

<b>REPORT DOCUMENTATION PAGE</b>			Form Approved OMB NO. 0704-0188	
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 comment regarding this burden estimates 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 Nov 96		3. REPORT TYPE AND DATES COVERED Final 27 Sep 93 - 26 Sep 96
4. TITLE AND SUBTITLE Novel Thin Films of Ferroelectric Materials for Opto-Electronics Applications			5. FUNDING NUMBERS DAAH04-93-2-0008	
6. AUTHOR(S)  Ram S. Katiyar				
7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES)  University of Puerto Rico Rio Piedras, Puerto Rico 00931			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)  U.S. Army Research Office P.O. Box 12211 Research Triangle Park., NC 27709-2211			10. SPONSORING / MONITORING AGENCY REPORT NUMBER  ARO 32455.18-PH-ISP	
11. SUPPLEMENTARY NOTES  The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.				
12a. DISTRIBUTION / AVAILABILITY STATEMENT  Approved for public release; distribution unlimited.			12 b. DISTRIBUTION CODE  <b>19970213 061</b>	
13. ABSTRACT (Maximum 200 words)  This project focused most of its efforts in two major strategic families of materials: nonlinear optical and dielectric. The selection of candidate materials and the proposed studies on them were made very carefully taking into account their potential impact on technologically important devices. Additionally, we have selected materials which have shown promise in various important devices but still have room to be improved upon either synthesis or understanding. The following flow chart summarizes the direction of our efforts. Also the present project has given us the opportunities to establish facilities to produce some of these materials at the UPR. This report covers the studies on materials which either are produced at some active external collaborative facility or produced at the developing materials facilities at UPR.				
14. SUBJECT TERMS			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

DTIC QUALITY INSPECTED 4

# FINAL PERFORMANCE REPORT

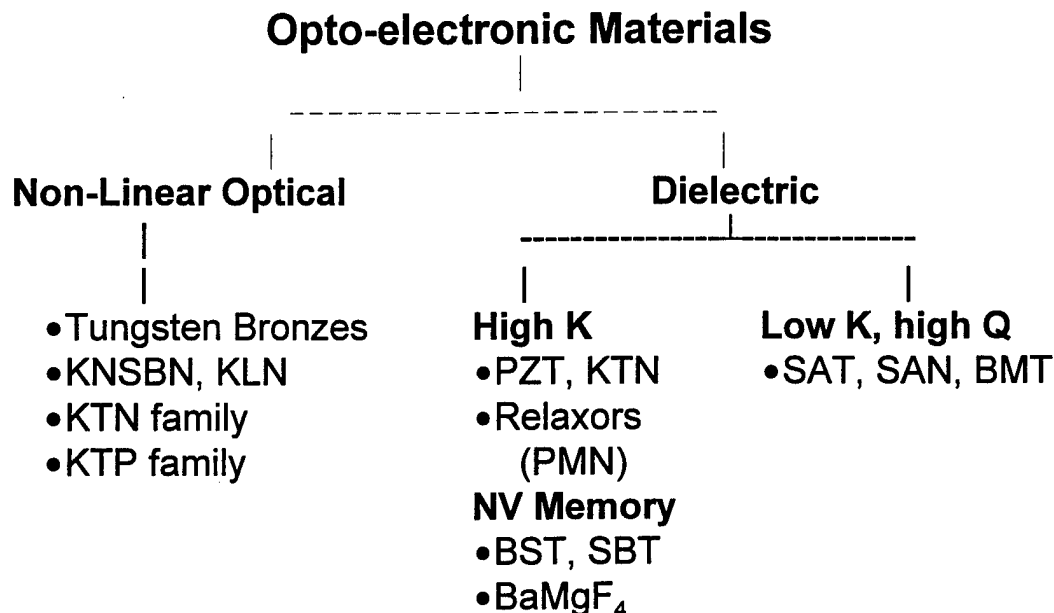
**Contract/Grant Number:** DAAH04-93-2-0008

**Project Title:** Novel Thin Films of Ferroelectric Materials for Opto-Electronics Applications

**Period:** September 27, 1993 through September 26, 1996

**Principal Investigator:** Dr. Ram S. Katiyar; **Co-PIs:** Dr. F. Fernandez, Dr. A. Martinez

This project focused most of its efforts in two major strategic families of materials: nonlinear optical and dielectric. The selection of candidate materials and the proposed studies on them were made very carefully taking into account their potential impact on technologically important devices. Additionally, we have selected materials which have shown promise in various important devices but still have room to be improved upon either synthesis or understanding. The following flow chart summarizes the direction of our efforts. Also the present project has given us the opportunities to establish facilities to produce some of these materials at the UPR. This report covers the studies on materials which either are produced at some active external collaborative facility or produced at the developing materials facilities at UPR.



KNSBN - (KNa)(Sr Ba) Nb<sub>2</sub>O<sub>6</sub>; KLN - (KLi)NbO<sub>3</sub>; KTP - KTiOPO<sub>4</sub>; KTN - K(TaNb)O<sub>3</sub>  
PZT - Pb(ZrTa)O<sub>3</sub>; BST - (Ba Sr)TiO<sub>3</sub>; SBT - SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>; SAT - Sr(AlTa)O<sub>3</sub>  
SAN - Sr(AlNb)O<sub>3</sub>; BMT - Ba(MgTa)O<sub>3</sub>; PMN - Pb(MgNb)O<sub>3</sub>;

## High-lights of the Research Report:

- Nb oxide and Ta oxide thin films of very good quality grown by PLD. This work offered an alternative route for KTN growth by the multilayer approach.
- Successful growth by PLD of KTN films using the multilayer approach. This allows growth with Ta/Nb composition control.
- From Raman spectra of SAT and SAN, it is evident that these materials are ordered in both ceramic and single crystal fibre forms, possessing Fm3m symmetry, at least in nanoregions. This is in contradiction to the X-ray data that shows Pm3m symmetry (complete disordered structure) in crystalline form. From a comparison of the phonon widths in Raman data one may conclude that the nanoregions are smaller in crystals than in ceramics.
- Similarity in the Raman spectra of  $\text{BaMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$  (BMT) with  $\text{SrAl}_{1/2}\text{Ta}_{1/2}\text{O}_3$  (SAT) clearly indicates that the BMT structure is Fm3m (1:1 arrangement at the B site, occupied by Mg & Ta) in the nano-regions, instead of P3m1 (1:2 arrangement) as reported by X-ray analysis. However, this arrangement will require some distortion or oxygen vacancies in order for the charge compensation. The extra weak Raman lines, observed in BMT spectrum, may be an indication of these distortions.
- The selection rules for Raman scattering in complex perovskites are controlled by a short range order in nanoscale regions. For example, the disappearance of Raman spectrum in BMT at higher temperatures, is an indication of complete disorder at the B site (occupied by Mg and Ta) at the nanoscale level. The average symmetry thus changes from Fm3m to Pm3m.
- Established the connection between the phonon spectra, dielectric losses, the real structure and the order-disorder behavior in SAT, SAN, BMT - the important microwave dielectric and HTSC substrate materials due to their low dielectric constant (25 -200) and high Q values (3,000 to 50,000). The spread in the dielectric values was found to be related with the nanoscale arrangement of the B site ions, as determined from Raman studies.
- Ferroelectric properties of perovskite materials depend on their grain sizes. For example, from Raman studies, nano-crystals of  $\text{BaTiO}_3$  with grain size as large as 110 nm, show a symmetry lower than tetragonal at room temperature, whereas the corresponding x-ray data show a pseudocubic symmetry. Analysis shows that as the grain size is reduced, the surface stress on spherical particles play an important role in varying the short range forces, and thus changing the FE behavior.
- A dynamic central peak was found in PMN (a relaxor FE) in the vicinity of both diffuse phase transition (~270 K) and electric field induced FE transition (~200 K). The anomalies in its relaxation time at these temperatures are quite pronounced. This was the first study about the transition dynamics of ferroelectrics with ordered nano-regions.

- Established for the first time, the soft-mode existence and hence the ferroelectric mechanism in the KTP family crystals utilizing Raman and Brillouin Scattering studies.
- From Dielectric properties measurements on KTP family crystals, it was determined that CTA is far superior material for non-linear optical applications than commonly used KTP. From the Cole-Cole plot it is evident that there exists only a single relaxation process in CTA, which is a dipolar process.
- A new glass model is proposed to characterize the frequency dependence of the temperature ( $T_m$ ) of the dielectric constant maximum for the relaxor ferroelectrics. The relation between the dielectric constant and the dielectric absorption was established.
- From Dielectric studies on Relaxor ferroelectrics, the existence of two polarization processes, namely relaxation polarization and resonance polarization, was established. The resonance polarization was verified by the dielectric behaviour under DC bias.
- Photoluminescence studies clearly throw light on the mechanism of the phase transition in relaxor ferroelectrics, such as PMN. The decrease in luminescence peak above the  $T_c$  (210 K) is associated with the decrease in the dimensions of the polar microregions as the temperature is increased.
- KNSBN:Cu from the tungsten bronze family of ferroelectrics is a material with the enhanced photorefractive properties. A stable structure is desirable in a wider temperature interval. We have found from Raman studies that there is an additional phase transition (not reported so far) in this material around  $T \sim 200$  K besides the known FE transition at  $T_c = 410$  K.

## TECHNICAL DETAILS

### PLD of Potassium-niobate-tantalate (KTN) Thin Films.

Our PLD system was recently improved by the substitution of the Nd:YAG laser by an excimer laser as the main light source. An immediate consequence of this is that we have been able to grow KTN thin films of very good quality. Since K-enrichment of the films is needed, evaporation of suitable potassium compounds must be included during deposition. This had proved impracticable with our older laser. A multilayer approach was used to grow this material. This required deposition of very thin layers (less than a monolayer) of  $\text{KTaO}_3$  and  $\text{KNbO}_3$ , in addition to  $\text{K}_2\text{NO}_3$  to provide excess potassium. We have now grown KTN in this manner on  $\text{MgO}$ ,  $\text{SrTiO}_3$ , and  $\text{KTaO}_3$  substrates, all with (100) orientation. It was not possible to grow KTN on Si (100) or glass substrates with the same growth conditions. A crystalline substrate with reasonably good lattice match seems to be a requisite. On the other hand, films grown even on  $\text{MgO}$  show very good orientation. The films are smooth and hard. Preliminary composition estimates, via XRD measurements of (n00) peaks, indicate  $\text{KTa}_x\text{Nb}_{1-x}\text{O}_3$  with x from 0.5 to 0.6, although this assumes

bulk lattice values and does not take lattice strain into consideration. For films grown on  $\text{KTaO}_3$  (100) substrates, due to the close lattice match, more detailed studies of the crystal structure will be required. Additional studies of these films are underway in collaboration with other group members. These will include spectroscopic and electronic property measurements. Suitable samples for these purposes are being prepared.

While KTN has been grown before by PLD, this had been achieved with fixed-composition KTN targets. The present work shows that it is possible to tailor the film composition by the multilayer approach. It will be of interest to verify if the full range of compositions is possible in thin film form.

### **PLD of Ta oxide and Nb oxide Thin Films.**

We have succeeded in growing good quality tantalum oxide and niobium oxide thin films by reactive PLD starting from both oxide or metallic targets. These oxides are of technological interest by themselves, but our interest was stimulated by the possibility of growing KTN thin films by using a  $\text{Ta}_2\text{O}_5 / \text{Nb}_2\text{O}_5 / \text{K}_2\text{NO}_3$  or  $\text{Ta} / \text{Nb} / \text{K}_2\text{NO}_3$  multilayer sequence. Since our results for films grown from the pentoxides are superior we will attempt this option next.

More detailed work was performed on Nb oxide films, partly because PLD growth of this material had not, to our knowledge, been reported before, but also because of its high refractive index (compared to other binary oxides). In addition, interesting nonlinear optical properties have been reported recently for Nb oxide. Nearly stoichiometric  $\text{Nb}_2\text{O}_5$  films were obtained in our depositions from pentoxide targets, in 100 mTorr flowing  $\text{O}_2$  atmosphere, with heated substrates (over 300 °C). Films are polycrystalline when grown at these temperatures. At lower temperatures films are amorphous, and oxidation state appears to be lower. Refractive index of the films is high. As determined by ellipsometry and uv-vis transmission, it approaches 2.4 in the blue. We have also grown Cr-doped Nb oxide films in order to allow spectroscopic studies.

### **Hot Wall Epitaxy Evaporator:**

The use of a hot wall epitaxy evaporator was explored to deposit  $\text{BaMgF}_4$  films. The attempts to deposit this material in our evaporator were not successful due to the inability of the source heaters to achieve a temperature of 1000 C necessary to obtain a plausible deposition rate. The systems inadequacy was isolated to the use of Nichrome wire in the heaters. Even though this alloy is related to temperatures of up to 1300 C, it began to sublime before the temperature in the source reservoir reached the 1000 C mark. This was evidenced by the deposition of Fe on the substrates as the results of Auger electron spectroscopy analysis indicated. The possibility of rewiring the evaporators heaters with a refractive material W or Mo was evaluated. Major rewiring of the system inside and outside of the vacuum system would have been required. It was decided to postpone the  $\text{BaMgF}_4$  growth efforts until the construction of the ultra high vacuum system as stated in the proposal. The hot wall system was used to deposit thin films of bismuth and antimony on silicon substrates. Multilayers of these materials have nonlinear optical properties in the infrared with possible energy related applications.

### **MBE Growth Chamber:**

We designed and ordered components for the construction of a molecular beam epitaxy system with two effusion cells based on a EPI MBE growth chamber. The components have been received and the system has been assembled. The electronics to control the effusion cells and interfacing between the temperature controllers and the power supplies were done in-house. The assembly of the vacuum components, as well as, the design and fabrication of these electronic components have been a valuable opportunity to the graduate students involved and allowed for the system to be built at great savings. We ordered and received  $\text{BaMgF}_4$  and  $\text{BaZnF}_4$  powders and these have been loaded into the two k-cells. Growth runs are being carried out as this report is being submitted. X-ray diffraction and Auger electron spectroscopy of the  $\text{BaMgF}_4$  and  $\text{BaZnF}_4$  source powder were performed to characterize the starting material. Both techniques confirm the chemical integrity of the powder sources.

### **Optical and Dielectric Investigations in Complex Perovskite Materials:**

Our current studies have been concentrated on complex perovskite materials of the  $\text{AB}'_x\text{B}''_{1-x}\text{O}_3$  type. The range of applications of these materials covers different practical needs, such as materials for capacitors with high dielectric permittivity on the one hand and materials with low and extra low dielectric losses on the other hand, as well as materials with high piezoelectric and electrostrictive effects and other properties, materials for dielectric resonators, filters, down converters and other elements in microwave sections and so on. There is a particular interest in materials with composite properties (smart structures).

One of the typical features for perovskite ferroelectric materials like  $\text{PbTiO}_3$ ,  $\text{BaTiO}_3$ , PLT, PZT etc. is that they possess a soft mode driven phase transition associated with the macroscopic properties, i.e. dielectric constant  $\epsilon$  ( $\epsilon \propto 1/\Omega^2$ ). Systematic investigations of the temperature, pressure, dopant and grain size-induced soft mode driven phase transitions can well lead to an understanding of the structure, phase transition, especially the origin of ferroelectric properties which are the basis for the above applications.

### **Raman and Infrared Spectroscopy:**

To start with, we studied the Raman scattering in several materials with remarkable microwave dielectric properties such as those with low dielectric constant and high Q value:  $\text{SrAl}_{1/2}\text{Ta}_{1/2}\text{O}_3$  (SAT),  $\text{SrAl}_{1/2}\text{Nb}_{1/2}\text{O}_3$  (SAN) and  $\text{BaMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$  (BMT). These materials were synthesized in two mostly appropriate forms for practical applications, viz as ceramics and as single crystal fibers grown by the laser heated pedestal growth technique (LHPG). SAT and SAN have a composition with the 1:1 ratio of two B ions while BMT is composed of two B ions with the 1:2 ratio. The B-site order-disorder in complex perovskites of the  $\text{AB}'_x\text{B}''_{1-x}\text{O}_3$  type determines unusual behavior of these materials in many aspects. For example, the dielectric response of different samples of BMT was found in the range 25-200, the reported Q values were widely scattered from 3000 up to 50 000, presumably due to the differences in the Mg and Ta arrangement and in the density of ceramics. So, the study of microscopic structure of the complex compounds like BMT is very important in order to create materials with desirable properties.

Comparative study of the 1:1 (SAT and SAN) and 1:2 (BMT) complex perovskites with low dielectric losses let us find the connection between phonon spectra and the real structure. In spite of different stoichiometric ratio for the constituent B ions, the microstructure was found likely to consist of nanoscale arrangement with the 1:1 ordering in the B sublattice. Raman scattering was found to be an appropriate and sensitive tool to distinguish all three possibilities of the arrangement: the simple perovskite structure  $Pm\bar{3}m$  ( $O_h^1$ ), the  $Fm\bar{3}m$  ( $O_h^5$ ) space symmetry with doubling of the unit cell or pseudo-layered  $P3m1$  ( $D_{3d}^3$ ) structure for the 1:2 ordered compounds.

Our approach allowed us to make some conclusion about the mechanism of charge compensation in such complex compounds like BMT. The real arrangement of two different B ions in nanodomains corresponds to the  $Fm\bar{3}m$  structure and remains invariable in the temperature range studied (up to 1000 K) while the Raman spectra changes drastically. In agreement with these new spectra, at high temperatures an effective size of the oxygen octahedrons is the same in average and the charge compensation is provided by large phonon amplitudes. When temperature decreases, the phonon amplitudes can provide only a partial charge compensation and the main effect of compensation arises from shifts of the oxygen atoms. As a result, two inequivalent oxygen octahedrons appear in the complex perovskite structure corresponding to the two unlike B ions. The oxygen atoms occupy local positions without the inversion center, and the A ions occur in non-centrosymmetrical positions as well. At least a short-range arrangement of this type is consistent with the  $Fm\bar{3}m$  space symmetry.

The most well-known compound between the materials with the 1:2 ratio for the B ions is  $PbMg_{1/3}Nb_{2/3}O_3$  (PMN) which is considered as a model relaxor ferroelectric. Two steps separate PMN from BMT. If on the first stage the  $Nb^{5+}$  ions in PMN are replaced by  $Ta^{5+}$ , one gets a new compound  $PbMg_{1/3}Ta_{2/3}O_3$  (PMT) which exhibits the relaxor ferroelectric behavior with slightly lower temperatures and with smaller values for the dielectric maximum, the remnant polarization, etc. However, the next step to substitute  $Ba^{2+}$  for  $Pb^{2+}$  in PMT leads to our BMT compound under discussion here, the dielectric response changing drastically. Only change in the ionic radii from 1.49 Å (Pb) to 1.60 Å (Ba) results in some tiny variations in the structure. A new material does not show any sign of ferroelectric properties and exhibits ultra low dielectric losses instead. Another reason for a drastic change in properties may originate from order-disorder variations in the B sublattice. In order to correlate the change in properties with the behavior of the phonon subsystem, we also studied Raman scattering in the PMT and PMN single crystals. This part of work has not been completed yet.

Preliminary studies show that the  $A_{1g}$  singlet mode is a sensitive probe to structural changes. The  $A_{1g}$  mode is due to simple motion of the oxygen atoms like the breath-type mode of a free oxygen octahedron. However, this mode reflects clearly the effect of subtle changes in the structure in statics as well as the dynamic phenomena in course of evolution to a ferroelectric state which is very specific in relaxors. An isotypical series of the  $AMg_{1/2}W_{1/2}O_3$  compounds with  $A=Ba, Pb, Sr$  and  $Ca$  shows a change in the  $A_{1g}$  mode frequency when the A cation radius decreases in a  $Ba \Rightarrow Pb \Rightarrow Sr \Rightarrow Ca$  sequence although the  $B'=Mg$  and  $B''=W$  cations and their oxygen surroundings remain without a formal change. An interesting correlation between the  $A_{1g}$  mode frequency and the tolerance factor,  $t$ , was found. It seems that the highest frequency corresponds to the most stable

Fm3m structure with  $t \approx 0.99$ .

The dynamical modification of the  $A_{1g}$  mode spectrum was studied on an example of  $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$  (PST). An evident structure of the initially singlet line appears when the temperature is lowered down to the vicinity of the ferroelectric phase transition. The complex structure of the  $A_{1g}$  mode is connected with a break down in the wave-vector selection rules, so some symmetry points elsewhere in the Brillouin zone contribute to the Raman scattering in the vicinity of the initial singlet line. We suppose that the loss of translational symmetry in PST occurs in a dynamic process initiated by heterophase fluctuations. The dynamic breaking of translational symmetry correlates with the appearance of a broad central peak in PMN which has the maximum intensity and the minimum width just in the vicinity of the main dielectric anomaly. We assume that the central peak in PMN determines the dynamics of the competing interactions between the two frustrated phase transitions. The first report about the transition dynamics of ferroelectrics with ordered nanoregions will be presented. This report summarizes our Raman studies of PMN and related materials with a special attention to the low-frequency Raman spectra.

Ferroelectric Potassium Lithium Niobate (KLN) has a diffusive ferroelectric (FE) to paraelectric (PE) phase transition at 400-550° C depending on the content of lithium in the composition. In a crystal of stoichiometric and low lithium composition with  $T_c = 540^\circ \text{C}$ , we have observed at least one high-pressure phase transition by Raman spectroscopy in a diamond-anvil cell. The phase transition was diffusive but first order in nature. At ambient temperature, the high pressure phase transition from tetragonal to orthorhombic symmetry was determined to occur at  $53 \pm 3$  kbar. We observed mode softening for the low frequency modes as well as the internal and external niobate modes. A peak at  $\sim 200 \text{ cm}^{-1}$  showed a marked intensity increase near the phase transition. We have calculated the mode Grüneisen parameters of 14 out of 20 Raman active  $A_1(z)$  modes polarized parallel to the ferroelectric axis.

For the better understanding of common features in the phonon behavior of different relaxor ferroelectrics, we have studied the Raman scattering in  $(\text{K}_{0.5}\text{Na}_{0.5})_{0.2}(\text{Sr}_{0.75}\text{Ba}_{0.25})_{0.9}\text{Nb}_2\text{O}_6$  doped with CuO (KNSBN:Cu) which belongs to another group of relaxors with the tungsten bronze structure. The vibrations of an oxygen framework in the tungsten bronze structure are considerably affected by disordering in the arrangement of cations. However, it seems that the structure of KNSBN does not predispose to discommensuration as in other closely related analogous materials. The present study shows that the structure of KNSBN remains to be stable in a wide temperature interval below the Curie point.

Sol-gel prepared lead titanate (PT) thin films on silicon substrate were studied. The frequency shift of the modes and the shift of the c-parameter with respect to the bulk material were associated with compressive stress in the films, which was not homogeneous. It is believed that the stress is caused by nonequilibrium defects and diffusion at the interface. The measured shift in the Raman frequencies suggested grain sizes  $< 1 \mu\text{m}$ . XRD indicated grain size of approximately 22 nm and an average stress around 1.3 Gpa. Raman and infrared spectroscopy was also used as a function of temperature to investigate sol-gel grown thin films of  $0.7\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - 0.3\text{PbTiO}_3$  (PMN-PT) deposited on Pt coated silicon as well as on  $\text{Al}_2\text{O}_3$ . The studies indicate strong disorder in the system due to the presence of defects, predominantly, in the B sites of the  $\text{ABO}_3$  perovskite

structure.

Single crystals of  $\text{KTiOPO}_4$  (KTP) family are very important materials for the non-linear optical and electro-optic applications. We have carried out Raman scattering experiments in four materials of this family, namely KTP,  $\text{KTiOAsO}_4$  (KTA),  $\text{RbTiOAsO}_4$  (RTA), and  $\text{CsTiOAsO}_4$  (CTA). The relative intensities of the low frequency bands increases noticeably with increasing temperature due to high mobility of alkali ions at higher temperatures. Moreover, some of the low frequency modes show an evident softening as the temperature increases. A soft mode like behavior is clearly seen in CTA, but the soft mode does not go to zero frequency at the transition temperature, suggesting the presence of a central mode or the acoustic mode softening close to  $T_c$ . Our recent measurements on Brillouin scattering do show the softening of the acoustic mode in these crystals.

We have also investigated by Raman scattering the insulator films of  $\text{Ta}_2\text{O}_5$  and  $\text{Nb}_2\text{O}_5$  that were grown by PLD technique in our laboratories. Both materials exhibit a large variety of crystallographic forms (monoclinic, orthorhombic, tetragonal and hexagonal forms). To our knowledge no analogous Raman scattering study has been published for tantalum and niobate pentoxides. The present Raman scattering study includes a comparative analysis of results obtained for the thin films and their powders. More complex structure of Raman spectrum in  $\text{Nb}_2\text{O}_5$  powder in comparison with that of  $\text{Ta}_2\text{O}_5$  evidences lowering the symmetry which is, probably, monoclinic and orthorhombic, respectively. The Raman spectra of thin films of both materials correspond to amorphous state.

### **Dielectric Spectroscopy:**

The dielectric properties of KTP family crystals have an important effect on its applications. Based on the dielectric behavior of these materials in the temperature range from  $-170^\circ\text{C} \sim 200^\circ\text{C}$ , a micro-model is proposed. The experimental relation between the dielectric constant and the dielectric absorption is given. The model can well explain the effect of alkali ions in the materials, the dielectric relaxation and conductivity of the materials, etc. Based on our model, it is expected that the conductivity at high temperatures will obey the following relation:

$$\sigma = \sigma_0 + a \omega^s$$

We plan to extend the dielectric measurements in the above materials at temperatures from  $200^\circ\text{C}$  to  $\sim 700^\circ\text{C}$  in the frequency range from 1 Hz to 10 MHz, in order to obtain more information about the micro polarization mechanism in these materials.

Relaxor ferroelectrics are very important kind of the functional materials. Based on the experimental study of their dielectric behavior, we proposed a new glass model to characterize the relation between the temperature of dielectric constant maximum and the frequency, which also gives the temperature dependence of the relaxation time in the materials. We get the temperature dependence of the static dielectric constant of these materials for the first time. Based on the specialty of the materials, we propose a reasonable distribution of the relaxation times in the materials. Thus, we can simulate both the temperature and frequency dependence of the dielectric behavior of the materials. The shortcoming of the research based on only the relaxation of the micro

region is given based on the study of the dielectric behavior, aging behavior and the effect of DC bias. A more complete micro picture about the materials is proposed, based on which, the behavior of the relaxor ferroelectrics can be explained and complex perovskite materials are classified. As an extension of the model to typical ferroelectrics, all the behavior of  $\text{BaTiO}_3$  are explained.

Besides dielectric studies, we are in the process of establishing the pyroelectric measurement system for single crystals, ceramics, and thin films. The system will have two method to measure the pyroelectric behavior. Because there are some contradiction and indeterminacy in the measurement of the pyroelectric coefficient with each method. The system with two methods will give us more insight about the behavior of the materials.

### **Publication/ Presentations:**

A list of publication record, scientific presentations in the international and local conferences, and details of the student's supervision were already submitted to U.S. Army Research Office on September 23, 1996. Accordingly there are 12 papers published in refereed scientific journals, 37 presentations in international conferences, 3 papers in the local presentations, and successful supervision of 2 students for their Master's degree during the above award duration.



September 23, 1996

Ms Patsy S. Ashe  
Grants Officer  
U.S. Army Research Office  
4300 South Miami Blvd.  
P.O.Box 12211  
Research Triangle Park, NC 27709-2211

Contract/Grant Number: DAAH04-93-2-0008

Project Title: Novel Thin Films of Ferroelectric Materials for Optoelectrics Applications

Period: September 27, 1993 though September 26, 1996

Principal Investigator: Dr. Ram S. Katiyar

### FINAL PERFORMANCE REPORT (Cumulative)

Following is the list of scientific publications or conference presentations that have resulted so far under the above Grant:

#### A. List of Publications:

104. Micro-Raman Study of BaTiO<sub>3</sub> Thin Films Prepared by the Metallo-Organic Decomposition Technique, E. Ching-Prado, R.S. Katiyar, and J.J. Santiago-Aviles, J. Raman Spectroscopy, **25**, 215 (1994).
107. Micro-Raman Study of PbTiO<sub>3</sub> Film Prepared by Sol-gel Technique, E. Ching-Prado, A. Reynes-Figueroa, R.S. Katiyar, S.B. Majumder, and D.C. Agrawal, *Materials Research Society Symposium Proceedings*, **343**, 469 (1994).
109. Structural and Thermal Study of Pb(Zr,Ti,Ce)O<sub>3</sub> Ceramics, E. Ching-Prado, R.S. Katiyar, Ajay Garg, and D.C. Agrawal, *Proceedings of the Ninth International Symposium on the Applications of Ferroelectrics* (IEEE Catalog #94CH3416-5, Edited By R.K. Pandey, M. Liu, and A. Safari, 1994), p 108.
112. Micro-Raman Spectroscopy of BaTiO<sub>3</sub> Thin Films from Metallo-organic Precursors, E. Ching-Prado, R. S. Katiyar, J.J. Santiago-Aviles, *Proceedings of the XIVth International Conference on Raman Spectroscopy* (Edited by N.T. Yu and X.Y. Li, John Wiley & Sons, John Wiley & Sons, 1994), p 852.
113. Raman Study of Low Temperature Phase Transitions in PbTiO<sub>3</sub>, E. Ching-Prado, C.E. Diaz, A. Reynes-Figueroa, and R.S. Katiyar, *Proceedings of the XIVth International Conference on Raman Spectroscopy* (Edited by N.T. Yu and X.Y. Li, John Wiley & Sons, 1994), p 1004.

119. Optical Study of  $\text{PbTiO}_3$  Thin Films Grown by Sol-Gel Technique, E. Ching-Prado, R.W. Tao, R.S. Katiyar, and A.S. Bhalla, *Materials Research Society Symposium Proceedings*, **361**, 191(1995).
122. Raman Spectroscopy and X-Ray Diffraction of  $\text{PbTiO}_3$  Thin Film, E. Ching-Prado, A. Reynes-Figueroa, R.S. Katiyar, S.B. Majumder, and D.C. Agrawal, *J. Appl. Phys.*, **78**, 1920 (1995).
129. Temperature Dependent Raman Scattering in  $\text{KTiOPO}_4$  and  $\text{KTiOAsO}_4$  Single Crystals, C.-S. Tu, A.R. Guo, Ruiwu Tao and R.S. Katiyar; Ruyan Guo and A.S. Bhalla, *J. Appl. Phys.* **79**, 3235 (1996).
130. Raman and Infrared Study of Sol-gel Grown Lead Magnesium Niobate: Lead Titanate Thin Films, E. Ching-Prado, R.W. Tao, A.R. Guo, R.S. Katiyar, and A.S. Bhalla, *Ferroelectric Letter*, **21**, 17 (1996).
132. Raman Investigation on Sol-gel Grown  $\text{PbTiO}_3$  Films, E. Ching-Prado, R.W. Tao, R.S. Katiyar, and A.S. Bhalla, *Ferroelectrics*, **175**, 261 (1996).
134. Raman Scattering in  $\text{CsTiOAsO}_4$  Single Crystal, A.R. Guo, C.S. Tu, Ruiwu Tao, R.S. Katiyar, Ruyan Guo, and A.S. Bhalla, *Ferroelectric Letters* **21**, 71 (1996).
151. High Pressure Raman Spectroscopy of Stoichiometric Ferroelectric Potassium Lithium Niobate. M.J.Massey, R.S.Kartiyar, B.M.Jin, and A.S. Bhalla, *J. Ferroelectric* (Accepted ).

#### **B. Presentations in International Forums:**

- 8) Raman Spectra of Stoichiometric Ferroelectric Potassium Lithium Niobate, APS March Meeting, Pittsburgh, March 1994.
- 10) Micro-Raman Study of  $\text{PbTiO}_3$  Film Prepared by Sol-gel Technique, MRS Spring Meeting, San Francisco, April 1994.
- 11) Structural and Thermal Study of  $\text{Pb}(\text{Zr},\text{Ti},\text{Ce})\text{O}_3$  Ceramics, The Ninth International Symposium on the Applications of Ferroelectrics, University Park (PA), August 7-10, 1994.
- 12) Raman Spectroscopy of Stoichiometric Ferroelectric Potassium Lithium Niobate, The Ninth International Symposium on the Applications of Ferroelectrics, University Park (PA), August 7-10, 1994.
- 14) Micro-Raman Spectroscopy of  $\text{BaTiO}_3$  Thin Films from metallo-Organic Precursors, XIVth International Conference on Raman Spectroscopy, Hong Kong, August 21-25, 1994.

- 15) Raman Study of Low Temperature Phase Transitions in  $\text{PbTiO}_3$ , XIVth International Conference on Raman Spectroscopy, Hong Kong, August 21-25, 1994.
- 20) Raman Study of  $\text{BaTiO}_3$  and  $\text{PbTiO}_3$  Thin Films, 8th Latin American Congress on Surface Science and its Applications, Cancun (Mexico), September 19-23, 1994.
- 23) Optical Study of  $\text{PbTiO}_3$  Thin Films Grown by Sol-gel Technique, Materials Research Society Fall Meeting, Boston, November 28 - December 2, 1994).
- 24) Optical properties of  $\text{Pb}(\text{Zr}, \text{Ti}, \text{Ce})\text{O}_3$  Ceramics, American Physical Society March Meeting, San Jose, March 20 -24, 1995.
- 28) Micro-Raman Study of Sol-Gel Grown PMN-PT Thin Films, Materials Research Society Spring Meeting, San Francisco, April 17-21, 1995.
- 29) Temperature Dependent Raman Scattering in PT and PMN-PT Thin Films, 42nd National symposium of the American Vacuum Society, Minneapolis, October 16 -20, 1995).
- 30) Raman Spectroscopy of Ferroelectric Perovskite Films, XV Congreso nacional de la Sociedad mexicana de Ciencia de superficies y Vacio, CINVESTAV Mexico, D.F., November 13 - 16, 1995 (Invited Lecture).
- 31) Temperature Dependent Micro-Raman Scattering in  $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{TiO}_3$  Thin Films, Materials Research Society Fall Meeting, Boston, November 27 - December 1, 1995.
- 32) Raman Studies on  $\text{Sr}(\text{Al}_{1/2}\text{Ta}_{1/2})\text{O}_3$  (SAT) and  $\text{Sr}(\text{Al}_{1/2}\text{Nb}_{1/2})\text{O}_3$  (SAN) Single-crystals Prepared by Laser Heated Pedestal Growth Technique, Materials Research Society Fall Meeting, Boston, November 27 - December 1, 1995.
- 33) Temperature Dependent Raman Scattering in  $\text{CsTiOAsO}_4$  Single Crystal, Materials Research Society Fall Meeting, Boston, November 27 - December 1, 1995.
- 35) Raman Scattering Studies in the Relaxor Ferroelectric PST, American Physical Society March Meeting, St. Louis, March 18 - 22, 1996.
- 36) Dynamic breaking of the Translational Symmetry in the Relaxor ferroelectrics, American Physical Society March Meeting, St. Louis, March 18 - 22, 1996.
- 37) Grain size Study of Fine and ultrafine  $\text{BaTiO}_3$  Particles, American Physical Society March Meeting, St. Louis, March 18 - 22, 1996.
- 41) Broad Central Peak in Light Scattering from the relaxor Ferroelectrics PMN and NBT, American Physical Society March Meeting, St. Louis, March 18 - 22, 1996.
- 42) Raman and Temperature Dependent Raman Studies in  $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$  (BMT),

Materials Research Society Spring Meeting, San Francisco, April 8-12, 1996.

- 43) Characterization of  $\text{Sr}_x\text{Ba}_{1-x}\text{TiO}_3$  pulsed laser deposited thin films, Materials Research Society Spring Meeting, San Francisco, April 8-12, 1996.
- 44) Grain Size Study of  $\text{BaTiO}_3$  Grown by Sol-Gel Technique, E. Ching-Prado, W. Perez, S. Sen, R. S. Kartiyar, M. H. Frey, and D. A. Payne, *XVth International Conference on Raman Spectroscopy*, Pittsburgh, August 11 -16, 1996.

**C. Presentations in Local Conferences: (1994-1995)**


- 1) Micro-Raman Spectroscopy of  $\text{BaTiO}_3$  Thin Films from Metallo-Organic Precursors, First Mini-Gordon Conference on Materials Science, Guánica, December 10-11, 1994.
- 5) Raman Study of Ferroelectric Materials, Sixth Puerto Rico EPSCoR Annual Conference, San Juan, May 6-7, 1994.
- 7) Raman Spectroscopy of Ferroelectric Perovskite Films, Seventh Puerto Rico EPSCoR Annual Conference, Dorado, April 28-29, 1995.

**D. Thesis supervision:**

- 1). Title: Optical and Electrical Measurements in  $\text{CsTiOAsO}_4$  single crystal.  
Submitted for the Master degree by Ruqian Guo.
- 2). Title: Raman Studies on New Potential Substrate Materials for HTSC.  
Submitted for the Master degree by Ruiwu Tao.

Please acknowledge the receipt. Thank you,

Sincerely yours-

  
Professor Ram S. Kartiyar  
Department of physics, P.O.Box 23343  
University of Puerto Rico  
Sun Juan, PR 00931-3343