Thermal Expansion of \( n \)-Type Doped \( \text{Bi}_2\text{Te}_{2.88}\text{Se}_{0.12} \) and \( p \)-Type Doped \( \text{Bi}_{0.52}\text{Sb}_{1.48}\text{Te}_3 \) Solid Solutions from \(-60^\circ\text{C}\) to \(+60^\circ\text{C}\)

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An automated dilatometric system was developed to measure the thermal expansion of solid materials from \(-60^\circ\text{C}\) to \(+400^\circ\text{C}\). This system was then applied to measure the linear thermal expansions of \( n \)-type doped \( \text{Bi}_2\text{Te}_{2.88}\text{Se}_{0.12} \) and \( p \)-type doped \( \text{Bi}_{0.52}\text{Sb}_{1.48}\text{Te}_3 \) solid solutions along the \( a \)-axis from \(-60^\circ\text{C}\) to \(+60^\circ\text{C}\). The experiments were performed using a vertical “tube/push rod” dilatometer under constant-temperature conditions. The initial alloys were synthesized from Bi, Te, and Se or Sb (each at 99.999 mass% purity) in stoichiometric ratios. The method based on the correlation between the thermal expansion and the heat capacity was proposed to calculate the axial expansion coefficients along the \( c \)-axis.

Key words: Thermoelectric materials, thermal expansion, thermal strain, dilatometer, heat capacity

INTRODUCTION

Bismuth-telluride-based solid solutions are state-of-the-art thermoelectric materials with the highest known figures of merit for thermoelectric cooling (TC) devices based on the Peltier effect. However, some problems of their crystal lattice dynamics, in particular specific features of their thermal expansion and its matching to other materials, are not sufficiently well studied.

The \( p \)-type doped \( (\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3 \) and \( n \)-type doped \( \text{Bi}_2(\text{Te},\text{Se})_{1-x} \) solid solutions formed from the isomorphous compounds \( \text{Bi}_2\text{Se}_3, \) \( \text{Bi}_2\text{Te}_3, \) and \( \text{Sb}_2\text{Te}_3 \) crystallize in the rhombohedral space group structure \((R3m)\), which can be easily represented by a hexagonal cell.¹ The hexagonal cell is formed by the stacking of layers, perpendicularly to the \( c \)-axis, of like or unlike atoms following the sequences:

\[
\begin{align*}
\text{\(a\)-axis:} & \quad \text{Te(Se)(1)-Bi-Te(Se)(2)-Bi-Te(Se)(1)} \quad \text{covalent-ionic bonding} \quad \text{van der Waals bonding} \quad \text{covalent-ionic bonding (I)} \\
\text{\(c\)-axis:} & \quad \text{Te(1)-Sb(Bi)-Te(2)-Sb(Bi)-Te(1)} \quad \text{van der Waals bonding} \quad \text{van der Waals bonding (II)}
\end{align*}
\]

for \( p \)-\( \text{Bi}_{0.52}\text{Sb}_{1.48}\text{Te}_3 \) (I) and \( n \)-\( \text{Bi}_2\text{Te}_{2.88}\text{Se}_{0.12} \) (II), respectively.
The Te\(^{(1)}\)-Te\(^{(1)}\) and Te\(^{(1)}\)-Se\(^{(1)}\) bonds are considered to be van der Waals interactions, whereas Te\(^{(2)}\)-Sb(or Bi) and Bi-Te(or Se)\(^{(2)}\) are covalent-ionic bonds. The lamellar structure of the compounds and the weakness of the van der Waals bond between two quintets are responsible for the easy cleavage along the planes perpendicular to the c-axis (i.e., along the basal planes). Besides this striking mechanical anisotropy, many of the transport parameters also possess strong anisotropy.

Due to this crystal structure, the solid solutions under study have highly anisotropic thermophysical properties. Because of this anisotropy, thermoelectric elements must be assembled into a cooling module so that the crystal growth axis is parallel to the length or height of each element, and therefore perpendicular to the ceramic substrates and the metal conductors (Fig. 1).

The linear thermal expansion coefficient is a very important parameter used for solving a wide range of theoretical and practical problems. TC devices operate over the temperature range of -120°C to +180°C under repeated thermal cycling with temperature gradients that are likely to be higher than 60°C/mm. Therefore, thermoelectric materials should have long-term thermal and mechanical stability. ¹

Accurate values for thermal expansion coefficients are necessary in practical procedures to determine the optimum structure of semiconductor thermoelectrics to meet the required specifications with minimum cost. Also they are necessary to understand the temperature dependence of the electronic properties, in the growth of single crystals, in the choice of substrate materials suitable for epitaxial growth of thermoelectric materials, etc. Furthermore, these values help to estimate the thermal strain arising in thermoelectric cooling modules under cyclic conditions. These effects radically increase the risk of failure, either in monolithic components or when joined to other materials. Unfortunately, the literature does not provide any information about the thermal expansion coefficients of n-type doped Bi\(_2\)Te\(_2.88\)Se\(_{0.12}\) and p-type doped Bi\(_{0.52}\)Sb\(_{1.48}\)Te\(_3\) solid solutions, which are very promising low- and medium-temperature thermoelectric materials.

This work is devoted to the study of the temperature dependence of the linear thermal expansion coefficients of n-type doped Bi\(_2\)Te\(_2.88\)Se\(_{0.12}\) and p-type doped Bi\(_{0.52}\)Sb\(_{1.48}\)Te\(_3\) solid solutions along the a-axis. These measurements were carried out for the temperature range of -60°C to +60°C. Additionally, a method based on the correlation between the average coefficient of linear thermal expansion and the heat capacity was proposed to calculate the axial expansion coefficients along the c-axis for the solid solutions examined herein.

**EXPERIMENTAL PROCEDURES**

**Samples**

The main errors in dilatometric measurements are due to sample preparation and the quality of the samples themselves (microcrack defects). In this study, n-type 0.11 wt.% CdCl\(_2\)-doped Bi\(_2\)Te\(_2.88\)Se\(_{0.12}\) and p-type 0.03 wt.% Te- and 0.14 wt.% TeI\(_4\)-doped Bi\(_{0.52}\)Sb\(_{1.48}\)Te\(_3\) thermoelectric materials were prepared by the vertical zone-melting method in evacuated quartz ampoules. High-purity bismuth, antimony, selenium, and tellurium (semiconductor grade, 99.999 mass% purity) were used in proportions corresponding to the general chemical formulas Bi\(_2\)Te\(_2.88\)Se\(_{0.12}\) and Bi\(_2\)Te\(_2.88\)Se\(_{0.12}\). The zone-melting experiments were carried out with zone travel rates of 0.2 mm/min to 2.0 mm/min with less than two zone passes. Furthermore, the chemical and structural homogeneity of the Bi\(_2\)Te\(_3\)-Bi\(_2\)Se\(_3\) and Sb\(_2\)Te\(_3\)-Bi\(_2\)Te\(_3\) solid solutions under study were monitored after zone melting. For this purpose, the solid solutions were subjected to x-ray diffraction and scanning electron microscopy/energy-dispersive x-ray spectroscopy (SEM/EDS) analyses using a Bruker D8 diffractometer and a JSM-6480LM microscope with an accuracy no worse than 4 vol.% and 5% for phase determination and elemental quantitative analysis, respectively. The values of the lattice constants for a were found to be equal to 0.43835 ± 5 × 10\(^{-5}\) nm, 0.42640 ± 5 × 10\(^{-5}\) nm, and 0.41340 ± 5 × 10\(^{-5}\) nm for the Bi\(_2\)Te\(_3\), Bi\(_2\)Se\(_3\), and Sb\(_2\)Te\(_3\) compounds, respectively. For the Bi\(_2\)Se\(_3\)-Bi\(_2\)Te\(_3\) and Bi\(_2\)Sb\(_2\)Te\(_3\) solid solutions, the a lattice parameters varied according to Vegard’s law in agreement with the equations a = 0.43835(1 - 0.25y) and a = 0.43835(1 - 0.12x), respectively. The resultant ingots up to 10 mm in diameter and 100 mm in length after zone melting were not single crystals, but consisted of very coarse grains oriented along the growth axis, which was parallel to the a-axis. Measurements showed that a high figure of merit Z, defined as Z = S\(^2\)σ/κ, where S is the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity, was

![](image)