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1. DISSERTATION DATA

1.1 TITLE OF DISSERTATION (TIT) (MANDATORY – To be completed in lower case)

The title exactly as it appears on the dissertation's title page.

Transport properties of thermoelectric $Bi_{0.5}Sb_{1.5}Te_3$ thin films and bulk alloys

1.2 LANGUAGE OF TITLE (MANDATORY)

The language in which the title is written Διατριβής.

English

1.3 TRANSLATION OF TITLE (MANDATORY – To be completed in lower case)

Complete any of the following that apply.

Greek: Ιδιότητες μεταφοράς του θεμοηλεκτρικού υλικού $Bi_{0.5}Sb_{1.5}Te_3$ σε μορφή λεπτών υμενίων και συμπαγούς κράματος.

English: Transport properties of thermoelectric $Bi_{0.5}Sb_{1.5}Te_3$ thin films and bulk alloys

1.4 LANGUAGE OF TEXT (MANDATORY)

The language in which the text is written.

English

1.5 TRANSLATION OF DISSERTATION

If the dissertation has been translated, please provide the language(s) it has been translated to.

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2. INDIVIDUALS INVOLVED

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2.3 MEMBERS OF EVALUATION COMMITTEE (MANDATORY – To be completed in lower case)
Provide the names of the members of the evaluation committee.

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2.3.1.2	Louka		Loukas
2.3.2.1	Dinescu		Maria
2.3.2.2	Gelbstein		Yaniv
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2.3.5.1	______	**2.3.5.2**	______
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2.3.7.1	______	**2.3.7.2**	______
2.3.8.1	______	**2.3.8.2**	______
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2.4 MEMBER OF EVALUATION COMMITTEE RESPONSIBLE FOR FINAL SUPERVISION
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3. AWARDING INSTITUTION **(MANDATORY – To be completed in lower case)**

3.1 HIGHER EDUCATION INSTITUTE: University of Cyprus

3.2 SCHOOL: Faculty of engineering
3.3 DEPARTMENT: Department of mechanical and manufacturing engineering
3.4 COUNTRY: Cyprus

4. COLLABORATING INSTITUTION

4.1 NAME
To be completed only if the dissertation was written in a research institute or laboratory, e.g. Institute of Neurology and Genetics.

____

____

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5. DATE OF PhD AWARD **(MANDATORY)**

5.1 YEAR: 2017 **5.2 MONTH:** February
Year and month the PhD was awarded, e.g. 1996 05

Date of release from the awarding institution χορηγών ίδρυμα (if applicable)

5.3 YEAR: ____________ **5.4 MONTH:** ____________

6. DISSERTATION IN PRINT FORM **(MANDATORY)**

PHYSICAL DESCRIPTION

6.1 NUMBER OF PAGES: 104
Provide the number of pages of the dissertation.

6.2 ATTACHMENTS (ACCOMPANYING MATERIAL)

No. of diskettes: ____________ **No. of maps:** 1

No. of CD-ROM: 1 **Other material:** ____________

NOTES (MANDATORY)

6.3 NUMBER OF CITED SOURCES IN BIBLIOGRAPHY: 130

6.4 INDEXES (check all that apply)

TERMS...NO.........TABLES........YES.....IMAGES......YES.......MAPS........NO....OTHER.....NO........

6.5 VOLUMES (MANDATORY) 1

The number of volumes constituting the dissertation.

6.6 TRANSLATION IN GREEK **NO**

Has the dissertation been translated to Greek? Please circle 'yes' or 'no' above. (To be completed only in case where the PhD has been awarded by a higher education institute outside Cyprus and Greece).

7. SUBJECT CONTENT OF DISSERTATION (MANDATORY – To be completed in UPPER case)

7.1 KEYWORDS (in Greek)

Words or phrases defining the topic. Each keyword must not exceed 60 characters, including spaces.

7.1.1 $Bi_{0.5}Sb_{1.5}Te_3$ ΛΕΠΤΑ ΥΜΕΝΙΑ

7.1.2 $Bi_{0.5}Sb_{1.5}Te_3$ ΣΥΜΠΑΓΕΣ ΚΡΑΜΜΑΤΑ

7.1.3 ΘΕΡΜΟΗΛΕΚΤΡΙΚΕΣ ΙΔΙΟΤΗΤΕΣ

7.1.4 ΕΝΑΠΟΘΕΣΗ ΜΕ ΠΑΛΜΙΚΟ ΛΕΙΖΕΡ

7.1.5 ΖΕΣΤΗ ΠΥΡΟΣΥΣΩΜΑΤΩΣΗ

7.1.6 ΖΕΣΤΗ ΠΥΡΟΣΥΣΩΜΑΤΩΣΗ-ΠΑΡΑΜΟΡΦΩΣΗ

7.1.8 ____

7.2 KEYWORDS (in English) (MANDATORY – To be completed in UPPER case)

7.2.1 $Bi_{0.5}Sb_{1.5}Te_3$ THIN FILMS

7.2.2 $Bi_{0.5}Sb_{1.5}Te_3$ BULK ALLOYS

7.2.3 THERMOELECTRIC PROPERTIES

7.2.4 PULSED LASER DEPOSITION

7.2.5 HOT PRESS

7.2.6 HOT DEFORMATION

7.2.8 ____

7.3 KEYWORDS (in the language of dissertation, in case neither 7.1 nor 7.2 apply)

7.3.1 ______________________________

7.3.2 ______________________________

7.3.3 ______________________________

7.3.4 ______________________________

7.3.5 ______________________________

7.3.6 ______________________________

7.3.7 ______________________________

7.3.8 ______________________________

7.4 ABSTRACT (in Greek) (MANDATORY – To be completed in lower case)

The abstract ***must not exceed 500 words*** *and must include the aim, methodology and findings/conclusions of the dissertation.*

Στις μέρες μας, ένα από τα πιο σημαντικά και πολυσυζητημένα προβλήματα είναι η κλιματική αλλαγή και κατά συνέπεια η υπερθέρμανση του πλανήτη αλλά και η ενεργειακή κρίση. Ένα μεγάλο μέρος της ενέργειας που χρησιμοποιείται καθημερινά από διάφορες οικιακές και βιομηχανικές διεργασίες μετατρέπεται σε άχρηστη θερμότητα. Τα θερμοηλεκτρικά υλικά μπορούν να μετατρέψουν αυτή την άχρηστη θερμότητα, σε ηλεκτρισμό και κατά συνέπεια να αποτελέσουν μέρος της λύσης του ενεργειακού αλλά και κλιματικού προβλήματος που αντιμετωπίζουμε σήμερα. Αν και η σημερινή απόδοση των θερμοηλεκτρικών διατάξεων είναι χαμηλή (~7), πρόσφατα έχουν εμφανιστεί υλικά, τα οποία υπόσχονται να αυξήσουν την απόδοση στο 15-20% (1). Η απόδοση των θερμοηλεκτρικών υλικών, σε bulk μορφή, καθορίζεται από τον αδιάστατο θερμοηλεκτρικό συντελεστή $ZT= S^2T/\rho\kappa$, όπου S,ρ, κ, S^2/ρ και T είναι ο συντελεστής Seebeck, η ειδική αντίσταση, η θερμική αγωγιμότητα, η θερμοηλεκτρική ισχύς (PF) και η θερμοκρασία. Η απόδοση των θερμοηλεκτρικών λεπτών υμενίων, καθορίζεται από την θερμοηλεκτρική ισχύς, διότι η μέτρηση της θερμικής αγωγιμότητας των λεπτών υμενίων είναι πολύ δύσκολη.

Η ένωση $Bi_{0.5}Sb_{1.5}Te_3$ (BST) χαρακτηρίζεται ως το “the state of art” θερμοηλεκτρικό υλικό σε θερμοκρασία δωματίου αφού παρουσιάζει πολύ υψηλή απόδοση σε bulk μορφή αλλά όχι συγκρίσιμη με τις μέχρι τώρα υπάρχουσες τεχνολογίες ($ZT=1.4$, $PF=3770$ $\mu V/K^2m$ στους 390K). Από την άλλη, η απόδοση των λεπτών υμενίων, τα οποία μπορούν να χρησιμοποιηθούν σε μικρής κλίμακας ηλεκτρονικές εφαρμογές, παραμένει χαμηλή. Οπόταν η περαιτέρω μελέτη αυτού του υλικού και στις δύο μορφές, κρίνεται απαραίτητη.

Η παρούσα διδακτορική διατριβή χωρίζεται σε δύο μέρη. Στο πρώτο μέρος, αναπτύχθηκαν λεπτά υμένια BST , με την μέθοδο παλμικής εναπόθεσης με λέιζερ, με σκοπό την επίτευξη μιας υψηλής θερμοηλεκτρικής απόδοσης συγκρίσιμης με αυτή των bulk υλικών. Για τον σκοπό αυτό, κατασκευάστηκαν και αποδομήθηκαν στόχοι με την επιθυμητή στοιχειομετρία για την ανάπτυξη λεπτών υμενίων πάνω σε υπόστρωμα γυαλιού.

Αρχικά μελετήθηκαν οι συνθήκες εναπόθεσης, ώστε να βρεθούν οι βέλτιστες, που να οδηγούν σε υψηλές θερμοηλεκτρικές αποδόσεις. Στη συνέχεια, τα λεπτά υμένια , αναπτύχθηκαν σε θερμοκρασία δωματίου και πέρασαν από ανόπτηση, ώστε να βελτιστοποιηθούν περαιτέρω οι ιδιότητες τους. Επίσης, μελετήθηκε κατά πόσο οι αναλογίες Bi/Te και Bi/Sb μπορούν να επηρεάσουν τις θερμοηλεκτρικές ιδιότητες των λεπτών υμενίων. Είναι αξιοσημείωτο, ότι η θερμική αγωγιμότητα στα λεπτά υμένια είναι μικρότερη από ότι στα bulk υλικά, λόγω σκεδάσεων των φωνονίων στις επιφάνειες και διεπιφάνειες. Έτσι, η επίτευξη ίδιας θερμοηλεκτρικής ισχύς με αυτήν των bulk υλικών μπορεί να οδηγήσει σε ένα υψηλότερο ZT. Η ανάπτυξη λεπτών υμενίων σε εύκαμπτα υποστρώματα βρίσκει πολλές εφαρμογές όπως για παράδειγμα σε ενδυτά ηλεκτρονικά. Έτσι, τέλος, αναπτύχθηκαν λεπτά υμένια σε εύκαμπτο υπόστρωμα ώστε να μελετηθεί κατά πόσο οι συνθήκες ανόπτησης και θερμοκρασίας υποστρώματος, επηρεάζουν τις θερμοηλεκτρικές ιδιότητες τους. Στο δεύτερο μέρος, ετοιμάστηκαν και χαρακτηρίστηκαν bulk BST υλικά με έξτρα προσθήκη Te, με την μέθοδο hot press και hot deformation, με σκοπό να επιτευχθεί ίδια ή και υψηλότερη θερμοηλεκτρική απόδοση από την υπάρχουσα (2).

Αποτέλεσμα αυτής της προσπάθειας, είναι η επίτευξη της υψηλότερης μέχρι σήμερα, θερμοηλεκτρικής ισχύς στα λεπτά υμένια και ίσης θερμοηλεκτρικής απόδοσης με αυτή της βιβλιογραφίας, στα bulk υλικά.

7.5 ABSTRACT (in English) (MANDATORY – To be completed in lower case)

*The abstract **must not exceed 500 words** and must include the aim, methodology and findings/conclusions of the dissertation.*

In recent years, researchers and industries are attempting to find solutions for the escalating energy crisis and the threatening global warming. The huge amount of waste heat generated from several domestic and industrial processes could be directly converted to electricity by using thermoelectric devices. However, currently available thermoelectric devices are not in common use, because of their low efficiency (~7%). The next generation of thermoelectric materials are expected to produce thermoelectric devices with conversion efficiency 15-20% (1).

The conversion efficiency of thermoelectric materials is expressed through the dimensionless figure of merit, $ZT = S^2T/\rho\kappa$ where S, ρ, κ, S^2/ρ and T are the Seebeck coefficient, the electrical resistivity, the total thermal conductivity, the thermoelectric power factor (PF) and the operation absolute temperature, respectively.

$Bi_{0.5}Sb_{1.5}Te_3$ (BST) is considered to be a state-of-the-art p-type thermoelectric material, for temperatures near room temperature. In bulk form, BST exhibits $ZT \approx 1.4$ and PF= 3770 $\mu V/K^2m$ at 390K. While these values are very encouraging, there is much more work to be done in order to develop higher-efficiency thermoelectric devices. In addition, for small-scale electronic applications, with small heat loads, thermoelectric thin films are more appropriate; however, the PF of BST thin films is still rather low.

My PhD thesis work is divided in two parts. The objective of the first part concerned the growth of BST films with bulk-like thermoelectric properties. To this end, we grew p-type BST thin films on fused silica substrates using pulsed laser deposition and home-made targets. Initially, we deposited BST films with different deposition conditions in order to obtain the optimum growth conditions. Then, the films were grown at room temperature followed by a post-deposition ex-situ annealing process in order to optimize their thermoelectric properties. Our results, concerning the PF value of the BST films, are very encouraging. Understanding the factors that influence the thermoelectric properties of BST (bulk and thin films) required further systematic investigations. To this end, we explored the effect of Sb-alloying on the thermoelectric properties of BST samples. Another issue we investigated concerned the growth and thermoelectric characterization of BST films on flexible substrates, as flexibility of these materials is an interesting feature for many applications such as wearable electronics. The influence of substrate temperature and annealing treatment on the thermoelectric properties of these films was studied. In the second part, we dealt with the preparation and thermoelectric characterization of bulk BST with the objective to achieve similar or higher ZT than the highest reported value (2). A series of p-type bulk $Bi_{0.5}Sb_{1.5}Te_3$-with excess Te samples were prepared by hot press (HP) and by hot deformation (HD) with varying processing conditions.

We have achieved the highest PF value, ever reported in the case of BST films on fused silica and Kapton substrates, which is comparable with the bulk value. While in the case of bulk BST we have achieved the same ZT value as the highest one reported in the literature.

7.6 ABSTRACT (in the language of dissertation, in case neither 7.4 nor 7.5 apply)

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First name	**Last name**	**Father's name**	**Academic supervisor**	Ioannis Giapintzakis
Elli	Symeou	Antonis		
School / Department	Faculty of engineering / Department of mechanical and manufacturing engineering		**Year of dissertation submission**	2016

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The author

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