysteresis found in ferrite materials. Idealised descriptions of hard and soft materials tend to focus on the shape of the ferroelectric hyesteresis loops, whereas in practice it is the magnitude of the loss, the area within the loop that most distinguishes hard and soft materials. Soft materials have a tan δ of the order of 0.02, whereas hard materials have losses an order of magnitude less.

More precise definitions of PZT materials are given by the so called Navy types, where six PZT types are distinguished by their electrical and mechanical properties, irrespective of the type of additions. These definitions come from a US Navy standard [3] for materials for sonar transducers and reflect their use currently and historically.

There has been much speculation that there will be a boom in the use of piezoelectric materials in smart applications, for example in active suspension systems in automobiles [4]. This need will be satisfied by current materials used in improved production techniques and technologies rather than improved material formulations. Don Berlincourt's estimate of the importance of PZT remains true and is likely to remain so until improved materials are discovered.

There was clear support for the need for work on both soft and hard materials typified by the PZT 4 and 8 types for the hard materials, and PZT 5 for soft materials:

The other area which needs to be considered is the effect of microstructure on the results of measurements. To look at the extremes of materials structures, it was decided to examine conventional sintered materials as an example of materials with poorer microstructure, and hot pressed materials as materials with a high quality microstructure.

Thus the four main different materials would be examined are hard and soft materials made by hot pressed and conventional sintering processing to obtain the necessary high quality and less good microstructures.

In addition to these materials some work would also be carried out under the associated EU funded project ACTUATE on multilayer materials.

Very little interest was shown for work on electrostrictive materials, and these will incorporated into the testing programme if resources allow.

A number of different suppliers are available for the supply of the necessary material and test samples, but after some consideration, particularly of the need to incorporate UK suppliers as much as possible into the programme, it was decided that conventionally sintered materials would be supplied by Morgan Matroc in the UK, with some additional materials supplied by Ferroperm.

Hot-pressed materials would be supplied by Advanced Ceramics Ltd, but some hot pressed samples obtained under project AM4 from GEC-Marconi would also be used.

TEST CONDITIONS

In this section, the overall limits for the test conditions used in the project will be considered. The two main concerns that were addressed were the industrial need expressed in the industrial survey, and the likely limits on the test conditions that would be imposed by the test equipment available for the project.

In considering the industrial need, a very rough classification of applications in terms of frequency of operation has been adopted. Thus Table 1 lists the different categories and their frequency range. This is recognised to be somewhat rough and ready, but nevertheless gives an approximate guide to the applications of concern in the relevant frequency ranges.

Table 1, Application areas and frequency of interest.

Application Area	Frequency of Interest
Actuators	< 40 kHz
Sensors	< 40 kHz
Audio (including sonar and hydrophones)	< 20 kHz
Low frequency ultrasound	> 20 kHz
High frequency ultrasound	> 20 MHz

Although the AM 4 and CAM 7 industrial surveys both show interest in the development of test methods for relatively high frequencies (Figure 2), there is also a considerable need for improved measurement methods at lower frequencies.

The requirement for increased frequency experiments and measurements in relation to fatigue and degradation is two-fold. Firstly the material may intrinsically behave differently to changes in frequency. In particular the behaviour of domain walls is likely to be governed by frequency, where inertial effects may restrict their movement at high frequencies. Secondly to investigate fatigue it is necessary to look at repeated applications of the loading cycle, and this can become experimentally inconvenient. For instance 10^6 cycles at 1Hz takes over 11 days, whereas at 100Hz this test is reduced to less than 3 hours.

In the future applications of multilayer actuators in control systems in automotive applications it is likely that the actuators will be operated by an on-off square drive. A square wave can be thought of as a sum of many sine waves with some high frequency components. A square wave is a notoriously difficult wave form to produce in a clean and controlled manner, however it might prove useful to use this form of drive to simulate actual applications.

In actual fact, although the consideration of applications is useful, the upper frequencies that will be used in project CAM 7 are more defined by the likely limitations of test systems. Thus, although power amplifiers are available which will give electrical stressing at frequencies up to several hundred kHz, the capabilities of the measurement equipment that will be used to measure the response of piezoelectric ceramics gives a much lower limit.

Similarly, the need for the application of well controlled mechanical stresses limits the upper frequency at which mechanical stresses can be applied.

These considerations lead to the choice of ceilings for electrical stressing experiments of < 20kHz, and < 1kHz for mechanical stressing.

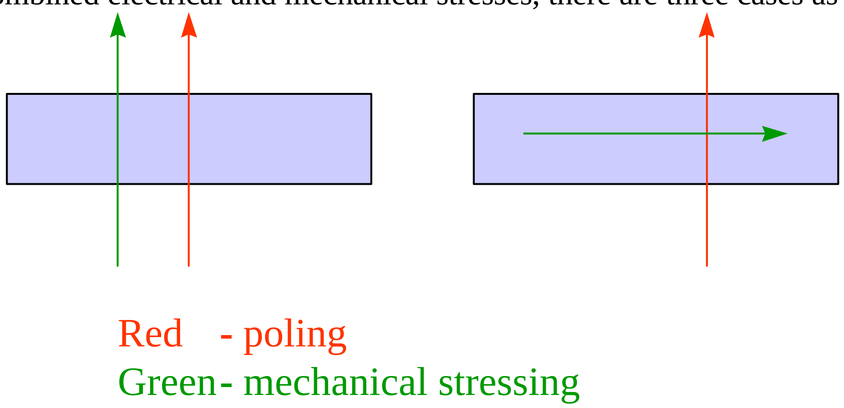
Butler et al. [5] carried out a survey of the literature and industry on how hard type I and III navy materials were actually being used. They found mechanical stresses of up to 170MPa were used in construction, and up to 100MPa in use, and electrical fields of up to 600volt/mm. They note that higher values of field and stress are possible in sonar transducers. Experimental evidence and manufacturers brochures suggest that for single point tests values much higher than this are possible. What happens after repeated applications will be the focus of the present program CAM7.

It will also clearly be important to limit the static and cyclic stresses are applied to less than the mechanical and electrical stress limits for the materials examined, and these parameters will be determined in mechanical and electrical strength tests carried out as part of project CAM 7.

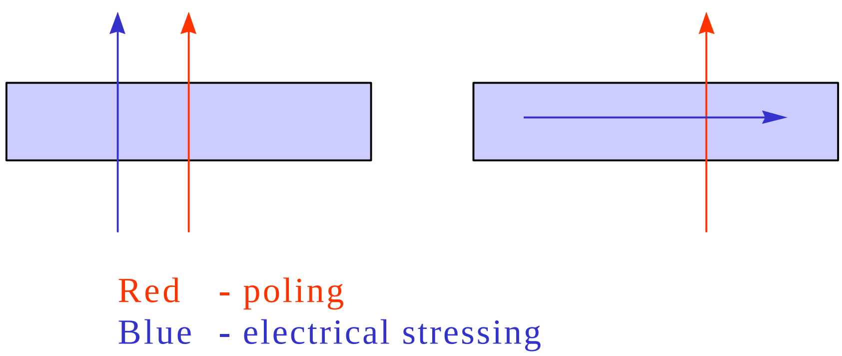
PROPOSED TEST GEOMETRIES

An important consideration when defining the test geometries which will be used in project CAM 7 is the orientation of the direction of application of stressing relative to the poling direction.

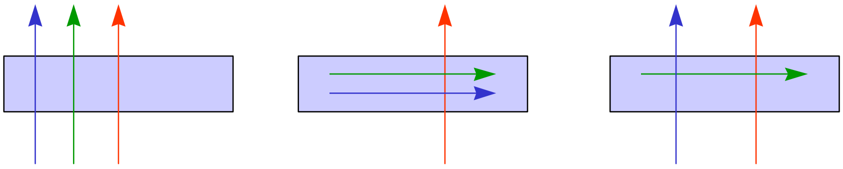
Figure 3 shows the different possibilities for the application of uniaxial stresses to a simple block of material. Thus for the application of only mechanical stresses, there are two possible orientations with the axis of stress application parallel or perpendicular to the poling direction. With only electrical stressing, there are also two different orientations. For the application of combined electrical and mechanical stresses, there are three cases as shown in Figure 3c.



a) application of mechanical stress



b) application of electrical stress



Red - poling
Green - mechanical stressing
Blue - electrical stressing

c) application of combined electrical and mechanical stresses

Figure 3, Consideration of orientation of stressing axes relative to poling direction.

It is clearly not possible to consider all these different testing orientations for testing in project CAM 7. In practice, two test geometries will be considered. These are to use uniaxial compression with the axes of mechanical and electrical stressing aligned with the poling direction. These tests will typically use disc samples with about a 10:1 diameter to thickness ratio. By varying this ratio, in conjunction with finite element analysis, the effect of stress uniformity due to edge effects can be investigated.

The second test geometry which will be explored will be to use a composite bend testing sample where a strip of piezoelectric material is cemented to a thick bar of metal. The composite sample is then subjected to flexure testing. By proper design of the composite sample, in particular the ratio of the thickness of the piezoelectric strip to the metal bar, it is possible to obtain a sample where the piezoelectric material is subjected to an effectively uniform stress. In this case the metal bar will act as an electrode to the piezoelectric material, and the mechanical stress will be perpendicular to the aligned electrical stressing direction and poling directions. However it may be that the development time for this test geometry will preclude its use in this project.

MECHANICAL TESTING SYSTEM

The bulk of the tests within the project will be carried out in a test frame which is being developed. This frame will enable two types of experiment to be carried out. Firstly a static load will be applied to the sample which will then have a sinusoidal field imposed, whilst measuring the dielectric and mechanical displacement of the sample. This load could be applied using a dead load but for stability is probably more easily applied using some sort of compliant spring. If the compliance of the loading system were an order of magnitude less than the ceramic then this would maintain the required load within a few percent throughout the test. A conventional strain gauged load cell would probably fulfil this requirement.

In the second type of experiment a sinusoidal mechanical load will be applied to the sample whilst measuring the dielectric and mechanical displacement. In order to enhance the frequency response of the system two different actuation systems will be used. The first of these is a magnetostrictive system which was purchased towards the end of project AM4, and the second is a piezoelectric actuator which is being purchased from Physik Instrumente.

A preliminary design for the frame is shown in Figure 4. One problem with using magnetostrictive or piezoelectric actuators as opposed to conventional motor driven screw actuators is the limited stroke of the former. Therefore in order that the load is transferred to the sample and not the loading frame it is essential that the frame is as stiff as possible, removing all compliant elements. Therefore the load cell in the system will have to be a quartz load cell. Additional problems are caused by the differing sizes of the magnetostrictive and piezoelectric load cell. The magnetostrictive actuator is much bulkier than the piezoelectric by virtue of the drive coil surrounding the magnetostrictor, and the larger the actuator the larger the frame needs to be to become stiffer.

Preliminary experiments with the actuators have shown that with the magnetostrictive actuator sinusoidal loads of up to 2.4kN peak to peak are possible at frequencies of up to 170Hz. Using the piezoelectric actuator loads of up to 9kN peak to peak are possible at 10Hz but higher frequencies are difficult due to current limiting of the power supply.

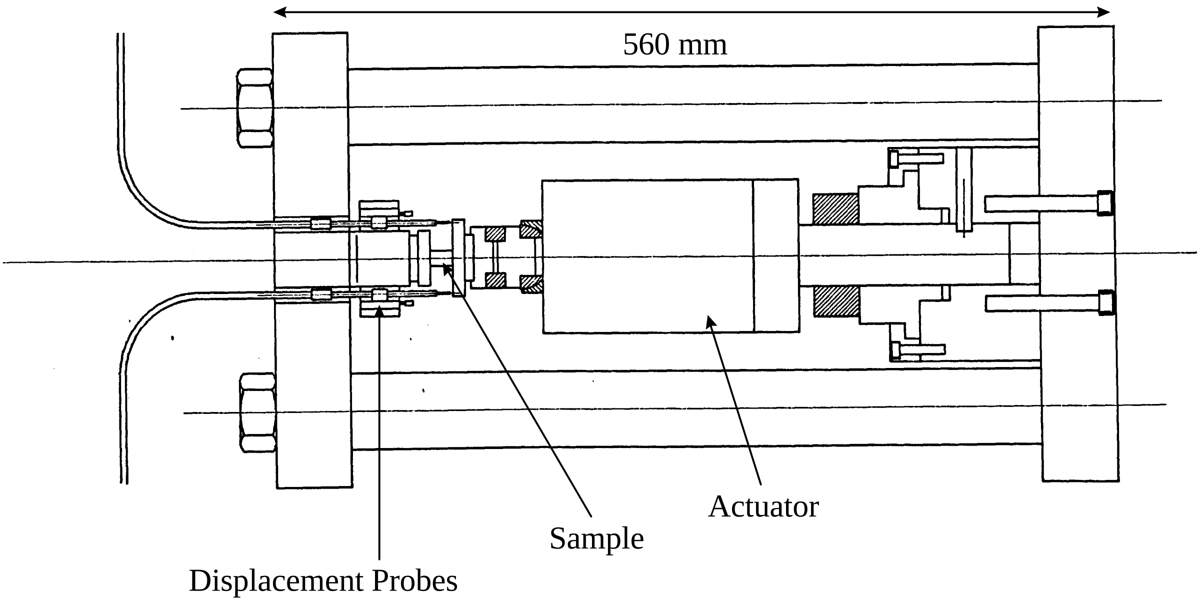


Figure 4, Preliminary design of mechanical testing frame

MICROSTRUCTURAL EXAMINATION

Experimental Techniques

Samples were cross sectioned, encased in either resin or moulded in bakelite, and their surfaces polished using water based diamond slurries (6µm, 3µm, 1µm) on soft polishing cloths, with final polishing using colloidal silica for 3 minutes. The microstructure was examined using a Field Emission Source Scanning Electron Microscope (Hitachi S4000) following the deposition of a thin conductive gold/palladium coating to eliminate the build up of charge under the electron beam. Representative images of the samples surface were recorded using Polaroid PolaPan Instant Sheet Film (Type 52). The same samples were then etched according to the following chemistry; HCl:HF (19:1) mixed with water to make a final solution of concentration 1 part acid mix to 40 parts water (distilled). The mounted samples were repolished to remove any conductive gold coating and immediately immersed into the etchent for 30 seconds, after which they were removed, rinsed thoroughly and dried. A second conductive coating was deposited prior to examination in the SEM.

Material Choice

A range of piezoelectric ceramics were chosen from the inventory that will be used in other stages of the CAM07 programme in an effort to as fully categorise the samples available for study as possible. Hard and soft piezoceramics, conventionally sintered and one hot pressed to near theoretical density were identified as representative of the many materials available and include, in detail the following:

Table 2, Samples chosen for the microstructural analysis.

CODE	**Description**	**Hard/Soft**	**Poled**	**Supplier**	**Composition**	**Serial #**
KSY	10mm Discs	Soft	Yes	Morgan Matroc TPD	PZT 5A	2648/10178
KWK	10mm Discs	Soft	No	Advanced Ceramics Ltd	ACL4050 Hot pressed	ACL4050
KSZ	10mm Discs	Hard	Yes	Morgan Matroc TPD	PZT4D	2643/10168
KTW	10mm Discs	Hard	Yes	Morgan Matroc Unilator	PC4D	PC4D
KKG	10mm Discs	Hard	Yes	Ferroperm	PZ26	95/0914,0915
KTX	10mm Discs	Soft	Yes	Morgan Matroc Unilator	PC5H	PC5H
KKH	10mm Discs	Soft	Yes	Ferroperm	PZ27	95/0198,0199

MICROSTRUCTURAL ANALYSIS

Polishing of these materials for microstructural analysis proved extremely difficult, as it was difficult to determine the effectiveness of the polishing procedure to reveal true microstructure and not grain tear out induced by polishing. Samples polished sufficient for SEM analysis were produced, where grain tear out is easily distinguished by its angular features compared with the true porosity consisting of rounded pores containing thermally etched grains. However for a more complete optical investigation using image analysis to determine pore size and distribution a more rigorous procedure will need to be developed. Figure 1 shows some optical images of KTY the soft PC5H material. It can be seen that the porosity in this sample is not randomly distributed, often there is a large pore, of the order 50 - 100μm surrounded by a ring of smaller pores. This outer ring is of the order of 200μm and is probably related to the granule size formed in the spray drying process. This linked network was less evident in the hard material made by the same manufacturer.

Images of the polished cross sections are compared in figures 6a) through 12a) at 500x magnification to highlight the general porosity, homogeneity and presence of any second phase present within the materials. Analysis of the micrographs yields estimates of the average sizes of pores present in the samples, Table 3. The pores present within piezoelectric materials can dramatically affect the material's electrical performance. Average grain size has been calculated using the linear intercept method and the images presented in figures 6b) through 12b), table 3.[1]

Table 3, Microstructural Features in Piezoceramic samples

CODE	Hard/Soft	Poled	Supplier	Composition	Largest Pore size, µm	Ave. Grain Size / µm
KSY	Soft	Yes	Morgan Matroc TPD	PZT 5A	22	3.6±0.5
KWK	Soft	No	Advanced Ceramics	ACL4050 Hot Pressed	3	2.6±0.1
KSZ	Hard	Yes	Morgan Matroc TPD	PZT4D	13	2.5±0.4
KTW	Hard	Yes	Morgan Matroc Unilator	PC4D	12	3.9±0.3
KKG	Hard	Yes	Ferroperm	PZ26	13	6.9±1.4
KTX	Soft	Yes	Morgan Matroc Unilator	PC5H	18	5.6±0.9
KKH	Soft	Yes	Ferroperm	PZ27	11	4.6±0.9

Evidence of some grain pull-out due to the polishing procedure is shown in the photomicrographs for some of the materials, and is especially evident in the etched materials, figures 6b) through 12b). A composite image, figure 13, aims to highlight the similarities and differences between the etched materials at one magnification. The distinguishing domain network patterns common to many of the images results from regions of the crystallites of differing polar axis orientation [6]. Imaging the domain patterns in the SEM is not trivial and so not all the poled and unpoled materials exhibit this feature. Additionally, the sample mounting process includes pressing at modest temperatures (<200°C) for times of less than 10 minutes, which might destroy or weaken the poled directionality. Indeed the pressure of the bakelite mounting process was sufficient to cause cracking in some samples, and was the reason for preferring the cold resin mounting process.

All materials had a closed porosity network, with the hard materials containing an even (modal) distribution of equiaxed grains, whereas some larger grains could be seen in the softer material. Generally the acceptor type dopants such as K^{+1} and Fe^{+3} used to give the piezoceramic harder electrical properties also tend to inhibit grain growth during the sintering process, thus leading to a smaller grain size in the hard formulations.

The homogeneity was determined from the grain shape and size and of course from the contrast uniformity across the samples surface. However, evidence of some second phase was found in samples, KKG, and KWK. Sample KKG was the Hard type Ferroperm material and sample KWK, the Soft Advanced Ceramics Ltd hot pressed material. Detailed chemical analysis of these phases was not conducted but both were of a lower contrast than the surrounding material ensuring it to consist of a lower average elemental atomic number.

Energy dispersive X-Ray Analysis

[1] Average Grain size = 1.56 C/MN where C is the line length, M the magnification of the print and N the number of grain intercepts along the line length.

A semi-quantitative energy dispersive X-ray (EDX) analysis was carried out on the samples to determine differences in composition. Generally this type of analysis on such complex oxides is difficult because of the lack of resolution and sensitivity of the method, however it does establish that all the materials are PZT compositions, and all contain strontium. The ratio of Pb:Zr:Ti was similar for all the materials, with the most significant difference being the increased level of Sr in the 5H material. The addition of isovalent strontium increases the dielectric constant and the d_{33} at the expense of a reduced curie temperature. This is indeed the electrical specification of a 5H Navy type VI material. Levels of additives less than one percent are difficult to detect using EDX, and are even less sensitive when peaks are overlapping, such as Nb between Zr and Pb peaks. In order to confirm the presence of dopants in small quantities such as Nb other techniques such as XRF must be used.

X-ray diffraction

Both of the hard samples and the 5A material showed lines corresponding the JCPDS pattern 33-784 which is a tetragonal and has a composition close to the morphotropic phase boundary (mpb) in the pseudo binary $PbTiO_3$-$PbZrO_3$ system (figure 14). The 5H material has similar crystallography, however the splitting of the 002 and 200 peaks is not pronounced and it is more likely that a slightly increased Zr content in addition to the increased Sr content has pushed the composition to the rhombohedral side of the mpb.
Comparison of the poled and unpoled patterns show the texture induced by poling (figure 15). In the unpoled state the intensity of the 200 (a-axis) peak is more than twice the 002 (c-axis), but on poling the intensities of the two peaks are roughly equal. It is also interesting to note that for the hot pressed material the intensity of the 002 axis is much higher than the 200 peak even in the unpoled state. This is evidence for texturing during the hot pressing process.

CONCLUSIONS

The electroceramic materials that are to be used in the DTI programme, CAM07, have been imaged using scanning electron microscopy. Salient microstructural features, pertinent to the remainder of the performance degradation programme, have been interpreted from micrographs taken at various magnifications of polished and etched surfaces. All materials, hard and soft, contain a certain small level of closed porosity, contain essentially single phase material possessing a mono-modal distribution of equiaxed grains. There is some evidence of liquid phase assisted sintering observed from small quantities of grain boundary residue present in some of the samples. Both poled and unpoled materials show evidence of a domain structure within individual grains. Due to the nature of the sample preparation it is not clear whether the poled materials have suffered reversion to their unpoled state. The information contained within this report will be of value during the remaining research contained in the CAM07 programme.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the support of DTI through its Materials Measurement Programme for this work.

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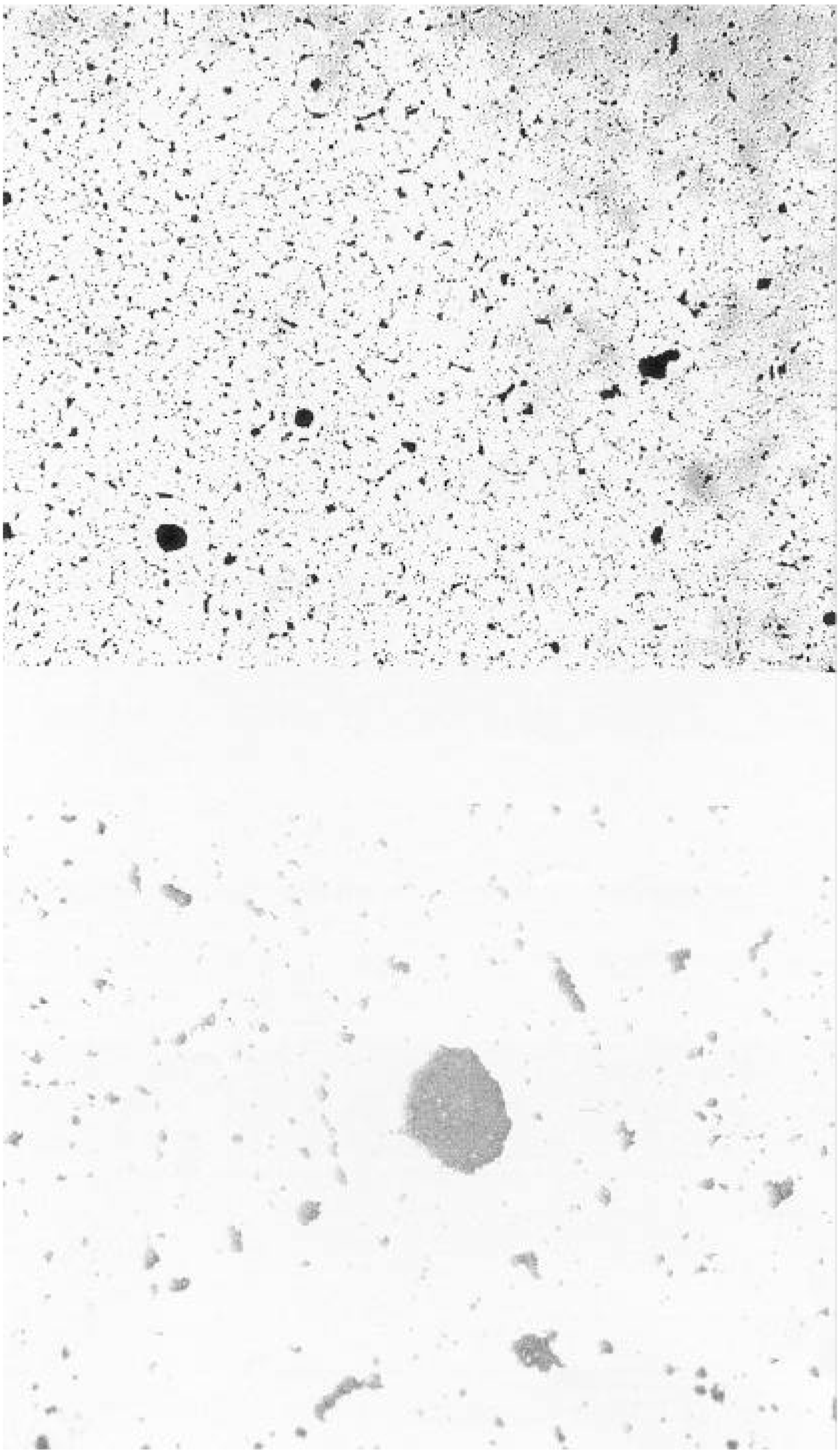


Figure 5 Optical micrographs of soft PZT material KTY at magnifications of x50 and x200 showing porosity probably caused by agglomerates in the spray drying process.

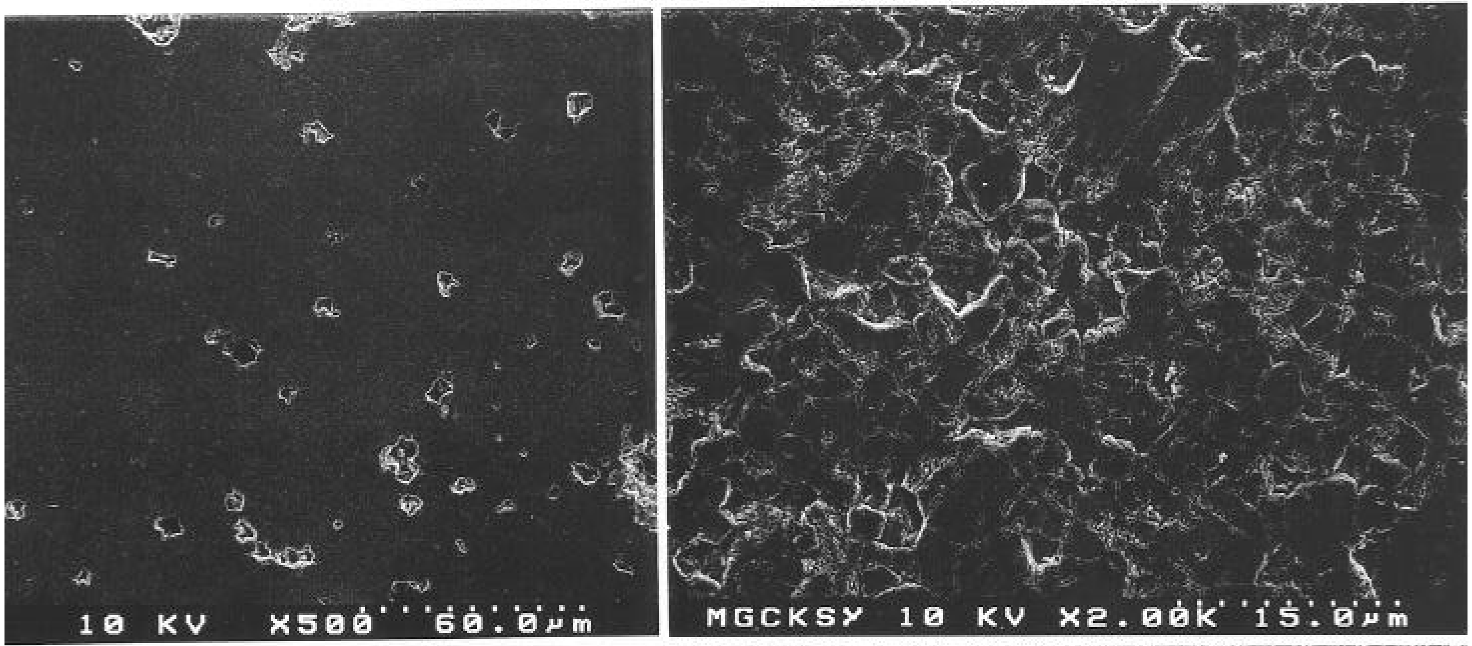


Figure 6a) Low Magnification Image of Sample KSY - Soft Piezo Ceramic - Morgan Matroc TPD & b) higher magnification of etched surface.

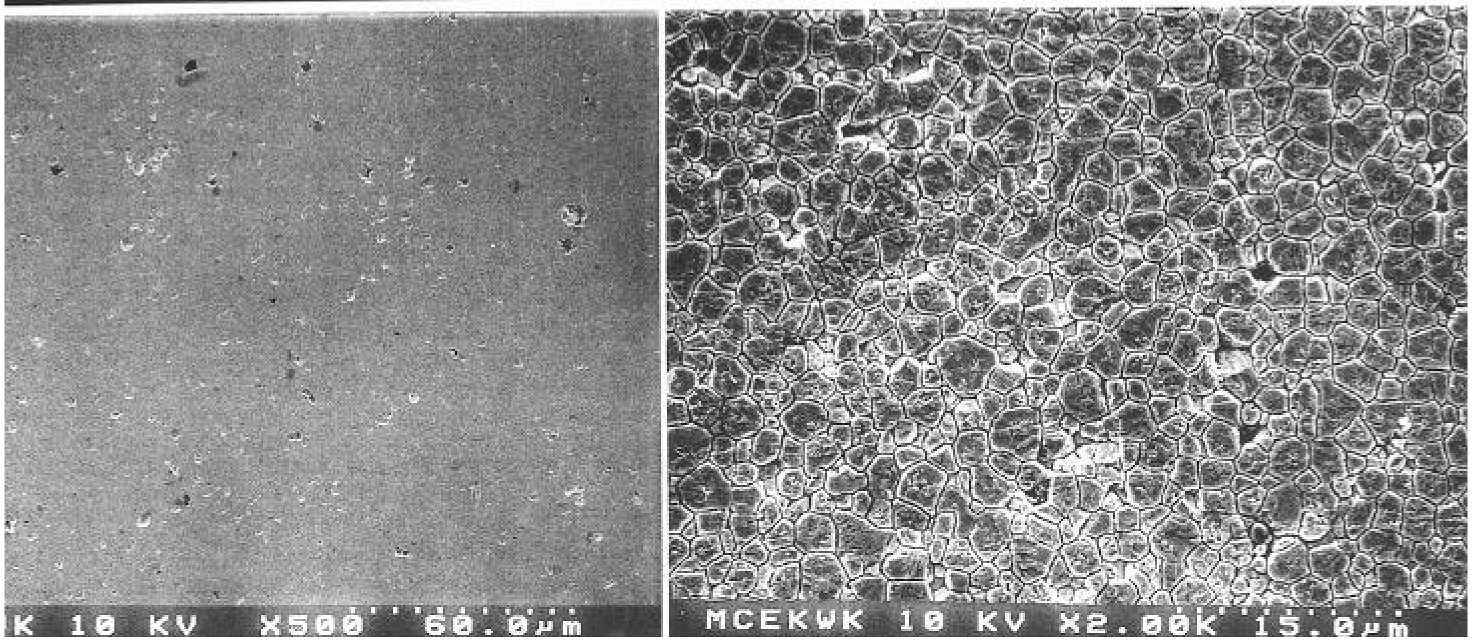


Figure 7a) Low Magnification Image of Sample KWK - Soft Hot Pressed Piezo Ceramic - Advanced Ceramics & b) higher magnification of etched surface.

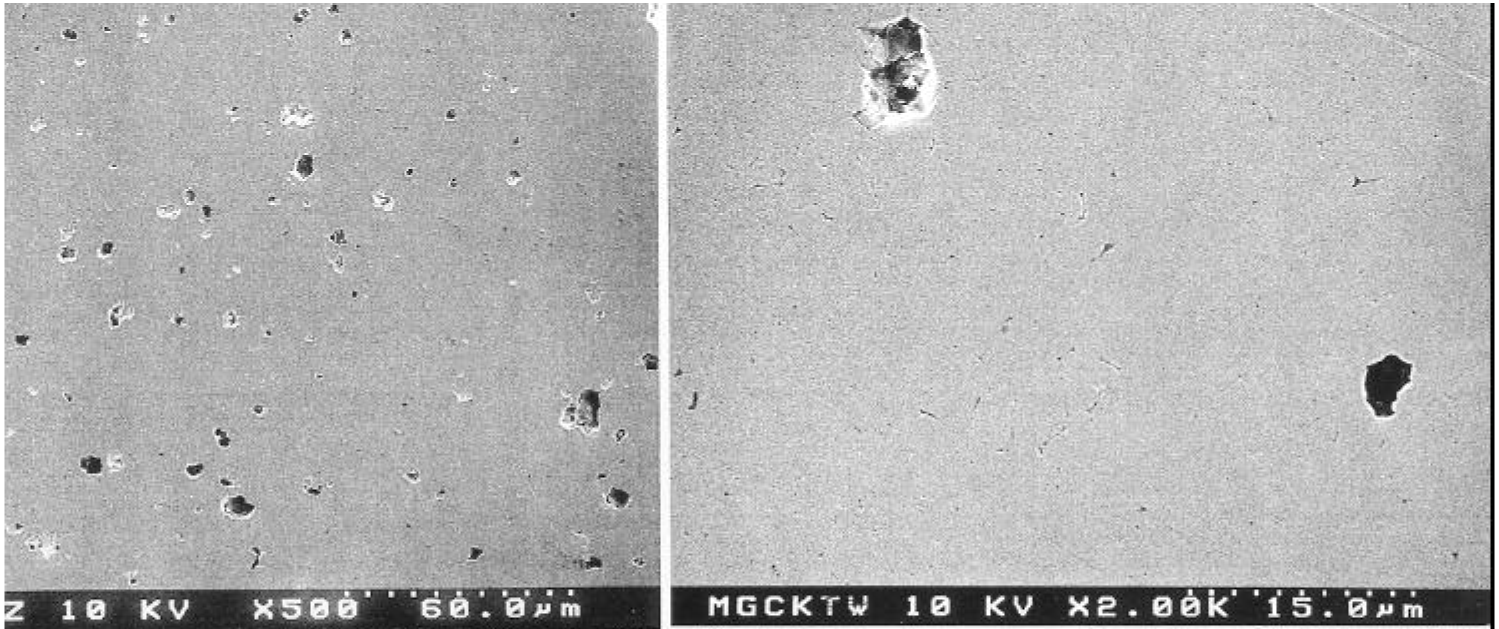


Figure 8a) Low Magnification Image of Sample KSZ - Hard Piezo Ceramic - Morgan Matroc TPD & b) higher magnification of etched surface.

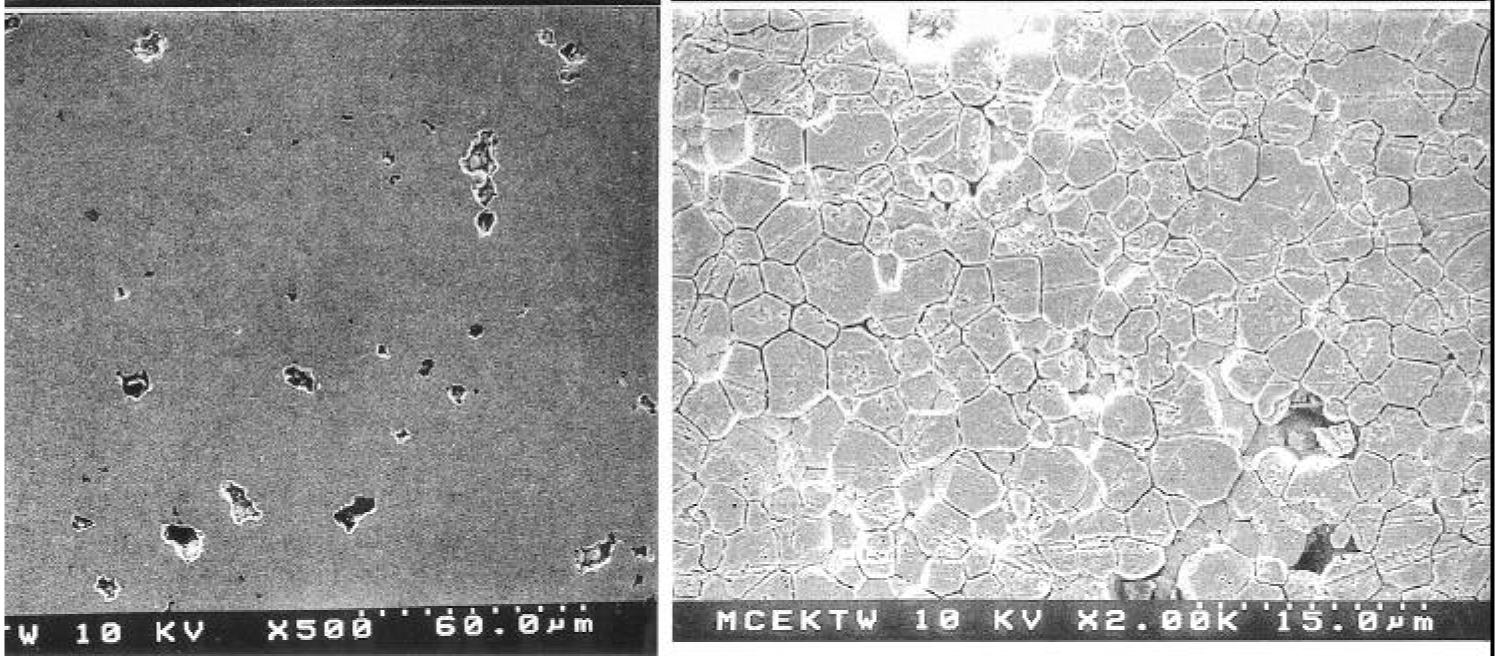


Figure 9a) Low Magnification Image of Sample KTW - Hard Piezo Ceramic - Morgan Matroc TPD & b) higher magnification of etched surface.

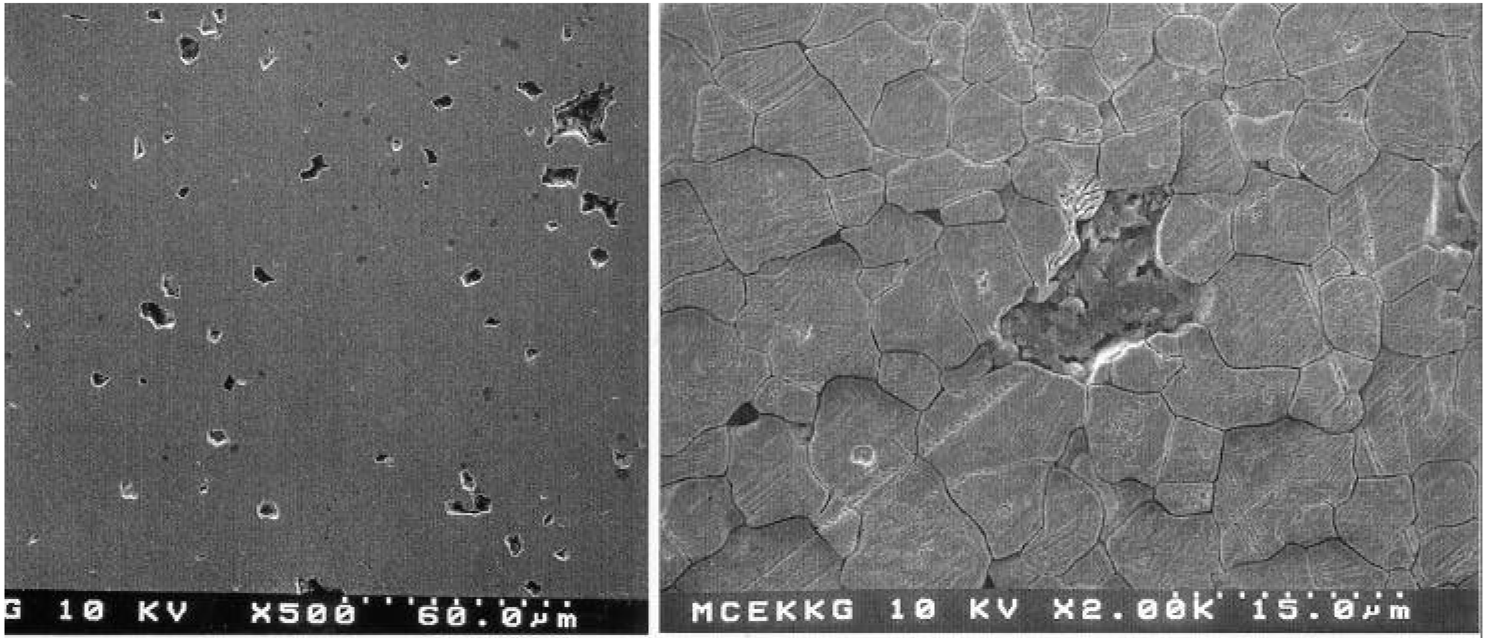


Figure 10a) Low Magnification Image of Sample KKG - Hard Piezo Ceramic - Ferroperm & b) higher magnification of etched surface.

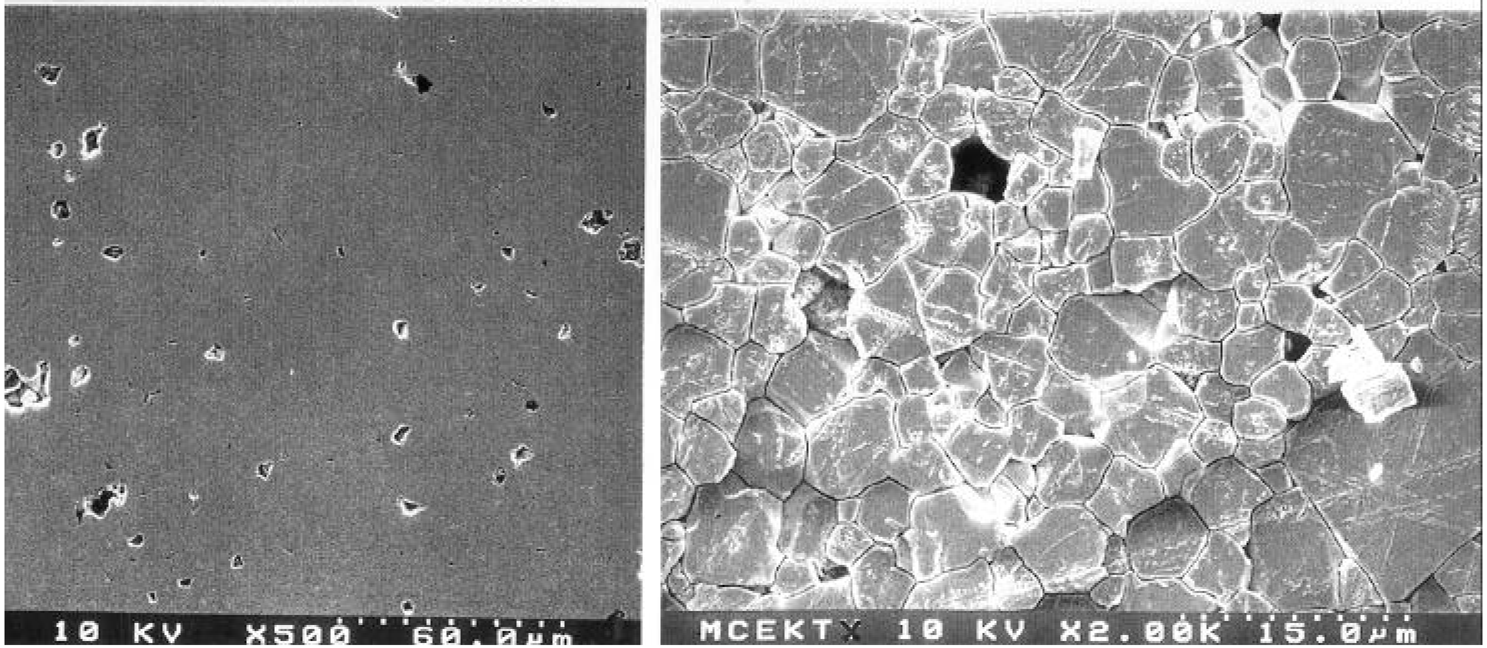
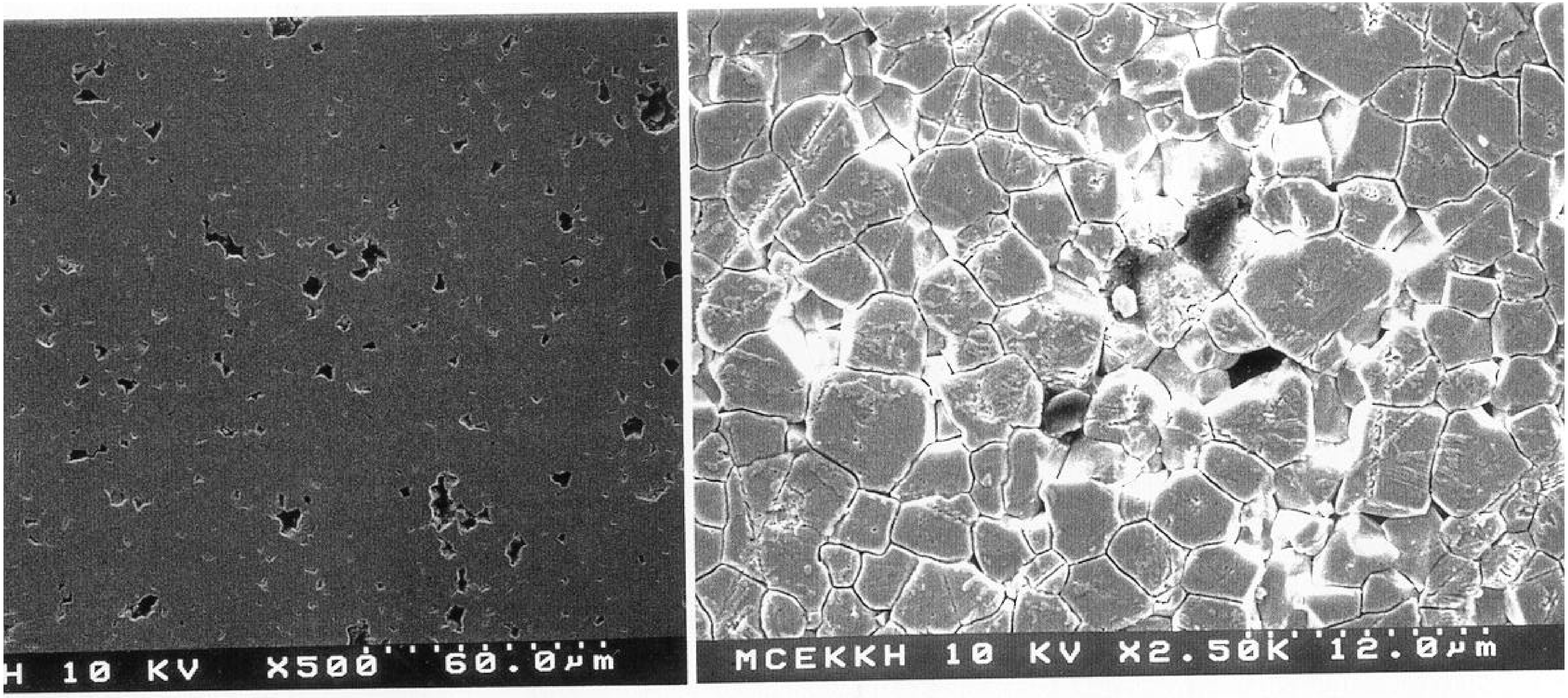


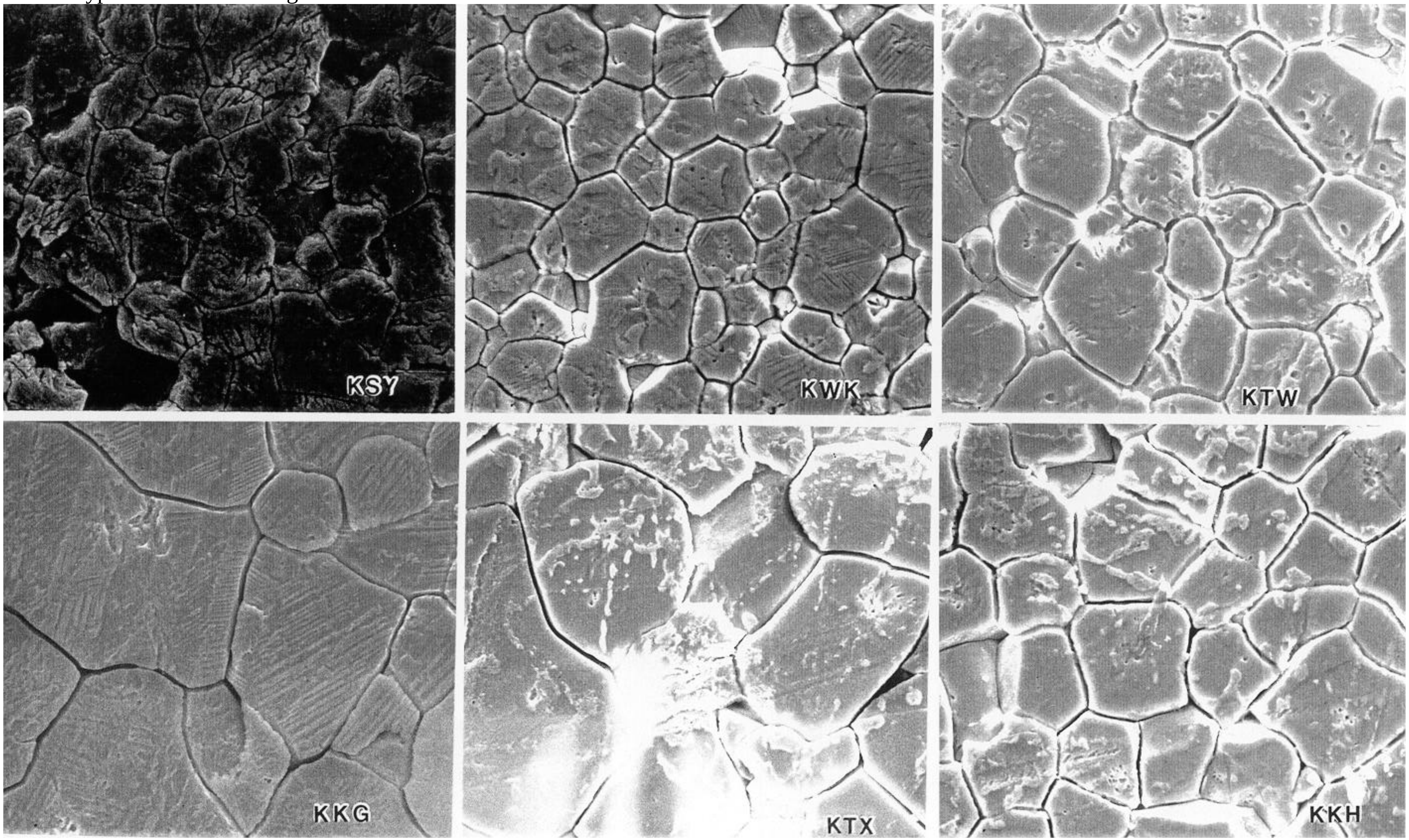
Figure 11a) Low Magnification Image of Sample KTX - Soft Piezo Ceramic - Morgan Matroc TPD & b) higher magnification of etched surface.



(a) (b)

Figure 12a) Low Magnification Image of Sample KKH - Soft Piezo Ceramic - Ferroperm & b) higher magnification of etched surface.

Figure 13: Scanning Electron Micrographs of etched surfaces at a magnification of 5000 times highlighting variation in grain size and evidence of domain type structures within grains.



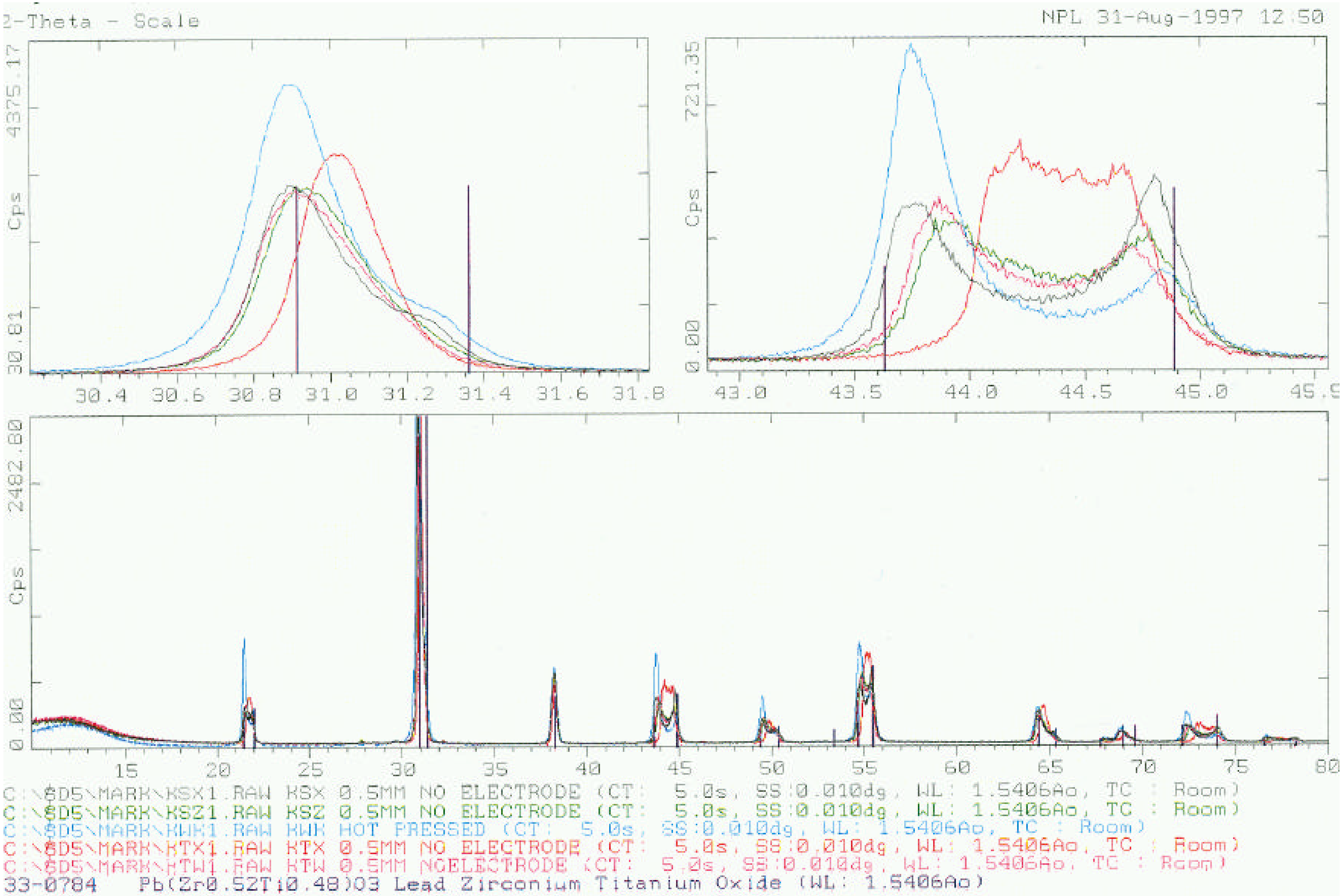


Figure 14 X-ray diffraction patterns of materials for CAM7

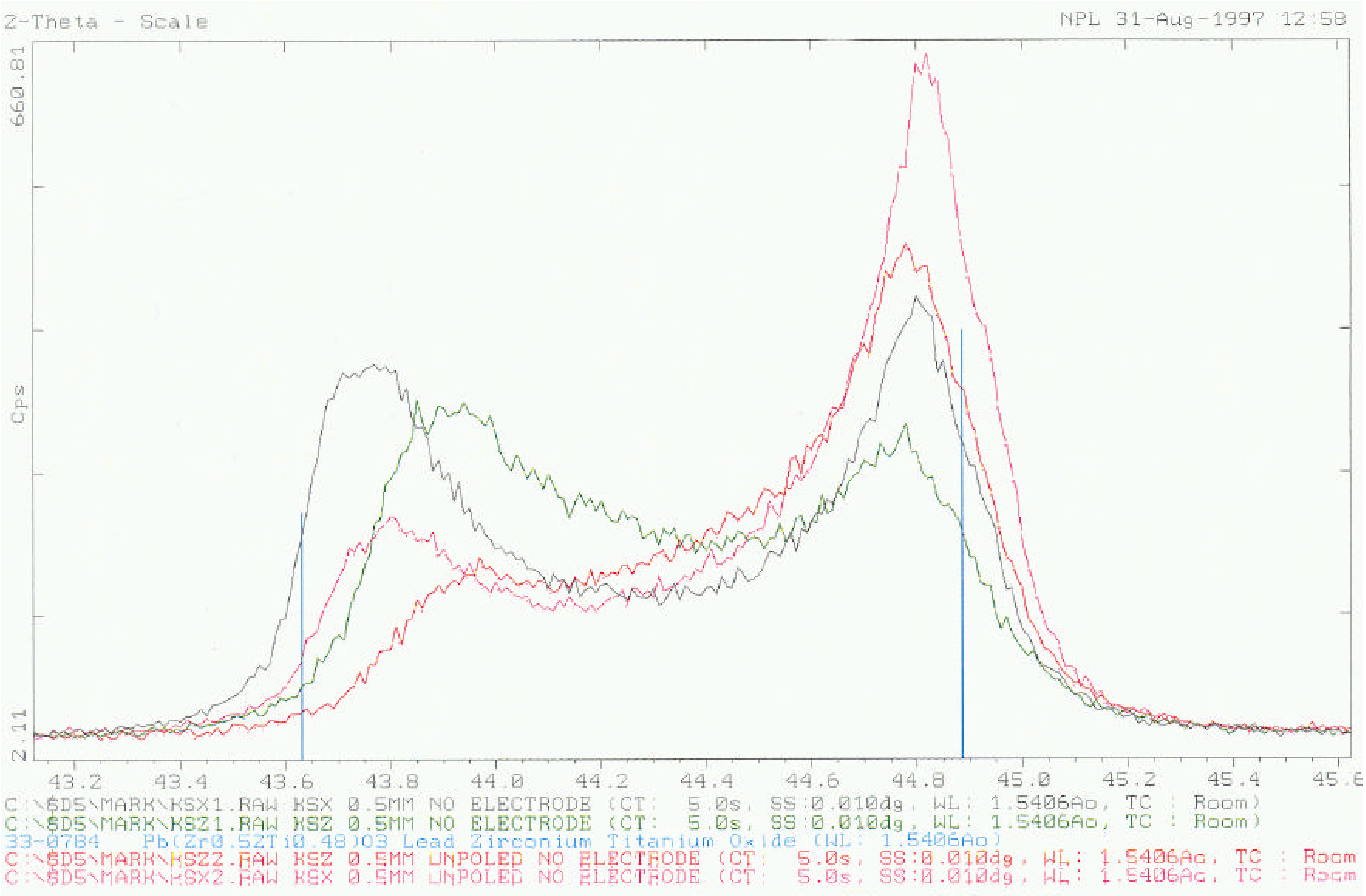


Figure 15 X-ray diffraction patterns of poled and unpoled materials for CAM7