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Thermophysical Properties of Thoriated Tungsten Above 3600 K by a Pulse-Heating Method[1]

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Thoriated tungsten (tungsten, 98% thorium oxide, 2%) is a widely used electrode material for inert-gas arc-welding. A subsecond pulse-heating technique was applied to rod specimens; radiance temperature was measured by high-speed pyrometry. Literature values of the temperature dependence of the normal spectral emissivity of tungsten were used to obtain true temperatures, with the melting point of thoriated tungsten as a calibration point. Experimental results obtained in the temperature range from 3600 K to the melting point (3693 K) are presented and discussed, along with data obtained during the initial part of the free cooling period. The electrical resistivity results show a regular behavior up to the melting point, indicating that thoria remains an insulator up to 3680 K. During heating, a heat capacity anomaly is found near 3666 K, interpreted as the melting point of thoria. During cooling, two anomalies are found, the first one with a peak near 3660 K and a second one (possibly a Frenkel disorder) with a peak near 3148 K.

KEY WORDS: electrical resistivity; Frenkel disorder; heat capacity; melting point; thoria; tungsten; welding electrodes.

1. INTRODUCTION

Measurements of thermophysical properties at very high temperatures (above 3000 K) are very difficult, on account of chemical reactions and severe experimental problems. In the present work, thermophysical properties of commercial thoriated tungsten (nominal composition, 98% wt

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tungsten and 2% wt thoria) above 3600 K and up to its melting point were measured with a subsecond pulse heating technique.

The work was performed in collaboration with a research group at the CSIRO Division of Applied Physics (CSIRO DAP, Sydney, Australia) that is working in the computer modelling of arc-electrode effects. Thoriated tungsten is a widely used arc electrode material and its thermophysical properties are important input data for the modelling.

Measurements were performed on commercial thoriated tungsten specimens, provided by CSIRO DAP, making use of the pulse heating apparatus available at the Istituto di Metrologia "G. Colonnetti" (IMGC, Torino, Italy). The experimental method is based on rapid resistive self-heating of the specimen from room temperature to high temperatures in times of the order of 1 s by the passage of an electrical current pulse. Complete technical details on the apparatus and on the measuring technique are given in earlier publications [1–3]. Thermophysical properties of thoriated tungsten were measured from 1200 K to the melting point [4]; this work describes the experimental results above 3600 K and specific phenomena occurring after the material has reached those temperatures.

2. MEASUREMENTS

The main technical characteristics of the experimental apparatus and some specimen data are reported in Table I.

Table I. System Characteristics and Specimen Data

Voltage and current measurement	Voltage drop across tungsten knife-edge probes and across standard resistor (1 mΩ)
Temperature measurement	High-speed pyrometer operating near 900 nm [5]
Specimen environment	High vacuum ($\cong 10^{-3}$ Pa) or flowing argon at atmospheric pressure
Number of specimens	3 (rod form, identified as S-1 to S-3)
Source[a]	Teledyne Wah Chang Huntsville Inc., Huntsville, AL, USA; commercial grade, 2% thoriated tungsten electrodes (nominal composition: 98% wt tungsten, 2% wt thorium oxide)
Dimensions (nominal)	Total length, 89 mm; effective length,[b] 30 mm; diameter, 3.2 mm
Mass and density	Total mass, 13.8 g; effective mass,[b] 4.65 g; density,[c] 18.872 g · cm^{-3}

[a] The supplier is identified in order to characterize the specimen adequately; such identification does not imply recommendation or endorsement by IMGC or CSIRO DAP.

[b] "Effective" refers to the portion of the specimen between the voltage probes.

[c] The density measurements were performed at CSIRO DAP.

Temperature measurements were made with a high-speed pyrometer [5] operating near 900 nm, using an interference filter with a bandwidth of 80 nm. Measurements in the high-temperature range were performed with a calibrated neutral density filter (nominal transmission, 0.25) in the pyrometer target path. The temperature range 1600–3700 K was covered in one experiment, using an autorange feature [6] on the pyrometer and the related data acquisition system.

The high-speed pyrometer focused on the surface of the rod specimen measured radiance temperatures: true temperatures were computed via normal spectral emissivity. The thoriated tungsten rods are made of 98% tungsten with thoria (ThO_2) particles finely dispersed in the tungsten matrix [7]. The temperature measurements are performed over a relatively large target area (circle of diameter, 300 μm) with respect to the typical size of the thoria particles (spheres of diameter, 1 μm). On account of these facts, it can safely be assumed that the melting point and the temperature dependence of the normal spectral emissivity of thoriated tungsten are the same as those for tungsten. The temperature dependence of the normal spectral emissivity at 900 nm was estimated from literature data [8–10], with a procedure previously used with good results in similar experiments on tungsten [11–12]. The emissivity curve was adjusted to the surface conditions of each specimen by using the melting plateau value (3693 K as indicated in Ref. 13) as a calibration point. Several measurements of the melting plateau were made for each specimen, using an experimental technique in which the specimen is taken to the melting point, but current is interrupted before complete fusion, preserving the specimen for additional experiments [14].

Experiments were performed with subsecond current pulses (duration, 0.4–0.7 s), with the heating rate in the range 4400–6700 $K \cdot s^{-1}$. High vacuum (better than 10^{-3} Pa) was used for most of the measurements. Some experiments done in flowing argon at atmospheric pressure did not indicate any significant difference. Measurements were performed on specimens S-1, S-2 (as received from the manufacturer), and S-3 (heat treated at temperatures higher than 3000 K for more than 3 h). Additional technical details on these measurements, including experimental results on thermophysical properties of thoriated tungsten in the temperature range 1200–3600 K, may be found in an earlier publication [4]. Physical changes occurring in tungsten and thoriated tungsten after pulse heating experiments are described in a complementary publication [7].

All the temperatures reported in this paper are based on the International Temperature Scale of 1990 [15] except where explicitly noted otherwise.

3. EXPERIMENTAL RESULTS

Thermophysical properties in the temperature range above 3600 K were computed directly from experimental data. The heating and cooling rates were obtained with a convolute method developed at Oak Ridge National Laboratory (ORNL) [16].

3.1. Electrical Resistivity (ρ)

The experimental values of the electrical resistivity are based on geometric dimensions at room temperature (293 K): no thermal expansion correction was applied. The electrical resistivity results above 3600 K are plotted in Fig. 1 as relative deviations with respect to the electrical resistivity of tungsten [11, 12] measured at IMGC. The data indicate a smooth behavior with the electrical resistivity of thoriated tungsten being approximately 4% higher than the resistivity of tungsten up to the melting point.

3.2. Heat Capacity (C_p)

All the experiments performed on specimens S-1, S-2, and S-3 indicate a heating rate anomaly in the region 3640–3680 K. The data for five

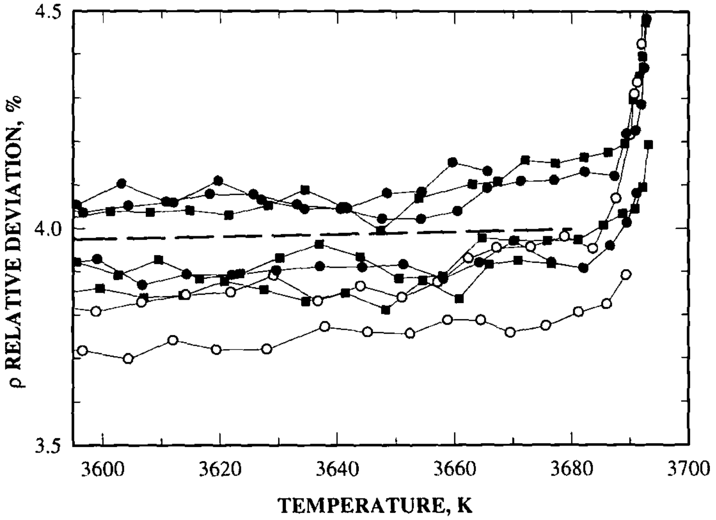

Fig. 1. Relative deviation of the electrical resistivity of individual experiments on thoriated tungsten above 3600 K from the electrical resistivity of tungsten [11]: (■) specimen S-1; (○) S-2; (●) S-3. The dashed line is the curve representing the electrical resistivity of thoriated tungsten in the temperature range 1200–3680 K [4]. One datum of two is plotted.

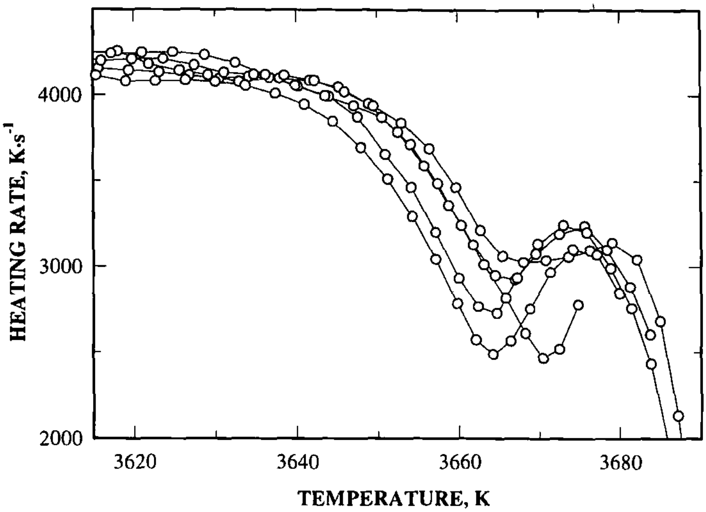

Fig. 2. Heating rate anomaly observed in five experiments on S-2.

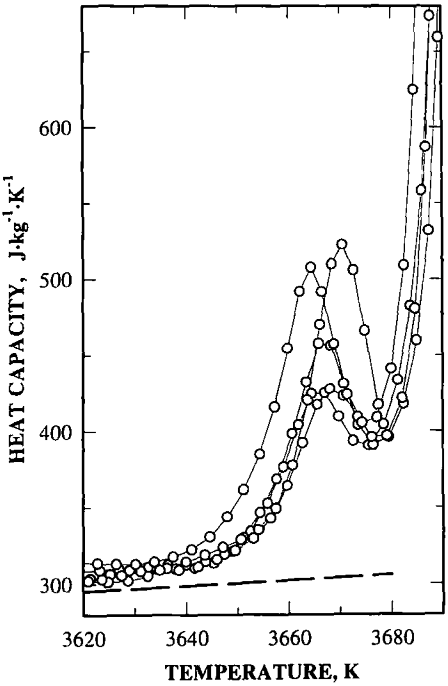

Fig. 3. Heat capacity of thoriated tungsten above 3620 K. The plotted data refer to the five experiments on S-2. The dashed line is the curve representing the heat capacity of tungsten in the temperature range 3600–3680 K [12].

Table II. Experimental Results on Thoriated Tungsten: for the Heating Phase the Peak Temperature of the Heating Rate Anomaly Is Reported; for the Cooling Phase the Temperatures of the First and Second Peak of the Cooling Rate Anomalies Are Reported

				Cooling phase	
Specimen	Experiment No.	Environment	Heating phase Peak temperature (K)	First peak temperature (K)	Second peak temperature (K)
S-1	13	High vacuum	3666	3650	Not measured
	14	High vacuum	3668	3664	Not measured
	20	High vacuum	3667	3666	Not measured
	24	Argon	3666	3688	Not measured
S-2	16	High vacuum	3665	3649	3147
	17	High vacuum	3666	3672	3156
	26	High vacuum	3670	3642	3149
	27	High vacuum	3668	3670	3157
	31	High vacuum	3664	3644	3153
S-3	12	High vacuum	3664	3647	3132
	13	High vacuum	3666	3667	3144

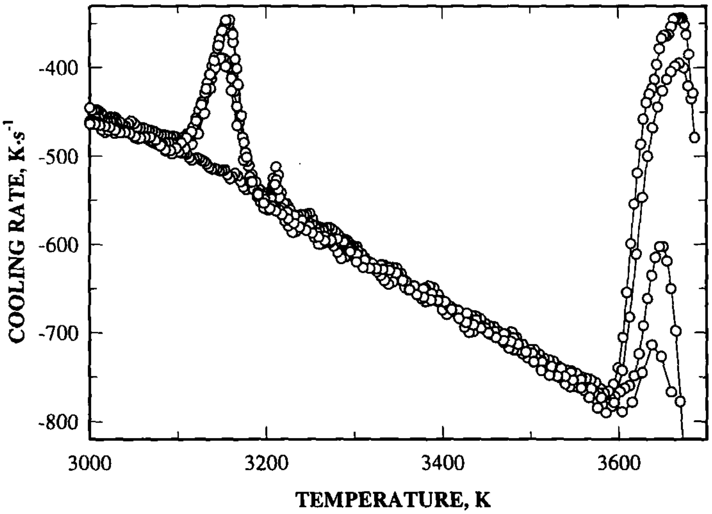

Fig. 4. Cooling rate anomalies observed on some experiments on S-2. One datum of three is plotted.

experiments performed on S-2 are reported in Fig. 2. It should be noted that, in all cases, the decrease is temporary, with the heating rate increasing again before the large decrease due to melting. Consequently, the heat capacity of thoriated tungsten exhibits a well-pronounced peak, as shown in Fig. 3 (results of measurements on S-2). This peak is interpreted as the melting of the thoria particles contained in thoriated tungsten, occurring over a range of approximately 40 K. The anomaly assumes various shapes and is spread over different temperature ranges, with no clearly identifiable behavior except for a well-reproducible peak value. Experimental data referring to all the specimens are reported in Table II. During heating the peak of the anomaly always falls in the range 3664–3670 K, with an average value of 3666 K and a standard deviation of 1.8 K.

Cooling experiments indicate a similar behavior, with the cooling rate decreasing sharply immediately after the melting plateau, but showing an

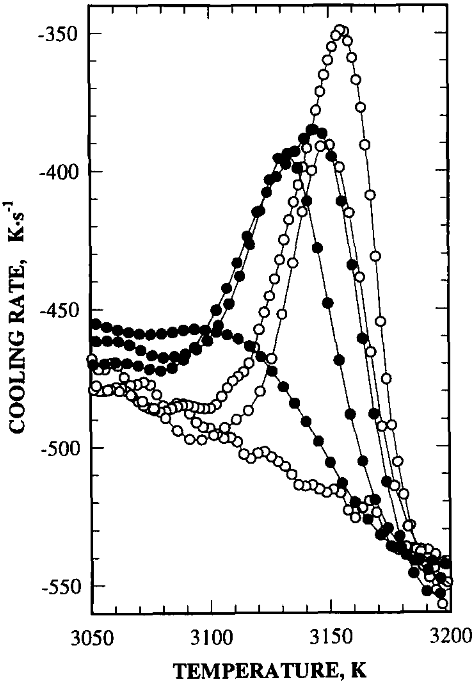

Fig. 5. Expanded view of the cooling rate anomaly occurring in thoriated tungsten around 3150 K. (○) Specimen S-2; (●) S-3. The shape of the humps depends on the highest temperature reached in the experiment. One datum of two is plotted.

extended hump from approximately 3680 to 3600 K. Typical data relative to S-2 are reported in Fig. 4, but the phenomenon is identical for all specimens.

Thoriated tungsten also exhibits a second cooling rate anomaly in the temperature range 3110–3180 K (see Fig. 4; details in Fig. 5). This anomaly is well reproducible only when the specimen has reached temperatures above 3680 K (when all the thoria has been melted). The anomaly is not present if the specimen does not reach the melting point of thoria (all experiments below 3640 K) and is partially present in the case of experiments with a maximum temperature in the range 3640–3680 K (probably on account of the incomplete melting of the thoria particles). Details of the peak temperatures of these cooling rate anomalies are also reported in Table II; the average value of the first peak is at 3660 K, with a standard deviation of 14 K, while the average value of the second peak is 3148 K, with a standard deviation of 9 K. However it should be noticed that the shape of the cooling rate anomalies is strongly dependent on the maximum temperature during heating and particularly if thoria was entirely melted.

4. DISCUSSION

The electrical resistivity data look physically sensible compared with tungsten, when it is realized that about 3% of the volume is now occupied by discrete particles of an "insulator," namely, thoria. It should be noted that, throughout the entire temperature range 1500–3680 K, the experimentally measured electrical resistivity of thoriated tungsten remains approximately 4% above the electrical resistivity of tungsten. Below 1500 K this difference percentage tends to increase [4], reaching about 5% at 1200 K (lowest temperature of measurements). No significant changes in electrical resistivity are seen in the range 3600–3680 K, with sharp increases after that temperature due to the onset of melting. From the detailed experimental results shown in Fig. 1, it should be clear that thoria does not significantly change its electrical resistivity on melting, remaining an insulator up to 3680 K.

The heat capacity curves (Fig. 3) also show a very large increase above 3680 K, which one may assume is due to melting or partial melting (i.e., a latent heat that may begin to appear in the impure material a few degrees below the melting point of pure unstrained tungsten).

As already mentioned, the peak at 3666 K is attributed to the melting of thoria. It should be remembered that in these measurements the thoria particles are constrained inside the tungsten matrix, therefore pressure effects may influence the result. Table III compares the result obtained in

Table III. Literature References on the Melting Point of Thoria: Original Values Are Reported, Not Corrected to ITS-90

Ref. No.	Year	Melting point (K)
17	1953	3573 ± 100
18	1969	3663
19	1972	3473 ± 40
20	1975	3643 ± 30
21	1980	3440
This work	1995	3666 ± 25

the present work with literature values (original data not corrected to ITS-90) on the melting point of thoria. The uncertainty of the present work was estimated by considering the uncertainty in the realized temperature scale (15 K) and an estimated uncertainty (20 K) for possible pressure effects. The reasonable agreement between the melting and freezing point of thoria in subsequent experiments provides strong evidence that there is no solubility of tungsten in the liquid thoria.

Also of interest are the second humps appearing on cooling between 3110 and 3180 K that are presented in detail in Fig. 5. These are likely to be associated with the oxygen Frenkel disorder, which has been studied in detail for other fluorite-structure compounds which are more accessible (temperaturewise) such as CaF_2, PbF_2, and $SrCl_2$. These compounds may be viewed as a simple cubic array of anions with alternate cube centers occupied by cations (Ca, Ba). They show a Schottky-type anomaly in heat capacity at a temperature about 85% of the melting point value (T_m) [22, 23], which is associated with thermal disorder in the anion lattice, that is, some anions (F, Cl) leave their lattice sites and sit near the cube-center interstitial sites. The dynamics of the defects and clustering behavior has proved complex. Studies of ThO_2 and UO_2 are important for nuclear reactor applications but more difficult because of the high melting points. Hiernaut et al. [24] have studied UO_2 from cooling curves of small samples initially laser heated to just below melting. They found anomalies in heat capacity (similar to other fluorides) at about 2700 K or 0.85 T_m. They observed that the anomaly was strongly dependent on stoichiometry and reducing/oxidizing atmosphere. Hutchings et al. [25, 26] studied single crystals of ThO_2 and UO_2 with neutrons to give direct evidence of thermally excited Frenkel disorder in the oxygen lattice akin to that in fluorides. Other investigators [27, 28] have also measured thermal properties of thoria and thoria–urania solid solutions and concluded that there is a solid–solid phase transition at 2950 K in thoria. The results of the present

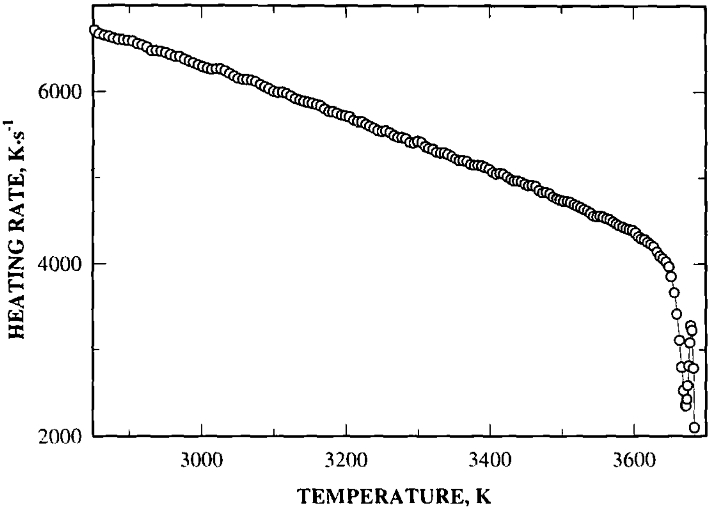

Fig. 6. Typical heating rate in the temperature range above 2800 K. The data refer to an experiment on S-3, performed with a data acquisition system acquiring one temperature every 100 μs. One datum of ten is plotted.

work indicate that the ratio of the averages of the heating rate anomaly and of the second peak observed on cooling is 0.86. With the fast heating rates used in the present work (4000–7000 K · s^{-1}), the Frenkel disorder is not observed during heating. Specific experiments performed with a data acquisition system capable of one measurement every 100 μs indicate a smooth behavior of the heating rate up to the melting of thoria. The heating rate above 2800 K in a typical experiment performed under these conditions is reported in Fig. 6. The shape of the humps appearing on cooling (Fig. 5) is strongly dependent on the maximum temperature reached during heating. Experiments that reached the melting point of thoriated tungsten exhibit a well reproducible and characteristic shape, experiments up to 3670–3680 K exhibit less pronounced humps and experiments that did not reach 3640 K do not present any cooling rate anomaly in the region around 3150 K.

5. CONCLUSIONS

This work presents experimental data on thoriated tungsten from 3600 K to the melting point. The results depend on the assumption that the melting point of tungsten taken from the literature [13] also applies to thoriated tungsten. Measurements performed with the heating rates (2000–5000 K · s^{-1}) and cooling rates (300–800 K · s^{-1}) used in this work indicate the melting point of thoria near 3666 K and a Frenkel disorder near 3148 K (observed only on cooling). The electrical resistivity results provide strong evidence that thoria remains an electrical insulator up to 3680 K (above the melting point).

The results of the present work prove that direct heating experiments on rods made of mixtures of tungsten and insulators may provide interesting experimental results in temperature ranges that are very difficult to reach with conventional techniques.

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REFERENCES

1. F. Righini, A. Rosso, and G. Ruffino, *High Temp. High Press.* **4**:597 (1972).
2. F. Righini, A. Rosso, and L. Coslovi, in *Proceedings of the Seventh Symposium on Thermophysical Properties*, A. Cezairliyan, ed. (ASME, New York, 1977), pp. 358–368
3. F. Righini and A. Rosso, *Measurement* **1**:79 (1983).
4. F. Righini, J. Spišiak, G. C. Bussolino, A. Rosso, and J. Haidar *Int. J. Thermophys.* **15**:1311 (1994).
5. L. Coslovi, F. Righini, and A. Rosso, *Alta Frequenza* **44**:592 (1975).
6. F. Righini, G. C. Bussolino, and A. Rosso, in *Temperature. Its Measurement and Control in Science and Industry, Vol. 6*, J. F. Schooley, ed., (American Institute of Physics, New York, 1992), pp. 763–768.
7. C. Horrigan, J. Haidar, and F. Righini, *Int. J. Thermophys.* **17**:1037 (1996).
8. J. C. DeVos, *Physica* **20**:690 (1954).
9. L. N. Latyev, V. Ya. Chekhovskoi, and E. N. Shestakov, *High Temp. High Press.* **4**:679 (1972).
10. A. P. Miiller and A. Cezairliyan, *Int. J. Thermophys.* **11**:619 (1990).
11. F. Righini, J. Spišiak, G. C. Bussolino, and A. Rosso, *High Temp. High Press.* **25**:193 (1993).
12. F. Righini, J. Spišiak, G. C. Bussolino, and A. Rosso, in *Proceedings Tempmeko '93* (Tech-Market, Prague, 1993), pp. 360–366.
13. A. Cezairliyan, *High Temp. Sci.* **4**:248 (1972).
14. F. Righini, G. C. Bussolino, A. Rosso, and J. Spišiak, *Int. J. Thermophys.* **14**:485 (1993).
15. H. Preston-Thomas, *Metrologia* **27**:3 (1990).
16. T. G. Kollie, D. L. McElroy, and C. R. Brooks, Oak Ridge National Laboratory Report ORNL-TM-2517 (1969).
17. W. A. Lamberston, M. H. Mueller, and F. H. Gunzel Jr., *J. Am. Ceram. Soc.* **36**:397 (1953).
18. R. Benz, *J. Nucl. Mat.* **29**:43 (1969).

19. F. Sibeude and C. Bonet, in *Colloques Internationaux CNRS No. 205* (CNRS, Paris, 1972), pp. 53-56.
20. M. H. Rand, in *I. Thermomechanical Properties in Thorium: Physico-Chemical Properties of its Compounds and Alloys*, Atomic Energy Review, Special Issue No. 5, O. Kubaschewski, ed. (IAEA, Vienna, 1975).
21. M. Bober, H. U. Karov, and K. Müller, *High Temp. High Press.* **12**:161 (1980).
22. W. Hayes (ed), *Crystals with the Fluorite Structure* (Oxford Press, Oxford, 1974).
23. W. Hayes, *J. Phys. Colloque* C6 **41**:C6 (1980).
24. J. Hiernaut, G. J. Hyland, and C. Ronchi, *Int. J. Thermophys.* **14**:259 (1993).
25. M. T. Hutchings, K. Clausen, W. Hayes, J. E. McDonald, R. Osborn, and P. Schnabel, *High Temp. Sci.* **20**:97 (1985).
26. M. T. Hutchings, *J. Chem Soc., Faraday Trans.* **83**:1083 (1987).
27. D. F. Fischer, J. K. Fink, and L. Leibowitz, *J. Nucl. Mater.* **102**:220 (1981).
28. J. Belle and R. M. Berman, in *Thermal Conductivity* 18, T. Ashworth and D. R. Smith, eds. (Plenum Press, New York, 1984), pp. 483–484. [See, also by the same authors, Report WARD-TM-1530 (1982).]