ARMY RESEARCH LABORATORY

Fabrication and Characterization of BSTO And Nonferroelectric Oxide Composites For Use In Phased Array Anntennas and Other Electronic Devices

L.C. Sengupta, E. Ngo, M.E. O'Day, S. Stowell, and R. Lancto

ARL-TR-652

December 1994

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	December 1994	

4. TITLE AND SUBTITLE
Fabrication and Characterization of BSTO and Nonferroelectric Oxide Composites for Use in Phased Array Anntennas and Other Electronic Devices

5. FUNDING NUMBERS

6. AUTHOR(S)
L.C. Sengupta, E. Ngo, M.E. O'Day, S. Stowell and R. Lancto

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Army Research Laboratory
Watertown, MA 02172-0001
AMSRL-MA-CA

8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-TR-652

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

A ceramic ferroelectric phase shifting device has been demonstrated using $Ba_{1-x}Sr_xTiO_3$ (BSTO) ceramics. As a part of an effort to optimize the electronic device performance in the phase shifter, various composites of BSTO combined with other nonelectrically active oxide ceramics have been formulated. In general, the composites have reduced dielectric constants, ε', where $\varepsilon = \varepsilon' - i\varepsilon''$, and loss tangents, tan δ. The low dielectric constant and low loss tangent reduce the overall impedance mismatch and the insertion loss of the device. In addition, the overall tunability, change in the dielectric constant with applied voltage, is maintained at a relatively high level. The combination of electronic properties of these materials offer substantially higher operating frequencies, 10 GHz and above. Another application for one of the composites is for use as a capacitor-varistor surge protector. The microstructures including grain size and phase analysis have been examined using SEM and X-ray diffraction. The analysis of the phase formation , compositional variations, and grain size will be related to the electronic properties of the materials.

14. SUBJECT TERMS	15. NUMBER OF PAGES
BSTO, Composites, Phased Array Antennas	13
	16. PRICE CODE

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

Contents

Figures

Tables

INTRODUCTION

Phased array antennas can steer transmitted or received signals either linearly or in two dimensions without mechanically oscillating the antenna. These antennas are currently constructed using ferrite phase shifting elements. Due to the type of circuit requirements necessary to operate these antennas, they are costly, large and heavy. Therefore, the use of these antennas has been limited primarily to military applications which are strategically dependent on such capabilities. In order to make these devices available for many other commercial and military uses, the basic concept of the antenna must be improved. If ferroelectric materials could be used for the phase shifting element instead of ferrites, phased array antennas would be totally revolutionized.

A ceramic Barium Strontium Titanate, $Ba_{1-X}Sr_XTiO_3$, (BSTO), phase shifter using a planar microstrip construction has been demonstrated [1]. In order to meet the required performance specifications, maximum phase shifting ability, the electronic properties in the low frequency (KHz) and microwave regions (GHz) must be optimized. As part of this optimization process, various composites of BSTO and non-ferroelectric oxides have been formulated.

Another application for one of these materials is a combined capacitor-varistor device. In general, this would be used as a protective device in parallel with electronic information processing circuits to protect against spurious voltage surges and voltage transients. The capacitive aspect of the device would guard against low-amplitude and high frequency transients which cause errors in signal processing or in stored signals. The varistor function of the device protects against high-amplitude voltage surges. The device combination is a replacement for a capacitor Zener diode combination which is often bulkier than the circuit it is protecting.

The capacitor-varistor device has been attempted previously by appropriately doping $SrTiO_3$ to form grain boundary phases or layers which exhibit the desirable characteristics [2]. Also discrete layers of ZnO and $Pb(Fe_{1/2}Nb_{1/2})O_3$-$Pb(Fe_{2/3}W_{1/3})O_3$ (dielectric constant of 27000 to 32000) have been fabricated [3]. The problem with the former scheme has been with the high loss tangents and high threshold voltages derived from the metallic additives and the semiconducting capacitor. The problem associated with the latter scheme is with the processing of the lead based capacitor compounds and the deleterious diffusion between the ZnO varistor layers and lead-based capacitor layers.

The composites will be designated as BSTO-Oxide II, BSTO-Oxide III, BSTO-Oxide II / BSTO-Oxide III, BSTO-Oxide III Compound, and BSTO-IV since they all have patents pending on their formulations. All of these composites possess improved electronic properties. The comparison of the compositions and phase formation of the various BSTO-oxide ceramic composites will be made and related to their electronic properties. This report will outline some of the initial findings for these new ceramic composites.

EXPERIMENTAL

Ceramic Processing

Powder forms of Barium Titanate and Strontium Titanate were obtained from Ferro Corporation, Transelco Division, Pen Yan, N.Y. (product nos. 219-6 and 218 respectively), stoichiometrically mixed to achieve $Ba_{0.6}Sr_{0.4}TiO_3$ and ball-milled in ethanol using 3/16" alumina media for 24 hrs. The resulting BSTO was then air-dried, calcined at 1100°C and mixed with an oxide (oxide II, oxide III, oxide II / oxide III, oxide III compound or oxide IV) in the proper weight percent and ball-milled again in a slurry of ethanol using the alumina grinding media for an additional 24 hrs.

Rholpex B-60A (Rohm and Haas Co., Philadelphia, PA) binder (3 wt%) is added to the resulting BSTO/oxide mixture. The mixture is then air-dried and uniaxially dry-pressed to a pressure of approximately 7000 p.s.i.. Sintering schedules were obtained by employing a deflectometer such as Mitutoyo digimatic indicator and miniprocessor (Mitutoyo Corp., Paramus N.J.). Porosity and liquid absorption was obtained by performing an immersion density in ethanol using a modified ASTM standard. It should be noted that all of the examined samples have liquid absorption of less than 2%.

Two metallization techniques were employed. One involved painting on two circular, aligned electrodes, one on either side of the specimens, using high purity silver paint (SPI Supplies West Chester, PA) and attaching wires using high purity silver epoxy, Magnobond 8000, made by Magnolia Plastics, Inc., Chamblee, GA. The other technique utilized the screen printing of electrodes using silver conductive ink (FERRO #3350, Electronic Materials Division, Santa Barbara, CA) and wires were attached by dipping the specimens in a bath of 2% silver, 62% tin and 36% lead solder.

Electronic Measurements

The dielectric constants, ε', loss, tan δ, and % tunability were determined for all composites. The % tunability of a material is determined using the following equation:

$$\% \text{ tunability} = \{ \varepsilon'(0) - \varepsilon'(Vapp)\}/ \{\varepsilon'(0)\} \qquad (1)$$

The tunability measurements were taken with an applied electric field which ranged from 0 to 3.0 V/micron (μm). The electronic properties given in the forthcoming tables were measured at a frequency of 1 KHz. Capacitance measurements for all materials were taken using an HP4284A LCR meter. Further calculations were done to correct for the effect of fringe capacitance.

RESULTS AND DISCUSSION

BSTO-Oxide III, BSTO-Oxide II / Oxide III, BSTO-Oxide III Compound Composites

SEM and X-ray Diffraction

No secondary phases (other than BSTO and Oxide III) were identified by X-ray diffraction for the BSTO-Oxide III composites. Also the SEM photographs did not reveal any evidence of

secondary phase formation. However, the BSTO-Oxide II/Oxide III composites revealed the existence of secondary phases at oxide additions of 10 wt%. Three distinct secondary phases were identified for these composites. The BSTO-Oxide III compound composites also revealed at least two secondary phases for oxide content above 30 wt%. These phases were evident as discolorations in the SEM photographs for both the BSTO-Oxide II/Oxide III and BSTO-Oxide III compound composites.

Electronic Properties

The electronic data for the BSTO-Oxide III, BSTO-Oxide II / Oxide III and BSTO-Oxide III compound composites are shown in Table 1. As shown in the table, the dielectric constants decrease with increase in oxide content and the tunability decreases slowly with increase in oxide content. In fact, the BSTO-Oxide III composites exhibit high tunabilities (>10%) up to 60 wt% oxide III which is not the case for the two other oxide additives. This difference could be due to the fact that the BSTO-Oxide III compounds do not exhibit secondary phases whereas the other two composites form multiple secondary phases as discussed previously. These non-ferroelectric phases will tend to inhibit tunability at high additive contents.

As shown in Fig. 1, the loss tangent of these composites are extremely low for most all compositions (decreasing slightly with an increase in oxide content).

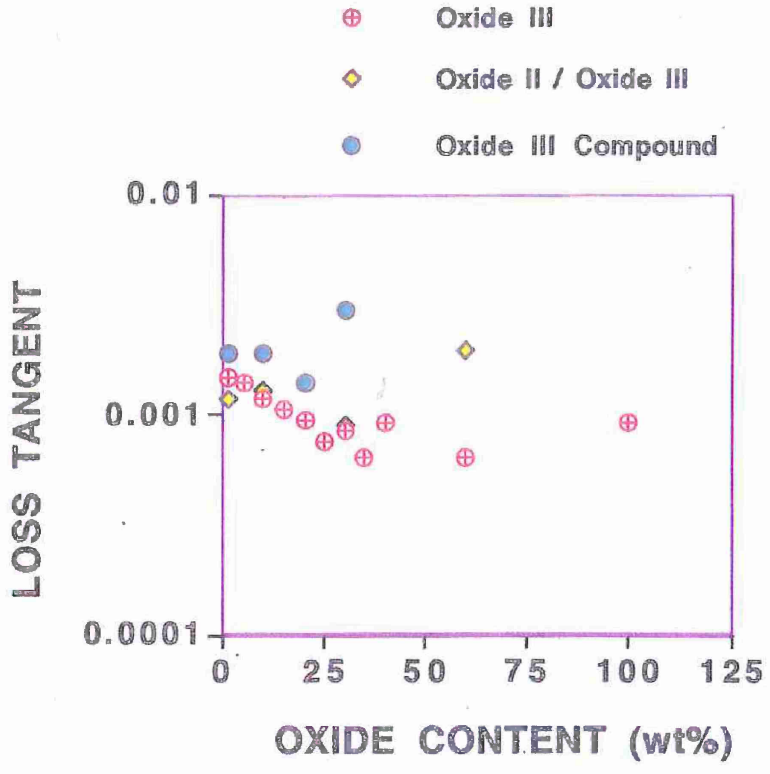


Fig. 1. Loss tangent vs. Oxide Content for BSTO-Oxide III, BSTO-Oxide II/ Oxide III and BSTO-Oxide III Compound Composites measured at 1 KHz.

TABLE 1. Electronic Properties of BSTO-Oxide III, BSTO-Oxide II / Oxide III and BSTO-Oxide III Compound Ceramic Composites Measured at 1 KHz.

BSTO-Oxide III

Oxide II Oxide III Content (wt%)	*Dielectric Constant*	*Loss Tangent*	*% Tunability*	*Electric Field (V Micron)*
0.0	3299.08	0.0195	19.91	0.73
1.0	1276.21	0.0015	16.07	2.32
5.0	1770.42	0.0014		
10.0	1509.19	0.0018		
15.0	1146.79	0.0011	7.270	1.91
20.0	1079.21	0.0009	15.95	2.33
25.0	783.17	0.0007	17.46	2.45
30.0	750.93	0.0008	9.350	1.62
35.0	532.49	0.0006	18.00	2.07
40.0	416.40	0.0009	19.81	2.53
50.0	280.75	0.0117*	9.550	2.14
60.0	117.67	0.0006	11.08	2.70
80.0	17.00	0.0008	0.61	1.72
100.0	13.96	0.0009		

BSTO-Oxide II / Oxide III

Oxide II Oxide III Content (wt%)	*Dielectric Constant*	*Loss Tangent*	*% Tunability*	*Electric Field (V Micron)*
0.0	3299.1	0.0195	19.91	0.73
1.0	2515.3	0.0011	12.24	1.14
10.0	1868.9	0.0013	11.63	1.56
20.0	1016.0	0.0327*	10.89	1.33
30.0	389.06	0.0009	1.607	1.34
60.0	93.591	0.0022	0.450	0.99

BSTO-Oxide III Compound

Oxide II Oxide III Content (wt%)	*Dielectric Constant*	*Loss Tangent*	*% Tunability*	*Electric Field (V Micron)*
0.0	3299.1	0.0195	19.91	0.73
1.0	2531.4	0.0019	18.58	1.66
10.0	1801.5	0.0019	13.29	1.34
20.0	959.27	0.0014	6.910	0.91
30.0	432.40	0.0030	7.347	0.51
60.0	63.192*	0.0176	1.054	1.00

* samples have poor contacts

BSTO-Oxide IV Composites

As mentioned previously, another application for one these composites, denoted as, BSTO-Oxide IV, is for use as a capacitor-varistor protection device. At high voltages, the varistor conducts current given by the power-law relation [4].

$$I = AV^{\alpha} \tag{2}$$

where V is the applied voltage, I is the current, A is the proportionality constant, and α is the index of nonlinearity. Current conduction through the varistor prevents the voltage from exceeding a critical value in the electronic circuitry that is being protected. The nonlinear electrical conduction in the ceramic composite is due to the addition of oxide IV (no secondary phases where observed from X-ray diffraction and SEM anaylsis) in which electron tunneling through the grain boundaries occurs.

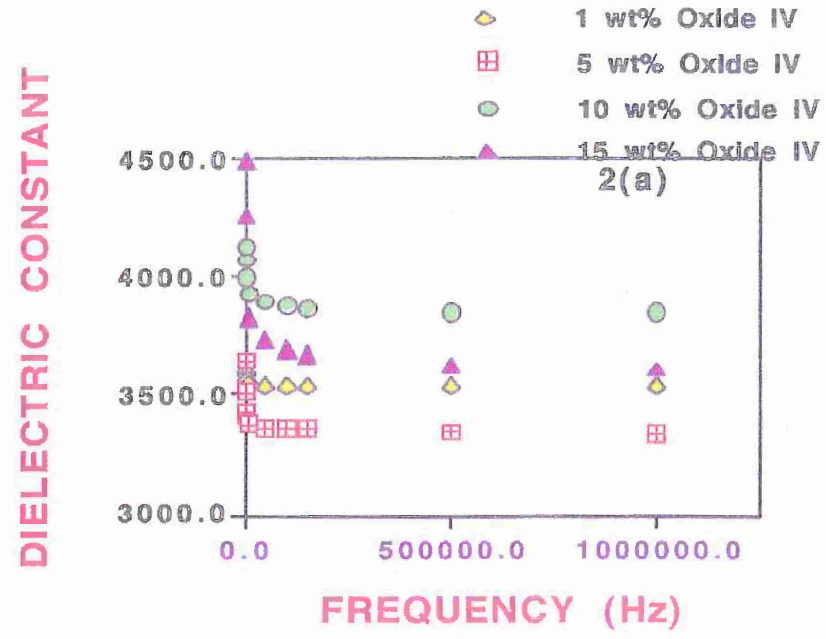
Electronic Properties

The electronic properties and the average grain size of the BSTO-Oxide IV composites are shown in Table 2. As shown in Figs. 2(a) and 2(b), the dielectric constant decreases with an increase in frequency. Also the loss tangent shows a decrease with increasing frequency as shown in Figs. 3(a) and 3(b). At low doping levels (1-15 wt%) the composites have

TABLE 2. Electronic Properties and Grain Size of BSTO-Oxide IV Composites Measured at 1 KHz.

Oxide IV Content (wt%)	*Dielectric Constant*	*Loss Tangent*	*Tunability*	*Electric Field (V/Micron)*
1.0	3756	0.00236	7.334	1.0
5.0	3416	0.01276	8.957	0.8
10.0	3908	0.01320	13.11	0.7
15.0	3942	0.03708	27.97	0.6
20.0	4685	0.19113	-----	---
25.0	7520	0.46976	-----	---
30.0	7859	0.46927	-----	---
50.0	71922	0.46891	-----	---

Oxide IV Content (wt%)	*Threshold Voltage*	*Nonlinearity Exponent*	*Grain Size (μm)*
1.0	-----	---	------
5.0	-----	---	10.24
10.0	-----	---	9.774
15.0	-----	---	8.610
20.0	100	6.510	8.387
25.0	25	5.390	7.514
30.0	20	10.290	6.806
50.0	5	8.349	5.909



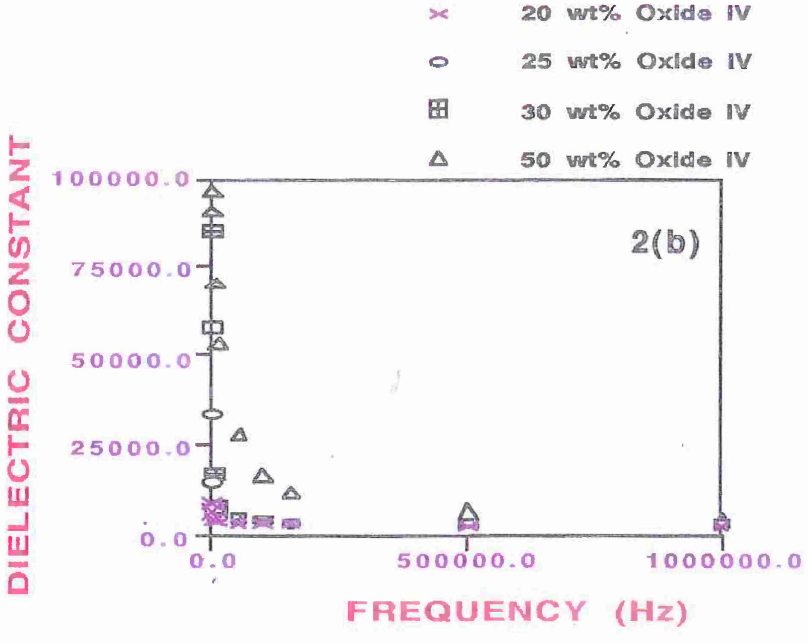
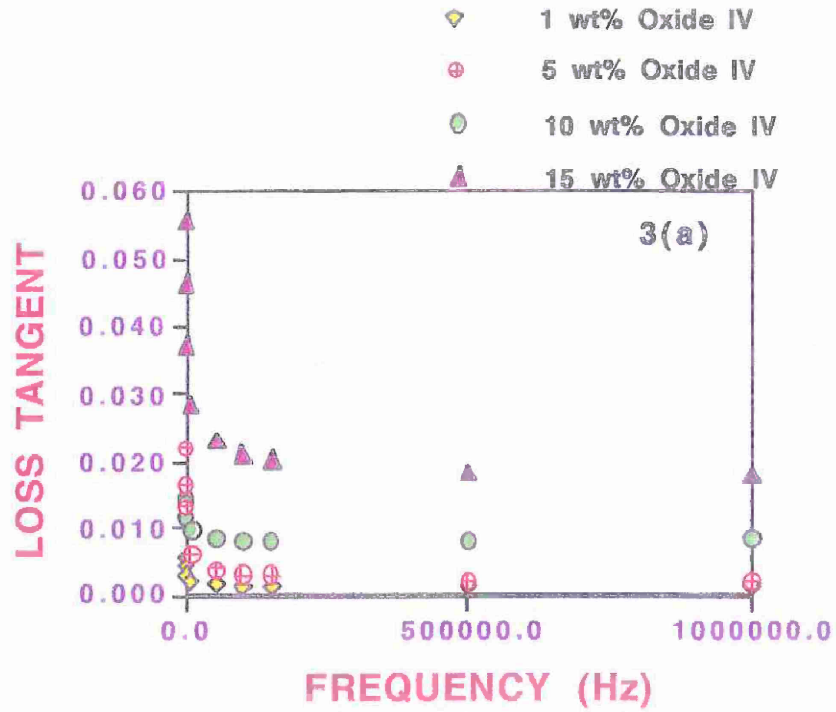


Fig. 2. (a) Dielectric Constant vs. Frequency for BSTO-Oxide IV Composites (1, 5, 10, 15 wt%) (b) for BSTO-Oxide IV Composites (20, 25, 30, 50 wt%).



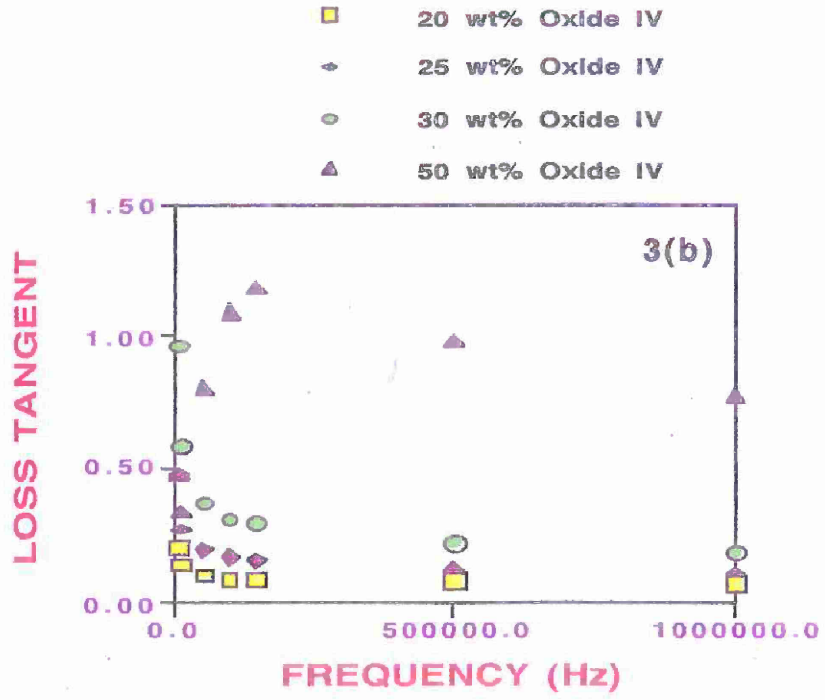


Fig. 3. (a) Loss Tangent vs. Frequency for BSTO-Oxide IV Composites (1, 5, 10, 15 wt%) (b) for BSTO-Oxide IV Composites (20, 25, 30, 50 wt%).

large dielectric constants and possess low loss tangents and reasonably high tunabilities. These properties meet the requirements for various antenna applications (especially low frequency applications). At higher levels (20 - 50 wt%), the addition of oxide IV content continues to increase the dielectric constant drastically especially at low frequencies, and the composites begin to conduct current and exhibit non-ohmic behavior and the threshold voltage is seen to increase with an increase in oxide IV content.

Fig. 4 (a) and (b) show the current versus voltage for several BSTO-Oxide IV (20, 25. 30 and 50 wt%) composites . It should be noted that as the oxide IV content is increased, the dielectric constant increases, and the non-linearity exponent increases. This increase in the non-linearity is definitely related to the decrease in the grain size as indicated in Table 2. However, contrary to the predicated behavior for pure oxide IV varistor compositions, the threshold voltage decreases with decrease in average grain size. Since the material formed is a composite it is difficult to determine if the grains of oxide IV are decreasing or if the BSTO grains are decreasing. The threshold voltage for the BSTO-Oxide IV (50 wt%) specimen is lower than reported for any bulk capacitor-varistor device (which was reported to be around 100 V)[2] and the capacitance is as high as that obtained for multilayered structures (nearly twice than that reported)[3]. Fig. 5 shows the dielectric constant versus temperature for the BSTO-Oxide IV (50 wt%). The figure shows that the dielectric is reasonably temperature stable at room temperature and above which is an important operating parameter for microelectronic circuits.

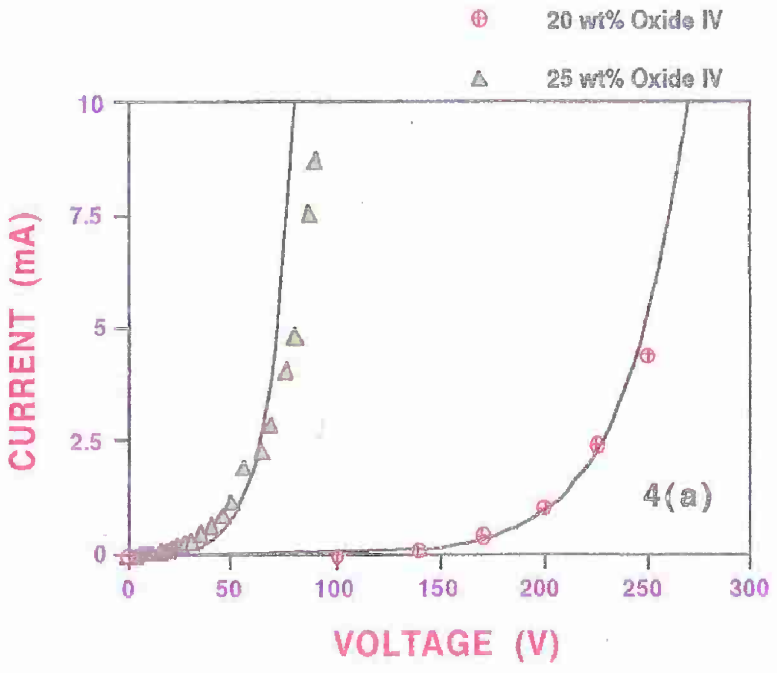


Fig. 4(a) Current vs. Voltage for BSTO-Oxide IV Composites (20 and 25 wt% oxide IV).

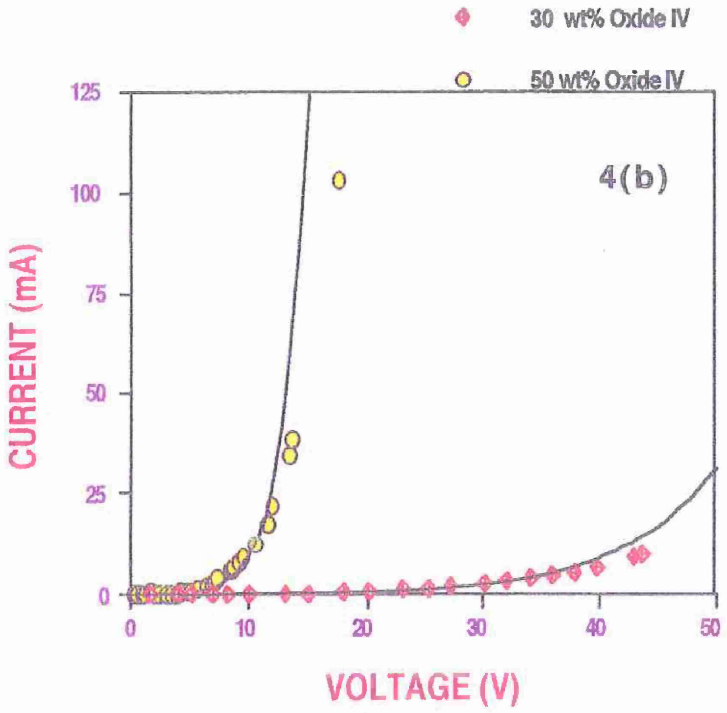


Fig. 4(b) Current vs. Voltage for BSTO-Oxide IV Composites (30 and 50 wt% oxide IV).

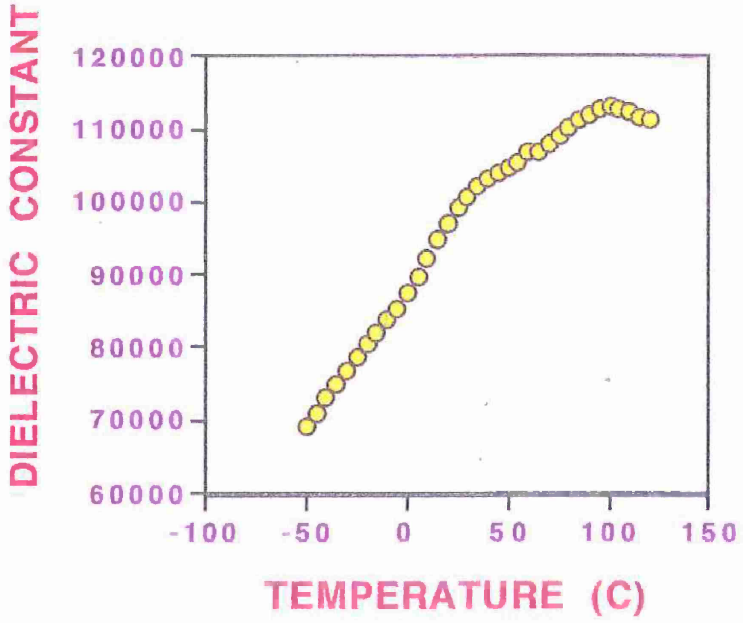


Fig. 5. Dielectric Constant vs. Temperature for a BSTO-Oxide IV (50 wt%) composite measured at 1 KHz.

CONCLUSIONS

The BSTO-Oxide III, BSTO-Oxide II / Oxide III and BSTO-Oxide III- compound ceramic composites possess extremely low loss tangents and high tunabilities. The data suggest that any composites containing oxide III or an oxide III compound will display similar electronic behavior. This is significant in that a family of composites has been identified which can potentially facilitate the operation of these ferroelectric phased array antennas at millimeter wave range frequencies due to much improved electronic properties.

The BSTO-Oxide IV materials exhibit behavior which renders them suitable for use both (at low oxide IV content < 15 wt%) in phased array antenna systems and (at high oxide IV content >15 wt%) as a capacitor-varisitor protection device for microelectronic circuits. The improved properties of these composites includes very low threshold voltages (@5 V), reasonable nonlinear coefficients, moderate to low loss tangents, tunable and extremely high dielectric constants, and temperature stability. It should be noted that the low threshold voltage accompanied by an extremely high dielectric constant was accomplished in a bulk ceramic (1mm thickness) and is less than that reported for thin film laminates [3].

REFERENCES

[1] R.W. Babbitt, T. E. Koscica, and W.E. Drach, "Planar Microwave Electro-optic Phase Shifters," *Microwave Journal* , vol. 35, pp. 63-79, June 1992.
[2] N. Yamaoka, M. Masuyama and M. Fukui, "$SrTiO_3$-Based Boundary Layers Capacitor Having Varistor Characteristics," *Ceramic Bulletin*, vol. 62, pp. 698-703, 1983.
[3] H.C. Ling, M.F Yan, and W. W. Rhodes, "A Monolithic Device with Dual Capacitor and Varistor Functions," *J. Am. Ceram. Soc.*,, vol. 72, pp. 1274 -1276 , 1989.
[4] M. Matsuoka, "Nonohmic Properties of Zinc Oxide Ceramics," *Japanese Journal of Applied Physics*, vol. 10, pp. 736- 746, 1970.

DISTRIBUTION LIST

No. of Copies	To
1	Office of the Under Secretary of Defense for Research and Engineering, The Pentagon, Washington, DC 20301
	Director, U.S. Army Research Laboratory, 2800 Powder Mill Road, Adelphi, MD 20783-1197
1	ATTN: AMSRL-OP-SD-TP, Technical Publishing Branch
1	AMSRL-OP-SD-TA, Records Management Administrator
	Director, U.S. Army Research Laboratory, 2800 Powder Mill Road, Adelphi, MD 20783-1197
1	ATTN: Technical Library
	Commander, Defense Technical Information Center, Cameron Station, Building 5, 5010 Duke Street, Alexandria, VA 23304-6145
2	ATTN: DTIC-FDAC
1	MIA/CINDAS, Purdue University, 2595 Yeager Road, West Lafayette, IN 47905
	Commander, Army Research Office, P.O. Box 12211, Research Triangle Park, NC 27709-2211
1	ATTN: Information Processing Office
	Commander, U.S. Army Materiel Command, 5001 Eisenhower Avenue, Alexandria, VA 22333
1	ATTN: AMCSCI
	Commander, U.S. Army Materiel Systems Analysis Activity, Aberdeen Proving Ground, MD 21005
1	ATTN: AMXSY-MP, H. Cohen
	Commander, U.S. Army Missile Command, Redstone Arsenal, AL 35809
1	ATTN: AMSMI-RD-CS-R/Doc
	Commander, U.S. Army Armament, Munitions and Chemical Command, Dover, NJ 07801
2	ATTN: Technical Library
	Commander, U.S. Army Natick Research, Development and Engineering Center, Natick, MA 01760-5010
1	ATTN: DFAS-IN-EM-TL, Technical Library
	Commander, U.S. Army Satellite Communications Agency, Fort Monmouth, NJ 07703
1	ATTN: Technical Document Center
	Commander, U.S. Army Tank-Automotive Command, Warren, MI 48397-5000
1	ATTN: AMSTA-ZSK
1	AMSTA-TSL, Technical Library
	Commander, White Sands Missile Range, NM 88002
1	ATTN: STEWS-WS-VT
	President, Airborne, Electronics and Special Warfare Board, Fort Bragg, NC 28307
1	ATTN: Library

No. of Copies	To
	Director, U.S. Army Research Laboratory, Weapons Technology, Aberdeen Proving Ground, MD 21005-5066
1	ATTN: AMSRL-WT
	Commander, Dugway Proving Ground, UT 84022
1	ATTN: Technical Library, Technical Information Division
	Commander, U.S. Army Research Laboratory, 2800 Powder Mill Road, Adelphi, MD 20783
1	ATTN: AMSRL-SS
	Director, Benet Weapons Laboratory, LCWSL, USA AMCCOM, Watervliet, NY 12189
1	ATTN: AMSMC-LCB-TL
1	AMSMC-LCB-R
1	AMSMC-LCB-RM
1	AMSMC-LCB-RP
	Commander, U.S. Army Foreign Science and Technology Center, 220 7th Street, N.E., Charlottesville, VA 22901-5396
3	ATTN: AIFRTC, Applied Technologies Branch, Gerald Schlesinger
	Commander, U.S. Army Aeromedical Research Unit, P.O. Box 577, Fort Rucker, AL 36360
1	ATTN: Technical Library
	U.S. Army Aviation Training Library, Fort Rucker, AL 36360
1	ATTN: Building 5906-5907
	Commander, U.S. Army Agency for Aviation Safety, Fort Rucker, AL 36362
1	ATTN: Technical Library
	Commander, Clarke Engineer School Library, 3202 Nebraska Ave., N, Fort Leonard Wood, MO 65473-5000
1	ATTN: Library
	Commander, U.S. Army Engineer Waterways Experiment Station, P.O. Box 631, Vicksburg, MS 39180
1	ATTN: Research Center Library
	Commandant, U.S. Army Quartermaster School, Fort Lee, VA 23801
1	ATTN: Quartermaster School Library
	Naval Research Laboratory, Washington, DC 20375
2	ATTN: Dr. G. R. Yoder - Code 6384
	Chief of Naval Research, Arlington, VA 22217
1	ATTN: Code 471
	Commander, U.S. Air Force Wright Research & Development Center, Wright-Patterson Air Force Base, OH 45433-6523
1	ATTN: WRDC/MLLP, M. Forney, Jr.
1	WRDC/MLBC, Mr. Stanley Schulman

No. of Copies	To
	U.S. Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD 20899
1	ATTN: Stephen M. Hsu, Chief, Ceramics Division, Institute for Materials Science and Engineering
1	Committee on Marine Structures, Marine Board, National Research Council, 2101 Constitution Avenue, N.W., Washington, DC 20418
1	Materials Sciences Corporation, Suite 250, 500 Office Center Drive, Fort Washington, PA 19034
1	Charles Stark Draper Laboratory, 555 Technology Square, Cambridge, MA 02139
	Wyman-Gordon Company, P.O. Box 8001, North Grafton, MA 01536-8001
1	ATTN: Technical Library
	General Dynamics, Convair Aerospace Division, P.O. Box 748, Fort Worth, TX 76101
1	ATTN: Mfg. Engineering Technical Library
	Plastics Technical Evaluation Center, PLASTEC, ARDEC, Bldg. 355N, Picatinny Arsenal, NJ 07806-5000
1	ATTN: Harry Pebly
1	Department of the Army, Aerostructures Directorate, MS-266, U.S. Army Aviation R&T Activity - AVSCOM, Langley Research Center, Hampton, VA 23665-5225
1	NASA - Langley Research Center, Hampton, VA 23665-5225
	U.S. Army Vehicle Propulsion Directorate, NASA Lewis Research Center, 2100 Brookpark Road, Cleveland, OH 44135-3191
1	ATTN: AMSRL-VP
	Director, Defense Intelligence Agency, Washington, DC 20340-6053
1	ATTN: ODT-5A (Mr. Frank Jaeger)
	U.S. Army Communications and Electronics Command, Fort Monmouth, NJ 07703
1	ATTN: Technical Library
	U.S. Army Communications and Electronics Command, Intelligence and Electronic Warfare Center, Fort Monmouth, NJ 07703-5211
1	ATTN: Frank Elmer, AMSEL-RD-IEW-TAE-M
	U.S. Army Research Laboratory, Electronic Power Sources Directorate, Fort Monmouth, NJ 07703
1	ATTN: AMSRL-EP-M, W. C. Drach
1	AMSRL-EP-M, T. E. Koscica
1	AMSRL-EP-M, R. W. Babbit
	Director, U.S. Army Research Laboratory, Watertown, MA 02172-0001
2	ATTN: AMSRL-OP-WT-IS, Technical Library
25	Authors