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Electroceramics Research in India

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Abstract. Electroceramics research is driven by the technology development needs and the device applications in the fields of microelectronics, communications, automation, energy conservation, MEMS and others. Ferroelectric ceramics have been technically exploited because of their unique properties such as high dielectric permittivity, high piezoelectric & electromechanical coupling and discovery of electrical poling process. Under certain circumstances they show high optical transparency and electro-optic coefficients. High permittivity barium titanate based piezoelectric ceramics and their polymer composites show unusual properties for a wide range of applications in sonars, ultrasonic cleaners, micro-accelerometers, hydrophones, surface acoustic wave filters, delay lines, and microactuators etc. A number of organizations in India viz. academic institutions, research laboratories and industries are involved in the preparation, characterization and device fabrication of the electroceramic materials. This paper presents an overview of the ongoing work and the future prospects.

Keywords: electroceramics research, piezoelectric devices, acoustic transducer, hydrophone, MEMS

Introduction

Ferroelectric ceramics have been technically exploited in industrial and commercial application of their unique properties, namely (i) high dielectric permittivity, (ii) high piezoelectric and electro-mechanical coupling, (iii) high pyroelectric coefficient. The transition in the history of ceramic materials occurred in 1940s during World War II, when it was observed that on external electric field could orient domains, within the grains of a polycrystalline material, thus producing a material similar in behavior to single crystals as far as its ferroelectric and piezoelectric properties are concerned. The second breakthrough occurred in late 1970s, when ferroceramics thin films were developed using vacuum deposition techniques and wet chemical methods. Integration of ferroelectric films to silicon chip was demonstrated in 1993 [1]. With this, electroceramics came to the threshold of a technological revolution preparing towards nanocomposite intelligent materials.

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The Electroceramic Devices

Advanced electroceramics are a class of functional materials that are utilized for their specific dielectric, ferroelectric, piezoelectric, pyroelectric and electro-optic properties [2]. The research performed in various organizations has focused on developing a scientific base for synthesis and characterization of electrocreamics under different ambient conditions [3]. The effect of electrical poling and characterization of polarization behavior have been studied. The applications include multilayer capacitors (MLCs), ferroelectric memories, piezoelectric transducers, pyroelectric detectors and non-linear optical devices. From high strength flaw detectors of mechanical parts, the use of fine ferroelectric ceramics in high dielectric constant multilayer capacitors, noiseless printing heads for bubble jet printers, ultrasonic devices and high resolution tomography has been demonstrated. Their applications range has been growing in micro-accelerometers, hydrophones, surface acoustic wave filters, delay lines, and microactuators.

The pyroelectric devices include night vision systems, thermal imaging, two dimensional arrays of thermally isolated bolometers and temperature sensors.

Under certain circumstances ferroelectric ceramics show high optical transparency and electro-optic coefficients. They provide options for developing nonvolatile ferroelectric random access memories (NFRAMs), high density optical storage and spatial light modulators. Integration approach with silicon is making it possible to develop micro-electromechanical systems (MEMS). Using MEMS technology, provisions for different type of sensors for space borne instruments, medicinal applications, aircraft payloads and operational hardware are being made.

Global Scenario

The global market for electroceramics has been growing most rapidly in last two decades and approaching 50 billion US dollars per year. The electroceramics technology in USA and Japan has focused on both bulk and surface machined MEMS based devices for applications in automotive industry. More than thirty types of sensors are used in automobiles as knock sensors, raindrop sensors and thermisters for sensing temperature of coolants or exhaust gases etc. The technical Universities in USA are leading in research on high precision pressure sensors for strategic uses in defense and space sectors, development of materials for NFRAMs and electrolytes for solid oxide fuel cells (SOFC).

Lead zirconate titanate has been the most studied material, but the current research focus is on new compositions, new processes and new device concepts in ceramic: polymer and silicon integration using micromachining. The role of interfaces and evaluation of piezoelectric characteristics of silicon integrated electroceramic structures using advance charge profiling techniques like pulsed electric acoustic and laser induced pressure pulse are gaining importance. Material integration approaches in ceramics-polymers-silicon have become the centre of attraction for emergence of niche applications in actuators and smart sensors.

Electroceramic Research in India

A number of organizations in India viz. academic institutions, research laboratories and industries are involved in the preparation, characterization and device fabrication of the electroceramic materials. In the academic sector, most research has been conducted at Universities and Indian Institute of Technologies (IITs). IIT Delhi is involved in the polarization studies in thin films of lead zirconium titanate (PZT) and modified PZT and their composites. The IITs at Kanpur and Kharagpur, IISc Bangalore and other universities are aiming at piezoelectric and electroceramic materials development for industrial use, doped PZT for monolithic MLCs and polarization switching studies. Notable work on electroceramics has been carried out at the Tata Institute of Fundamental Research, Mumbai. National research laboratories are also concerned with electroceramics for the strategic use. A few industries have been the major players in electronic components for defense applications and materials.

Academic Institutions

The lead role in the research field of electroceramics is being taken by the technical Institutes in India. The Indian Institutes of Technology (IITs) as part of rich Indian tradition in engineering education were founded in 1950s in the different parts of country. Most IITs are providing the main thrust for innovative research in the preparation, characterization and device fabrication for their use in industries.

One of the first and finest research activity on electroceramics was started at IIT Kanpur by Prof. E.C. Subbarao and co-workers, who gave inspiration to many fellow Indians working in India and abroad, to take up this activity. The advanced ceramics laboratory in the Physics Department of IIT Delhi has been actively involved in the development of thin films of lead zirconium titanate (PZT), modified and doped PZT, its composites with polymers for acoustic transducers, hydrophone arrays, vibration sensors and infra detectors. An electroacoustic transducer used to generate and receive acoustic signals, makes use of PZT: polymer composites. Series of ceramic: polymer composites have been prepared and tested for different applications. A 16 element and a 64 element hydrophone receiver array using ceramic: polymer 1:3 composites were designed and fabricated for hydrophone applications. A summary of the rare earth doped lead zirconate titanate (PZT) work carried out in the laboratory is shown in Fig. 1.

The micro-electromechanical system (MEMS) sensor device having lanthanum doped PZT (PLZT) thin films with composition 8/60/40 have also been fabricated using silicon micromachining technology. This device has been characterized as a vibration sensor

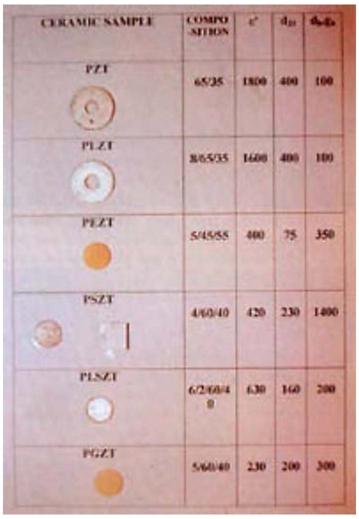

Fig. 1. Rare earth modified PZT characteristics.

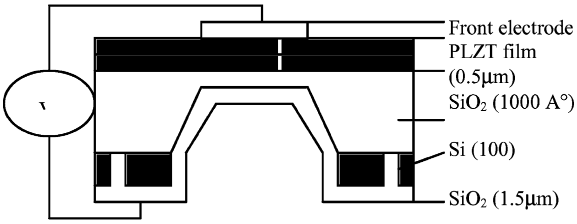

Fig. 2. The structure of the MEMS fabricated device.

(Fig. 2). Work on Ca doped PT and ferroelectric relaxor ternary system has been pursued for infrared detectors and MLCs.

The research work carried out at IIT Mumbai has focused on the amorphous and nano-crystalline thin films of elemental semiconductors and their alloys such as Si-H, Si-C, Si-N etc. Dielectric properties of thin films of PZT ceramics and lead magnesium niobate (PMN) have been studied for correlation with grain size, thickness etc. [4]. Using Chemical Vapor Deposition enhanced by either a hot filament (HFCVD) or RF plasma (RPCVD), development of devices and material modification by low energy ion immersion technique have been targeted. A successful effort has been made to develop stable solid electrolytes with high ionic conductivity using polymeric materials with an inorganic salt-polymer blend.

A large number of electroceramic materials such as lead germinate oxide ($PbGeO_3$), PZT, PLZT, lead magnesium niobate-lead titanate PMN-PT, barium titanate ($BaTiO_3$), barium strontium titanate (BST), strontium bismuth tantalate (SBT) and others have been developed at Department of Physics, IIT Kharagpur [5]. The investigations have aimed at device applications such as monolithic multiplayer capacitors, varistors, electrostrictive and pyroelectric devices. A large amount of work has also been carried out on modified $PbMoO_3$ and $PbWO_3$ materials for their use as varistors. Compounds with K_2SO_4 structure have also been investigated exhibiting successive ferroelectric, paraelectric commensurate-incommensurate phase transitions.

The areas of research interest at Materials Research Centre, Indian Institute of Science (IISC), Bangalore are thin film deposition involving a variety of techniques such as multi-ion beam reactive sputtering, plasma assisted growth, excimer laser ablation and metalo–organic chemical vapor deposition (MOCVD). Low energy ion induced effects in multi-component oxide films, ion-surface interactions and epitaxial growth in ferroelectrics and high permittivity oxide films for dynamic random access memories (DRAMs), development of epitaxial pyroeletric thin films for IR detection using ECR plasma are some of the ongoing areas of research. Backward switching effect observed in PZ and PZS thin films show promising result for microelectronics applications in high-speed charge coupling capacitors [6].

IIT Kanpur is involved in the synthesis of the doped $BaTiO_3$ materials in bulk and thin film forms for their applications in transducers and other piezoelectric devices. The emphasis is on development of new processing methods and materials integration issues with the objective of developing a lead free and environmental friendly material. Among universities, theoretical and experimental work on thin films and bulk ceramics began quite early at the University of Delhi. Recent collaborative work with Jammu University has led to development of high performance lead titanate ceramics with improved hardness characteristics. Allahabad University and Jabalpur University have carried out work on impedance and hysteresis measurements of electroceramics.

Research Laboratories

There are a number of research laboratories involved in the preparation and characterization of various parameters viz. structural, dielectric, piezoelectric, pyroelectric and optical parameters of electroceramics in bulk as well as thin film forms. The pioneer work has been done in the National Physical Laboratory (NPL) and Solid State Physical Laboratory (SSPL), New Delhi, Central Glass & Ceramic Research Institute (CGCRI), Kolkata, Naval Materials Research Laboratory, Mumbai, Armament Research and Development Establishment (ARDE), Naval Science & Technology Laboratory (NSTL), C-Met Trissur and National Physical Oceanographic Laboratory (NPOL), Cochin.

Temperature and frequency characterization of dielectric and electromechanical properties of electroceramics is quite useful for transducer applications A series of piezoelectric (soft PZT) materials were developed at NPL, New Delhi for low power applications. These materials are; NPLZT-5 for acoustic sensing devices and probes for flaw detectors, NPLZT-5A for impact type gas igniters and low power transducers, NPLZT-5B for flaw detectors and NPLZT-5H_1 for gramophone-pickups and hydrophones [7]. Utrasonic velocity measurements have been adopted for characterization of piezoelectric properties of donor doped lead zirconate. The SSPL, New Delhi is engaged in the fabrication of, La doped PZT, PCT and BST ceramics prepared by high temperature solid state reaction and pulsed laser deposition (PLD) techniques. MEMS devices based on Si technology are also the main thrust area of this laboratory.

Research activities at CGCRI, Kolkata involve study of doped zirconia fibers with high temperature insulation characteristics. Such materials may find application in copper vapor laser systems for thermal insulation. Detail studies on Laser damage resistant high reflection and antireflection coatings on glass have been carried out systematically. The development of such coatings may be useful for optical elements in solid state laser systems. Development of rare earth doped silica glass by sol-gel processing is also studied in detail.

The scientists at NPOL, Cochin are working towards the development of advanced technologies for SONAR system design, acoustic signal processing, information technology displays and underwater transducers by using a variety of electroceramic materials. Both bulk and thin film electroceramics have been studied at NMRL, Mumbai. The initial work has been on preparation, compactation and sintering of powders prepared using fine particle technology and study of phase transformations in sintered ceramics. To overcome disadvantages of monolithic PZT ceramics, PZT-polymer composites having 1–3 connectivity and better compatibility for hydrophonic and sonar projectors have been tested for underwater applications [8].

Industrial Involvement in Electroceramics

A few public and private industries have facilities for large scale production of PZT based materials and design & development of hydrophone arrays. The public sector industries viz. Central Electronics Limited, Sahibabad and Bharat Electronics Limited, Bangalore have been producing electroceramic materials like PZT-4, PZT-5 and others for electronic components. They are also supplying different compositions in pellet form to educational as well as research organizations. The private industry like Cabonrundum Universal Ltd. and Concord Industries, Delhi have undertaken fabrication of commercial piezo transducers, hydrophone receivers and arrays based on PZT materials.

Conclusions

Electroceramics is a growing research area in the technical institutions in the country. The research and development on ceramics started in late 1960s. The work on MEMS based piezo-restrictive and piezo-capacitative materials has begun in number of organizations. Study of polarization, optical switching and non uniform charge distribution in electroceramics has been conducted only at a few places. Most research has been through sponsored projects by different government agencies. However, the industry has not played much innovative role in commercial production, except to meet strategic requirements.

In the recent years, there has been considerable interest in combining desirable properties of PZT and different piezoelectric polymers to forms electro active materials for advance sensors. The materials oriented research is becoming more and more interdisciplinary and nanotechnology methods offer new challenges for materials integration as well as modeling studies. In the future, the field of electroceramic materials will continue to grow and unfold new application domains requiring vision and strategic planning in the technological advancement and indigenous capability building.

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