# Electric resistivities of liquid $Sb_2Te_3$ and $Ge_2Sb_2Te_5$

R Endo, S Maeda, Y Jinnai, M Kuwahara*, Y Kobayashi and M Susa
Dept of Metallurgy and Ceramics Science, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152-8552, Japan
*Center for Applied Near-Field Optics Research (CAN-FOR), AIST, Central 4,
1-1-1 Higashi, Tsukuba, Ibaraki 305-8562, Japan
Corresponding author's e-mail address: rie@mtl.titech.ac.jp

## ABSTRACT

The chalcogenide including $Ge_2Sb_2Te_5$ (GST) plays an important role in phase change memory (PCM) devices, because (i) the difference between electric resistivities of GST in crystallized and amorphous states can be utilized for data storage and (ii) the phase transformation between crystalline and amorphous states can be controlled by Joule-heating and cooling processes. Accordingly, accurate values for electric resistivity for chalcogenides are indispensable to thermal and electrical designing of PCM devices. However, there are few data reported about electric resistivities of the liquids. Thus, the present work aims to determine electric resistivities of liquid $Sb_2Te_3$ and $Ge_2Sb_2Te_5$.

Electric resistivities were measured using the four-terminal method. First, measurements were made on liquid Ga and Sn to confirm the applicability of this method, and then on liquid $Sb_2Te_3$ and $Ge_{1.6}Sb_{2.0}Te_{5.0}$ over the temperature ranges between the respective melting temperatures of the samples and 1020 K. The electric resistivities of liquid $Sb_2Te_3$ and $Ge_{1.6}Sb_{2.0}Te_{5.0}$ have been determined to be 4.35 μΩm at 991 K and 4.11 μΩm at 923 K, respectively. It has also been found that both resistivities decrease with a temperature rise, which suggests that both liquids behave as semiconductors.

**Key words**: Electric resistivity, $Sb_2Te_3$, $Ge_2Sb_2Te_5$, liquid, four-terminal method

## 1. INTRODUCTION

Phase change memory (PCM) is expected to lead the next generation memory technology, in which Te-based materials such as $Sb_2Te_3$ and $Ge_2Sb_2Te_5$ are used as memory material[1,2)]. PCM utilizes an electric resistance contrast associated with phase change for data storage; namely, the amorphous phase has much higher resistance than the crystalline phase. For bit writing, the phase change material is melted by Joule heating with high power pulse current and then quenched rapidly, forming an amorphous bit. For bit erasing, the amorphous bit is heated with low power pulse current to a temperature above glass transition temperature to form a crystal bit. Accordingly, electric resistivities of phase change materials are essential to optimal operation of PCM devices. There are many data reported for electric resistivities of liquid Te alloys containing transition metals[3-6)]; however, only a few reports are available for electric resistivities of Sb-Te alloys and $Ge_2Sb_2Te_5$ even for bulk materials. For example, Onderka et al.[7)] have measured electric resistivities of bulk Sb-Te alloys in solid and liquid states in the Te concentration range less than 60 %, and Vukalovich et al.[8)] have measured on liquid $Sb_2Te_3$ only; however, these reports have shown a discrepancy of about 1 μΩm between the values for liquid $Sb_2Te_3$. As to $Ge_2Sb_2Te_5$, on the other hand, Kato et al. [9)] and Lankhorst et al.[1)] have measured electric resistivities of thin films in amorphous, crystal and liquid states as functions of temperature. However, there are no extant data available for bulk $Ge_2Sb_2Te_5$. Thus, the aim of the present study is to measure electrical resistivities of $Sb_2Te_3$ and $Ge_2Sb_2Te_5$, especially in liquid states, as functions of temperature.

## 2. EXPERIMENTAL

### 2.1 Principle

Figure 1 shows a schematic diagram of the measurement system developed in this work. The system consists of two parts, a sample container and a measurement probe having four lead wires. The container was a one-end-closed fused

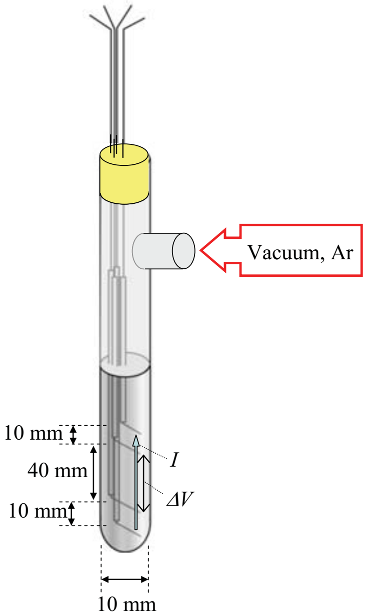

Fig. 1 Experimental setup for electric resistivity measurements

silica tube (8 mm in inner diameter) having a branch tube. The lead wires were W or Pt of 0.5 mm in diameter, and each end was bent into the shape of "L", which portion served as electrode. The distance between the inner electrodes was about 40 mm, and the distance between the inner and outer electrodes was about 10 mm. The wires other than the ends were insulated by mullite tubes, which were fixed with alumina cement to keep the probe structure. The current ($I$) was supplied between the outer electrodes, and the potential difference ($\Delta V$) was measured between the inner electrodes. The electric resistance of the sample between the inner electrodes can be derived on the basis of Ohm's law as follows:

$$R = \Delta V / I \qquad (1)$$

In experiment, the resistance was determined from the slope of a linear portion in the plot between $I$ and $\Delta V$. The electric resistivity ($\rho$) of the sample can be derived from the resistance from the equation

$$\rho = RA / l \qquad (2)$$

where $A$ and $l$ represent the cross-sectional area and the distance between the inner electrodes, respectively. The value of $A$ can be determined from the following equation:

$$A = \pi(r_1^2 - 2r_2^2) \qquad (3)$$

where $r_1$ is the inner radius of the container and $r_2$ is the outer radius of the mullite tube.

Prior to measurements on liquid $Sb_2Te_3$ and $Ge_2Sb_2Te_5$, the reliability of this method was confirmed by measuring electric resistivities of Ga (99.99 %) and Sn (99.9 %) in the temperature ranges 308 – 338 K and 700 – 850 K, respectively. In measurements at high temperature, thermal expansion of materials for the electrodes, container and insulating tubes should be corrected, and the calculation of eq.(2) was made using linear coefficients of thermal expansion given in Table 1.

Table 1 Linear coefficients of thermal expansion

| Materials | Coefficients /K$^{-1}$ | | | | References |
|---|---|---|---|---|---|
| Pt | 773 K | $9.617 \cdot 10^{-6}$ | 1273 K | $1.021 \cdot 10^{-5}$ | 10 |
| W | | $5.732 \cdot 10^{-6}$ | | $4.608 \cdot 10^{-6}$ | 10 |
| Fused silica | | $5.5 \cdot 10^{-7}$ | | $5.5 \cdot 10^{-7}$ | 11 |
| Mullite | | $4.96 \cdot 10^{-6}$ | | $4.96 \cdot 10^{-6}$ | 12 |

### 2.2. Measurements

Sample used in this study were $Sb_2Te_3$ (99.9 %) and $Ge_2Sb_2Te_5$ ($Ge_{1.6}Sb_{2.0}Te_{5.0}$). The samples were melted in a vacuum condition to keep from oxidation and evaporation during the sample preparation and measurements. First, the probe was placed in the empty container, as shown in Fig. 1, and was fixed to the container with epoxy resin at the open end of the container, which was completely sealed at the same time. Second, sample powders were inserted into the container from the branch tube, using which the container was evacuated by a rotary pump. After two-step argon purge, the container was finally closed with a vacuum valve. Samples were heated at temperatures above the respective melting points in an electric furnace, as shown in Fig. 2. When the sample was melted, the container was shaken by hand to remove bubbles between the container and the sample. Electric resistivity measurements were carried out over the temperature ranges between the melting temperatures of the samples and 1020 K in both cooling and heating cycles. Temperature was measured with a K-type thermocouple beside the sample, and supplied electric currents were in the range 0.3 – 0.7 A. Chemical compositions of the samples were analyzed by a scanning electron microscope with an energy dispersive spectrometer (SEM-EDS) after electric resistivity measurements.

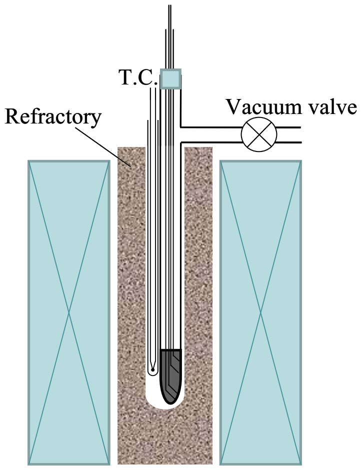

Fig. 2 Sample set up in electric furnace

## 3. RESULTS & DISCUSSION

Figure 3 shows a relation between the current (*I*) and the voltage (*ΔV*) in a measurement of liquid $Sb_2Te_3$ at 991 K. There is good linearity obtained between *I* and *ΔV*. The resistance of the sample is calculated from the slope of the straight line, and the electric resistivity in turn is calculated from eq.(2). At this temperature, the electric resistivity of $Sb_2Te_3$ has been calculated to be 4.35 ± 0.06 μΩm. The uncertainty in the electric resistivity is determined to be 3 % according to GUI (Guide to the expression of uncertainty in measurement)[13] with the coverage factor $k = 2$, providing a level of confidence of approximately 95 %. Major sources of uncertainty in electric resistivity measurements are (i) the resistance, (ii) the inner diameter of the container, (iii) the outer diameter of the insulating tubes, and (iv) the distance between the electrodes. The uncertainty in this measurement is almost the same as reported for the four-terminal technique[14]. On the other hand, the electric resistance measured at 1100 K decreased with the holding time, and SEM-EDS analysis after the measurement has shown that 0.5 mass% of W was contained in the sample, suggesting that reliable measurements would be limited to those up to 1000 K.

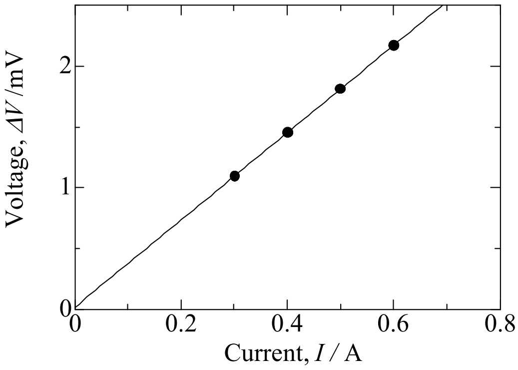

Fig. 3 Relation between current (*I*) and voltage (*ΔV*) in measurement of liquid $Sb_2Te_3$ at 991 K

Figure 4 shows the electric resistivity of liquid $Sb_2Te_3$ as a function of temperature in comparison with reported values. The results recorded in three measurements in this study show very good agreement and is also close to those reported by Onderka[7]. The electric resistivity values of liquid $Sb_2Te_3$ are two orders of magnitude greater than those for common

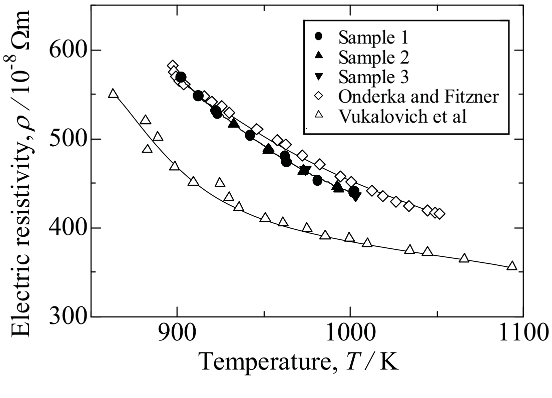

Fig. 4 Temperature dependence of electric resistivity of liquid $Sb_2Te_3$ using W electrodes with values reported by Onderka[7] and Vukalovich[8]

liquid metals[15], including Ga and Sn measured in the present study. These findings suggest that the present technique can be applied to conducting materials having electric resistivities of less than ~ 1 μΩm. Figure 5 shows the electric resistivity of $Ge_2Sb_2Te_5$ as a function of temperature. Similar to $Sb_2Te_3$, $Ge_2Sb_2Te_5$ also shows negative temperature dependence in the electric resistivity. Figures 4 and 5 indicate that these materials are likely to be semiconductors in liquid states, and the same behavior has also been reported for amorphous thin film of $Ge_2Sb_2Te_5$ by Kato et al[9].

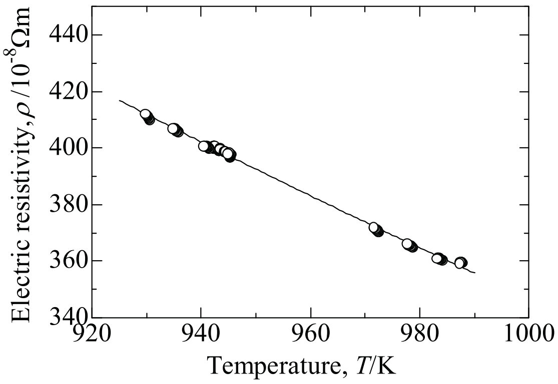

Fig. 5 Temperature dependence of electric resistivity of liquid $Ge_2Sb_2Te_5$ using Pt electrodes

## 4. CONCLUSIONS

Electric resistivities of liquid $Sb_2Te_3$ and $Ge_{1.6}Sb_{2.0}Te_{5.0}$ have been measured using the four-terminal method over the temperature ranges between the respective melting temperatures of the samples and 1020 K. For reliable measurements, special sample containers were applied to prevent samples from oxidation and evaporation during the sample preparation and measurements. It has been found that the electric resistivities of liquid $Sb_2Te_3$ and $Ge_{1.6}Sb_{2.0}Te_{5.0}$ decrease with increasing temperature, which suggests that these liquids are likely to be semiconductors. The uncertainty in the electric resistivity of $Sb_2Te_3$ is about 3 % at 991 K with the confidence of 95 %.

## REFERENCES

1. M.H.R. Lankhorst, B.W.S. M.M. Ketelaars, and R.A.M. Wolters: Nat. Mater. **4** (2005) 347.
2. D. Lencer, M. Salinga, B. Gravowski, T. Hickel, J. Neugebauer, and M. Wuttig: Nat. Mater. **7** (2008) 972.
3. S. Takeda, S. Ohno, and S. Tamaki: J. Phys. Soc. Jpn. **40** (1976) 113.
4. A. C. Bames, D. Laundy, and J. E. Enderby: Phil. Mag. B **55** (1987) 497.
5. T Okada, and S. Ohno: J. Phys. Soc. Japan **56** (1987) 1092.
6. R.J. Newport, R.A. Howe, and J.E. Enderby: J. Phys. C: Solid State Phys. **15** (1982) 4635.
7. B. Onderka and K. Fitzner: Phys. Chem. Liq. **6** (1998) 215.
8. M. P. Vukalovich, V.I. Fedorov, A.S. Okhotin, V.m. Glazov: Izvestiya Akademii Nauk SSSR, Neorganicheskie Materialy 2 (1966) 844.
9. T. Kato and K. Tanaka: Jpn. J. Appl. Phys. **44** (2005) 7340.
10. A. Buch: *Pure metals Properties, A Scientific-Technical Handbook* (ASM International, Ohio, 1999) p.183, p.219.
11. A. K. Varshneya, *Fundamentals of Inorganic Glasses* (The Society of Glass Technology, Sheffield, 2006) p.257
12. H. Ikawa, T. Watanabe, K. Urabe, and S. Udagawa, Yogyo-Kyokai-Shi, **93** (1985) 762.
13. BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIMl, Guide to the expression of Uncertainty in Measurement (ISO 1995)
14. B.J. Monaghan: Int. J. Thermophys. **20** (1999) 677.
15. M. Shimoji: *Liquid metals* (Academic Press, 1977) p.318

**Biography**

Name: Rie Endo

Nationality: Japanese

Present address: Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology

Education:

| | |
|---|---|
| 1995-1999 | Department of Metallurgical Engineering, Tokyo Institute of Technology |
| 1999-2001 | Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology<br>Awarded the Degree of Master in Engineering, supervised by Prof Susa |
| 2001-2003 | Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology<br>Awarded the Degree of Doctor in Engineering for a thesis entitled by “Molecular dynamics study on surface melting of Cu and γFe-C alloy”, supervised by Prof Susa |

Research and professional experience:

| | |
|---|---|
| 2003 | JSPS Research Fellow |
| 2003-present | Assistant Professor at the Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology, working with Profs Susa and Kobayashi on Thermophysical Properties of Metals and Glasses at High Temperature. |