Project no.**17569**

Project acronym: **IMMEDIATE**

Project title: **INEXPENSIVE, HIGH-PERFORMANCE, LEAD-FREE PIEZOELECTRIC CRYSTALS AND THEIR APPLICATIONS IN TRANSDUCERS FOR ULTRASONIC MEDICAL DIAGNOSTIC AND INDUSTRIAL TOOLS AND EQUIPMENTS**

Instrument: **CRAFT**

Thematic Priority: **HORIZONTAL RESEARCH ACTIVITIES INVOLVING SMES COOPERATIVE RESEARCH**

Title of report
Final Activity Report

Period covered: from 1.0.7.2005 to 30.09.2007

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Start date of project: 1.07.2005

Duration: 24 months + 3 months extension

Project coordinator name: Prof. N. Setter
Project coordinator organisation name: LC-EPFL

Revision [2]

1. Project execution

(It should include a summary description of project objectives, contractors involved, work performed and end results, elaborating on the degree to which the objectives were reached. It briefly describes the methodologies and approaches employed and relates the achievements of the project to the state-of-the-art. It should explain the impact of the project on its industry or research sector. It includes, if available, diagrams or photos illustrating the work of the project, a project logo and a reference to the project website.)

Project objectives:

Concerned with toxicity of lead (Pb) contained in most high performance piezoelectric materials, recent legislations in EU and other regions (notably Japan) require replacement of lead based materials with non-toxic alternatives, whenever this is possible, i.e., when alternatives can assure the same functionality as existing products. This is particularly important for medical devices employing piezoelectric materials: thousands of lives are saved and illnesses cured using ultrasonic imaging and therapy based on piezoelectric devices. The alternative materials thus must meet or surpass the performance of the existing lead-based products. Recent engineering and scientific advances in Japan have suggested that materials based on potassium sodium niobate may be comparable in performance with classical lead zirconate titanate ceramics, presently most widely used piezoelectric material. This project represents a European effort to seek alternative lead-free solutions for piezoelectric materials used in medical and industrial devices and a broad spectrum of other applications.

This main objective is pursued through the following activities, focusing on the need of participating SMEs:

(1) Investigate Solid State Crystal Growth (SSCG) method for preparation of inexpensive lead-free, potassium niobate, $KNbO_3$, and modified potassium niobate $(K_{1-x-y}Na_xLi_y)(Nb_{1-z-w}Ta_zSb_w)O_3$ crystals. The method is based on template-assisted growth of single crystals from high-density ceramic substrates and presents a potentially cost effective way to obtain crystals of complex compositions that are difficult to prepare with standard techniques,
(2) Development of medical and industrial transducer components based on high performance piezoelectric crystals and ceramics of lead-free, potassium niobate KNbO3 and novel modified potassium niobate $(K_{1-x-y}Na_xLi_y)(Nb_{1-z-w}Ta_zSb_w)O_3$ compositions. The morphotropic compositions of $(K_{1-x-y}Na_xLi_y)(Nb_{1-z-w}Ta_zSb_w)O_3$ and special crystal orientations of $KNbO_3$ exhibit performance advantages over standard presently used lead based piezoelectric ceramics.

The specific devices targets are high frequency probes for ophthalmology, Doppler transcranial probes, and liquid level sensors. Piezoelectric crystals and ceramics developed in the project are applicable for a broad range of other piezoelectric applications.

The long term objective of the project is to help: (i) reduce lead-based toxic waste during production of piezoelectric materials and components, (ii) eliminate toxic, lead based compounds from medical and industrial ultrasonic imaging devices and thus ensure their safer disposal, and (iii) develop biocompatible piezoelectric materials.

It should be mentioned that additional activities in lead free piezoelectric materials are carried out in other EC FP6 projects (e.g., MINUET) with participation of IMMEDIATE partners Ferroperm, IMASONIC, MTB, EPFL and JSI and other industrial partners such LEGO, FIAT Research Center and others. Thus the spectrum of possible end-products expected from these combined efforts is much wider than that considered in IMMEDIATE alone. Other activities on lead free materials are carried out in the framework of FP6 Network of Excellence MIND and future European Piezo Institute created by the members of this Network with financial support of EC.

Continuation of the work on lead-free piezoelectrics is envisaged in the framework of FP7 projects (1 proposal already submitted, others pending) with various industrial partners, which will again help broadening the application area of these materials.

See below for continuation of activities emerging directly from IMMEDIATE project.

Contractors involved

-Ceramics Laboratory of Ecole Polytechnique Federale de Lausanne, Switzerlan (LC-EPFL), an RTD partner specialized in properties studies of piezoelectric materials and the project coordinator

-Laboratory for Electronic Ceramics of Jozef Stefan Institute, Slovenia (IJS) , an RTD partner, specialized in processing of piezoelectric ceramics

-Forschungsinstitut für mineralische und metallische Werkstoffe - Edelsteine/Edelmetalle- GmbH, Germany (FEE), an SME specialized in crystal growth.

-Ferroperm Piezoceramics A/S, Denmark (Ferroperm), an SME specialized in production of piezoelectric ceramics for a broad spectrum of applications

-Imasonic S.A., France (IMASONIC), an SME specialized in development and fabrication of various types of medical and industrial transducers

-CERAM, Sweeden, (CERAM) an SME specialized in development and production of liquid level sensors

Medizintechnik Basler AG, Switzerland, an SME specialized in development and fabrication of Doppler devices for medical use.

Work performed and end results:

Work performed during the project was carried out according to the plan with minor modifications as explained below.
To reach the project goals and finish all deliverables, an extension of the duration of project activities was asked and obtained form the EC. Thus the project was officially ended 30.09.2007. Comparison with the state of the art is given for each result, were applicable.

The major results of the 2-year (+3 months) work can be summarized as follows.

1. **Development of monodomian and domain engineered $KNbO_3$ based piezoelectric elements.** This activity involved development of crystal growth conditions, crystal poling into monodomain and domain engineered state and preparation of $KNbO_3$ (KN) elements for transducers (e.g., cutting, thinning and polishing) .
   Special cuts of KN crystals exhibit low dielectric permittivity (clamped permittivity below <30) and high thickness coupling coefficients (69%) that are particularly well suited for high frequency single element transducers. Such piezoelectric elements are presently not commercially available. One reason for this is difficulty in growth and preparation of KN crystals and the other is the high cost of monodomain crystals which were until now prepared only for optical applications. Both issues were addressed in this project.

   Calculations by LC-EPFL have shown that a crystal cut convenient for crystal preparation exhibits equally good properties as the special cut with maximal piezoelectric properties originally reported in the literature. FEE, which is a world leader in growth of optical quality KN crystals, has developed a method for preparation of monodomain crystals cut in the optimal direction while preserving or nearly preserving the monodomain state. Functional characterization by LC-EPFL has shown that in samples with a small density of residual domains, the high piezoelectric properties are preserved. As a consequence, the procedure usually used for production of optical quality crystals could be relaxed, leading to cost reduction.

   A further step toward cost reduction was made by showing that poling crystals along a special crystallographic direction leads to so called domain engineered state in the crystal with the same properties as in a monodomain crystal. A procedure for domain engineering of KN crystals was developed at LC-EPFL and implemented by FEE; thus, it was shown that in principle a monodomain state is not needed for piezoelectric applications. As the monodoman state was directly linked to a high cost of optical crystals, this major obstacle in application of KN crystals for transducer applications has been passed. As a consequence, the cost of crystals for ultrasonic transducers could be reduced by roughly an order of magnitude compared to crystals prepared for optical applications. Nevertheless, FEE has developed a method for cutting and thinning KN crystals to samples with thickness of 50µm by maintaining monodomain state. These crystals were used for first prototypes of high frequency probes. Additional samples with large size (diameter 12-16 mm) were made for low frequency transducers. In all cases the properties of the crystals were excellent and close to those theoretically predicted.

From the point of view of crystal growth and preparation (including domain engineering) the partners have accomplished all the goals from the initial plan. To our best knowledge there are no other activities worldwide with similar results.

The main partner involved in this activity was FEE, while poling studies and characterization were performed by LC-EPFL and FEE. The main end-user is IMASONIC, which has interest in using KN crystals for medical imaging in ophthalmology. The prototypes of KN-based transducers for low frequency applications was made by CERAM for liquid sensor applications and MTB for transcranial Doppler measurements (see below for further details).

The activities in further development of KN based devices for high frequency applications will continue at FEE, EPFL and IMASONIC after completion of project.

The impact of these activities on FEE is important as it could expand its range of products to piezo devices, and not only those considered in the consortium. This will have a positive impact on the stability of FEE's workforce.

2. **Development of 50 MHz transducers based on KN.** High frequency ultrasonic probes (operation at 50 MHz) for medical imaging have been constructed using KN crystals with joint effort of IMASONIC (composite and probe fabrication), FEE (KN crystal preparation and thinning) and LC-EPFL (electroding and re-poling of probes into domain engineered state). The transducers are to be used for medical imaging in ophthalmology and possibly other high frequency applications.
The initial goals of IMASONIC have been achieved: high frequency prototypes based on KN have been built and tested showing performance comparable to those made with classical PZT materials. This by itself is an important result demonstrating that alternatives for lead-based devices may be found. The main technical issue not solved during the project duration, is partial depoling of crystals during transducer fabrication. Repoling of transducers has been tried by LC-EPFL. It was partially successful (kt was recovered to 56%, compared to 69% expected in fully poled monodomain or domain engineered crystals). These partially poled crystals already have the same performance as existing PZT based transducers. The modeling shows that if KN crystal within transducer is fully re-poled into domain engineered state, its performance should be superior to that of already existing product based on PZT. In-situ repoling of transducers continues to be investigated with joint efforts of Imasonic, FEE and EPFL. In particular, optimization of poling conditions (into domain engineered state) will continue by EPFL after the end of the project. If these efforts are successful, the product (first prototypes) could be commercialized by IMASONIC as early as 2008.
To our best knowledge there are no competing products with similar properties and potential.

3. **Development of transcranial Doppler probes using $KNbO_3$ crystals**
Doppler probes for transcranial measurement of cerebral blood flow velocity were successfully constructed using KN crystals. The main technical issue is the low dielectric permittivity of KN making the electrical impedance of the probes too high at low frequencies. MTB has shown that the impedance mismatch can be compensated electrically. When compensation was implemented, the performance of probes was superior to those using lead-based transducers. An obstacle in commercialization of probes could be the high price of large crystals (16 mm) needed for 2 MHz probes. However, the price issue is being considered by FEE and significant decrease in fabrication cost of crystals has been already achieved during the project. While KN-based probes represent a technically viable lead-free alternative to classical PZT based devices, a more convenient solution for low frequency applications would be lead-free materials with a higher permittivity and the same high coupling coefficient as KN. As planned in the DoW, this problem was addressed by developing ceramics and crystals with modified compositions. These activities will continue within future activities of FEE, Ferroperm, JSI and LC-EPFL. In the present situation, no commercialization of probes is envisaged before 2008, but if materials with more suitable properties are available, it could be as early as 2008.

The partners involved in these activities were MTB (probes construction), FEE (crystal supplier), and LC-EPFL (electroding and characterization).

4. **Conception and fabrication of water level sensors using $KNbO_3$ crystals.** Transducers using KN crystals were constructed by CERAM, and prototypes tested as planned in DoW. In general, probes show poorer performance than transducers prepared by standard PZT materials. However, under suitable driving conditions, the transducers can be used, if needed, for intended application.

Technical and non-technical obstacles, possible solutions and possibility of commercialization are nearly identical to those for MTB described in item 3 above (both end users use probes at 2 MHz, under similar operating conditions). No competing products based on lead-free materials presently exist on the market.

The partners involved in this activity were CERAM (transducer construction), FEE (supply of crystals) and LC-EPFL (characterization and electroding). The activities in developing more suitable materials will continue after project is officially finished.

5. **Development of the SSCG method for producing KN and KNN single crystals.** SSCG method was chosen as one of the possibilities to achieve cost reduction in production of KN based crystals. Prior to work in IMMEDIATE, to our best knowledge, no attempts were made in growth of KN based materials by SSCG technique. Growth conditions (such as temperature, pressure, time), substrate choice and matrix used for the growth were investigated and developed. Crystals sufficiently large for property characterization (up to 4mm) were grown for the first time. Because of the low crystal growth rate the size of the crystals was, however, too small for prototype construction. Thus, the cost reduction efforts were concentrated on developing TSSG domain engineered crystals (described in (1) above) that could be used in prototypes during the project duration. From the scientific and research point of view the demonstrated possibility of growth of KN based crystals is significant. It is shown that this technique is useful for exploratory growth of single crystals of KN based materials that are difficult to grow with standard methods.

   Partners involved were JSI (development of growth conditions and crystal growth) and FEE (supplier of substrates). Presently, commercial utility is remote but results will be used for education purposes and activities will be continued by JSI.

6. **Growth of Li and Ta doped $(K_{1-x},Na_x)NbO_3$ crystals.** Li and Ta modified KNN crystals were grown and functional properties tested. From the point of view of crystal growth, the original plan was achieved by demonstrating that Li and Ta doped crystals can be grown by TSSG technique. Difficulties were encountered in incorporating sufficient concentration of Li into crystals. Toward the end of the project, however, a significant breakthrough was made by growing crystals containing as much as 4% Li (determined by dielectric measurements). No prototypes were made since the size of grown crystals was not sufficiently large for low frequency applications and poling procedure could not be developed before the project completion. Ta concentration needs to be optimized, but first results show that Ta can be incorporated into the structure. The first grown crystal was off the target by about 5% Ta, which is encouraging considering difficulties in simultaneous control of concentrations of K, Na, Li, Nb and Ta. Equally important is that as grown, unpoled crystals possess high kt (>50% and in some cases >60%, promising even better properties in poled state) and higher permittivity than KN (up to 300 in <100> pseudocubic direction) suitable for low frequency applications. Poling conditions need to be developed and optimized to allow exploitation of the full potential of these crystals, in particular for low frequency applications of CERAM and MTB (see items 1,2,3,4). To our best knowledge, efforts in the framework of IMMEDIATE are the first worldwide to successfully produce Li and Ta based KNN crystals.

   Partners involved were FEE (crystal growth) and LC-EPFL (poling, characterization), with potential users MTB and CERAM. The activities in growth (FEE) and characterization (LC-EPFL) will be continued. MTB, CERAM, and IMASONIC are ready to test crystals with properties suitable for transducers after project is finished. Introducing crystals with new compositions (besides KN) would be important for new market opportunities and visibility of FEE in the field of piezoelectric materials .

7. **Preparation of ceramics of modified KNN.** In agreement with the DoW, it was demonstrated that examined systems could potentially be used in ceramic form as a replacement for PZT. Moreover, prototypes were fabricated for all intended applications and tested. In particular, it was demonstrated that machinability of ceramics is excellent allowing production of small elements (tens of microns size) for composite transducers. Excellent properties were obtained in some ceramic samples prepared in JSI and LC-EPFL, exceeding those reported in the literature; however, the properties degraded with time. Upscaling of production from laboratory to industrial level was also accomplished although not optimized before completion of the project.

   Thus, lead–free ceramics with properties comparable to those of PZT are not yet commercially available. While potential of lead-free ceramics was demonstrated in IMMMEDIATE, the materials were found to suffer from a poor reproducibility and degradation of properties with time. However, some of the ceramics prepared by Ferroperm are of high enough quality to be used for selected applications. It should be mentioned that this project, together with related efforts within FP6 projects MINUET and NoE MIND are the first concentrated efforts in Europe to develop lead-free ceramics for piezoelectric applications (other efforts were reported by Bosch and Siemens at the European Ceramics Society meeting held in Berlin, in June 2007).

The partners involved were Ferroperm, as industry that is interested in commercializing developed compositions, and LC-EPFL and JSI involved in ceramic preparation and testing. Ferroperm will continue working on development of ceramics and powders after the project is finished as will LC-EPFL and JSI. Once reproducibility problems are solved, the possible end users are IMMEDIATE partners IMASONIC, CERAM and MTB and many of the large number of Ferroperm customers. Ferroperm has a world-wide network of contacts among end-users and well developed network for distribution of its products.

We emphasize that a vast number of potential applications are open for lead-free materials: in consumer sector (e.g., for toys), for biocompatible and implantable piezoelectric actuators and sensors, as biocompatible elements for passive energy dissipation (e.g., for toughening of dental protheses), for medical diagnostics and therapy, sensors, nondestructive testing and many others. KNN-based powders as a separate product are now commercially available from Ferroperm.

2. Dissemination and use

(Publishable results of the Final plan for using and disseminating the knowledge (see format in Appendix 1).

Considering that many of the results are trade secrets of end-users, the consortium is not yet ready to publish project results on CORDIS public web page. Selected results of the project haves been presented at conferences (8 international conferences) and scientific publications (6). Please see details in the Final plan for using and disseminating knowledge. The dissemination of the activities will continue at international conferences and in scientific publications after the project is completed (1 PhD thesis work is carried out at EPFL).

The project web page (http://lc.epfl.ch/lc/electro/Projects/ImmediatePublic/Home.htm) was created and maintained by the coordinator. This page was used for external dissemination of information about project activities and for internal distribution of information to project partners.