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CONTRACT NUMBER DAMD17-96-C-6024

TITLE: Combat Surgical Ultrasound System and Probes with Multi-Modality Image Fusion for Front Line Surgical Guidance and Telesurgery

PRINCIPAL INVESTIGATOR: Doctor David R. Pickrell

CONTRACTING ORGANIZATION: TRS Ceramics, Incorporated
State College, Pennsylvania 16802

REPORT DATE: October 1996

TYPE OF REPORT: Final, Phase I

PREPARED FOR: Commander
U.S. Army Medical Research and Materiel Command
Fort Detrick, Frederick, Maryland 21702-5012

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REPORT DOCUMENTATION PAGE

Form Approved
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Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	October 1996	Final, Phase I (1 Mar 96 - 31 Aug 96)

4. TITLE AND SUBTITLE
Combat Surgical Ultrasound System and Probes with Multi-Modality Image Fusion for Front Line Surgical Guidance and Telesurgery

5. FUNDING NUMBERS
DAMD17-96-C-6024

6. AUTHOR(S)
Doctor David R. Pickrell

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
TRS Ceramics, Incorporated
State College, Pennsylvania 16802

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Commander
U.S. Army Medical Research and Materiel Command
Fort Detrick, Frederick, MD 21702-5012

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

19961113 105

11. SUPPLEMENTARY NOTES

DTIC QUALITY INSPECTED 2

12a. DISTRIBUTION / AVAILABILITY STATEMENT
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13. ABSTRACT *(Maximum 200*

This TRP-SBIR project addressed the synthesis and characterization of single crystal relaxor ferroelectrics for high performance bio-medical transducers. The ability to grow single crystals of various relaxor-based compositions with specific crystallographic orientations offers piezoelectric, dielectric and electro-mechanical properties not achievable in polycrystalline PZT ceramics. Limitations associated with the multi-domain state of polycrystalline ceramics are eliminated in single crystals. Consequently, these single crystals will exhibit better temperature stability allowing devices to operate in adverse environments and be sterilized with an autoclave technique. In addition, the single crystal form of these materials will be more easily fabricated into high frequency (MHz) transducer arrays where the elemental scale approaches that of the microstructural features in polycrystalline ceramics.

The Phase I research provides a basis for further crystal growth studies, characterization, and testing in Phase II leading to a new family of laparoscopic imaging probes for both the military battlefield and domestic diagnostic care.

14. SUBJECT TERMS Relaxor, Bio-Medical, Ferroelectric, Transducer, Crystal, Ultrasound

15. NUMBER OF PAGES
21

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	Limited

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David Pickett 9/18/96

PI - Signature Date

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I. INTRODUCTION

The SBIR Phase I program titled "Single Crystal Relaxor Ferroelectrics for High Performance Bio-medical Ultrasound Transducers" is an embedded SBIR in the TRP program titled "Combat Surgical Ultrasound System and Probes with Multi-modality Fusion for Front Line Surgical Guidance and Telesurgery," led by Tetrad Corp. of Englewood, CO, a TRP consortium.

The consortium members include of the following:

Tetrad Corporation
Siemens Medical System, Inc.
Surgical Navigation Technologies, Inc. (A division of Sofamol Damek Group)
Materials Systems, Inc.
TRS Ceramics, Inc.

The Vision Statement is as follows:

> Create an ultrasound device which, when operated with other co-displayed imaging techniques, provides diagnosis and therapy guidance during surgery. This highly portable device includes miniature surgical probes made with novel materials and integrated electronics for the purpose of rapid diagnosis and minimally invasive treatment of wounded soldiers. The device provides a cost effective alternative for emergency and open surgery procedures in both government and civilian medical care, and enables a new level of intervention in battlefield surgery.
>
> At the end of two years, the program will produce a prototype miniature surgical probe coupled with an ultrasound imaging system integrated into a surgical work station for image fusion. At the end of five years portable, high performance ultrasound imaging systems will be commercialized for general imaging and surgical intervention.
>
> Tetrad will be responsible for probe development using novel transducer materials supplied by MSI and TRS Ceramics. Highly integrated ultrasound imaging electronics will be supplied by Siemens, and image fusion software and display will be produced by Surgical Navigation. Surgical stand alone product for defense and commercial applications will be marketed by Siemens. Surgical work stations will be marketed by Surgical Navigation.

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Purpose of the Work

In the Phase I program, TRS Ceramics' goal was to develop single crystal ferroelectrics for use as autoclavable transducers in high performance bio-medical ultrasound probes. Through interaction with Tetrad Corp, single crystals were to be evaluated for potential use in array type transducers, and subsequently, actual transducers using these single crystals were to be fabricated and tested. Tetrad's evaluation program, however, extends through Phase I of the TRS Ceramics SBIR with further work to be concluded in the Phase II program.

Background

Today, ultrasonic imaging is an integral part of diagnostic medicine. A major drawback of this imaging modality, however, its relatively poor spatial resolution which limits image quality. In reference to remote combat casualty care, current bio-medical ultrasound systems do not meet the field use requirements of low power consumption, are not readily functional in adverse environments, and do not satisfy the proposed autoclave sterilization method (TRP Parent Program).

Conceptually, poor image quality can be improved through the use of high frequency (>5 MHz) or multidimensional imaging (1.5 and 2-D arrays), however, several materials issues relevant to the transducer must be addressed. In addition to high piezoelectric, dielectric, and electromechanical coupling, temperature stability is an important issue for a battle field unit which has to function over a broad range of temperature as well as perform upon exposure to severe environmental conditions.

For high frequency linear/curved arrays, each of the transducer elements must be subdiced to a very small size in order to suppress spurious transverse modes. The requirement of high aspect ratio demands the element size to be on the order of a few hundred microns for MHz range transducers. This is a technically challenging processing problem for polycrystalline ceramics since small grain sizes correspond to degraded electrical properties.[(1)] Furthermore, associated with small elements are small capacitance values and hence inadequate electrical impedance matching.

The *next generation* of noninvasive and minimally invasive ultrasound imaging transducers requires more advanced materials with better piezoelectric, dielectric and coupling constants, as well as the ability to fabricate fine scale arrays. Currently, the materials of choice for bio-medical ultrasound transducers are based on the $PbZrO_3$-$PbTiO_3$ (PZT) solid solution system near the morphotropic phase boundary (MPB). See Figure 1. Single crystal growth of these compositions is very difficult, which restricts the use of these materials to polycrystalline ceramics with grain sizes on the order of 3 to 10 microns. To optimize dielectric and electromechanical properties, compositional modifications are generally used to reduce the Curie temperature (T_c) of the material, the temperature of which the onset of ferroelectricity occurs. The T_c of the material dictates the transducer performance by imparting a strong temperature dependence on the

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properties and limits its use temperature above which depolarization may occur. As a rule of thumb, the maximum usage temperature is one-half of T_c. As a note, 60-70% of the piezoelectric activity in ferroelectric ceramics is associated with extrinsic domain wall contributions and hence are sensitive to external electrical and mechanical stresses. Of significance to this program, the above limitations associated with polycrystalline ceramics will not be an issue with single domain single crystal ferroelectrics.

The Approach

As stated above, piezoelectric ceramics are generally based on the morphotropic phase boundary (MPB) found in the perovskite system $PbZrO_3$-$PbTiO_3$ (PZ-PT) near the compositional ratio Zr:Ti of 52:48.[(2)] Single crystal growth of these compositions is very difficult, which restricts the use of these materials to polycrystalline ceramics. Morphotropic phase boundaries also exist in numerous compositions of the perovskite family as shown in ternary system in Figure 1. These compositions have the general formula $Pb(B_1B_2)O_3$-$PbTiO_3$ with B_1-Mg^{+2}, Zn^{+2}, Ni^{+2}, Sc^{+3}, Fe^{+3}, In^{+2}, and B_2=Nb^{+5}, Ta^{+5}, W^{+6}. Previous studies by Nomura and Kuwata [(3,4)] on $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PZN-PT) and by Shrout, Markgraf, Kim and Chang[(5)] on $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) both reported anomalously high piezoelectric properties for single crystals with compositions near their respective morphotropic phase boundaries. Electromechanical coupling coefficients (k_{ij}) > 90% and piezoelectric d_{33} values $\geq$ 1500 pC/N were reported. These values are significantly larger than those associated with any polycrystalline ferroelectric ceramic as contrasted in Table I. In addition, for the (1-x)PZN-x(PT) system, dielectric loss values less than 0.002 for the tetragonal phase (x=0.11) and 0.008 for the rhombohedral phase (x=0.05) have been reported.[(6)] These data coupled with high permittivities (K_s>4000) make these materials ideal candidates for high frequency transducers in bio-medical imaging systems. Furthermore, the scalability limits in polycrystalline ceramics due to grain size are eliminated by the use of single crystals, opening up a plethora of applications including a wide range of specialized imaging probes.

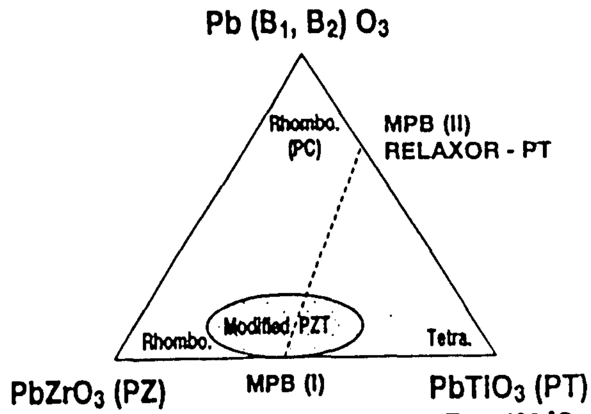

Figure 1: Ternary system for $PbZrO_3$-$PbTiO_3$-$Pb(B_1B_2)O_3$ showing the PZ-PT-MPB-1 and $Pb(B_1B_2)O_3$-PT-MPB-2 regions. Note: Crystal growth MPB-2>>MPB-1 (Ref. 7).

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Table 1: Selected parameters for polycrystalline piezoelectric ceramics and single crystal relaxor ferroelectric transducers.

Transducer Materials	T_c	Dielectric Constant	Piezoelectric Coupling (k_{33})	d_{33} pC/N	Comments
PZT-5 *rhombohedral	~350°C	1000 - 2000	60-70%	~300–500	• crystal growth not possible
PZT-5H *rhombohedral	~130°-190°C	3000–4000	70-75%	~600–700	• scale-grain size limited • 1/2 T_c temp. limit
Relaxor ferroelectrics $Pb(B_1B_2)O_3$-$PbTiO_3$ rhombo/tetra	~150°-300°C	1,000–10,000	80–92%	600–1600	• crystal growth possible • *no* grain size limitations • *no* domains

* In contrast to rhombohedral phases, tetragonal compositions possess inferior electro-mechanical properties.

Scope of the Work

To address the needs of the next generation of high performance bio-medical transducers that are autoclavable, the growth and characteristics of single crystals based on relaxor-PT compositions was proposed. Specific objectives deemed significant to the TRP program are given in the following objectives:

- Single crystal growth [high temperature solvent (flux)] of $Pb(B_1,B_2)O_3$-$PbTiO_3$ compositions, specifically $Pb(Zn_{1/3}Nb_{2/3})O_3$:$PbTiO_3$ [(1-x)PZN:(x)PT] near the respective MPB, with x=0.09 and $x \geq 0.15$ for high T_c materials.
- Determination of dielectric, piezoelectric and elastic properties, e.g., K_{ji}, k_{ij}, loss and s_{ijkl}, as a function of crystal composition, structure and orientation.
- Determination of key performance parameters as a function of temperature (-50° to 100°C) as well as thermal stability tests to mimic exposure to adverse environments and sterilization by an autoclave.
- Selection of optimum crystal compositions and orientation for evaluation and fabrication of high frequency array transducers by the TRP parent organization, namely Tetrad Corporation (contact Dr. Clyde Oakley).

The research program included five primary tasks:

(1) compositional selection; (2) crystal growth; (3) electro-mechanical characterization; (4) environmental testing. A fifth activity was the preparation of the Final Report. The milestone chart used is provided in Figure 2.

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Figure 2: Milestone Chartb

Task/Milestone	Months After Project Initiation 1	2	3	4	5	6
Task 1: Composition Selection	▒	▒	▒	▒	▒	
Task 2: Crystal Growth						
A. TRS Ceramics, Inc.	▒	▒	▒	▒		
B. Crystal Associates		▒	▒	▒		
Task 3: Characterization			▒	▒	▒	
Task 4: Environmental Testing					▒	▒
Task 5: Final Report						X

II. EXPERIMENTAL METHODS AND RESULTS

Task I: Composition Selection

High electromechanical coupling (k), low dielectric loss, and relatively high T_c were guidelines for selecting compositions. Crystals of the following compositions listed below were selected for growth. All the compositions have T_c's > 150°C. For optimum electromechanical coupling, compositions B and E are morphotropic phase selected systems. Composition C is expected to have a T_c > 170°C with a tetragonal structure allowing a single domain state upon poling giving rise to good temperature stability for autoclavable transducers.

Relaxor-PT compositions selected are identified on the PZN-PT and PMN-PT phase diagrams shown in figures 3 and 4 and listed below:

$Pb(Zn_{1/3}Nb_{2/3})O_3$ --------------- (A) PZN
$0.905Pb(Zn_{1/3}Nb_{2/3})O_3 - 0.095PbTiO_3$ --------------- (B) PZN-PT
$0.65Pb(Mg_{1/3}Nb_{2/3})O_3 - 0.35PbTiO_3$ --------------- (E) PMN-PT
$0.85Pb(Zn_{1/3}Nb_{2/3})O_3 - 0.15PbTiO_3$ --------------- (C) PZN-PT
$0.92Pb(Zn_{1/3}Nb_{2/3})O_3 - 0.08PbTiO_3$ --------------- (B-1) PZN-PT
$0.89Pb(Zn_{1/3}Nb_{2/3})O_3 - 0.11PbTiO_3$ --------------- (C-1) PZN-PT

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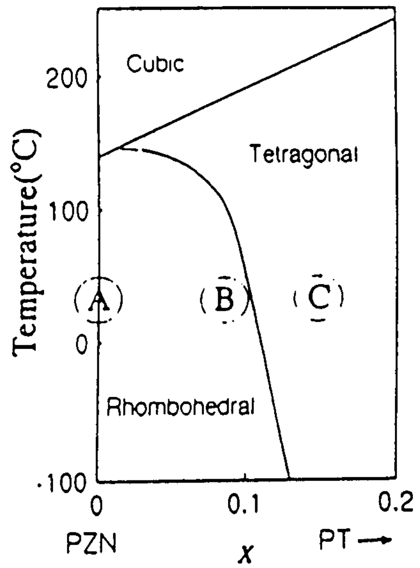

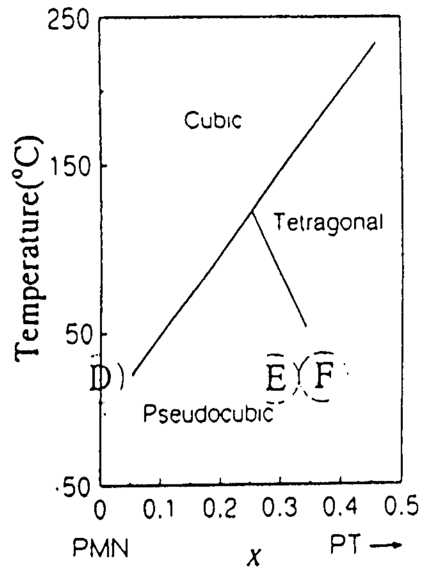

Nomura et al., J. Phys. (1969)
J. Kuwata et al., Ferroelectrics (1981)

S. W. Choi et al., Ferroelectrics (1989)
T. Shrout et al., Ferroelectric Letters (1990)

Figures 3 and 4: PZN-PT and PMN-PT phase diagrams. Compositions B, C, and E were grown in the program.

Task II: Crystal Growth

Crystals of selected compositions were grown by the flux technique, schematically shown in Figure 5. Powders of Pb_3O_4, ZnO, $MgCO_3$, Nb_2O_5, and TiO_2 with high purity (>99.9%) were used. The raw powders were mixed and loaded into a Pt. crucible. The Pt. crucible was then placed in an alumina crucible which was sealed with an alumina lid and alumina cement to minimize volatilization of the Pb rich phase. The crucible with the powder was then placed in the furnace and held at a soaking temperature (1150~1200°C) for 10 hours, followed by cooling at the rate of 1°C/hour down to 900°C. The flux was leached out by hot HNO_3 (20%). The size and quality of the crystals were reasonable enough to make test samples for compositions B and E. Crystal growth of composition C was not found to be successful due to a furnace instability problem. Crystals of composition C contained larger amounts of second phases and their size was significantly smaller than crystals of B and E, size $\leq$ 1 cm^3. To reduce the amount of inclusions, the PT content was lowered hence the reason for composition C-1.

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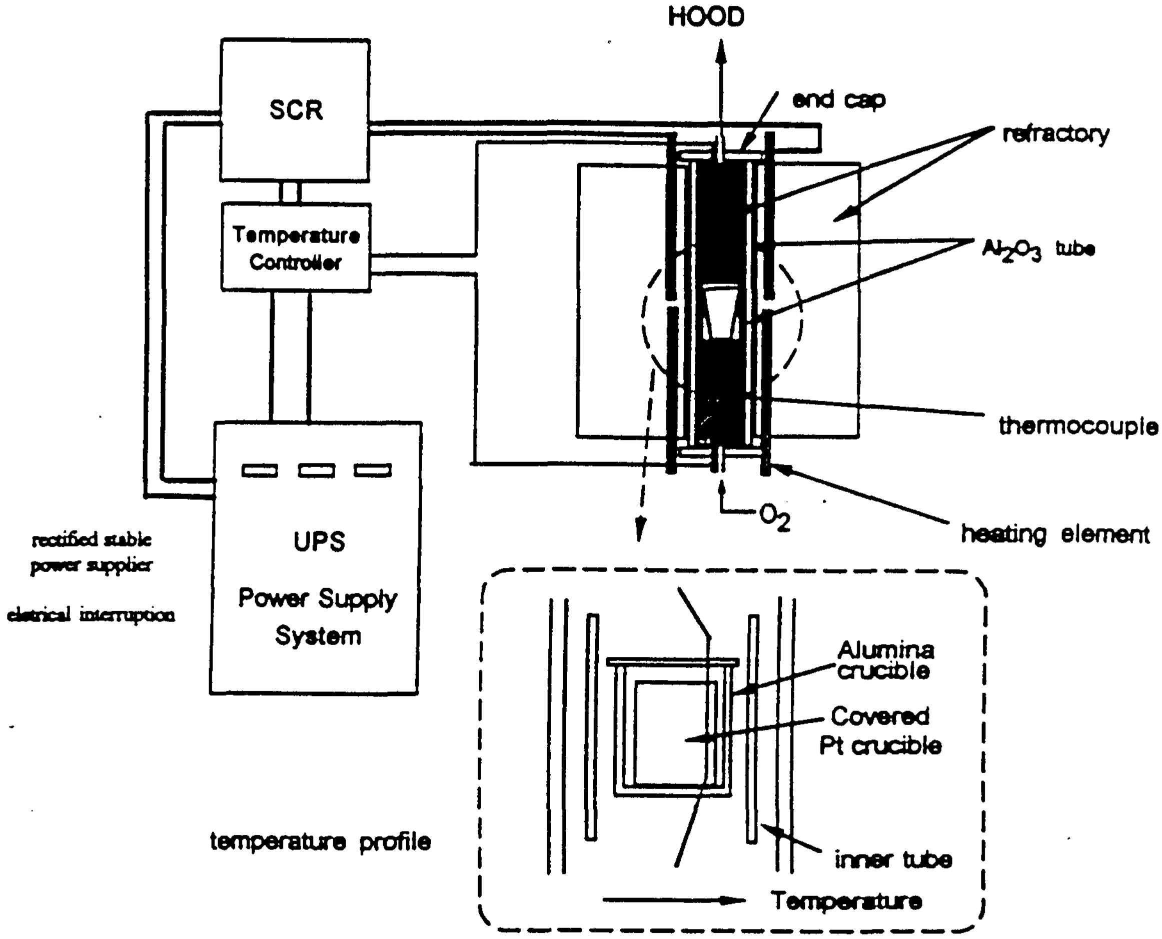

Figure 5: Schematic of modified flux growth system.

In parallel to TRS Ceramics' work, crystals of composition E were given to Crystal Associates, Inc. (subcontractor to this work). This effort is in relation to the ultimate commercialization of single crystals at economical costs.

Figure 6 shows photomicrographs of selected crystals grown using the flux technique. As shown, the crystal was < 1cm^3 in size with irregular crystallographic morphology.

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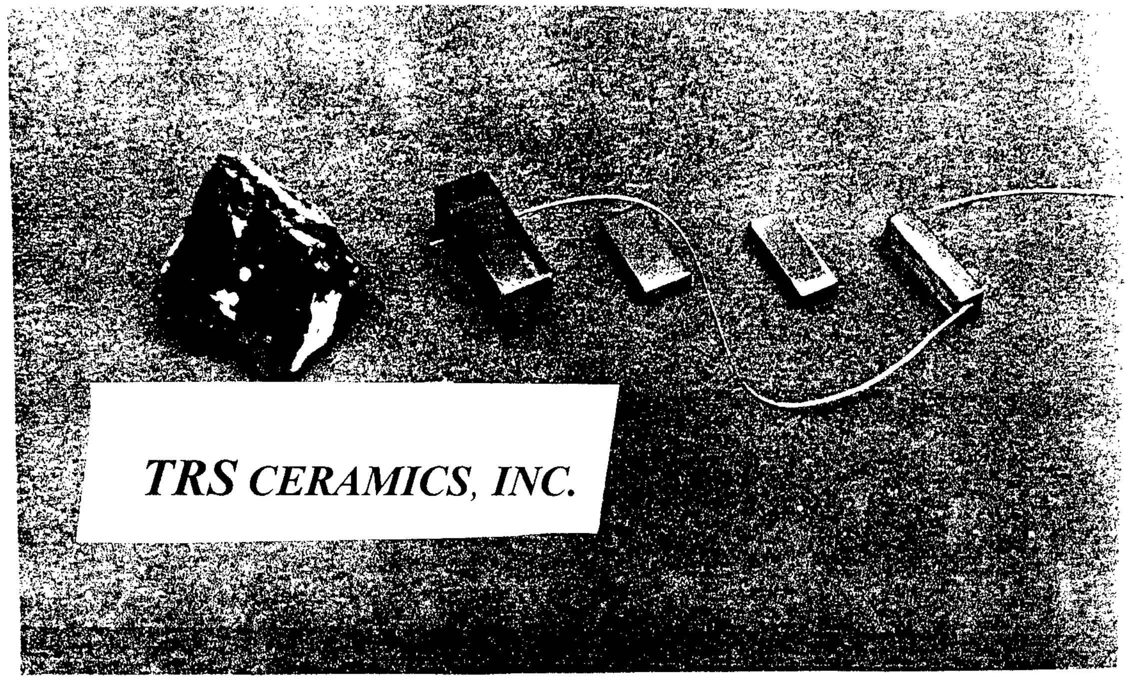

Figure 6: Photomicrography of flux grown crystals and test samples.

Task III: Electrical Property Characterization

Sample Preparation

Various dielectric, piezoelectric, and electromechanical properties were determined as a function of crystal composition, crystallographic structure and orientation. Samples with both <001> and <111> crystallographic orientations were made with an emphasis on <001>.

Crystals were oriented along the pseudocubic (001) direction using a Laue back reflection camera. Oriented crystals were cut and polished based on the crystallographic relationship. Figure 6 shows an example of a prepared sample with very small dimensions due to the small crystal starting size and poor quality, i.e., second phase inclusions, in some cases. Prepared samples were then electroded and poled by applying 5~10kV/cm while cooling from a temperature higher than T_c.

Dielectric and Piezoelectric Properties

Table 2 summarizes the dielectric properties of compositions B, E, and C, (orientation <001>) with corresponding dielectric temperature behavior given in Figures 7-9. As presented, the compositions have $T_c > 150°C$ with the highest found for compositions with the highest level of PT. The dielectric properties were determined from capacitance measurements using a HP multiple frequency (LCR) meter Model 4194A in conjunction with a computer controlled temperature oven.

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Table 2 - Dielectric Properties of Crystals (1kHz)

Composition	K_{virgin}	K_{poled}	$Loss_{virgin}$	$Loss_{poled}$	$T_c(°C)$
B	10800	1400	0.012	0.004	172
E	2900	3100	0.029	0.014	160
C	2500	1072	0.026	0.041	210

The high dielectric maximums K_s >30,000, and low loss reflected at all frequencies measured reflects a good crystal quality. Due to numerous inclusions in composition C, however, C-1 was focused upon. Also a slightly lower PT (8%) rhombohedral crystal B-1 was selected for further work.

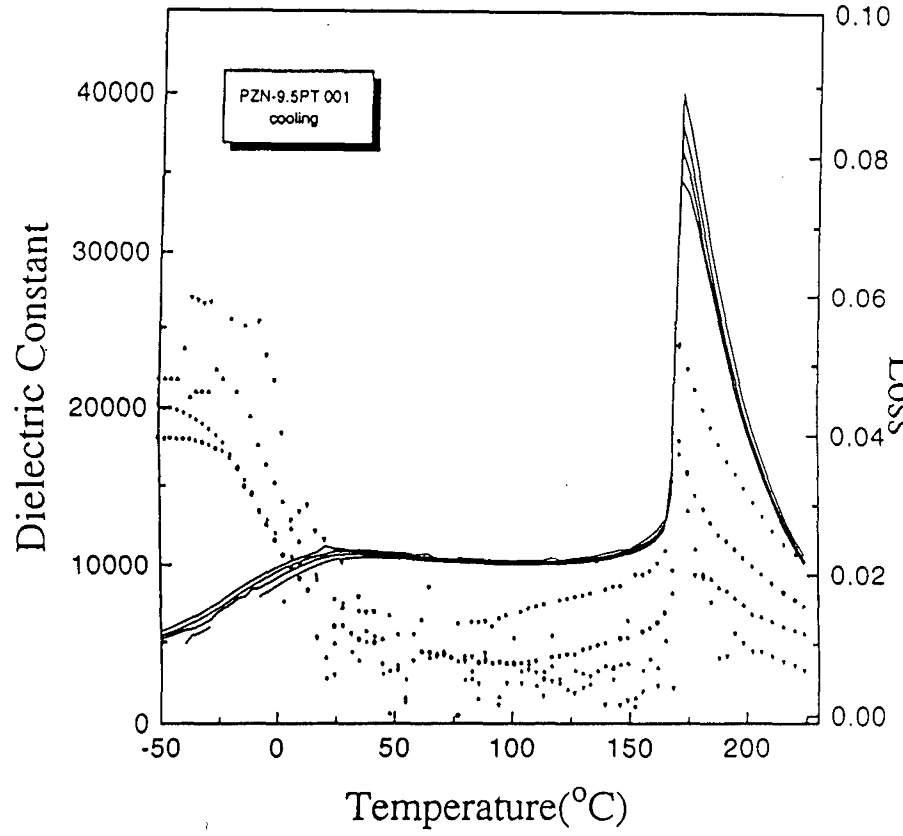

Figure 7: Dielectric constant and loss for single crystal - Composition B. Dotted lines represent dielectric loss. Frequency range - 100 Hz, 1 kHz, 10 kHz and 100 kHz.

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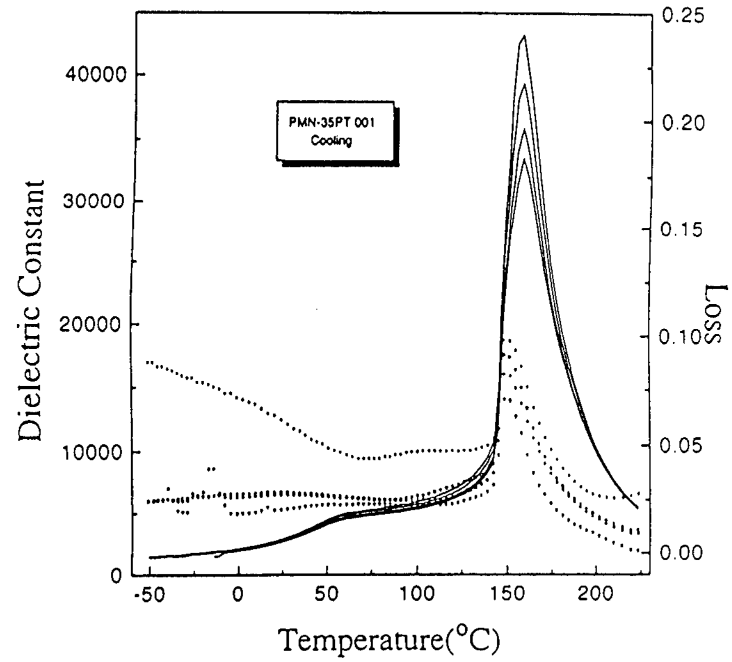

Figure 8: Dielectric constant and loss as a function of temperature for Composition E.

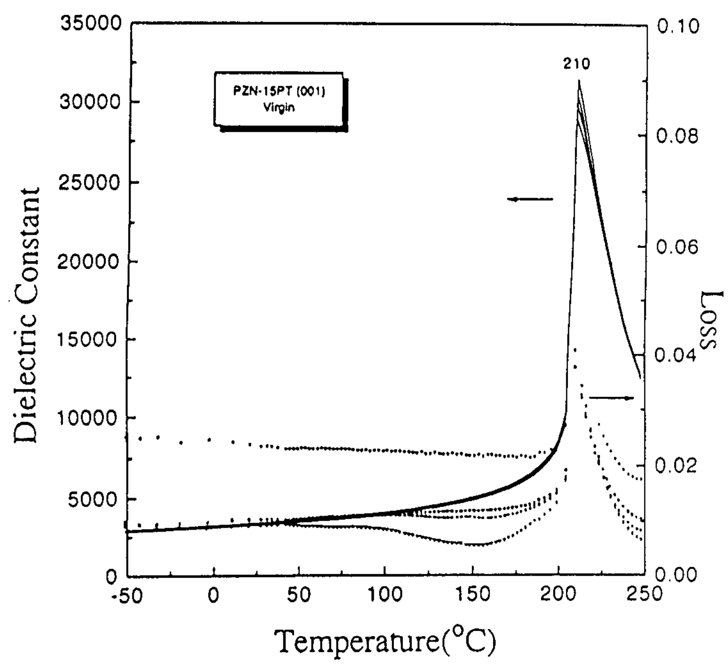

Figure 9: Dielectric constant and loss for single crystal - Composition C.

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The dielectric and piezoelectric properties for all the crystal compositions are summarized in Table 3, being determined with an HP impedance gain phase analyzer and based on IEEE standard (1982).

Table 3: Dielectric and Piezoelectric Properties of crystals (k_{33} mode samples).

Composition	Cut	Tmax(°C)	Dielectric Constant (Loss)	Coupling
A	111	~140	900 (0.012)	0.377
	001		3600 (0.008)	0.852
B-1	111	~170	2150 (0.012)	0.395
	001		4200 (0.012)	0.938
B	111	~176	4300 (0.007)	0.644
	001		1400 (0.004)	0.894
E	001	~160	3100 (0.014)	0.923

Table 4: Dielectric and Piezoelectric Properties k_T mode sample.

Composition	Cut	Coupling	K_{3T}	Loss
A	001	0.493	2732	0.013
B-1	001	0.481	4450	0.017
B	001	0.541	1553	0.024
C-1 (PZN-11%PT)	001	0.638	890	0.024
E (PMN-35%PT)	001	0.541	4540	0.031

As presented, longitudinal coupling coefficients $k_{33} > 85\%$ were found for all the crystals with the highest values found for compositions near the MPB, in particular compositions B and B-1.

Of significance to single element transducers, K_t values > 63% were measured for the tetragonal composition C-1 (Table 4), being associated with the relatively high anisotropy of tetragonal materials.

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Sample Delivery

Based on the results above, delivery of prototype samples to Tetrad for transducer evaluation was made on May 7, 1996 and samples with the following dimensions were delivered.

(B) - Composition $0.905Pb(Zn_{1/3}Nb_{2/3})O_3$ - $0.095PbTiO_3$
- Crystal Orientation (001)
- $k_{33} = 0.89$, $k_T = 0.54$
- Sample Size: x= 2.38 mm, y= 4.18 mm, z (thickness) = 0.17 mm
  x= 1.97 mm, y= 3.77 mm, z (thickness) = 0.17 mm
- Electrode: 3 min. sputtered gold
- Poling (5/3/96)
  Applying 10kV/cm, cooling at the rate of 4°C/min. from 210°C.

Sample crystals of composition B were also sent for preliminary dicing studies.

A second generation of crystals were delivered on August 7, 1996 as given below:

(B-1) - Composition $0.92Pb(Zn_{1/3}Nb_{2/3})O_3$ - $0.08\ PbTiO_3$
- Crystal orientation (001)
- $k_{33} \cong 0.93$, k_T - 0.48
- Sample size: #1 x=2.92 mm, y=4.06 mm, z (thickness)=0.12 mm
  #2 x=1.89 mm, y=3.68 mm, z (thickness)=0.18 mm
- Electrode: 3 minutes sputtered gold

The dielectric data (1kHz) after poling was:

K = 3400 (#1) and 4800 (#2), respectively.

Problem Areas

1.) The variation of K for the above crystals may be the result of compositional fluctuations.

2.) The dicing of fine scale arrays is of concern for quality transducers. Preliminary dicing experiments revealed the following:

Edge chipping at the surface

The dicing conditions used were as follows:

- ♦ K&S (Kulicke & Soffe) Saw
- ♦ Blade Thickness: 0.9 mil
  - Cut crystal with 27 μm width, 140 μm depth (blade exposure, 300 μm)

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- Spindle Speed: 40,000 rpm
- Entry speed and cut speed: 0.15 mm/sec

To achieve the exactness for fine scale array fabrication, further dicing studies must be carried out, requiring numerous samples.

Task IV: Environmental Testing

The dielectric and piezoelectric properties of composition B-1 were selected for evaluation as a function of temperature. The relatively low d_{33} values for the higher T_c samples, composition C & C-1 excluded them at this time. Figure 10, presents the dielectric constant as a function of temperature showing the rhombohedral-tetragonal transition of ~100°C. Up to this point, the samples could be thermally cycled without degradation of properties, as shown in Figure 11. Going higher in temperature resulted in a decrease in properties, however, upon cooling, returned to 90% of the original value.

For a high T_c, tetragonal composition (C-1), a thermal stability study was performed by inserting the sample into an environmental chamber at various temperature intervals beyond T_c. (Note: Hold time 10 minutes) As presented in Figure 12, the K_T and K values measured at room temperature after temperature disturbance actually increased up to ~ 180°C the T_c, demonstrating good autoclavable capability. The increase in properties is believed to be the result of domain contributions being enhanced through the thermal disturbance as found for PZT ceramics [(2)].

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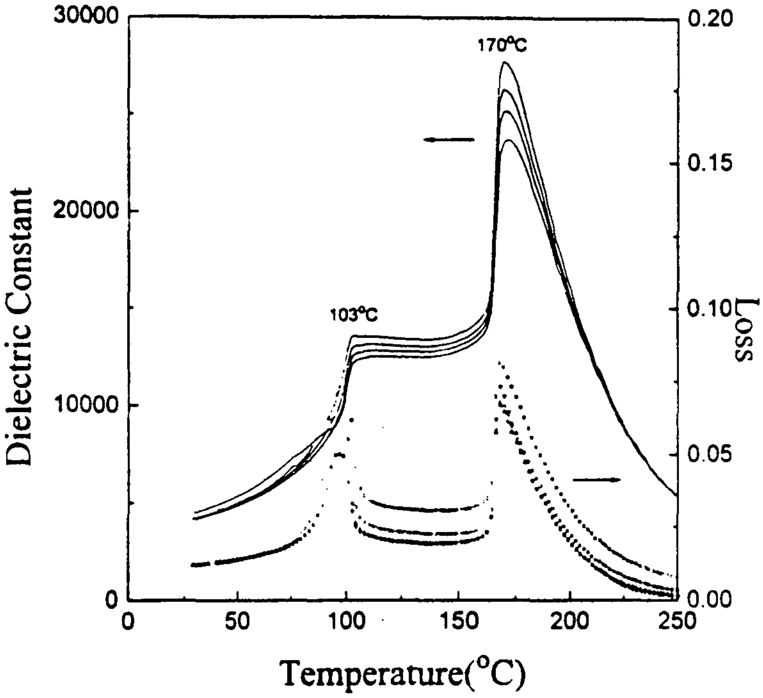

Figure 10: Dielectric constant and loss as a function of temperature for B-1.

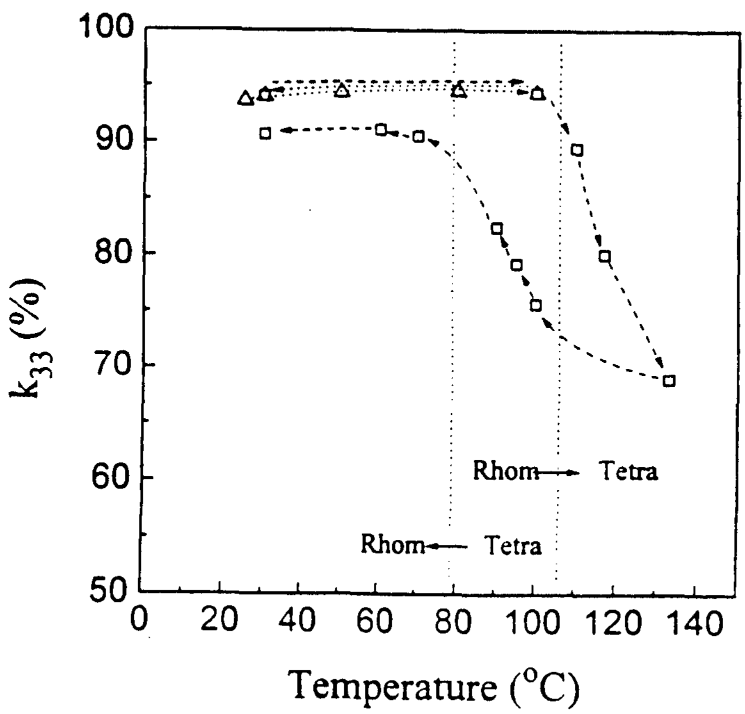

Figure 11: The longitudinal coupling coefficient (k_{33}) as a function of thermal cycling for B-1.

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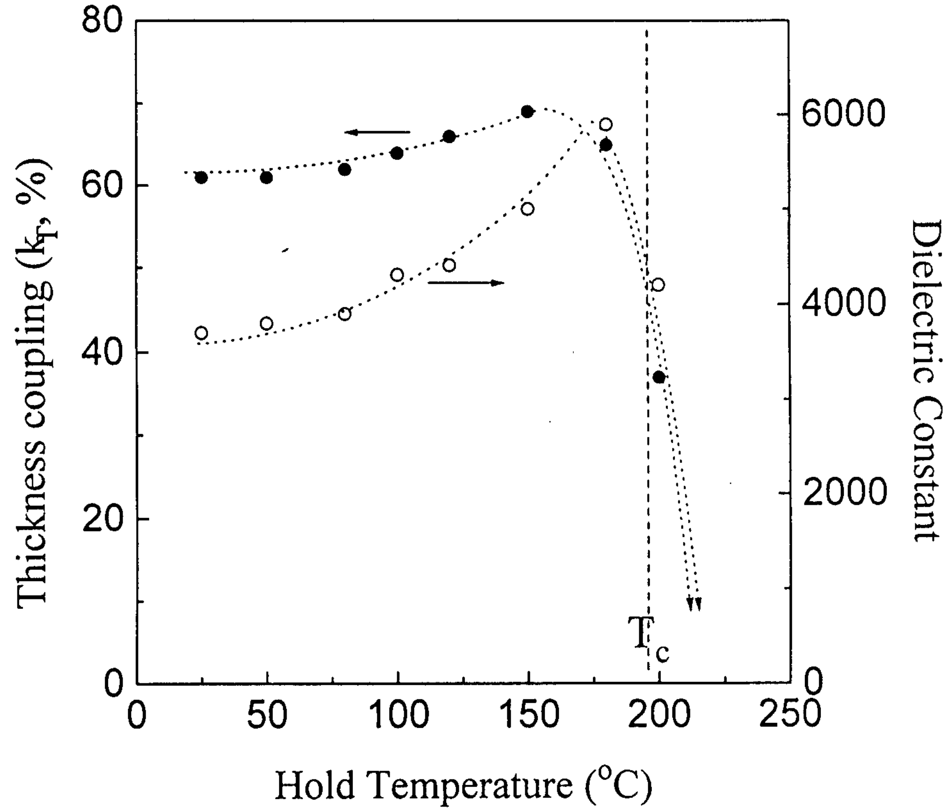

Figure 12: Thermal depolarization of k_T and K for PZN-11PT Crystals. Hold time ~ 10 minutes.

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Bibliography

List of Personnel:

Wesley S. Hackenberger is Director of R&D for TRS Ceramics. He received a B.S. in Nuclear Engineering in 1989 and a Ph.D. in Materials in 1995 both from Penn State University. He worked as a summer intern at American Electric Power in Columbus, Ohio from 1987-1990. Dr. Hackenberger is responsible for all new product and process development at TRS. His research experience includes sintering and microstructural development of multilayer and thick film ceramic materials for electronics applications; ceramic powder processing techniques; constrained sintering and viscoelastic properties of porous materials at elevated temperature; design and development of thermal analysis instrumentation. Dr. Wesley Hackenberger has communicated more than 10 publications and technical presentations in various journals and society meetings.

David J. Pickrell is General Manager of TRS Ceramics. He obtained a B.S. (1984) in Ceramic Engineering from The Ohio State University, and an M.S. (1987) and Ph.D. (1990) in Solid State Science from Penn State University. As General Manager for TRS (1994-pres) he is responsible for all aspects of the business. Sales have grown from a level of $250,000/year to $1million/year during his tenure. Prior to joining TRS, Dr. Pickrell was a Product Development Manager at Diamonex, Inc. His professional experience includes product and process development, team-based manufacturing, quality programs, as well as marketing and business planning for the commercialization of new products. His technical interests include processing-structure-property relationships in materials, piezoelectric and electrostrictive materials, and ceramic powder processing. Dr. Pickrell has communicated more than 25 publications and technical presentations in various journals and societies and is co-author on two book chapters.

List of Personnel Receiving Pay From This Effort:

Dr. Wesley Hackenberger, Director of R&D
Dr. David Pickrell, General Manager
Jim Perryman, Manufacturing Team Leader
Judy Stover, Research Technician

Presentations

TRP Kick-off Meeting - Dr. Wesley Hackenberger presented on August 5, 1996 at MSI, Inc., in Andover, MA.

Conclusions

The TRP-SBIR Phase I Program addressed the synthesis and characterization of single crystal relaxor ferroelectrics based on the $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ and $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ systems. The ability to grow single crystals of compositions near their respective morphotropic phase boundaries (MPBs) (x-0.09 PZN-PT and x-0.35 PMN-PT) using high temperature flux techniques was demonstrated resulting in crystals $<1 cm^3$. Compositions with relatively high PT content, however, contained inclusions and were of poorer quality. Based on IEEE standards resonant-antiresonant techniques, crystals with longitudinal coupling coefficients >90% were found for <001> oriented crystals with relatively high dielectric constants (3,000-5,000) and low loss <0.01, making them exceedingly promising for high performance bio-medical ultrasound transducers. In relation to single element

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transducers, thickness coupling coefficient, k_T >63% were achieved for tetragonal materials 0.89 PZN-0.11PT.

Preliminary environmental studies found thermal stability to ~100°C for rhombohedral PZN-0.08PT crystals, and up to ~ 100°C near the T_c for tetragonal crystals.

The above properties offer dramatic improvements in properties relative to currently available polycrystalline PZT ceramics. Problem areas of compositional variation as reflected by ranges in dielectric properties and sample preparation by dicing were recognized as k_{ij} issues for device fabrication.

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US ARMY MEDICAL RESEARCH AND MATERIEL COMMAND
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REPLY TO
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MCMR-RMI-S (70-1y) 4 Dec 02

MEMORANDUM FOR Administrator, Defense Technical Information Center (DTIC-OCA), 8725 John J. Kingman Road, Fort Belvoir, VA 22060-6218

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2. Point of contact for this request is Ms. Kristin Morrow at DSN 343-7327 or by e-mail at Kristin.Morrow@det.amedd.army.mil.

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