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New Piezoelectric ceramics with T, > 1O(KFC for Operation up to 800”C

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Abstract

The goal of this project has been to develop a piezocerarnic which can be operated to higher temperatures than existing piezoelectric polycrstalline materials. The properties required of the ceramic are density >95 % th., d_{33} >7 pCN_[l], k_t >0.3 and both resistivity > 10^3 S2 and zero oxygen loss at < 800”C. The materials selected are lithium niobate, $LiNb0_3$,’ based ceramics. The former is only available as a single crystal and is limited to use below 650”C by oxygen loss and the later limited by low resistivity. By following an in depth study of the effects of composition and of the fabrication conditions, from powder to ceramic and electrode ceramic, a polycrystalline material that can operate at SOO”C without depoling and without oxygen loss have been identified. In addition a compatible electrode material has been developed for operation over this temperature range. The investigations have been supported by two material end users, who have tested the materials *in two high* temperature prototype devices, an accelerometer and an ultrasonic probe.

Introduction

There is an ever increasing drive to develop piezoelectric devices that operate at high temperatures. At the time this program commenced the range of materials available for operation at working temperatures above 250*C was very restricted and of these, only LiNbO~ single crystals and tourmaline were suitable for use above 500”C.

A/though tourmaiine is stable to 700°C its use is limited by its poor piezoelectric properties, (k~ ~ 0.1 and dss = 1,5 pCN_[l]) as weil as being expensive and difilcult to obtain in high quality. Thus, at present, the main contender for high temperature applications is single crystal LiNbOs. However, despite having a high Curie temperature of 1200”C, the operating temperature of LiNbOq is limited to < 650*C. Above this temperature oxygen is lost to the environment, increasing the conductivity of the crystals. To increase the operating temperature range of piezoelectric materials it is necessary either to find a more stable material or to stabilise LiNbOs against oxygen loss.

Little work has been reported concerning the fabrication of $LiNb0_3$ bulk ceramics. Instead most research has been concentrated on the production of thin films for use as wave guides and surface acoustic wave devices In this area, the preparation of high density, fine grained microstructure have successfully been achieved by a number of techniques, including; sol-gel, rf sputtering and chemical vapour deposition. In contrast, the preparation of dense bulk ceramics of pure LiNbOs has not been possible using the mixed oxide route. Maximum

densities obtained have been as low as 80°A of the theoretical density. To date there are no reported results of $LiNb0_3$ bulk ceramics being prepared from chemically prepared powders, although, powders have been prepared from alkoxide precursors.

Experiments have shown that the stability of LiNbOs single crystals against o~gen 1oss can be improved to 700°C by additions of Na. Here, efforts have been made to improve the temperature stability of $LiNb0_3$ ceramics through adjustments in composition, processing and microstructure. Ceramics have been chosen for their relative ease of fabrication and alteration of composition as well as reduced in fabrication cost as compared to single crystals.

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In the course of the compositional study the most promising compositions were determined as those based on the lithium sodium niobate, Within this Na_20-$LiNb0_3$ system a series of compositions with the stoichiometric compositional formula Lil.xN%NbOs was studied ftily,; these are commonly referred too as LNN:x for brevity, where x denotes the atomic percentage sodium.. In order to have Tc > 10OO°C, the range of values of x were from O to 25.

Precursor powders have been prepared by three separate routes, namely, the traditional solid state reaction or mixed oxide method and two non-traditional chemical routes, a sol-gel route (see Figure 1) and an inorganic chemical route (see Figure 2). Mixed oxide powders makes use of high purity raw materials of lithium and sodium carbonates and the niobium oxide powders. Reactive powders were prepared by first batching and then milling the raw materials in isopropanol for 5 hours followed by drying and calcination at the temperature/time appropriate to the system. A comrnhwtion process (either by ball or attritor milliig) reduced the agglomerates to a desired size and distribution and binder was added to aid compaction and formation of the green body.

The processing route represented in the schematic in Figure 1 has been successfully used to prepare (Li,Na)NbOz gels and powders with different Na contents tlom O*A up to 100% to include a more comprehensive study of the overall behaviour of materials in this system. Gels were dried as usual and caicined at 350°C/ 3 hours for HT-XRD and at 700°C/ 10 hours for Differential Scanning Calorimetry.

The optimum sintering conditions were determined for each composition and powder source. In some cases the samples were subjected to a post-sinter hot isostatic pressing, with an atmosphere of 20°A Oz and 80°A Ar, in an efFort to increase the bulk density.

X-ray powder d~fiaction analysis of sintered ceramic discs confirmed the observations from the phase analysis performed on all the powders prepared.

Further to the phase analysis of lithium niobate samples a full structural characterisation of the samples was performed using a Philips EM430 transmission electron microscope (TEM), by a combination of selected area electron diffraction and high resolution imaging techniques.

In an attempt to obtain the widest possible characterisation of piezoelectric, dielectric and elastic properties, for all the mixed oxides LN based ceramics, efforts are concentrated on the use of the iterative method recently developed by C. Alemany et al. ‘l]. To facilitate the measurements of dielectric and piezoelectric properties at high temperature a complete measurement system was created. Two designs for high temperature cell (one open, one closed to allow work to be carried out in a specific atmosphere) were developed and constructed and *in* addition two flunaces and corresponding temperature controllers were also assembled. Computer programs were developed for controlling a HP4194A impedance analyser, storage, conversion and dispiay of impedance (modulus and phase) data, from 102 Hz to 100 MHz and

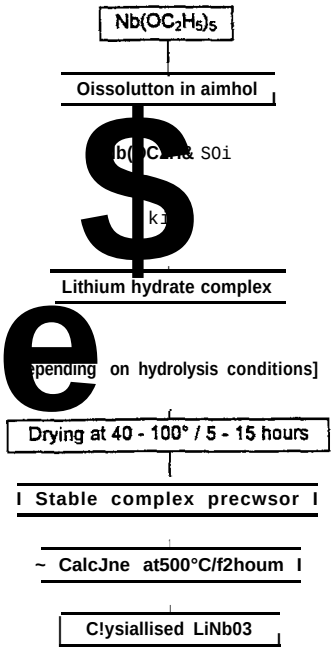


Figure 1: "Sol-Gel Chemica!" preparation route

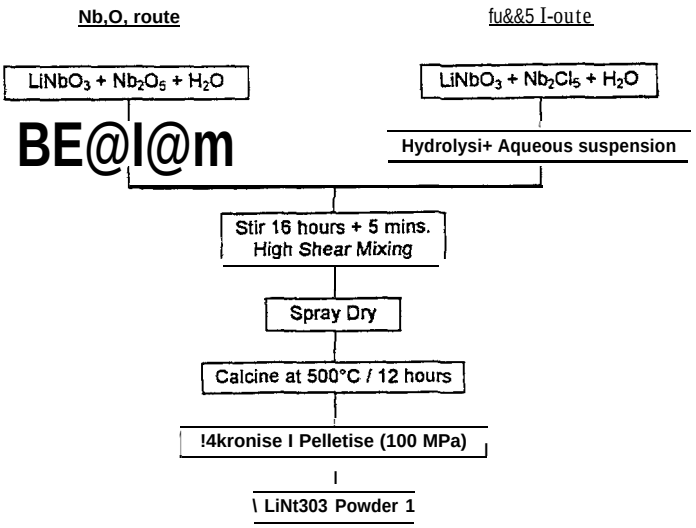


Figure 2. "inorganic Cheinicai" preparation routes.

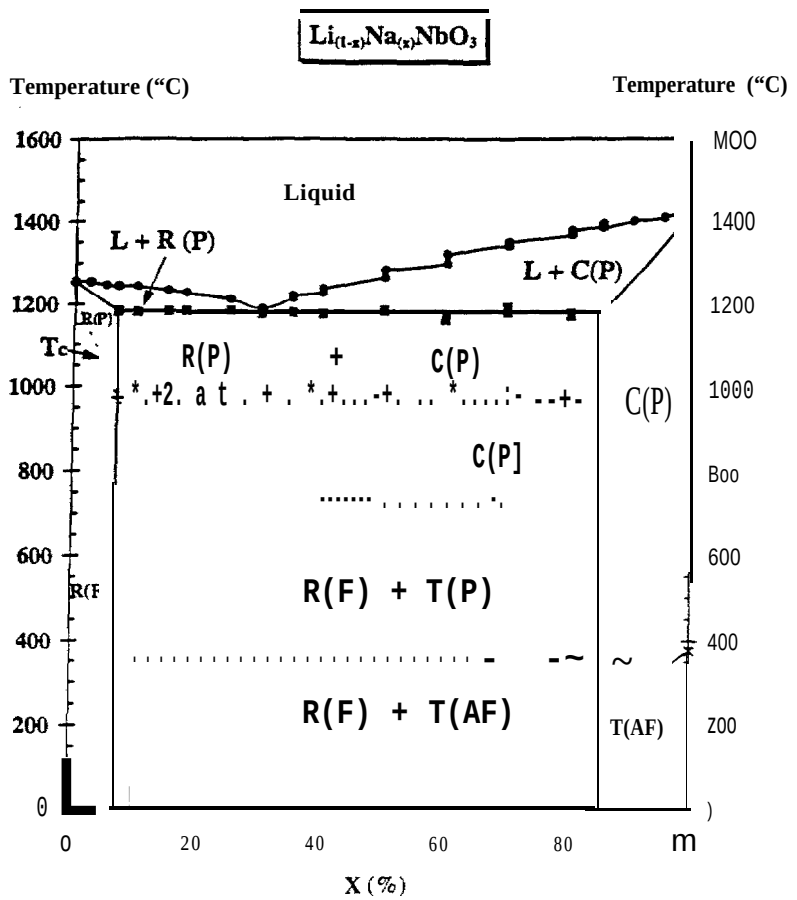


Figure **3:** *Phase diagram for Lil.JVaJVbU3 ~stern: R@), ~kombohedrai ~araelectric); RF) &hombohea'rai @jerroelectric); T@), Zetragonal Earaelec@ic); T@F), ~etragonal (A_nti-~erroelectric) and C(P), @bit ~araeiectric,).*

fiorn 10O°C to 105O”C. From this data, the values of 8’, e”, o,. and A4 (dielectric modulus) have been calculated.

Quantitative oxygen loss anrdysis was performed on sintered discs up to 800°C using a Systech ZR893 zirconia oxygen cell with a detection range of 100% to 0.01 ppm.

Powders and ceramics were characterised by optical, scanning and transmission microscopy,

A study of the temperature behaviour of the isotropic quasi-static (I - 10 Hz) elastic modulus was carried out cm unpoled LNN ceramic samples (with 15, 18 and 25°A Na). The elastic modulus was determined by the three points bending test on rectangular bars, at increasing and decreasing temperature with a 5°C/ minute rate, Loads of 10 mN have been applied in order to give mechanical stresses of 5.105 Pa.

Results *and Discussion*

The result of this investigation is that all of the sodium-doped lithium niobate sample studied are found to exhibit a high degree of twinning, whereas *the* undoped lithium niobate samples are twin free. The obsenmd twin planes have been characterised in terms of the pseudo-cubic modification of the unit cell of LiNbOg (a = b = c = 7.5292 ~ and ct = B = 7 ⁻86.2720), as oriented along the (1OO)C crystallographic plane. It would appear from this work that the twin planes form a mechanism by which the LiNbOs structure may accommodate the lattice strain induced by the substitution of Li^+ by Na^+ ions in the crystaI lattice.

In a post sintering process the various compositions were subjected to Hot Isostatic Pressing, HIP, in an atmosphere of 20% Oz and 80% Ar in an effort to increase the bulk density. Due to the inherent high and interconnected porosity of the sintered ceramic the HIPing process did not increase the density significantly, however, the strength and room temperature piezoelectric properties were to some extent increased.

DSC analysis was carried out between room temperature and the melting point on materials with compositions covering the whole $LiNb0_3$-NaNbOs range. The results confirm the solid solution range as well as the liquidus and solidus cu~es [eutectic composition close to 23°/0 mol N% eutectic temperature: 1180”C). In addition, three invariant lines were obsemed at about 1140”C (the possible Curie temperature), 970”C (phase transition) and 350°C (only for Na-rich samples). A tentative interpretation of the phase diagram is given in Fi~re 3.

Table 1 represents a selection of the findings for the dielectric and piezoelectric properties obtained from LNN samples at room temperature. From the prelimina~ studies for the lithium-sodium niobate (LNN) composition it has been noted that there is no significant increase of the electromechanical coefficient with increasing the sodium contents up to 25 at.^{O}/O, therefore, the study of thermal behaviour was extended to include the fill range of modified and the unmodified LNN ceramics. As a consequence of the HIP process an increase in the piezoelectric response (higher k, d_{33} and h_{33}) and lower dielectric losses was observed in the three samples.

Figure 4 shows the comparison of permittivity, .s’, and A. C-. conductivity, a, as a finction of the temperature compared for a set of samples measured at 1 MHz. SEM obsemations indicate that the differences in porosity and grain size in this ceramics are not significant between samples. An increase in s’ is observed with corresponding increasing in Na content. Figure 5 shows the thermal behaviour of e’, s“ and u for measurement frequencies of 1, 10, and 100 EHz for LNN:7Y0 Na, measured with increasing and decreasing temperature. The behaviour shown in this figure are common to all the ceramics of the above series. From the study of permittivity as fimction of temperature it is evident that all the ceramics exhibit

anomalies, consisting of a wide maximum, in the vicinity of 300°C and 450”C. These become more enhanced with both lower measurement fi-equency and as the Na content is increased. The temperatures at which these anomalies occur do not change significantly with the Na content or the measurement frequency. There is a continuous increase of E’ as the temperature increases from temperatures which is also dependent on the measurement frequency, It is a repeated observation that the anomalies in e’(T) measured with increasing temperature are more enhanced than those when measuring with decreasing temperature.

Sample	&33*	t a d (?'?')	d_{33} @2'v'j	k, (%)	A33 RF Em-1	-@f (C339	N, (kHZmm)
IAN 15 I080″C	51	1.0	5	4	5.3	7.6	1930
LNN:15 HIP	l\4710.7[9~9[H. o 19.511950						
LNN:15* 1040″C	‖53 I 1.4 I 11 I9 I 10.5 t 6.6 I 1970						
LNN:15* HIP#	49	0.9	12	10	12.6	6.8	1940
LNN25 1100″C	!6011.11 9{9I10.7I12.5I 2150						
LNN25 HIF	55	0.5	11	12	15.6	16.4	2280

*].5 *aPA No + 0.1 wt!% h% + 0.1 wtf% Mg.*

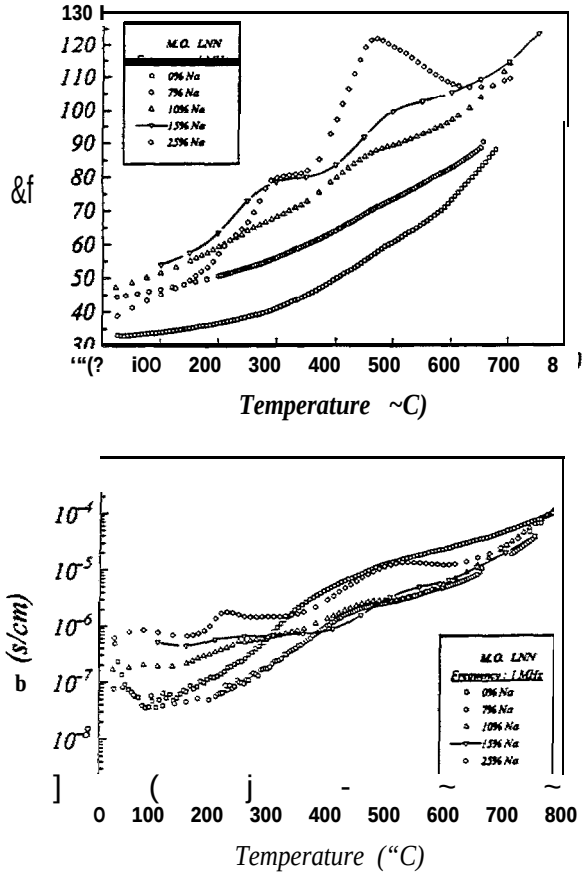
**Measured with a* $V_{=tiil\text{•}tiO}$. *= 0.1 volts: all others* $V\sim_{CillofiO}$. *= 0.5 volts*

Ta/n’e 1: Room temperatzire pkzoe!ectric and dielectric properties at resonance of mixed oxides LNN sintered and HIPed ceramics.

The data for conductivity versus temperature indicate a strong minimum at low temperature (=140”C), which becomes more enhanced the lower the frequency. As the content of Na increases, the frequency at which this minimum disappears becomes lower. The materials have a negative temperature coefficient, NTC, behaviour below 140°C and a positive temperature coefficient, PTC, behaviour above, indicating the competition between two ionic conduction mechanisms.

The plot of logs’ and logE” as a finction of the ilequency, as calculated horn the impedance modulus and phase measurement are represented in Figure 6 for LNN7 material (18’% Na - Nb doped). What is observed is a universal dielectric response in which the ratio s’/ s” remains constant as a fbnction of the frequency. For all the samples s’ and s” show a strong dispersion, revealing a behaviour of the type: e’, e” = Q“-l, where n <1. The value of n decrease as the temperature increases. It is currently considered that for n <. 0.5 a carrier hopping mechanism leads to the behaviour observed in the dielectric losses. For lower n values, at higher temperatures, the D.C. conductivity begins to play a role on this behaviour.

Figure 7 shows the thermal behaviour of the quasistatic elastic moduli of LNN:25 sample. LNN samples with 15, 18 and 25% Na exhibit similar behaviour, characterised by a strong hysteresis between 400°C and 800°C when measurements are made with increasing and decreasing temperature. With increasing temperature, there are soft anomalies at =300 and =500°C, followed by a sharp increase up to six times the value found at *morn* temperature at =800*C, at higher temperature there are no marked change in values. With decreasing temperature, there are two anomalies at =800”C and between =600 - 400°C, followed by a sharp decrease at =400°C. There is a noticeable increase in the elastic modulus of the samples.



Figwe *4: Comparison ofpermittivi& E', andA.C. conductivi~, g as u function of temperature (1 MHz).*

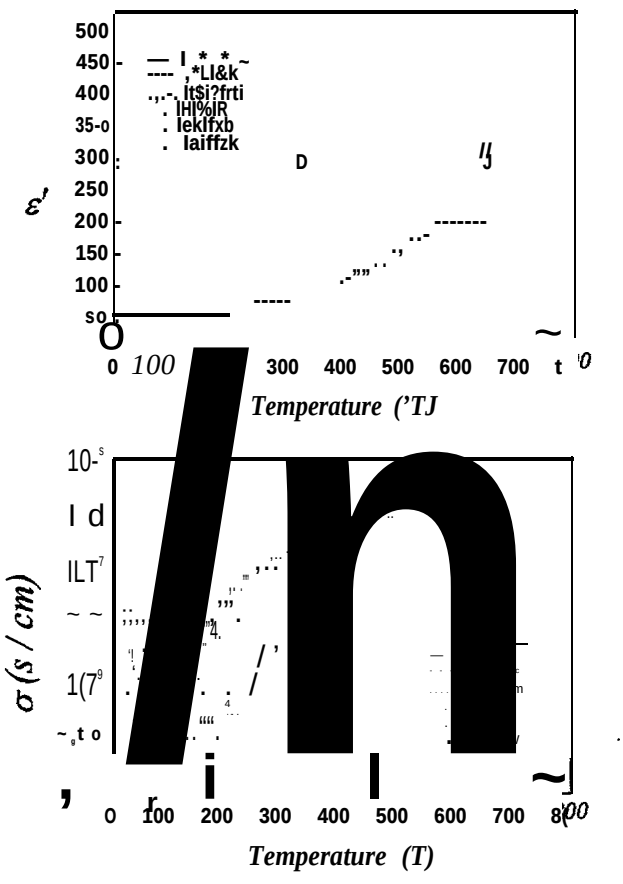


Figure 5: Comparison ofpermittiviy, E: andAC, G conductivip as a function of temperature at 1, 10 and 100 kHz

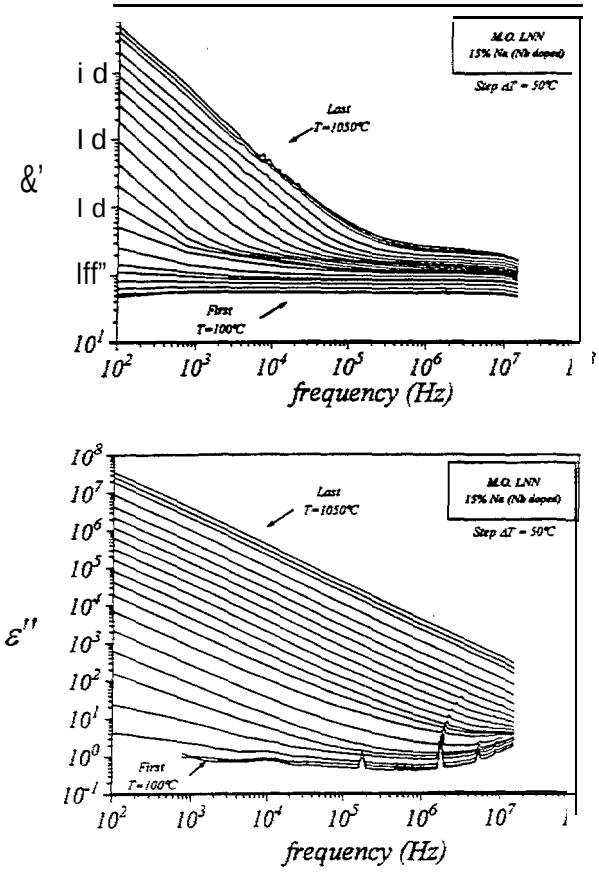


Figure 6: Plot of log E', and log s" as a function of thej-equency.

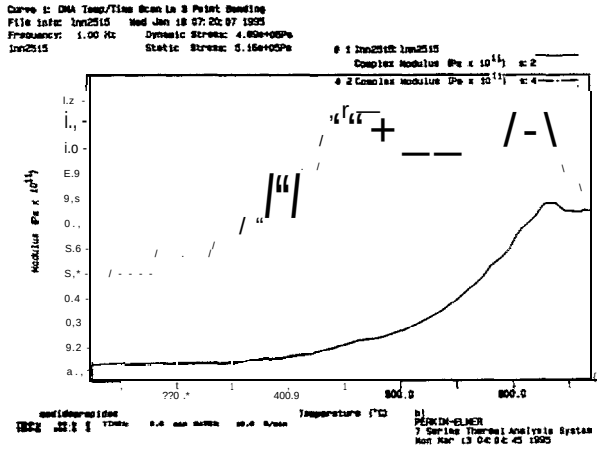


Figure 7: Thermal behaviow of the quasi-static (1 - i O Hz) elastic modulus.

at room temperature after the thermal cycle .

The normal thermal behaviour for the isotropic elastic modulus of a solid is that of a continuous decrease as a function of the temperature. However, when the solid experiments a structural phase transition, *there is* a sharp increase of the modulus when heating in the vicinity of the transition temperature. This is very dependent on the magnitude of the structural modifications that take place in the transition and it can account for up to 20-30°/0 of the value of the elastic modulus. The soft changes on heating observed at 500*C can then be interpreted as a consequence of a phase transition, that gives place to dielectric anomalies at the same temperature. In this particular case the transition occurs with a change of the spontaneous polarisation of the phases together with the structural change. At this temperature the polarisation change couid account for a 12- 15°A change in the elastic modulus, which can not be solely attributed to the very smrdl change of the structure parameters at the transition '2]. The sharp and significant increase of the elastic modulus at 800°C indicates a ferroelastic character of the samples, which is supported by the strong thermal hysteretic behaviour. The hysteresis indicates that the structural change, taking place when heating, is fixed in the interval i?om =800 to =400°C and rearrangement takes place only below this temperature. A corresponding dielectric anomaly is not observed at 800°C, probably due to the samples conductivity at this temperature.

Figure 8 shows the thermal behaviour of the following properties for as sintered and HIPed LNN ceramics with 25% Na: electromechanical thickness coupling coefficient, kt , elastic constant, $c33^D$, piezoelectric constant h_{33}, permittivity at resonance frequency E^S33, frequency number, N_t, mechanical Q factor, as defined by Q_M = real(css~t imaginary(cqs~. The results of the measurements show that all LNN mixed oxides ceramic samples are piezoelectric up to temperatures of 800*C or above. Attempts to apply Alemany's method '[2-4] to find the temperature dependence of the piezoelectric, elastic and dielectric complex coefficients were not successful for all the samples or at some temperatures for some samples. The results for LNN mixed oxides ceramics with 7, 10, 15, 18 and 25?40 Na show some common features:

i) The electromechanical thickness coupling coefficient decreases as a fl.mction of the temperature up to a temperature in the range of 350- 450°C, in coincidence with the first observed anomaly in the dielectric measurements, and increases above it.

ii) The elastic constant $C3s^D$ decreases very slowly up to 300- 350°C and above this temperature region increases sharp and continuously.

iii) The piezoelectnc coefficient shows similar behaviour to that of the electromechanical coupling factor described in i).

iv) The perrnittivity measured at the resonance frequency, show a good comparison with the measurements taken at different frequencies, with anomalies also obsemed at $30C1^0$C and 450- 500°c.

v) The thickness resonance shows an important fi-equency shift of the spectra to higher frequencies at temperatures of 300- 350°C, which coincide with those seen for the dielectric anomaly. Below this range of temperature the shift in the resonance spectra is smaller and is towards lower fi-equencies, In the expected working range of the ceramic, 800- 900*C, there is a small displacement of the resonance spectra. At room temperature, N!s 1500-2000 kHz.mm, whereas, at 800°C Nt = 2500-3000 kHz.mm for all the LNN materiais.

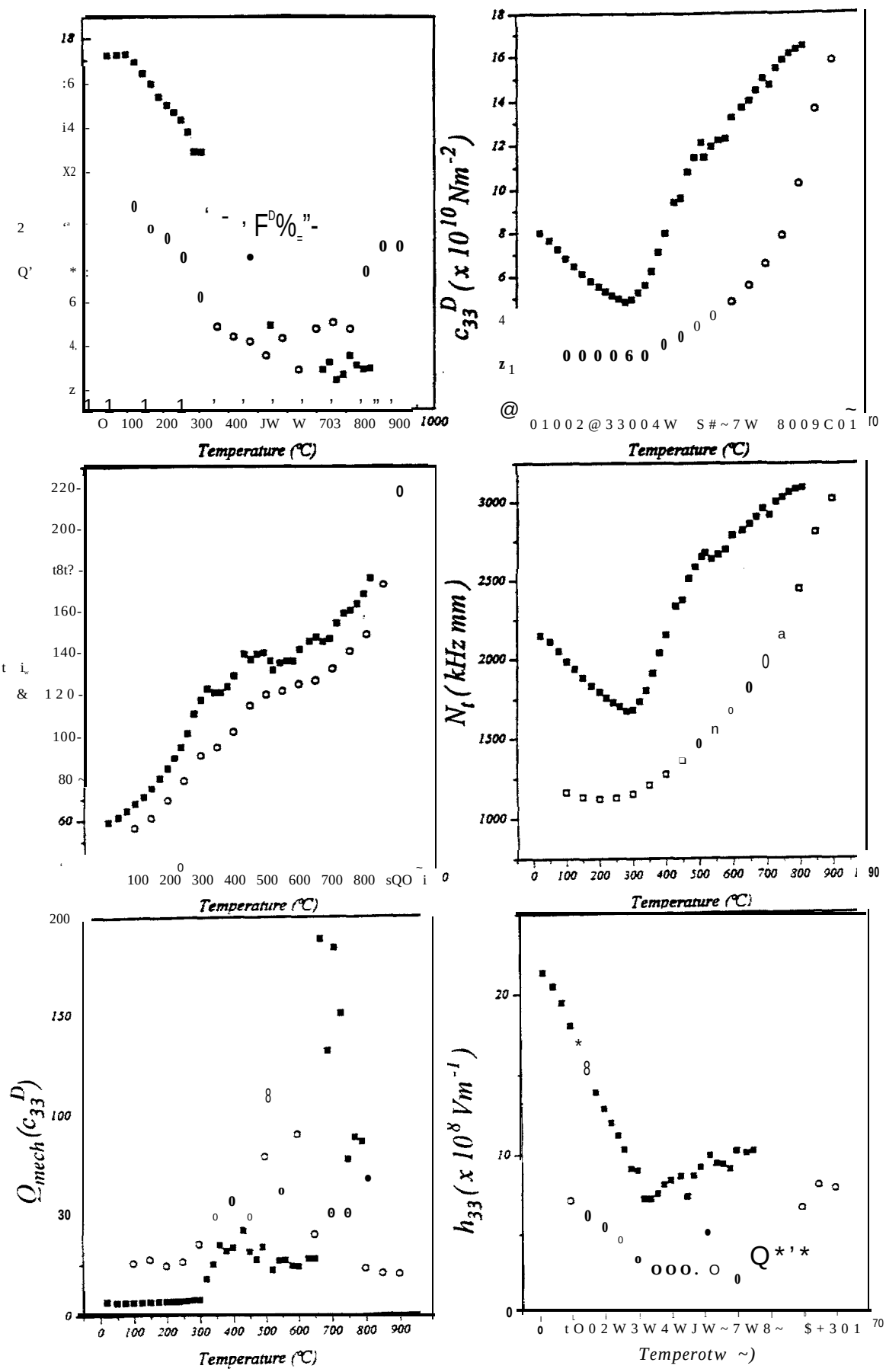


Figure 8: Therntai behvmw ofk:, C33^{D}, E 33', Mt, ~nwh and l?Hfor sintered and HIPed .LNN:25% ceramic. B Sintered and o Hot lsostizticaiiy Pressed

vi) The mechanical Q factor, defined as Q_M = real(c_{33}^D)/ imaginary(css~, which considers only the purely mechanical contribution and is not comparable with the Q_M calculated in IEEE standard piezoelectric characterisations, shows a maximum over the temperature interval 350- 45V'C.

In comparison with the corresponding as sintered ceramic, the post-sintering HIY treatment produces what can be considered as an homogenizing effect that results in a softening and widening of piezoelectric, elastic and dielectric responses as a fimction of the temperature.

From the data collected over the fill range of compositions it can be concluded that with increasing the Na content an increase in the room temperature piezoelectric coefficients is obsewed. However, this also results in a corresponding reduction in the temperature stability.

All the ceramics studied show piezoe[ectric response up to temperatures of 800"C or above, with typical values, at SOO°C, of kt and hss of 7- 12°/0 and 6-10 X10^8 V.m^{-1} respectively. This, together with the resistivity of =$10^{\$}$ ohms.cm at this temperature, makes them interesting materiak to be used as high temperature transducers. The main draw back for these materials being the change of the electromechanical parameters as a fimction of the temperature.

For increasing Na content, the associated reduction in thermal stabiiity can be correlated to the increasing content of a phase enriched in $NaNb0_3$ (NN). It has been previously reported that for pure NN '[2] and for LNN '[3] with Na substitutions from 12°/0 to 85*A, two phase transitions have been observed below and above 37$0^0$C. The lower temperature transition involves a phase change horn antifen-oelectric - orthorhombic (pseudotetragonal) with slight dii%erences in the crystal structure. For the higher temperature a paraelectric-orthorhombic (pseudocubic) phase change has been reported. Both give rise to dielectric anomalies that are in good comparison with those found *h this* investigation. For the till spectrum of samples amdysed it should be note that the thermal stability is highest for the LNN composition with **7%'o** Na content.

It has been reported that for pure $LiNb0_3$ [4] a die~ectric anomaly was obsewed at 600"C which was interpreted as a transition between two ferroelectric phases and accompanied by an small change in the cell parameters of the structure. In addition, a second anomaly was found at 900"C which was associated with changes that occur in the domain structure. These could possibly explain the high temperature dielectric anomaly and rnechanica~ behaviour observed.

Finally, similar thermal dependence of the conductivity has been observed in sodium and lithium niobates and tantalates, due to a change in the type of conductivity of low mobiiity localised charge carriers, such us Li^+ or Na^+ vacancies, fi-om a tmnelling to a hopping conduction mechanism 'G- ']'.

A study was carried out on ceramic samples of Lil.XNaXNbOs nominal composition with x = 0.00, 0.05, 0.07, 0.10, 0.50, 0.75, 0.90 and 1.00 prepared by a sol-gel method and P2. Samples were poled at 180°C with fields from 50 to 100 to 100 kV/cm, depending on the Na content, the higher the Na content the lower the field needed.

Figure 9a) & b) shows the real part of the dielectric permittivity, s', and the conductivity, o, as a fimction of the temperature for different Na contents; measured at 1 MHz.

As the content of Na increases, the perrnittivity, e', increases. This is true for all the samples containing Li and the oniy exception is found with the pure NaNbOq sample, which is associated with the lower density of **d37°/0** of theoretical, as compared with the rest of the samples with densities between 93- 95°/0 of theoretical.

When measurements are made with increasing temperature, two anomalies, consisting of wide maximums, at s3 OO°C and =450°C are evident for samples with greater than 10"A Na (Figures 9a) & b)). These becomes more enhanced with increasing Na content and decreasing

fi-equency. The temperature at which the second anomaly occurs is seen to shifi to lower temperatures with increasing Na content.

For the pure NaNbOs samples the second anomaly appears with increasing temperature as a sharp jump at x360*C. For measurements with decreasing temperature this anornaiy appears at 250”C (Figure 10 a)). The NWOS samples show also an insight of an anomaly at 550°C (Figure 10 a)).

In Lil.XNa.Nb03 ceramic samples with x >0.10 the two above mentioned dielectric anomalies are observed separately only in measurements with increasing temperature. When measurements are made with decreasing temperature, these two peaks collapse in a wide one due to a shiil to lower temperatures of the anomaly at 400- 450°C, as shown in Figure 10 b) for x= O.50.

As shown in Figures 9 a) and b), there is a minimum at T * 150°C in the plot of A.C. conductivity versus temperature. This tends to disappear as the flequency increases and shifl down towards T - 10O°C as the Na content increases. The two anomalies observed in the permittivity at 250*C and 400°C are also found as local maximum in the conductivity for Na content of x >0.50. As illustrated in Figure 10 b) they become more enhanced as the Na content increases and as shown in Figure 11, for the sample with Na content of x = 0.75, the flequency decreases. The above phenomena are consistent with those shown by all the samples measured.

Piezoelectric characterisation as a fi.mction of the temperature was carried out for thickness mode resonance and for samples with Na contents x $^{=}$0.07, 0.10, 0.50, 0.75 and 1.00. For low Na concentration the piezoeiectric activity, i.e., a resonance spectra is found over the whole range of measurement, up to 700- 800°C. However, from x $^{=}$0.50, the resonance above s 400 - 450°C is so weak that it mrdces it impossible to calculate the piezoeiectric coefficients. VWhen measurements are made with decreasing temperature there is a certain recovery for the values of the piezoelectric coefficients. Only the x = 1.00 (NaNbOs) samples suffer a non-recoverable and sharp disappearance of the piezoelectric activity, and this occurs at= 300”C.

Results fiorn XRD analysis were used to characterise the phases present as the Na content increases from LiNbOs to NaNb03. For compositions between these two compositions, the difllaction patterns indicate the presence of only two other coexisting phases, namely, the solid solutions of LN~ and N&.

For pure $NaNb0_3$ material there is no structural or ferroelectrk transition reported in the temperature range from -200°C to 355”C. However, in this study of $NaNb0_3$ ceramic samples, a dielectric anomaly is observed at N370*C during the heating temperature cycle, and at =250°C with decreasing temperature. This is associated with a phase transition fhm antferroelectric - orthorimmbic to paraelectric - orthorhombic (A-P). The much softer anomaly observed at 53 O°C corresponds to a transition from a pseudotetragonal to a tetragonal paraelectric phases[2]. The paraelectric character of the high temperature phases is confirmed by the non-reversible disappearance of the piezoeiectric activity at this temperature. The slight increase of the temperature of the A-P phase transition as the Li content increases indicates the formation of a solid solution, NN_{-} with partial substitution of Na^{+} for the smaller Li’ ion, which has a limit at relatively low Li content (O. 90> x 20. 75), The ceramics with Na content of x = 0.75, 0.50 and 0.10 show comparable transition temperatures (450”C) indicating that they contain different amount of a NaNbOs solid solution with the same composition. Changes in the lattice parameters of $NaNb0_3$ by Li substitution were not detectable by XRD.

The different thermal behaviour (Figure 10 b)) of the perrnittivity for all the LNN ceramics when measurements are made at increasing and decreasing temperature is due to the

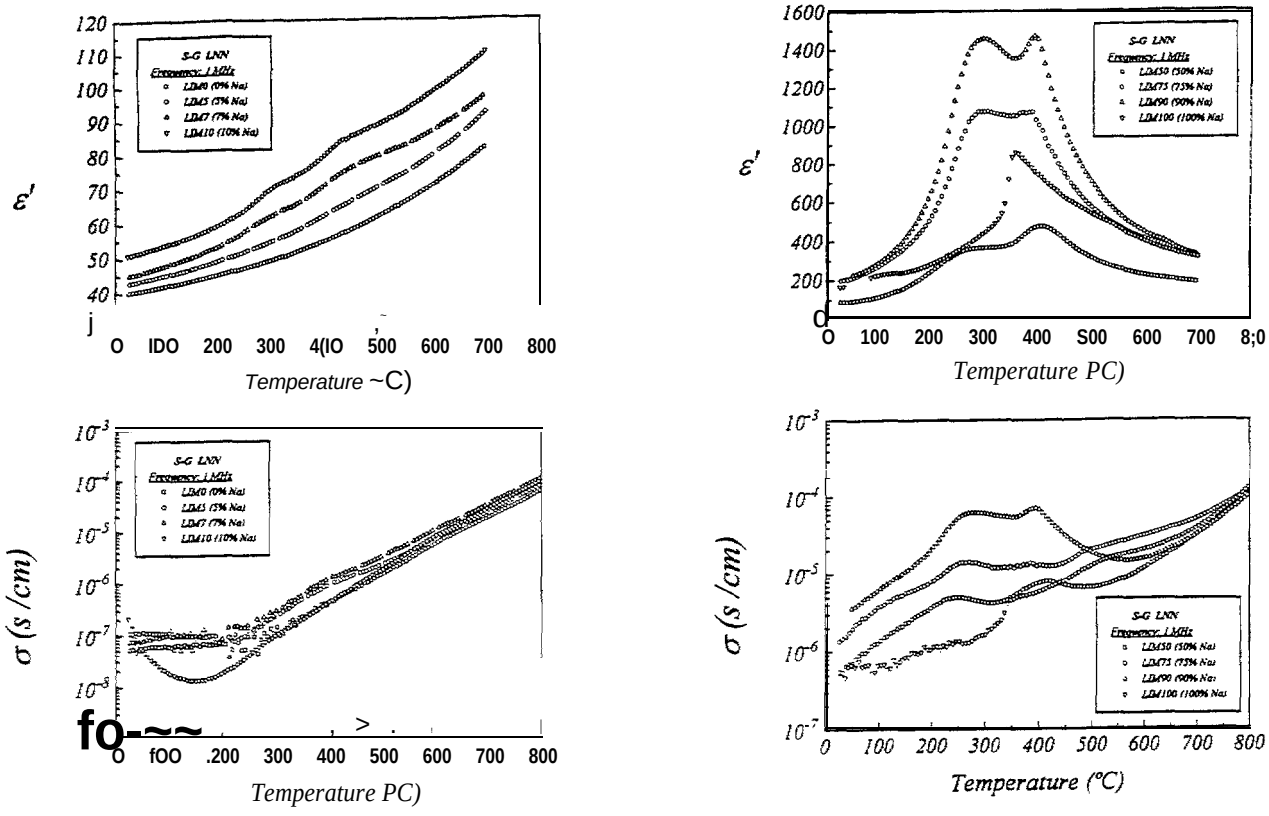


Figure 9: Permittivity, E', and conductivity, q as a function of the temperature for Na corttertts Q) U - if?% and b) 50- 100%: 1 MHz.

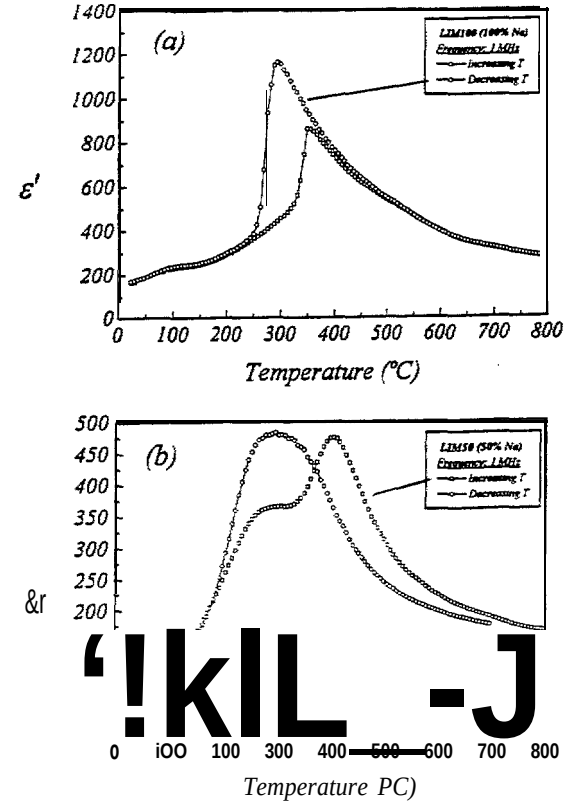


Figure 10: Perrnittivity, E', as a function of the temperature for a) NaNbt1₃and b) LAW(? (50% Na): heating and cooling cycles.

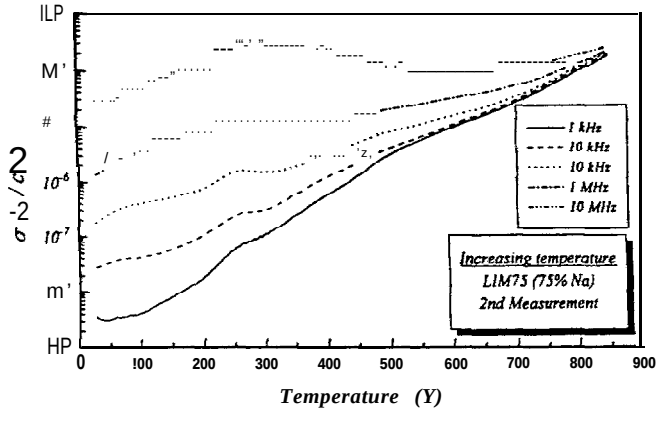


Figure 11: Conductivity as a function of temperature and frequency fop .UW75 {7S% Na) ceramic

characteristic thermal hysteresis of the A-P NaNbOs phase transition '2]. The displacement of the peak corresponding to the A-P transition at 400 - 450"C to lower temperatures, for measurements with decreasing temperature, results in an overlap with the peak of the anomaly at 250°C. As this remains unaltered the resukant effect is a wide unique peak. A hysteretic behaviour of the dielectric permittivity, similar to the one we observe in NaNbOs, was also reported in single crystals with Na content of x = 0.30 'g], but was not mentioned for x = 0.20 '** The low frequency (c 10 kHz) and [ow temperature (< 150°C) change in the temperature coefficient of the conductivity appearing as a minima (Figures 9 a) & b) was also found in ceramics processed by mixed oxides for the range of Na contents such that 0.00> x >0.25 at T = 150"C and similar frequencies [2,11], and in lithium 'b' and sodium "1 niobates and sodium tantalate '[8] at similar temperature and lower frequencies (10^{-3}-1 Hz). Also the anomaly in the dielectric permittivity at S300°C was found in the mixed oxide ceramics for Na substitution of 0.00> x >0.25 '[2,11]. Both the dielectric anomaly and the minimum in conductivity could be correlated to the possibie existence of a small polaron (locaiised charge carriers - existing due to a certain degree of stn.ictural disorder or if the surrounding region of the charged particle is polarised enough 'g]) conduction mechanism at low temperature. These mechanisms (short range-tunnelling) give place to conductivity values corresponding to long range hopping with activation energies that require higher temperatures, due to the low mobility of these localised charge carriers. The minimum in the thermal behaviour of the conductivity, c, is, therefore, explained as a result of a change in the conductivity mechanisms, ilom tunneling to hopping, f?om short range to long range mechanisms; at this temperature '7].

The piezoelectric behaviour as a fimction of the temperature vanishes at = 300°C in NaNbOs and, contrary to the results found in Li containing ceramics, does not recover when cooling to room temperature. Therefore, for Li containing ceramics the recoverable piezoelectric activity can be associated with the $LiNb0_3$ or LNS content, for which the activity extend up to the ferro-paraelectric transition above 11 OO°C and only ferro to ferroeiectric transitions were reported '[4] in the range of temperatures of our measurements.

Develot.nnent of Electrode Material

A parallel investigation was undertaken with the aim of which was to develop a thick film electrode material that could be applied to the different piezoceramic compositions, with adherence >10 N/m^2, solderability yielding a metallised surface area >95 % and conductivity as high as possible. Several approaches were undertaken, namely, direct firing, co-firing and sputtered of the electrodes. Close attention was paid to the composition of the paste, including the type and content of metal powder, mineral binders, glass phases, organic phases and other additives.

Under conditions, representing actual working conditions the adhesion is good and weil maintained after ageing tests, with the most promising method and composition being that of direct firing at low temperature, and the platinum based paste number 576402. In addition from it was found that there was no notabie change in the electrode when the ageing atmosphere was either air to oxygen.

Impedance measurements as a fimction of frequency (100 kHz -4 MHz) show two main resonant modes. For the samples under investigation, the resonant frequencies are =200 kHz for the pianar mode and =2 MHz for the thickness mode.

Significantly, for the piezoelectric behaviour, afler 50 cycles at 850°C in air, the piezoactivity of the poled materials is stiil present.

After ageing, three modifications of the frequency spectra can be obsewed:

- the frequency at which both modes occur is shiiled towards low values (from 250 kHz to 160kHzandfiorn 1.6 MHzto 1 MHz)
- both resonance values are mu-rower
- the thickness mode is more complicated.

Devekwrnent of Prototwe Devices

Two prototype high temperature devices have been developed, an accelerometer and an ultrasonic probe. For the former the new design has been established based on several designs of existing accelerometers having a temperature limit of 500°C to 650°C.

In order to maintain the high electrical impedance of the sensing element, it has been necessaxy to protect the elements from environmental influences, such as humidity and pollution. Therefore, the sensing elements have been placed in a hermetically sealed, welded housing. For the output wires, a hermetic ceramic to a metal brazed feed through has been used.

The major requirements for the high temperature piezoceram"cs can be derived as follows:

1. The dss piezoelectric constant should be at least 7 pCN
2. The sensitivity deviation with temperature should be of maximum 10 to 15% over the whole temperature range,
3. The typical values for the internal resistance of the accelerometers are 10~1 !i2 at room temperature with a minimum of 10^4 Q at 800°C.
4. The piezoceramics shall withstand a permanent static preload in the direction of the poling axis.
6. The material must be able to survive in an hermetically sealed housing with an internal controlled atmosphere.

The accelerometers were tested using both an open configuration and an hermetically sealed housing with various controlled internal atmosphere (o~gen, air and vacuum). The pefiormance of the piezocerarnic materials in accelerometers under actual operating conditions has been determined using a specific test installation. The *configuration* and characteristics of the equipment are the following:

- The room temperature sensitivity is based on a back to back calibration against a standard accelerometer

  The vibration level is kept to a constant level of 5g with a reference accelerometer outside the oven

The accelerometers were characterised under various experimental conditions and the following tests have been carried out:

Internal resistance, capacitance and sensitivity at room temperature and as a fhnction of temperature

Influence of static preload on the device sensitivity

Capacitance as a function of fi-equency and static preioad

Internal resistance, capacitance and sensitivity as a ti.mction of heat treatments and internal atmosphere

Sensitivity deviation with temperature

Long-term stability

In general the results were promising with devices satis&ing some if not aII of the above criteria. For most devices the sensitivity deviation was higher than the target values set and problems were identified with the internal atmosphere, which will require fiuther investigation. The tli.iture aim should be to develop a device specifically for these new range of piezoe]ectrk materials.

The ultrasonic probe was designed solely with the to use of LNN materials in mind. For general purpose comparison and qu-mtitative assessment of mechanical, thermal, and ultrasonic properties of the ultrasonic probe components in the temperature range up to 800”C, a high temperature device has been designed and manufactured using the following components:

Damping body
High voltage electrode connected to the high temperature signai cable
- Ground connection
- Coupling medium
Protection coating of metal components of ultrasonic probe:
- Pressure spring
Piezo material coupling.

The knowledge gained horn investigations on the different ultrasonic probe’s components has been compiled and matched to give a prototype probe designed for a circular piezo ceramic of 20 mm diameter, because this size has proved to be very effective.

At 600”C the sensitivity reached its highest value, but dropped by 8 dB (factor of 2.5) to 650”C. Mter a consecutive long term experiment over 18 hours at this temperature, the sensitivity dropped by another 18 dB (factor of 8), which was accompanied by a worsened pulse shape.

The sensitivity of the LNN - piezoceramics with has been measured and compared to the one of eider LNN - ceramics with 10 mm diameter and of single crystal $LiNb0_3$ piezo membranes and show a pronounced resonance behaviour referencing a higher sensitivity than measured before on the 10 mm diameter LNN - ceramics. The LNN - ceramic “ 15 1100 H69 No. 1” which has been estimated to have the highest sensitivity has been incorporated and its properties have been measured using the reference set-up. It could be shown that the relative sensitivity was 6 dB higher than that of the 10 mm diameter LNN-ceramics. The LNN - ceramic “15 1100 H69 No. 2“ only was 4 d3 lower in sensitivity than the single crystals, while the 10 mm diameter LNN - ceramics were lower in sensitivity by 2? -28 dB.

It is evident that from the investigations that with respect to the temperature, the piezo ceramic developed a higher and higher sensitivity, with an upper limit in the proximity of 760”C - 780°C. However, this upper limit seems to be of only theoretical importance, as at this temperature the present echo is of too low a performance for practical purposes. Nevertheless, for ultrasonic inspectio~ i.e. wail thickness measurement, this piezo ceramic will be applicable up to temperatures of roughly 700”C

Conclusion

Through the compositional study periiormed it has been identfied that bulk ceramic materials produced with sodium modfied lithium compositions gave the best overall properties. From the parallel investigations that were conducted in an effort to enhance material properties the use of chemical additives with the pure and sodium modiki Miurn *niobate* invariably produced materials that although they produced an increase in one particular property this was at the expense of the other properties.

Powders prepared from the traditional mixed oxide route showed promising properties, however, reproducibility of the properties in the sintered ceramics has yet to be proved. Although the typical values for density of the siitered ceramic are not as high as those produced by the sol-gel route the generaI properties of the ceramic exhibited superior electromechanical properties: again their is difkulty achieving reproducible results. This process, in addition to being the most cost effketive of the routes, can be used as one of the easiest ways to study compositional modification.

From a processing stand poin$ the sol-gel route is highly versatiie and flexible powder synthesis route. A high purity reactive powder can be produced with relative ease and with good reprodueibtity, with quality powder produced within a broad processing window. It is considered that scaling up to yield industrial quantities of this process is fmible.

Choice of electrode material is crucial to the behaviour of a piezoelectric material, particularly at elevated temperatures. Efforts have been focused on the development of a high temperature eIectrode material with good compatibility with the ceramic material under actual working conditions. High quaIity co-fired electrodes have been developed that show good adherence, conductivity and integrity before and after ageing studies.

The resistivity, dielectric and piezoelectric properties of the ceramics produced were determined from room temperature to 1000”C. Finally, the oxygen loss behaviour as a finction of temperature and time have been established. The results obtained were used to improve composition and fabrication.

The most promising materials were selected for each of the particular devices. Prototype accelerometer and ultrasonic probe devices were designed and constructed to investigate the material properties under actual working conditions. These tests, as well as giving va.IuabIe inilormation as to the behaviour of different materials, have enabled device design to be improved. Therefore results have been used to fimther adjust ceramic composition and processing and to modifj device design.

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