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Development of Advanced Materials for Electro-Ceramic Application Final Report CRADA No. TC-1331-96

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Development of Advanced Materials for Electro-Ceramic Applications

Final Report
CRADA No. TC-1331-96
Date Technical Work Completed:
Symetrix: October 1999
General Atomics: December 1999
Soliton Russia: March 1999

Date: September 27, 2001 Revision: 3

A. Parties

This project was a collaboration between Lawrence Livermore National Laboratory, Symetrix International USA, General Atomics USA and Soliton-NTT, Scientific and Production, Russia.

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Soliton was indirectly a party to the CRADA. The Russian Institute was a subcontractor to LLNL, and its activities were funded by a Russian Procurement placed through LLNL.

B. Project Scope

The goal of this project was to further develop and characterize the electrochemical methods originating in Russia for producing ultra high purity organometallic compounds utilized as precursors in the production of high quality electro-ceramic materials. Symetrix planned to use electro-ceramic materials with high dielectric constant for microelectronic memory circuit applications. General Atomics planned to use the barium titanate type ceramics with low loss tangent for producing a high power ferroelectric tuner used to match radio frequency power into their DIII-D fusion machine.

Phase I of the project was scheduled to have a large number of organometallic (alkoxides) chemical samples produced using various methods. These would be analyzed by LLNL, Soliton and Symetrix independently to determine the level of chemical impurities thus verifying each other's analysis. The goal was to demonstrate a cost-effective production method, which could be implemented in a large commercial facility to produce high purity organometallic compounds.

In addition, various compositions of barium-strontium-titanate ceramics were to be produced and analyzed in order to develop an electroceramic capacitor material having the desired characteristics with respect to dielectric constant, loss tangent, temperature characteristics and non-linear behavior under applied voltage. Upon optimizing the barium titanate material, 50 capacitor preforms would be produced from this material demonstrating the ability to produce, in quantity, the pills ultimately required for the ferroelectric tuner (approx 2000-3000 ceramic pills).

In Phase II of the project, we planned to begin the commercial development of facilities both in Russia and the US to produce the above electroceramic materials and precursors for use in the microelectronics industry. In addition, a 10-Megawatt ferroelectric tuner was scheduled to be built (using barium titanate material developed in Phase I) and tested on DIII-D fusion facility at General Atomics. Soliton would produce and perform quality control for the thousands of ceramic pills, which were to be produced.

The technical work for Phase I was completed in a timely manner after the Russian subcontracts, CRADA and disposition of monies were in place. However, there was a major delay in allowing the technical work to proceed due to the 18-month cycle getting the CRADA document through DOE.

The goals and deliverables described above for Phase I were met.

The significant change to plans in the original project was termination of the project after Phase I by consent of all parties because:

1) Phase II would have begun in the fall of 1999, however, the money was not automatic; and DOE would have to approve funds. In addition, at this time all Russian subcontracts through IPP were put on hold due to DOE issues with Russian taxes. The consequence was that payments on new or existing contracts would be delayed by over one year. With long delays again anticipated, it was not considered cost-effective by LLNL($125 K) to continue the project.
2) General Atomics made a strategic decision to no longer pursue the development of the ferroelectric tuner.
3) Symetrix found elsewhere a more immediately available and cost-effective source for their required organometallic precursors and no longer wished to pursue their commercialization interests with the Russian group.

C. Technical Accomplishments

The technical accomplishments were:

1) Development of electrochemical and other techniques for the synthesis of high-purity chemicals used in the manufacture of ceramic materials
2) Development of barium/strontium titanate ceramic capacitors with low electrical dissipation and large coefficient of non-linearity making possible the construction of a high power (10 MW) ferroelectric tuner used in plasma heating.

Chemical Synthesis

A large number of chemical samples were produced by various methods and then analyzed for impurities. In particular, these consisted of: Tantalum butoxide, Tantalum ethoxide, Tantalum Methoxide, Tantalum isopropoxide, Niobium ethoxide, Niobium butoxide, Niobium methoxide, Ziconium isopropoxide, Zirconium butoxide, Bismuth 2-ethylhexacoate, Tungsten butoxide. The concentration of trace impurities were determined at LLNL using inductively coupled plasma atomic emission spectroscopy

and inductively coupled plasma mass spectroscopy. The impurities of interest consisted of sodium, lithium, iron, cobalt, nickel and chromium.

In the first batch of chemicals the impurity levels were all at levels lower than the maximum allowable required as specified by Symetrix except for lithium. The methods for production were improved and by the third batch, the impurity level for lithium was also within specification. The group at Symetrix independently verified the impurity levels which were determined by the analytical sciences division at LLNL. The Soliton group was successful at developing techniques for producing high purity alkoxide and organometallic precursors.

Barium Strontium Titanate Capacitors

Various compositions of Barium Strontium Titanate ceramic material were produced to determine how the material dielectric constant and loss tangent behaved as a function of temperature, frequency and applied external voltage. Extensive measurements of the dielectric constant and loss tangent were performed to finally arrive at a material composition that satisfied the specifications required in order to built a 10MW ferroelectric tuner. Powders of this optimum composition were produced. The powders were formed into green ceramic preforms and then optimally sintered to produce ceramic pills 1cm in height and 1cm in diameter faced with gold electrodes on each end.

The dielectric constants were in the range 3000-6000 and the loss tangent was in the range .003-.005. There were 50 of these ceramic pills produced and delivered to LLNL. The composition of the pills was:

$$BaTiO_3(54.7\%), SrTiO_3(21.2\%), CaTiO_3(16\%), MgO(8.1\%).$$

The Soliton group was successful in developing an electroceramic material having the required properties to be used as the dielectric material for a 10MW ferroelectric tuner.

A quality control method for producing the large number of preforms required (2-3 thousand) was also demonstrated.

D. Expected Economic Impact

The goal of this project was to develop electrochemical techniques for the production of ultra pure electroceramic precurser materials and electroceramics for worldwide use in the microelectronics industry. These techniques have been proven scientifically but must be shown to be cost-effective and available on a large scale in order to have economic benefit.

D1. Specific Benefits

The specific benefits will be to General Atomics, Symetrix, and Soliton Russia.

General Atomics now has the key material component for a ferroelectric tuner if they decide to build such a device in the future.

Symetrix has detailed information on the electrochemical techniques for producing ultra pure electroceramic precursor materials, which could be used commercially at some future date.

Soliton Russia has demonstrated their electrochemical techniques for producing ultra pure electroceramic precursors, which could allow for future business opportunities with other companies worldwide.

E. Partner Contribution

Symetrix

Symetrix specified the various chemical compounds to be synthesized for use in making electroceramics. They determined what the goals and specifications were as to the impurity levels, which were to be satisfied. Finally, Symetrix provided information as to the commercial applications for development of these ceramic materials and precursors.

General Atomics

General Atomics provided the initial design concept for the ferroelectric tuner and the specifications on the dielectric ceramic material, which would be required for such a tuner.

LLNL

LLNL further developed the designs for the ferroelectric tuner and oversaw the development of the barium strontium titanate dielectric pills needed for the tuner. The Analytic Sciences group at LLNL did the analysis of the Russian samples to determine the impurity concentrations.

Soliton — Russia

Soliton developed their electrochemical processes to produce a variety of ultra-pure precursor materials used in the manufacture of electrocermics. They also synthesized and analyzed various barium strontium titanate compounds thus producing the characteristics required for use in ferroelectric tuners. They produced 50 ceramic pills and performed extensive measurements before delivery to LLNL.

F. Documents/Reference List

Reports

1. Choice of low electrical loss material for ferroelectric tuner. Production of alkoxy-derived barium titanate powders using electrochemical methods for producing precursors. Production of tantalum butoxide precursor with ultra low impurity content.

2. Optimum composition of barium titanate compounds for tuner capacitors. Analytic methods for controlling barium and strontium in (Ba,Sr)TiO3 systems. Comparative study of electrochemical and chemical techniques for synthesis of bismuth alkoxide precursors. Production of Niobium butoxide with ultra low impurity content.

3. Temperature and frequency dependence of complex dielectric constant for various (Ba,Sr)TiO3 compositions. Comparative study of electrochemical and chemical techniques for synthesis of zirconium alkoxides.

4. Temperature and frequency dependence of complex dielectric constant under different bias voltages for four different (Ba,Sr)TiO3 compositions. Comparative study of electrochemical and chemical techniques for synthesis of tantalum and niobium alkoxides.

5. Improving temperature and frequency characteristics of complex dielectric constant for various materials made with (Ba,Sr)TiO3 compositions. Electrochemical techniques using a membrane for synthesis of bismuth 2-ethylhexanoate. Production of tantalum butoxide with ultra low impurity content.

6. Temperature and frequency dependence of dielectric constant of different composition of (Ba,Sr)TiO3 with additives under different external voltage bias fields. Synthesis of tantalum and niobium ethoxides with low chlorine content.

7. Final choice of barium compound composition to be used in making capacitor preforms. Comparative study of chemical and electrochemical techniques for synthesis of molybdenum alkoxides and bismuth 2-ethylhexanoate. Production of tantalum butoxide and tantalum ethoxide with ultra low impurity content.

8. Best methods for preparing green ceramic composition in making preforms for capacitors. Comparative study of electrochemical and chemical techniques for synthesis of tungsten alkoxides. Methods for the synthesis of the salts of dicarboxylic acids.

9. Optimum sintering conditions for making ceramic capacitor preforms.

10. Testing of powder batches used for sintering ceramic preforms. Production of barium titanate thin films using alkoxy-carboxylates in sol-gel synthesis. Production of transition metal alkoxides.

11. Optimization of process to produce capacitor preforms. Synthesis of Ti, Nb and Ta alkoxy-carboxylates for application in preparing oxides. Production of alkoxy derived barium titanate powders and sintered ceramic preforms for capacitors.

12. Electrical tests of the ceramic capacitors developed for the prototype ferroelectric tuner. Low temperature methods for synthesis of titanates, niobates, and tantalates of alkaline earth elements. Study of the synthesis of hetero-metallic carboxylates with oxo-bridges between dissimilar metal atoms. Production of metal alkoxides with low impurity content.

13. Memorandum, August 1998, Analytical Sciences Division, LLNL, "Analysis of samples of Ta and Nb alkoxides to determine free alcohol concentration, Ta and Nb concentration and trace metal contamination"

14. Memorandum, May, 1999, Analytical Sciences Division, LLNL, "Analysis of trace metal impurities in organometallic solutions from both Soliton Russia and Symetrix"

Patent/Copyright Activity

There were no copyright or patents filed as part of this CRADA. There was no copyrighted software developed.

Subject Inventions

There were no subject inventions disclosed during this CRADA

Background Intellectual Property (BIP)

LLNL BIP:
Measurement techniques and hardware system for determining the complex dielectric constant of small ceramic samples as a function of temperature and external electric bias field.

General Atomics BIP:
Design of prototype RF tuner

Symetrix
1. Process of preparation of metal 2-ethylhexanoates
2. Synthesis of metal 2-ethylhexanoates
3. Process of plating complex metal alkoxides using a liquid precursor
4. Electrochemical synthesis of metal alkoxides using fractional distillation
5. Electrochemical synthesis of metal alkoxides using alternative processes
6. Electrochemical synthesis of metal alkoxides using rotary evaporator
7. Electrochemical synthesis of metal alkoxides using branched alkoxide exchange
8. New MOD process chemistry relating to reactions of metal alkoxides with metal carboxylates

Soliton BIP:
1. Process for preparation of titanium alkoxides
2. Process for preparation of barium titanate and magnesium titanate
3. Reactions of Ti,Ta, Nb alkoxides with 2-ethylhexanoic acid
4. Electrochemical synthesis of metal methoxyethoxides in methoxyethanol
5. Technique for synthesis of tantalum alkoxides
6. Technique for synthesis of niobium alkoxides
7. Technique for synthesis of metal 2-ethylhexanoates

G. Acknowledgement

Participants' signature of the final report indicates the following:

1) The Participant has reviewed the final report and concurs with the statements made therein.
2) The Participant agrees that any modifications or changes from the initial proposal were discussed and agreed to during the term of the project.
3) The Participant certifies that all reports either completed or in process are listed and all subject inventions and the associated intellectual property protection measures generated by his/her respective company and attributable to the project have been disclosed or are included on a list attached to this report.
4) The Participant certifies that if tangible personal property was exchanged during the agreement, all has either been returned to the initial custodian or transferred permanently.
5) The Participant certifies that proprietary information has been returned or destroyed by LLNL.

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Lawrence Livermore National Laboratory

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Soliton Russia has demonstrated their electrochemical techniques for producing ultra-pure electro-ceramic precursors which could allow for future business opportunities with other companies worldwide.

D. Benefits to DOE

The main benefit of this project to DOE is to promote the goals of the IPP program (Initiative for Proliferation Prevention). These goals are to develop collaborative commercial enterprises in Russia which will provide permanent employment for Russian Scientists previously employed in weapons research. The goal is to prevent proliferation by keeping Russian scientists gainfully employed inside Russia while at the same time developing new technologies in the US of benefit to both Industry and DOE. This project has achieved these goals in part by developing new electro-ceramic materials which can be used in the micro-electronics industry as well as in high power ferroelectric tuners for future use in the DOE fusion program.

E. Project Dates

Project Began: January 1998

Technical Work Completed:
General Atomics: December 1999
Symetrix: October 1999
Soliton: March 1999 (Acknowledged no patents to disclose, May 2001)