Thermochimica Acta, 19 (1977) 240–243

Note

Emissivities of arsenic, antimony, and bismuth single crystals

CLIFTON W. DRAPER and GERD M. ROSENBLATT
Department of Chemistry, The Pennsylvania State University, University Park, Pa. 16802 (U.S.A.)
(Received 19 July 1976)

For a variety of reasons, information on some of the thermophysical properties for many elements is limited. Arsenic is one of these elements[1]. To our knowledge the emissivity of arsenic has never been reported. This note reports determinations of the low-temperature radiative emissivity of arsenic (111) single-crystal cleavage surfaces, polycrystalline arsenic, and oxidized As (111) single-crystal surfaces. The emissivities of antimony and bismuth (111) single-crystal cleavage surfaces have also been determined. The measurements are made by a radiation pyrometer technique.

EXPERIMENTAL

Arsenic, antimony, and bismuth single crystals are grown in this laboratory, using the Bridgman technique[2], from granular elemental starting material with a quoted purity of 99.999% or better. Single crystal wafers 0.5–3.0 mm thick are prepared by cleaving along (111) immediately before an experiment with a new razor blade. The resulting mirror-like cleavage surfaces have surfaces areas of the order of 1–2 cm^2. The surfaces are similar to those whose surface reaction properties have received considerable attention in this laboratory[3]. Polycrystalline arsenic samples are prepared by rapidly quenching the melt from the crystal growth furnace. Polycrystalline wafers are cut and planed with a spark cutter[4], then polished with No. 400 emory paper and No. 925 crocus cloth. The polycrystalline arsenic samples are heated in vacuum (10^{-5} Torr) at 200°C for 15–20 min to remove almost all of the volatile surface oxide and are stored in evacuated (10^{-5} Torr) pyrex ampoules. Oxidized As (111) single crystal surfaces are prepared by exposing cleaved wafers to the atmosphere for about two weeks. After this exposure the originally metallic, mirror-like, cleavage surfaces are covered with a dull, reddish-gray oxide coating.

Emissivities are measured using a modified Mikron 10 infrared pyrometer covering the range 0–150°C. The pyrometer detection element consists of two matched thermistor bolometers, one shielded and one exposed to radiation from a 7 mm diam area of sample. The bolometers form two arms of a Wheatstone bridge. The detection circuit includes a precision potentiometer linear in emissivity. The spectral response of the infrared sensor is 1–20 μm, which encompasses about 60% of the total radiative flux emitted by a blackbody at 400 K. The inaccuracy of the calibrated instrument is less than ±2°C in the temperature and ±8% in the emissivity. Checks of the instrument which compare temperatures determined with the pyrometer from a black painted surface of unit emissivity with thermocouple measurements are well within this uncertainty. For general information on this and other commercial pyrometers, see the recent review by Warnke[5].

The heat source is a small hot plate covered by 5 mm of asbestos sheet rock and a 3 mm thick aluminum slab. This system has a temperature drift of less than 1/2°C over the time span of a measurement, about a minute. The pyrometer is supported 50 mm (the instrument focal length) above and perpendicular to, the sample surface.

Two methods of measurement are used. In the first, the temperature of the aluminum slab, which is covered with flat black paint so that it very closely approximates a blackbody is measured with the emissivity potentiometer of the pyrometer set at 1.0. The pyrometer is then focused on the sample and the emissivity potentiometer adjusted until this temperature again is indicated on the pyrometer. Differential thermocouples are used to insure that the blackbody and sample are indeed at the same temperature. In the second method, the sample temperature is determined by a spot welded 0.076 mm chromel–alumel thermocouple positioned just outside the pyrometer's field of view. The temperature is monitored continuously with a Keithley model 160 digital microvoltmeter or model 180 nanovoltmeter. The emissivity potentiometer is adjusted until the pyrometer indicates this same temperature. This second method has the advantages that aluminum foil can be positioned around the sample in order to eliminate the background radiative flux, and no repositioning of the pyrometer or sample is required after the instrument is initially focused. These are important factors in the present measurements since the sample sizes approach the 7 mm diam field of view of the instrument.

RESULTS AND DISCUSSION

The results of the emissivity measurements are presented in Table 1. The emissivities should be classified as (nearly) total, normal emittances since the instrument spectral response is restricted to 1–20 μm. Emissivities are very sensitive to surface preparation, and therefore, only the freshly cleaved (111) surface results are expected to be reliably reproducible from one sample to another.

The measured emissivities can be compared with the limited literature values available for the Group V semimetals. Coblentz[6] in 1911 measured the spectral reflectance of a room temperature antimony single crystal surface, and of an antimony mirror formed by cathode sputtering, over the range of 1–10 μm. Emissivities of 0.45 and 0.30 at 7 μm may be inferred from the reported reflectivities

TABLE 1

EMISSIVITIES OF GROUP V SEMIMETALS

Sample	*Temp. range (K)*	*Emissivity (averaged results)*
Arsenic single crystal (111)	395–420	0.17±0.04
Polycrystalline arsenic	408–415	0.23
Oxidized arsenic (111)	405–411	0.37
Antimony single crystal (111)	405–416	0.28±0.02
Bismuth single crystal (111)	394–423	0.34±0.04

by Kirchhoff's law. However, a number of experimental difficulties led Coblentz to conclude that the values obtained should receive little weight. Room temperature spectral reflectances of ground and polished bismuth mirrors reported[7] in 1903 lead to spectral emissivities of 0.29–0.18 in the range 3–14 μm. However, here also the authors noted concern with the surface condition of their bismuth mirror. Schmidt and Eckert[8] in 1935 report a total normal emittance for "bright" bismuth at 353 K of 0.340, which may be compared with the value in Table 1. Although no previous reports of the emissivity of arsenic appear in the literature, the values in Table 1 seem reasonable when compared to the other Group V semimetals. The measured emissivity ε of As (111) is consistent with measurements of the thermal accommodation coefficient γ of $As_4(g)$ on As (111)[9]. The thermal accommodation measurements yield the ratio $\gamma/\varepsilon = 5.68$. Combination of the experimental value of γ/ε with $\varepsilon = 0.17$ gives $\gamma = 0.98 \pm 0.28$, a result consistent with other work on the $As_4(g)$–As (111) system[3,9].

The instrumentation and methods used here appear to be useful for surfaces with emissivities approaching values as low as 0.05. We determine the emissivity of the aluminum foil shielding to be 0.076, in agreement with the normal spectral emittances determined by Reynolds:[10] $0.05 < \varepsilon < 0.10$, in the range 2–15 μm.

ACKNOWLEDGEMENTS

The authors wish to thank the National Science Foundation (Grant CHE 75–04801) for financial support of this work.

REFERENCES

1 Y. S. Touloukian, R. W. Powell, C. Y. Ho and M. C. Wicolaou (Eds.), *Thermophysical Properties of Matter*, Vol. 10, IFI/Plenum, New York, 1973, p. 9; C. Y. Ho, R. W. Powell, and P. E. Liley, *J. Phys. Chem. Ref. Data*, Vol. 3, Suppl. 1 (1974) 63.

2 L. R. Weisberg and P. R. Celmer, *J. Electrochem. Soc.*, 110 (1963) 563.

3 G. M. Rosenblatt, in J. M. Thomas and M. W. Roberts (Eds.), *Surface and Defect Properties of Solids*, Vol. 5, Specialist Periodical Reports, The Chemical Society, London, 1976, p. 36.

4 F. N. Lin, *Doctoral Dissertation*, The Pennsylvania State University (1974). University Microfilms No. 74-21012, Ann Arbor, Mich.

5 G. F. Warnke, in H. H. Plumb (Ed.), *Temperature: Its Measure and Control in Science and Industry*, Vol. 4, Instrument Society of America, Pittsburgh, 1972, p. 503.

6 W. W. Coblentz, *Bull. Nat. Bur. Std.*, 7 (1911) 197.

7 E. Hagen and H. Rubens, *Ann. Phys.*, 11 (1903) 873.

8 E. Schmidt and E. Eckert, *Forsch. Geb. Ingenieurw.*, 6 (1935) 175; E. Eckert, in W. M. Rohsenow and J. P. Hartnett (Eds.), *Handbook of Heat Transfer*, McGraw-Hill, New York, 1973, p. 15:21.

9 R. S. Lemons and G. M. Rosenblatt, *Surface Sci.*, 59 (1976) 293.

10 P. M. Reynolds, *Brit. J. Appl. Phys.*, 12 (1961) 111.