UNIVERSITI PUTRA MALAYSIA

STRUCTURAL AND DIELECTRIC PROPERTIES OF SUBSTITUTED STANNATE COMPOUNDS

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FSAS 2003 30

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DOCTOR OF PHILOSOPHY

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By

IFTETAN AHMAD TAHA

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

October, 2003

UPM

DEDICATION

To My Father
with respect and Love
I dedicate this work

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Doctor of Philosophy

STRUCTURAL AND DIELECTRIC PROPERTIES OF SUBSTITUTED STANNATE COMPOUNDS

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IFTETAN AHMAD TAHA

October, 2003

Chairman: **Professor Abdul Halim Shaari, Ph.D.**

Faculty: **Science and Environmental Studies**

The alkaline-earth stannates having the general chemical formula $MSnO_3$ (M = Ca, Sr and Ba) have been projected as potential electronic ceramics such as thermally stable capacitors, humidity sensor, carbon dioxide sensor. There is no reliable technical information on the effect of substitutional doping on $MSnO_3$ system that appears to exist in the published literature. In view of the information gaps in the reported research, vigorous and systematic investigation has been carried out on two systems; $SrSnO_3$ and Mg_2SnO_4.

The two systems $Mg_{2-x}M_xSnO_{4\pm\delta}$ where M = Ca and Nb and $Sr_{1-x}N_xSnO_{3\pm\delta}$ where N = Ba, La and Zn, have been thoroughly studied with respect to synthesis, processing and characterisation – physical, microstructural and electrical. Conventional solid state technique has been used in the preparation of the samples. Two sintering temperatures are employed for $Mg_{2-x}M_xSnO_{4\pm\delta}$ system; 1300 °C for 24 h and 1500 °C for 6 h. While for $Sr_{1-x}N_xSnO_{3\pm\delta}$ system the

sintering temperatures are 1300 °C for 24 h and 1400 °C for 12 h. The effect of substitutional doping and sintering temperature on the structural, microstructural and dielectric properties of the two systems have been studied

The results of the X-ray diffraction analysis on the $Sr_{1-x}N_xSnO_{3\pm\delta}$ system revealed that a single-phase solid solution has formed with Ba as substitutional element. The system has low solid solubility when substituted with La and Zn. The results of the XRD analysis on the $Mg_{2-x}M_xSnO_{4\pm\delta}$ system showed that a single phase solid solution has formed with Nb – substituted sample up to x = 0.05. The system has low solid solubility when substituted with Ca.

Scanning electron micrographs of the samples for all the compositions in the $Mg_{2-x}M_xSnO_{4\pm\delta}$ and $Sr_{1-x}N_xSnO_{3\pm\delta}$ systems, in general showed that the grains were spherical in shape and associated with some degree of porosity. In some samples even after sintering at temperature as high as 1500 °C / 6 h, there is still some degree of porosity. For Ca-substituted sample with x = 0.4 sintered at 1500 °C / 6 h, the shape of the grains has totally changed from spherical to cubic.

A thorough analysis of the measured electrical data in the frequency range of 10^{-2} to 10^6 Hz for $Sr_{1-x}N_xSnO_{3\pm\delta}$ samples substituted with Ba and La showed that the effect of changing sintering temperature and duration from 1300 °C / 24 h to 1400 °C / 12 h has resulted in a decrease in the relative permittivity and loss tangent. In Nb-substituted $Mg_{2-x}M_xSnO_{4\pm\delta}$ samples with $0 \leq x \leq 0.1$ increasing sintering temperature to 1500 °C / 24 h has resulted in the increase of the relative permittivity. In general, low capacitance, high resistance (in the order of 10^9-

$10^{10}\Omega$) and low dielectric loss were the most observed features of all compositions in the two systems under study.

The equivalent circuit of $Sr_{1-x}Ba_xSnO_3$ and $Sr_{1-x}La_xSnO_{3\pm\delta}$ samples with x = 0, 0.1, 0.2, 0.4, 0.6, 0.8 and 1 samples sintered at 1300 °C / 24 h can be expressed by the combination of parallel network of quasi-dc, dipole, and C_{inf} in series with the electrode resistance (Rs)

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia bagi memenuhi keperluan untuk ijazah Doktor Falsafah

STRUKTUR DAN SIFAT DIELEKTRIK BAGI SEBATIEN STANNAT GANTIAN

Oleh

IFTETAN AHMAD TAHA

Oktober 2003

Pengerusi: **Profesor Abdul Halim Bin Shaari, Ph.D.**

Fakulti : Sains dan Pengajian Alam Sekitar

Stannat-alkalin-bumi yang mempunyai formula kimia am $MSnO_3$ (M=Ba, La dan Zn) telah diutarakan sebagai seramik elektronik yang berpotensi seperti kapasitor stabil terma, sensor kelembapan, sensor karbon dioksida. Tiada maklumat teknikal yang boleh dipercayai kesan penggantian keatas sistem $MSnO_3$ yang boleh didapati daripada sorotan ilmiah. Memandangkan terdapat jurang maklumat dalam penyelidikan yang telah dilaporkan, satu kajian sistematik dan mendalam telah dijalankan keatas sistem, $SrSnO_3$ dan Mg_2SnO_4.

Kedua-dua sistem tersebut iaitu $Mg_{2-x}M_xSnO_{4\pm\delta}$ dengan M=Ca dan Nb, dan $Sr_{1-x}N_xSnO_{3\pm\delta}$ dengan N=Ba, La dan Zn, telah dikaji sepenuhnya dari segi sintesis, pemerosesan dan penentuan ciri fizik, mikrostruktur dan elektrik. Teknik keadaan pejejal lazim telah digunakan dalam penyediaan sampel. Dua suhu pensinteran telah digunakan untuk sistem $Mg_{2-x}M_xSnO_{4\pm\delta}$: iaitu 1300 ^oC selama 24 jam dan 1500 ^oC untuk selama 6 jam. Sementara untuk sistem $Sr_{1-x}N_xSnO_{3\pm\delta}$, suhu

sintering adalah 1300 °C selama 24 jam dan 1400 °C untuk selama 12 jam. Kesan penggantian pendopan dan suhu sinteran keatas struktur, mikrostruktur dan ciri elektrik sistem tersebut telah dikaji.

Keputusan analisis pecahan sinar-X keatas sistem $Sr_{1-x}N_xSnO_{3\pm\delta}$ menunjukkan satu larutan pepejal fasa tunggal telah terbentuk dengan Ba sebagai unsur gantian. Sistem tersebut mempunyai kelarutan pepejal yang rendah bila digantikan dengan La dan Zn. Keputusan analisis XRD keatas sistem $Mg_{2-x}M_xSnO_{4\pm\delta}$ telah menunjukkan bahawa satu larutan pepejal fasa tunggal terbentuk pada sampel yang digantikan dengan Nb sehingga 0.05 sistem ini mempunyai larutan pepejal yang apabila digantikan dengan Ca.

Mikrograf imbasan elektron keatas sampel untuk semua kandungan dalam sistem $Mg_{2-x}M_xSnO_{4\pm\delta}$ dan $Sr_{1-x}N_xSnO_{3\pm\delta}$, secara umumnya menunjukkan butiran adalah berbentuk sfera dan berkait rapat dengan darjah keporosan. Terdapat iuga sampel yang masih menunjukkan darjah keporosan walaupun disinter pada suhu setinggi 1500 °C / 6 jam. Untuk sampel gantian Ca dengan x = 0.4 yang disinter pada suhu 1500 °C / 6 jam dari berubah bentuk sfera ke kubus.

Satu analisis yang menyelurah bagi data elektrik yang diukur dalam julat frekuensi 10^{-2} hingga 10^6 Hz untuk sampel $Sr_{1-x}N_xSnO_{3\pm\delta}$ yang digantikan dengan Ba dan La menunjukkan bahawa kesan peningkatan suhu sinteran dari 1300 °C / 24 jam hingga 1400 °C/ 12 jam telah menyebabkan penurunan dalam ketelusan relatif dan kehilangan tangen. Dalam $Mg_{2-x}M_xSnO_{4\pm\delta}$ yang digantikan oleh Nb dengan $0 \leq x \leq 0.1$ persinteran sehingga 1500 °C / 24 jam telah menghasilkan

penambahan ketelusan relatif. Secara umum, kapasitan rendah, kerintangan tinggi (pada peringkat 10^9-10^{10} Ω) dan kehilangan dielektrik rendah adalah sifat yang paling banyak dicerap bagi semua komposisi di dalam sistem yang dikaji.

Litar setara bagi sistem $Sr_{1-x}Ba_xSnO_3$ dan $Sr_{1-x}La_xSnO_{3\pm\delta}$, dengan x = 0, 0.1, 0.2, 0.4, 0.6, 0.8 dan 1 yang disinter pada 1300 °C/ 24 jam boleh diungkap secara kombinasi rangkaian selari kuasi-dc, dwikutub dan C_{inf} sesiri dengan rintangan elektrod (Rs).

ACKNOWLEDGEMENTS

Firstly, I am very grateful to " ALLAH " s.w.t. for giving me the strength, and patient to complete this research within the specified time.

It is my pleasure to extend my sincere gratitude to, Professor Dr. Abdul Halim Shaari for his continuos supervision, guidance. Also I want to express my acknowledgment to my co-supervisor Associate Professor Dr. Wan Mohd. Daud Wan Yusoff for his assistance and fruitful discussion. I am also pleased to thank my co-supervisor Professor Dr. Lee Chnoong Kheng for her comments, suggestions throughout the research work

I am grateful to all the lecturers in the Physics Department for their kindness. Special thanks are due to Dr. Noorhana Yahya and Dr. Jumiah Hassan, for their assistance, discussion and moral support.

I would like to express my sincere gratitude to my lab mates: Dr. Imad Hamadneh, Ms. Ari Sulistyo Rini, Zohra, Mr. Kabashi, Mr. Mustafa, Mr. Ali, Mr. Ramadan, Mrs. Azizah, Mrs. Halema, Ms. Huda, Mr. Som and also I want to thank all postgraduate students in the Physics Department.

I want to thank Ms. Azilah, Mrs. Faridah, Mr. Ho and all members of Electron Microscopy Unit, UPM for their kind assistance.

My very special thanks go to my family in Iraq, my father Prof. Ahmad Al-Haje Taha from Mosul University, Iraq, my mother for her prayer for me and my kids, my lovely sisters, my brother-in-law, Mr. Radwan for their support from far.

Finally, I want to thank my husband Associate Professor Dr. Waleed A. Thanoon from Faculty of Engineering for his generous support and assistance during my studies. Thanks to my kids Dalia, Kaldoon and Zadoon for their love, understanding and time they missed their mother.

May Allah Bless You All

I certify that an Examination Committee met on 2nd October to conduct the final examination of Iftetan Ahmad Taha on her Doctor of Philosophy thesis entitled "Structural And Dielectric Properties Of Substituted Stannate Compounds" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

Signature

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Date : 8.01.2004

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