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Tentative design for measurements of absolute value of thermal conductivity of semi-conducting thermoelectric elements

G. KAVEI[1], Y. ZARE and A. SEYYEDI

[1]Material and Energy Research Centre, P.O. Box 14155-4777, Tehran (Iran)

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ABSTRACT

Thermal conductivity is an important characteristic of materials in particular semi-conductors and ceramics. Since it varies within a wide range and is measured in a variety of methods, no commercial device has, so far, been established to measure thermal conductivity. Hence, it sounds necessary to develop a device to meet all needs of scholars in laboratory with a general application. Development of such a device, beside relevant calculations, is evaluated in this paper where thermal conductivity of a thermoelectric semi-conductor ingot (approximately 8 mm in diameter and 24 mm in length) at the range of room temperature is considered. At lower temperatures, thermal conductivity is almost invariant and measured in both comparative and absolute methods. Absolute value method is still widely used at temperatures below room temperature. A great deal of practical error is due to heat leakage via radiation, convection and heat transfer. Within the range of room temperature, heat leakage shares a smaller contribution in error, but not an ignorable one. At higher temperatures heat leakage plays more important role and increasing temperature makes it more and more difficult parameter to define. Hence, for fabricating a device for thermal conductivity measurement taking into the account the errors and the involved parameters it is necessary to review the scientist comments in this subject which. we have a coverage of their idea.

Key words: Thermal conductivity, Thermal diffusivity, Thermocouples, Heat flow, Heat rate.

INTRODUCTION

Measuring thermal properties of a semi-conductor

Phrase “Thermal properties” refers to properties varying with heat, such as thermal expansion, specific heat, thermal diffusivity, thermal conductivity, etc. Among these properties, only thermal conductivity appears in relation of figure-of-merit factor which defines one of the most intrinsic characteristics of thermoelectric materials.

$$Z = \frac{\alpha^2 \sigma}{k}$$

where α is Seebeck coefficient, σ and κ are electrical and thermal conductivities, respectively. Owing to its contribution in preceding relation, measuring of the thermal conductivity has drawn scientists’ attention and many methods have been developed to measure it.

For a semi-conductor whose heat flux is comparable to that of surroundings, measurement of thermal conductivity is inconvenient and time consuming due to heat exchange. Steady-state condition is vitally important in such measurements. Therefore, during recent decades, thermal diffusivity (a) techniques have been applied to determine thermal transport data, and consequently, thermal conductivity ($\kappa = a\rho c$, where a thermal diffusivity, ρ is density and c is specific heat). Still, the more accurate value for c leads to more reliable thermal conductivity value.

Thermal diffusivity techniques provide larger volumes of data in shorter period of time, and are broadly used for measurements above room temperature on bulk materials.

Thermal transport properties of various categories of materials have been studied over temperature range up to 2000K[1], or as low as 100K[2]. Measurements for bulk and thin film materials are performed in different methods. Different techniques are applied depending on temperature range and materials.

Absolute method to measure heat flow is the most common method at low temperatures, which slightly differs from technique used by Lee, 100 years ago[3]. A brief review of experimental requirements of his device is represented by White[4]. As shown in Fig. 1, source supplies heat at the rate of:

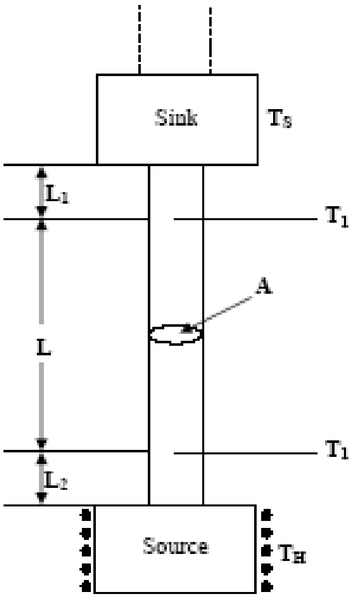

Fig.1: Heat supplied by the source (T_H) is conducted along an ingot of uniform cross-section *A*, in which a pair of thermometers is fixed at points 1 (T_1) and 2 (T_2), separated by distance *L*.

Heat is conducted along an ingot of uniform cross-section *A*, in which a pair of thermometers is fixed at points 1 and 2, separated by distance *L*.

Thermal conductivity at any point is given by

$$k(T) = \frac{\dot{Q}}{A}\frac{\partial L}{\partial T}$$

The mean thermal conductivity between points 1 and 2 in Fig.1 is:

where $\Delta T = T_2 - T_1$. It is assumed that temperature is uniformly distributed across any element (length *L*) of cross-section and heat leakage through surrounding gases, insulators, electrical connectors and by radiation is negligible.

The geometry of device depends on sensibility of thermometers and maximum value of . In practice, *L* should be greater than diameter of cross-section. For materials with low conductivity (e.g. thermoelectric materials) diameter of 3 to 4 mm and *L* /*A*d≤10 is preferred[5].

ange, heat sink ater or electric e heat sink. oth resistance es[6-9]. Typical e applications wires joint. For romel/Alumel and Copper/ 0.03 Fe/Cr) ecommended.

been done at above room oses effect[10-15]. t leakage from adiation losses. are located in eratures are entional device for thermal conductivity measurement at high temperatures is represented by Laubitz[17]. Such devices have been used to measure thermal conductivity of semi-conductors and thermoelectric materials, but being recently abolished by recent techniques.

Comparative methods for thermal conductivity measurements

Comparative methods determine thermal conductivity (k) of a material with respect to that of a proper reference material. The sample whose thermal conductivity is to be measured is sandwiched between two cylinders made of reference material whose thermal conductivity is exactly known. Temperature gradient in sample and reference are measured. If cross-sections of sample and reference are equal, then:

$$\kappa = \frac{\kappa_{ST}(\Delta T/\Delta x)_{ST}}{(\Delta T/\Delta x)}$$

where κ_{ST} is the known thermal conductivity of the standard reference and $(\Delta T/\Delta x)_{ST}$ and $(\Delta T/\Delta x)$ are the temperature gradients of reference and sample, respectively.

Thermocouples are located near the interfaces of sample and reference (which are both shielded in a cylindrical guard). A schematic of thermal conductivity measurement device is represented by Francl and Kingry[18], in which Chromel/Alumel thermocouples are located on silver plates separating the sample and reference. Thin layers of indium amalgam are used to overcome the problem of contact resistance. A modified version of this device is reviewed by Hust[19].

Comparative methods are not focused in this paper, because of lack of a standard reference; although, using comparative methods, the measurements would be more convenient and straight forward, complicated computation would not be necessary and instruments would be calibrated accurately. Having a standard reference, a more precise measurement would be accomplished following structure below:

The sample and the reference are located consequently in a thermal conduction instrument. A thermal flow $\dot{Q}$ passes along both sample and reference and T_1, T_2, $\Delta T = T_2 - T_1$, , T_{O2}, $\Delta T_O = T_{O2}$, T_{O1}, l, l_o A_1 and A_o are measured, where last four are lengths and cross-sections of sample and reference, respectively. Knowing thermal conductivity of reference (κ_O), that of sample will be:

$$\kappa = \kappa_o \frac{A_o}{A} \frac{l}{l_o} \frac{\Delta T_o}{\Delta T}$$

Thermal diffusivity method for thermal conductivity measurements

Non-steady-state methods to measure thermal transport were the matter of practice in 19th and early 20th centuries, and through the efforts made by scientists, impressive collections of mathematical calculations and practical approaches were provided[20,21]. Among these techniques was thermal diffusivity method in which thermal diffusivity (κ') is measured and substituted in thermal flow differential equation:

$$\kappa' = \left(\frac{\partial^2 T}{\partial x^2}\right) = \frac{\partial T}{\partial t} + \mu T$$

where μ is heat loss coefficient of surface lost by radiation, conduction and convection, t is time interval between consequent measurements, and x is distance between two points whose temperatures are to be measured. Depending on boundary conditions, a wide range of solutions to Fourier's equation are possible, and many ingenious techniques have been recently developed. Two factors are responsible for these developments: First, time is measured more accurately by the means of recent advanced equipments such as oscilloscopes, digital data acquisition systems and microcomputers. Second, when measurement time is short, heat losses decrease significantly and can be accurately taken into account by manipulating the differential equation or by properly calibrating equipments.

This approach is entirely different from steady-state methods in which heat leakage must be precisely quantified or eliminated to avoid large errors. Ref[22] has more about non-steady-state methods.

Angstrom's method for thermal conductivity measurements

Angstrom's Method developed in 1861 and gained widespread acceptance[23]. According to this method, a heat source whose temperature sinusoidally varies with time is attached to the end of a semi-infinite radiating ingot (x=0). Temperature waves will propagate along the ingot with velocity $v=\omega/\beta$, where w is angular velocity and β is phase shift per unit length. Thermal diffusivity is then obtained as[24]:

$$\kappa' = l.v/2\ln(q)$$

where l is distance between two thermocouples, and q is amplitude decrement in temperature wave.

Instrumentation

Development and trial of methods to measure absolute value of thermal conductivity

In thermal conductivity measurement instruments, thermal transport (needed for temperature difference at a certain distance from one end of a semi-conductor ingot of cross-section A) must be accurately defined. Having mentioned restrictions, a device (as illustrated in Fig. 2) is widely used to define thermal transport at room temperature and its arrangement is as follow: The sample (1) is located between two heaters (3). To avoid heat leakage, a guard (4) shields the measurement tools. Finally, the equipments lay on the device base (2). Heater supplies a heat flow in the sample and provides a temperature gradient (T_2- T_1) about 5 to 10 °C at a distance l (about 12mm) which is measured by a pair of Chromel/Alumel thermocouples. Diameter and height of the guard is critically important.

The guard is designed as tightly fit as possible to reduce free unused space and resultant errors due to radiation (some researchers have filled free space by thermal insulator powders, such as alumina[25]). Nevertheless, heat flow (heat rate lost by surroundings) does exist for surroundings and must be subtracted from heat generated by heater (3). Throughout the measurements, the guard temperature is measured by thermocouples as well, to estimate the heat leakage more precisely. The guard is usually made of copper to conduct thermal equilibrium or, in other words, to specify leaked heat flow accurately.

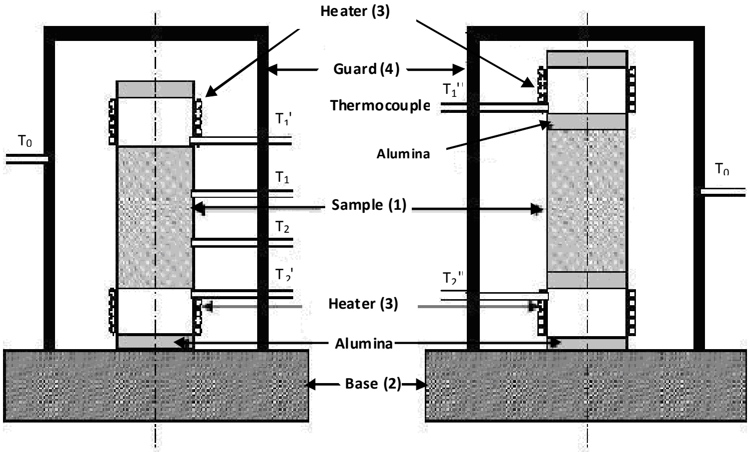

Fig. 2: A device for characterization of thermal conductivity and its arrangement is widely used at room temperature and its arrangement

Thermal conductivity from standard relation of steady-state is given by:

$$\kappa = \frac{(W - \Delta \dot{Q}')\, l}{A\, \Delta T}$$

where W=VI is electrical power consumed by heater (3), $\Delta\dot{Q}'$ is the heat rate lost by surroundings, L total length of the sample, A is cross-section of sample, l is distance between thermocouples 1 and 2 and DT is temperature gradient along l.

Heater is made of Nickel wires of 0.3 mm diameter. All electrical contact (including earth contacts) should be checked. Tip of thermocouples must be sharp enough. Two thermocouples are located on the sample, one on the guard and two at the ends of sample, under heaters. Thermocouples are tightened in holes of 0.5mm diameter and 2mm depth.

Heat flow, temperature gradient and chemical reaction of sample are three major factors one must consider when designs a system to measure thermal conductivity of the sample at high temperatures.

This research is a confirmation to develop an instrument to measure thermal conductivity by absolute method at room temperature. Accomplishing semi-practical calculations, measuring required quantities and substituting them in following semi-practical relation, one can obtain a more accurate value for thermal conductivity[26]:

$$\kappa = \frac{l}{A}\left[\frac{W_1 - K_1\Delta T_1' + K_2\Delta T_2'}{2\Delta T}\right] - \left[\frac{W_1 - K_1\Delta T_1' - K_2\Delta T_2'}{4(\Delta T_1 + \Delta T_2)}\right]\left[L/A - l^2/3LA\right]$$

$$\Delta T_1'' = T_1'' - T_o \qquad \Delta T_2'' = T_2'' - T_o$$

$$\Delta T_1' = T_1'' - T_o \qquad \Delta T_2' = T_2'' - T_o$$

$$\Delta T_1 = T_1' - T_o \qquad \Delta T_2 = T_2' - T_o$$

$$\Delta T = T_2 - T_1$$

$$W_1 = 0.24 R_1 I_1^2 \qquad W_2 = 0.24 R_2 I_2^2$$

$$K_1 = \frac{W_1}{\Delta T_1''} \qquad K_2 = \frac{W_2}{\Delta T_2''}$$

where R_1, I_1, R_2 and I_2 are resistance and current passing though upper and lower heaters, respectively. Other quantities are illustrated in Fig. 2. Potential differences V (in mV) produced by Chromel/Alumel thermocouples were measured and is substituted in the below formula to achieve an approximated temperature of above environment temperature[25].

$$T = \frac{V(\mu V)}{40}$$

Thermocouples producers are presenting tables of experimentally measured values of the voltage and calibrated temperatures, which are accurate and easy to use.

Selecting of a guard to control heat transfer is very important. Optimal guard size occurs when its walls are perfect reflectors and its internal diameter is small compared to dimensions of sample and heater. However, semi-practical calculations for the guard can be found in Ref. [27]. Surface of guard (which is made of copper whose emission coefficient is half of that of black-body) loses the heat by rate of $6\text{x}10^{-3}$ cal/s.cm^2.°C. This implies thermal conductivity to be measured more accurately by absolute method and that careful calculations still involve significant errors.

CONCLUSION

Thermal conductivity is an important physical property of materials. Measurement of this property is easy for good conductors, but not for semiconductors and insulators. Absolute value method is still widely used at temperatures below room temperature. Development of a device to measure thermal conductivity at room temperature, beside relevant calculations, was evaluated. A computational method to estimate the thermal conductivity in acceptable level was represented. Practical errors at room temperature depend on heat leakage by radiation, convection and heat transfer. Within room temperature, this dependence is less sensitive, but still necessary to measure. At higher temperatures heat leakage plays more important role and increasing temperature makes it more and more difficult parameter to define.

REFERENCES

1. Wood, C., Materials problems in high temperature thermoelectric conversion, in the First European Conference on thermoelectrics, Rowe, D.M.,Ed.,Peter Peregrinus, London, 1 (1988).
2. Goldsmid,H.J., Electronic refrigeration, in the First European Conference on thermoelectrics, Rowe,D.M.,Ed., Peter Peregrinus, London, 342 (1988).
3. Less,C.H., Conductivities of methods and alloys at low temperatures, *Philos. Trans. Royal Soc*.A, **208,** 301 (1908).
4. White,G.K., Measurement of solid conduction at low temperature, in Thermal Conductivity, volume 1,Tye,R.P.,Ed., Academic Press, London, 69 (1969).
5. Taylor R., CRC hand book of thermoelectric, Ed. Rowe M.D., (CRC Press , Boca Raton, FL), 165, (1995).
6. Black, W.C., Rosch, W.R.,and Wheatley, J.C., Speer carbon resistors as thermometers for use below 1°K, *Rev. Sci. Instrum.,* **35**: 587 (1964).
7. Kunzler, J.E., Gabelle, T.H., and Hull, G.W., Germanium resistance thermometers suitable for low temperature calorimetry, *Rev. Sci. Instrum.,* **28**: 96 (1957).
8. Lindenfield, P., Carbon and semiconductor thermometers for low temperatures, in Temperature. Its Measurement and Control in Science and Industry, Vol. 3, Part 1, Herzfeld, C.M.,Ed.,Reinhold, New York, 399 (1962).
9. Klein,M.V., Phonon scattering in sodium chloride containing oxygen, *Phys. Rev.,* **122**: 1393 (1961).
10. Slack, G.A., Thermal conductivity of CaF_2, MnF_2, CoF_2 and ZnF^2 crystals, *Phys. Rev.,* **122,** 1451 (1961).
11. Berman, R., Brock, J.C.F., and Huntley, D.J., Properties of gold + 0.03 at% iron thermoelements between 1 and 300°K and behaviour in a magnetic field cryogenics, **4**: 233 (1964).
12. Brinson, M.E. and Dunstan, W., Thermal conductivity and thermoelectric power of heavily doped n-type silicon, *J. Phys. C Solid State phys.,* **3**: 483 (1970).
13. Ditmars, D.A. and Ginnigs, D.C., Thermal conductivity of beryllium oxide from 40° to 750°C, *J.Res. Natl. Bur. Stand.,* **59**: 93 (1957).
14. Armstrong, L.D. and Dauphine, T.M., Thermal conductivity of metals at high temperatures. I. Description of the apparatus and measurements on iron, *Can J. Res. A,* **25**: 357 (1947).
15. Poiwell, R.W. and Tye, R.P., Thermal and electrical conductivities of nickel- chromium (Nimonic) alloys, *Engineer,* **209**: 729 (1960).
16. Busch, G. and Steigmier, E.F., Thermal and electrical conductivities, Hall effect and thermoelectric power of InSb, *Helv. Phys. Acta,* **34**: 1 (1961).
17. Laubitz, M.J., Measurement of thermal conductivity of solids at high temperature by using steady state linear and quasi- linear heat flow, in Thermal Conductivity, Vol. 1, Tye, R.P., Ed., Academic Press, London,111 (1969).
18. Francl, and Kingery, W.D., Thermal conductivity. IV. Apparatus for determining thermal conductivity by a comparative method, *J.Am. Ceram. Soc.,* **37**: 80 (1954).
19. Morris, R.G. and Hust, J.G., Thermal conductivity measurement of silicon from 30° to 425°C, *Phys. Rev.,* **124**: 1426 (1961).
20. Carslaw, H.S. and Jaeger, J.C., Conduction of Heat in Solids, 2nded, Oxford University Press, New York (1959).
21. Jakob, M., Heat Transfer, John Wiley & Sons, New York (1949).
22. Danielson, G.C. and Sidles, P.H., Thermal diffusivity and other non- steady state methods, in Thermal Conductivity, Vol. 2, Tye, R.P., Ed., Academic Press, London, (1989).
23. Angstrom, A.J., Neue Mathode des Warmeleitungsvermogen der Korper zu bestimmen, *Ann. Phys. Chem.,* **114**: 513 (1861).
24. Sidles, P.H. and Danielson, G.C., Thermal diffusivity measurements at high temperature, in Thermoelectricity, Egli, P.H., Ed., John Wiley & Sons, New York, 270 (1960).
25. petrov A.V., Thermoelectric properties of semiconductors Ed. Kutasov, 17-22 (1964).
26. Devyatkova E.D., Petrov A.V. and Moizhes B.Ya., Fiz. Tverd. Tela **2**: 738 (1960).
27. Abeles B., *J. Phys. Chem. Solids,* **8**: 340 (1959).