



**AUSTRALIAN ATOMIC ENERGY COMMISSION  
RESEARCH ESTABLISHMENT  
LUCAS HEIGHTS**

**LINEAR THERMAL EXPANSION OF THORIA, URANIA-THORIA,  
AND THEIR DISPERSIONS IN BERYLLIA IN THE RANGE  
20–1000°C TOGETHER WITH IMPROVED DATA FOR BERYLLIA**

by

**D. N. TURNER  
P. D. SMITH**

**August 1967**



AUSTRALIAN ATOMIC ENERGY COMMISSION  
RESEARCH ESTABLISHMENT  
LUCAS HEIGHTS

LINEAR THERMAL EXPANSION OF THORIA, URANIA-THORIA,  
AND THEIR DISPERSIONS IN BERYLLIA IN THE RANGE  
20-1000 °C TOGETHER WITH IMPROVED DATA FOR BERYLLIA

by

D. N. TURNER

P. D. SMITH

ABSTRACT

Differences in the thermal expansion properties of the dispersed phase and matrix of a beryllia based fuel can give rise to stresses in the material on cooling. In beryllia the strains can be very large. By means of a dilatometric method the linear thermal expansion properties of thoria, urania-thoria [(U,Th)O<sub>2</sub> with U:Th = 1:10] and dispersions of 20 vol. per cent of each in beryllia for the range 20-1000 °C have been measured. The results are given, together with some improved data for beryllia.

The data obtained for thoria are compared with published data and the thermal expansion of composite bodies is discussed. There is evidence that the particles of the dispersed phase are bonded to the matrix.



## CONTENTS

	Page
1. INTRODUCTION	1
2. SPECIMEN PREPARATION	1
2.1 Thoria	1
2.2 (U,Th)O <sub>2</sub>	1
2.3 Dispersions	1
3. METHOD	1
4. RESULTS	1
5. DISCUSSION	2
5.1 Thoria — Comparison with Published Data	2
5.2 Thermal Expansion of Composite Bodies	2
6. CONCLUSIONS	3
7. ACKNOWLEDGEMENTS	4
8. REFERENCES	4

Table 1 Specimens and Numbers of Measurements for Thermal Expansion Determinations

Table 2 Mean Coefficients of Linear Thermal Expansion

Table 3 Instantaneous Coefficients of Linear Thermal Expansion

Table 4 Mean Coefficients of Linear Thermal Expansion of Thoria Obtained from Published Data

Table 5 Impurity Contents of Specimens

APPENDIX Thermal Expansion of Beryllia

Figure 1 Mean Percentage Linear Thermal Expansion of BeO, ThO<sub>2</sub>, and BeO + 20 v/o ThO<sub>2</sub> v. Temperature

Figure 2 Mean Percentage Linear Thermal Expansion of BeO, (U,Th)O<sub>2</sub> and BeO + 20 v/o (U,Th)O<sub>2</sub> v. Temperature

Figure 3 Mean Coefficients of Linear Thermal Expansion of BeO, ThO<sub>2</sub>, and BeO + 20 v/o ThO<sub>2</sub> for Temperature Range 20–T °C v. Temperature "T"

Figure 4 Mean Coefficients of Linear Thermal Expansion of BeO, (U,Th)O<sub>2</sub>, and BeO + 20 v/o (U,Th)O<sub>2</sub> for Temperature Range 20–T °C v. Temperature "T"



## 1. INTRODUCTION

In ceramic fuels of the dispersion type, differences in the thermal expansion properties of the dispersed phase and the matrix are important because such differences cause strains to be introduced on cooling which give rise to stresses in the material. This is particularly important in a fuel based on a matrix of beryllia because with its high Young's modulus, even small strains give rise to substantial stresses.

The thermal expansion properties of thoria, urania-thoria [(U,Th)O<sub>2</sub> with a ratio of U:Th = 1:10], and dispersions of 20 vol. per cent of each of these in beryllia for the temperature range 20–1000 °C are given in this report. Of these materials, thoria is the only one for which thermal expansion data were found in the literature. The thermal expansion properties of beryllia fabricated at Lucas Heights have already been reported (Turner and Smith 1965); improved data incorporating a greater number of measurements are given in the Appendix.

## 2. SPECIMEN PREPARATION

2.1 Thoria: The powder was produced by calcining thorium oxalate for 12 hours at 900 °C in air. It was fabricated by isostatically pressing at 20 tons/in<sup>2</sup> followed by sintering for 2 hours at 1700 °C in dry nitrogen. The density was 94.5 per cent of theoretical. Cylindrical specimens 4 mm dia. x 40 mm long were finished to size by centreless grinding.

2.2 (U,Th)O<sub>2</sub>: This was prepared by co-precipitation from solution. The method was based on that described by Nowak and Wessling (1962); a brief outline follows: A solution of the mixed nitrates was formed with the uranium and thorium present in the ratio 1:10. This solution was added to an ammonia solution in such a way that excess ammonia was always present, and a precipitate of ammonium di-uranate and thorium hydroxide was formed. This was filtered, washed, and dried for 12 hours at 200 °C in air. It was then reduced in hydrogen for 2 hours at 700 °C. The mixed oxide powder so obtained was fabricated by isostatically pressing at 20 tons/in<sup>2</sup> followed by sintering for 2 hours at 1700 °C in dry nitrogen. The bulk density was 88 per cent of theoretical. The cylindrical specimens were finished to size by centreless grinding.

2.3 Dispersions: Sintered thoria and (U,Th)O<sub>2</sub> were crushed and screened to give particles of approximately 150–200 microns. These were each mixed with beryllia powder and the mixtures were isostatically pressed at 20 tons/in<sup>2</sup> and sintered for 1½ hours at 1500 °C in dry nitrogen.

## 3. METHOD

A Leitz dilatometer, model UBD, was used; a description of the method of operation of this instrument appears in Turner and Smith (1965). Only the direct method of measurement was used in this work.

## 4. RESULTS

The numbers of specimens, and of measurements on each specimen, are listed in Table 1. All measurements were made at least in duplicate.

The method of polynomial regression was used to obtain Equations 1 to 4 which define the percentage linear thermal expansion of each of the four materials as functions of temperature in degC for the temperature range 20–1000 °C, with 95 per cent confidence limits.

### Thoria

$$\text{Per cent Expansion} = 9.19 \times 10^{-4}(T-20) - 5.17 \times 10^{-8}(T-20)^2 + 1.15 \times 10^{-10}(T-20)^3 \pm 1.02 \times 10^{-2} \dots(1)$$

Plotted in Figure 1.

(U,Th)O<sub>2</sub>

$$\text{Per cent Expansion} = 9.99 \times 10^{-4} (T-20) - 2.45 \times 10^{-7} (T-20)^2 + 2.33 \times 10^{-10} (T-20)^3 \pm 1.25 \times 10^{-2} \dots(2)$$

Plotted in Figure 2.

20 vol. per cent ThO<sub>2</sub> in BeO

$$\text{Per cent Expansion} = 7.73 \times 10^{-4} (T-20) + 2.59 \times 10^{-8} (T-20)^2 + 1.39 \times 10^{-10} (T-20)^3 \pm 1.39 \times 10^{-2} \dots(3)$$

Plotted in Figure 1.

20 vol. per cent (U,Th)O<sub>2</sub> in BeO

$$\text{Per cent Expansion} = 7.31 \times 10^{-4} (T-20) + 1.72 \times 10^{-7} (T-20)^2 + 3.92 \times 10^{-11} (T-20)^3 \pm 0.76 \times 10^{-2} \dots(4)$$

Plotted in Figure 2.

The mean coefficients were obtained by dividing the above expressions by (T-20) and substituting the appropriate values of T; they are given for 100 °C intervals in Table 2 and plotted in Figures 3 and 4. The instantaneous coefficients were obtained by differentiating expressions for expansion in terms of T and substituting the appropriate values of T; they are given for 100 °C intervals in Table 3. The most recent thermal expansion data for beryllia obtained at Lucas Heights are given in the Appendix and are plotted in Figures 1 to 4.

## 5. DISCUSSION

### 5.1 Thoria — Comparison with Published Data

Published thermal expansion data for thoria were used to yield the values of mean coefficients listed in Table 4; the coefficient obtained in the present work is also included.

The data cover a range of values from 8.47 to 10.6 x 10<sup>-6</sup> degC<sup>-1</sup> although all but two values are within the much smaller range of 9.0 to 9.76 x 10<sup>-6</sup>. The value obtained in the present work is comparable with those obtained by three groups of workers, namely Baskin et al. (1960), Geller and Yavorsky (1945), and Lang and Knudsen (1956), who employed telemicroscope, dilatometer, and interferometer techniques respectively. Other values listed are all somewhat lower than these.

Differences in thermal expansion data can be due to experimental errors, to variations in material purity, and to crystal anisotropy. Anisotropy is not present in this case because the thoria crystal lattice is cubic; differences must therefore be due to one or both of the other two reasons. Impurity levels in the specimens used in the present work are given in Table 5. Relatively large amounts of impurities must be present to affect the thermal expansion, particularly as many of the impurities when present as oxides have thermal expansion properties close to those of thoria. The levels of impurities present are not considered to be high enough to affect the thermal expansion measurements significantly.

Sources of experimental error have been discussed elsewhere (Turner and Smith 1965); the good reproducibility obtained in the present work leads to confidence in the data for the thoria specimens used.

### 5.2 Thermal Expansion of Composite Bodies

The mean thermal expansion coefficient of a body made up of several components which have different thermal expansion and elastic properties and which are completely and intimately

joined together may be calculated by using an expression derived by Turner (1946). In Turner's analysis the datum temperature  $T_0$  is the lowest temperature at which all components are unstrained. On cooling below  $T_0$  (to  $T_1$ ) elastic strains arise in the components due to their physical dissimilarities and the lack of stress relaxation. For a body made up of two components which have equal values of Poisson's Ratio, Turner's expression is as follows:

$$\alpha_{M(T_0-T_1)} = \frac{E_1 V_1 \alpha_{1(T_0-T_1)} + E_2 V_2 \alpha_{2(T_0-T_1)}}{E_1 V_1 + E_2 V_2} \quad (5)$$

where  $\alpha_{M(T_0-T_1)}$  = Mean thermal expansion coefficient for the composite body for the temperature range  $T_0-T_1$

and  $\left. \begin{array}{l} \alpha_{1(T_0-T_1)} \\ \alpha_{2(T_0-T_1)} \end{array} \right\}$  = Mean thermal expansion coefficients of the components for the temperature range  $T_0-T_1$

$E_1$  and  $E_2$  = Young's Moduli of the components at temperature  $T_1$

$V_1$  and  $V_2$  = Volume proportions of the components.

This expression was applied to the dispersion of thoria in beryllia using the following values for the Young's Moduli and thermal expansion coefficients of these two materials:

BeO:  $E$  at  $20^\circ\text{C}$  =  $51.5 \times 10^6$  p.s.i. (Veevers and Rotsey 1965)  
 Mean  $\alpha_{(20-1000^\circ\text{C})}$  =  $9.28 \times 10^{-6}$  degC $^{-1}$  (Appendix)

ThO<sub>2</sub>:  $E$  at  $20^\circ\text{C}$  =  $34.9 \times 10^6$  p.s.i. (Watchman and Lam 1959)  
 Mean  $\alpha_{(20-1000^\circ\text{C})}$  =  $9.78 \times 10^{-6}$  degC $^{-1}$  (Table 2).

The datum temperature  $T_0$  was taken to be  $1000^\circ\text{C}$  because a significant increase in the creep rate of beryllia had been observed at this temperature (Kelly 1967). Equation 5 then gave the result that the mean coefficient for the dispersion for the temperature range  $20-1000^\circ\text{C}$  was  $9.36 \times 10^{-6}$  degC $^{-1}$ . This compares with the measured value of  $9.32 \times 10^{-6}$  degC $^{-1}$  (Table 2). This agreement indicates that the dispersed particles were bonded to the matrix because that condition is assumed for the theoretical analyses.

This conclusion is supported by the expansion curves in Figure 1 which show that the expansion of the dispersion was greater than that of beryllia right from room temperature. If the particles had not been bonded to the matrix, the expansion of the dispersion would have been the same as for beryllia from room temperature up to some temperature at which the particles made effective contact with the matrix.

For these materials, thermal expansion measurements alone do not provide a very sound basis for the above conclusion because of the difficulty of measuring the small differences in their thermal expansion properties. For example, the difference in the measured values of the mean thermal expansion coefficients of beryllia and of the dispersion of 20 vol. per cent thoria in beryllia for the temperature range  $20-1000^\circ\text{C}$  is only  $0.04 \times 10^{-6}$  degC $^{-1}$  (0.4 per cent). However, Veevers and Rotsey (1966), from measurements of Young's Modulus, also concluded that the particles were bonded to the matrix and the present work confirms that conclusion.

## 6. CONCLUSIONS

1. Expressions have been obtained for the percentage thermal expansions of the four materials, thoria, urania-thoria, and two dispersions of 20 vol. per cent of each of these in beryllia, in terms of temperature in degC for the temperature range  $20-1000^\circ\text{C}$ , with 95 per cent confidence limits.

2. The thermal expansion data for thoria obtained in this work compare favourably with other published data.

3. There is evidence that the particles of the dispersed phase are bonded to the matrix.

## 7. ACKNOWLEDGEMENTS

The authors are indebted to Mr. I. M. Binns for helpful discussions on the theoretical aspects of this work. The specimens were made by the Ceramics Group.

## 8. REFERENCES

- Baskin, Y., Harada, Y., and Handwerk, J.H. (1960). - J. Am. Ceram. Soc. 43 (9): 489.
- Brett, N.H. and Russell, L.E. (1960). - Plutonium 1960. Proc. 2nd Int. Conf. on Plutonium Metallurgy, 397.
- Duwez, P., Odell, F. and Taylor, J.L. (1947). - ATI23217, Jet Propulsion Lab., Calif. Inst. of Technology, Pasadena, Calif.
- Geller, R.F. and Yavorsky, P.J. (1945). - J. Res. Nat. Bur. Stand. 35: 87.
- Grain, C.F. and Campbell, W.J. (1962). - U.S. Bur. of Mines, BM-RI5982.
- Kelly, J.W. (1967). - AAEC/E176.
- Lang, S.M. and Knudsen, E.P. (1956). - J. Am. Ceram. Soc., 39: 415.
- Mauer, F.A. and Bolz, L.H. (1955). - WADC Tech. Rept. 55-473.
- Nowak, W.B. and Wessling, B.W. (1962). - USAEC NMI-1248, 36.
- Ohnysty, B. and Rose, F.K. (1964). - J. Am. Ceram. Soc. 47 (8): 398.
- Skinner, B.J. (1957). - Am. Mineral, 42: 39.
- Turner, D.N. and Smith, P.D. (1965). - AAEC/TM300.
- Turner, P.S. (1946). - J. Res. Nat. Bur. Stand. 37: 239.
- Veevers, K. and Rotsey, W.B. (1965). - AAEC/TM290.
- Veevers, K. and Rotsey, W.B. (1966). - J. Mats. Sci. 1(4): 346.
- Watchman, J.B. Jr. and Lam, D.G. Jr. (1959). - J. Am. Ceram. Soc. 42 (5): 254.
- Watchman, J.B., Scuderi, T.G., and Gleek, G.W. (1962). - J. Am. Ceram. Soc. 45: 319.
- Whittemore, O.J. Jr. and Ault, N.M. (1956). - J. Am. Ceram. Soc. 39: 443.

TABLE 1  
SPECIMENS AND NUMBERS OF MEASUREMENTS FOR  
THERMAL EXPANSION DETERMINATIONS

Material	No. of Specimens	No. of Measurements on Each Specimen
Thoria	2	2
(U,Th)O <sub>2</sub>	4	2
20 v/o ThO <sub>2</sub> in BeO	1	3
20 v/o (U,Th)O <sub>2</sub> in BeO	1	4

TABLE 2  
MEAN COEFFICIENTS OF LINEAR THERMAL EXPANSION

Temperature Range °C	Mean $\alpha$ ( $10^{-6}$ degC <sup>-1</sup> ) with 95% Confidence Limits			
	ThO <sub>2</sub>	(U,Th)O <sub>2</sub>	20 v/o ThO <sub>2</sub> in BeO	20 v/o (U,Th)O <sub>2</sub> in BeO
20-100	9.15 ± 1.28	9.81 ± 1.56	7.76 ± 1.74	7.45 ± 0.95
20-200	9.13 ± 0.57	9.62 ± 0.69	7.82 ± 0.77	7.63 ± 0.42
20-300	9.13 ± 0.36	9.48 ± 0.45	7.91 ± 0.50	7.82 ± 0.27
20-400	9.16 ± 0.27	9.39 ± 0.33	8.03 ± 0.37	8.02 ± 0.20
20-500	9.20 ± 0.21	9.35 ± 0.26	8.17 ± 0.29	8.22 ± 0.16
20-600	9.27 ± 0.18	9.35 ± 0.22	8.35 ± 0.24	8.43 ± 0.13
20-700	9.36 ± 0.15	9.40 ± 0.18	8.55 ± 0.20	8.66 ± 0.11
20-800	9.48 ± 0.13	9.49 ± 0.16	8.78 ± 0.18	8.88 ± 0.10
20-900	9.62 ± 0.12	9.63 ± 0.14	9.03 ± 0.16	9.12 ± 0.09
20-1000	9.78 ± 0.10	9.82 ± 0.13	9.32 ± 0.14	9.37 ± 0.08

TABLE 3  
INSTANTANEOUS COEFFICIENTS OF LINEAR THERMAL EXPANSION

Temperature °C	Instantaneous $\alpha$ ( $10^{-6}$ degC $^{-1}$ )			
	ThO <sub>2</sub>	(U,Th)O <sub>2</sub>	20 v/o ThO <sub>2</sub> in BeO	20 v/o (U,Th)O <sub>2</sub> in BeO
100	9.13	9.64	7.80	7.59
200	9.11	9.33	7.96	7.96
300	9.17	9.16	8.20	8.36
400	9.29	9.13	8.53	8.78
500	9.48	9.24	8.94	9.23
600	9.74	9.49	9.43	9.69
700	10.07	9.89	10.01	10.19
800	10.47	10.42	10.66	10.70
900	10.94	11.09	11.41	11.24
1000	11.47	11.90	12.22	11.80

TABLE 4  
MEAN COEFFICIENTS OF LINEAR THERMAL EXPANSION  
OF THORIA OBTAINED FROM PUBLISHED DATA

Authors	Method	Mean $\alpha$ ( $10^{-6}$ degC $^{-1}$ ) 20-1000 °C
Grain and Campbell (1962)	X-Ray Diffractometer	9.3
Mauer and Bolz (1955)	X-Ray Diffractometer	9.0
Skinner (1957)	X-Ray Camera	8.47
Baskin et al. (1960)	Telemicroscope	9.76
Whittemore and Ault (1956)	Telemicroscope	9.3
Ohnysty and Rose (1964)	Telemicroscope	9.45
Geller and Yavorsky (1945)	Dilatometer	9.6
Brett and Russell (1960)	Dilatometer	9.33
Duwez et al. (1947)	Dilatometer	10.6
Turner and Smith (1966)	Dilatometer	9.78
Lang and Knudsen (1956)	Interferometer	9.62
Watchman et al. (1962)	Interferometer	9.45

TABLE 5  
IMPURITY CONTENTS OF SPECIMENS

Material	Impurity (p.p.m.)									
	MgO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Na <sub>2</sub> O	MnO	PbO	Cr <sub>2</sub> O <sub>3</sub>	CuO	BeO
BeO	140	450	260	160	170					
ThO <sub>2</sub>	80	5	10	300		1	1	3	1	
(U,Th)O <sub>2</sub>	200	20	60	<20				<5	1	100

## APPENDIX

### THERMAL EXPANSION OF BERYLLIA

The data given below were obtained from seven specimens of Brush UOX beryllia fabricated by the method already described (Turner and Smith 1965); measurements were made in duplicate on four specimens to give a total of eleven sets of data. The method of polynomial regression gave the following equation which defines the percentage linear thermal expansion of beryllia as a function of temperature in degC for the temperature range 20–1000 °C, with 95 per cent confidence limits.

$$\text{Per cent Expansion} = 6.41 \times 10^{-4}(T-20) + 3.29 \times 10^{-7}(T-20)^2 - 3.64 \times 10^{-11}(T-20)^3 \pm 1.34 \times 10^{-2}$$

Plotted in Figures 1 and 2.

The mean and instantaneous coefficients of linear thermal expansion for temperatures in the range 20–1000 °C are given in the following Table. The mean coefficients are plotted in Figures 3 and 4.

### MEAN AND INSTANTANEOUS COEFFICIENTS OF LINEAR THERMAL EXPANSION OF BERYLLIA

Temperature T °C	Mean $\alpha$ , 20–T °C ( $10^{-6}$ degC $^{-1}$ )	Instantaneous $\alpha$ at T °C ( $10^{-6}$ degC $^{-1}$ )
100	6.67 ± 1.67*	6.93
200	6.99 ± 0.74	7.56
300	7.30 ± 0.48	8.16
400	7.60 ± 0.35	8.75
500	7.90 ± 0.28	9.31
600	8.19 ± 0.23	9.85
700	8.47 ± 0.20	10.37
800	8.75 ± 0.17	10.87
900	9.02 ± 0.15	11.35
1000	9.28 ± 0.14	11.80

\*95% Confidence Limits



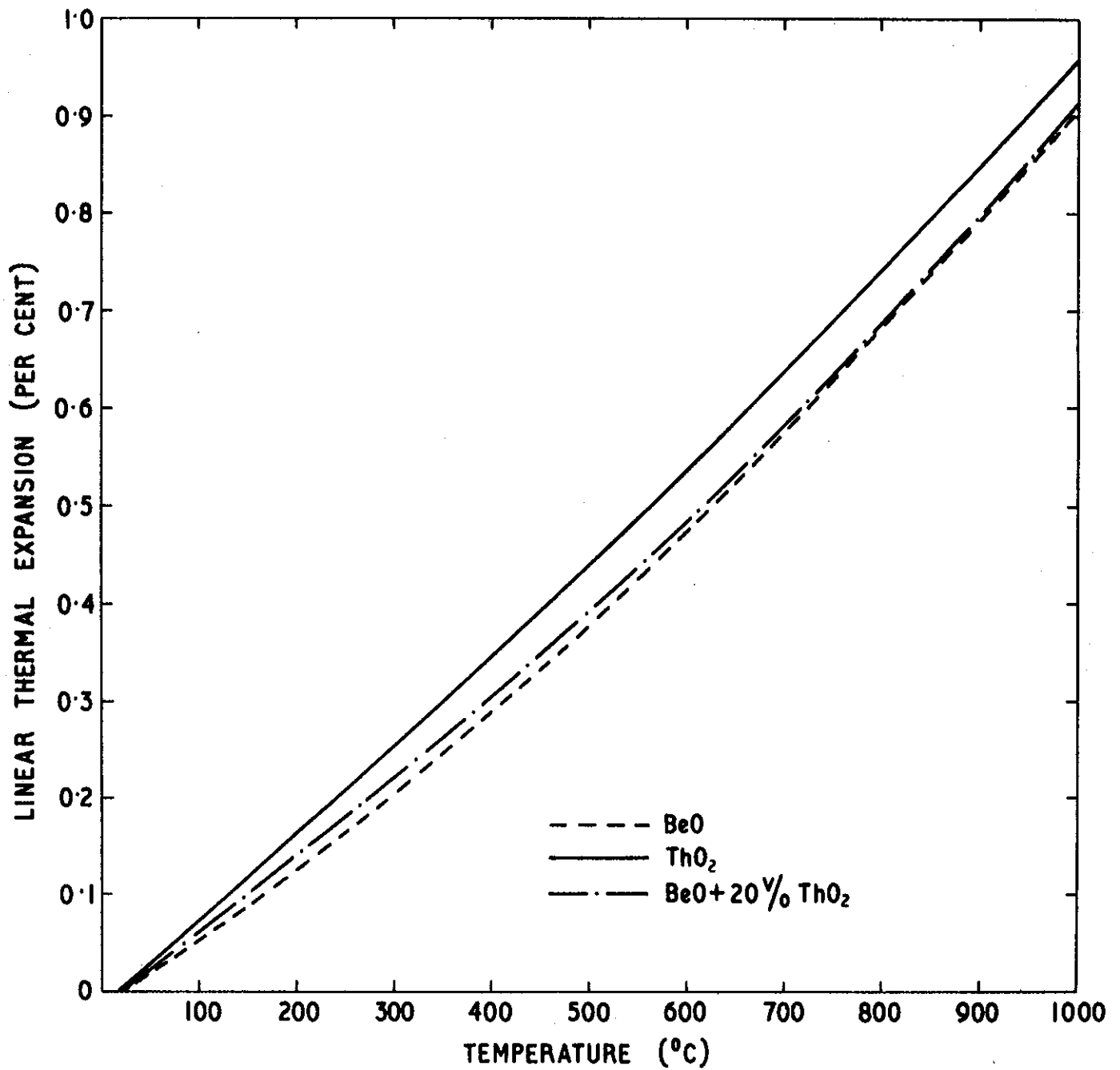


FIGURE 1. MEAN PERCENTAGE LINEAR THERMAL EXPANSION OF BeO, ThO<sub>2</sub> AND BeO + 20 VOL. PER CENT ThO<sub>2</sub> v. TEMPERATURE

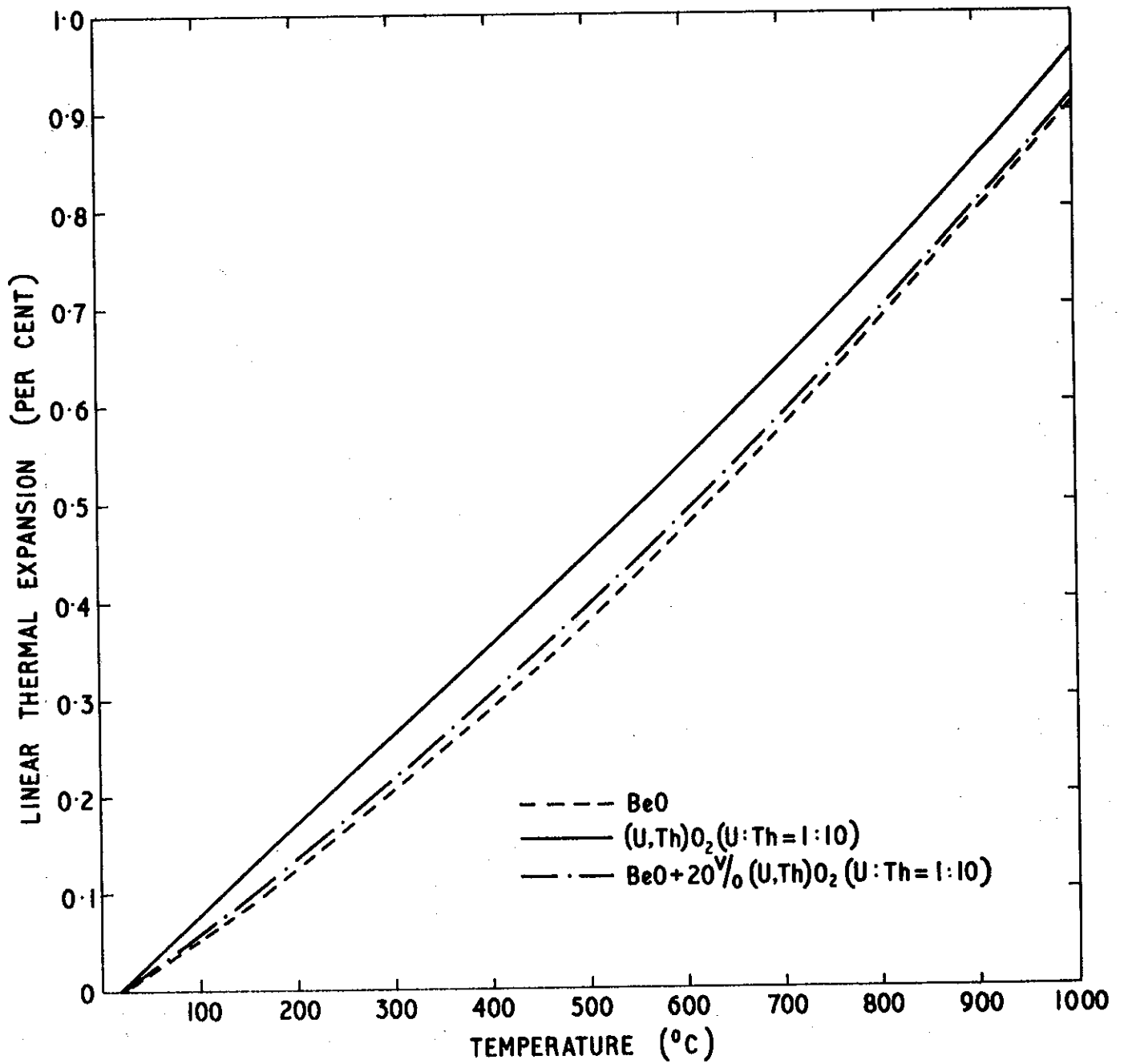


FIGURE 2. MEAN PERCENTAGE LINEAR THERMAL EXPANSION OF BeO, (U,Th)O<sub>2</sub> AND BeO + 20 VOL. PER CENT (U,Th)O<sub>2</sub> v. TEMPERATURE

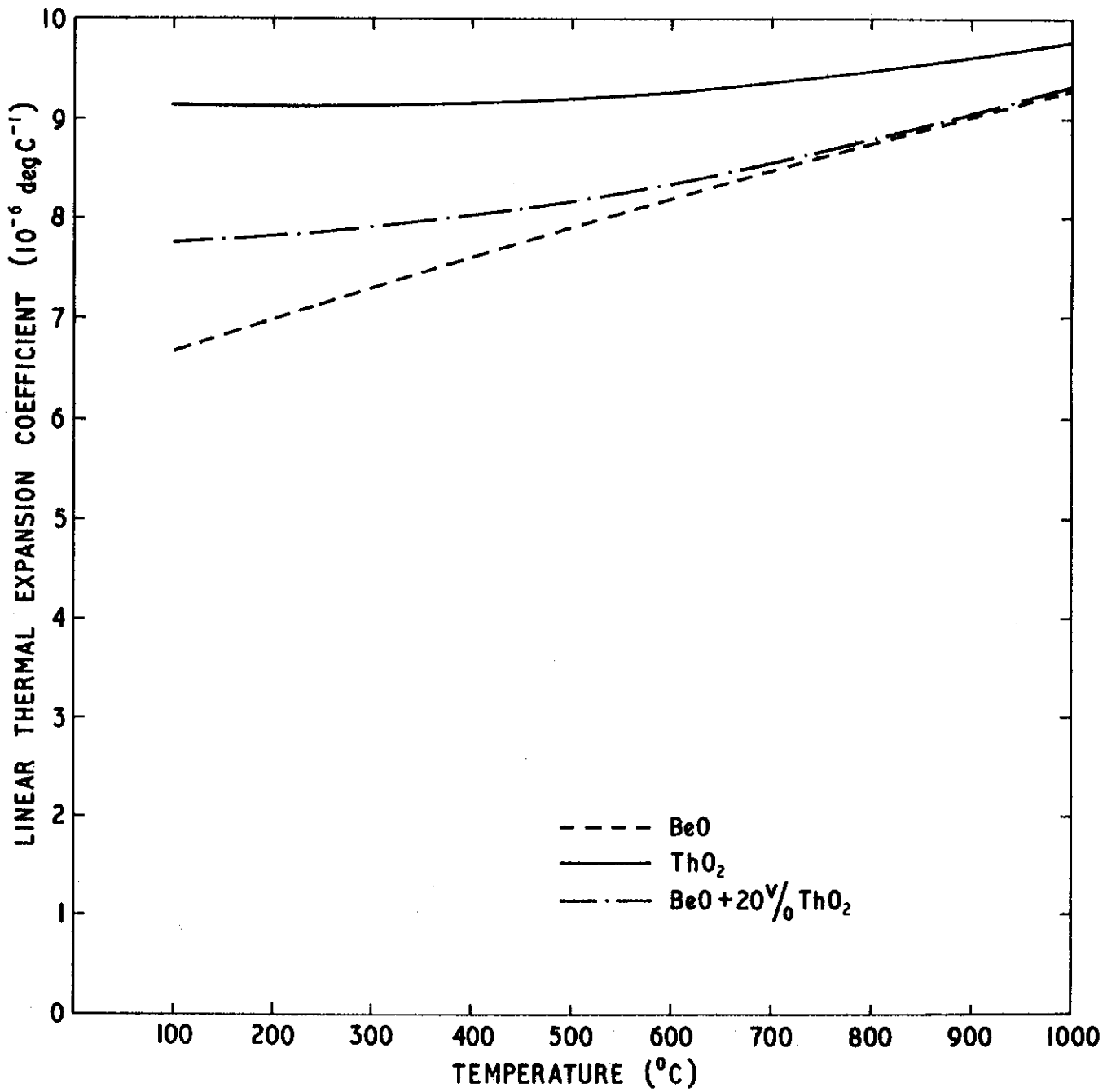


FIGURE 3. MEAN COEFFICIENTS OF LINEAR THERMAL EXPANSION OF BeO, ThO<sub>2</sub> AND BeO + 20 VOL. PER CENT ThO<sub>2</sub> FOR TEMPERATURE RANGE 20 - T°C v. TEMPERATURE 'T'

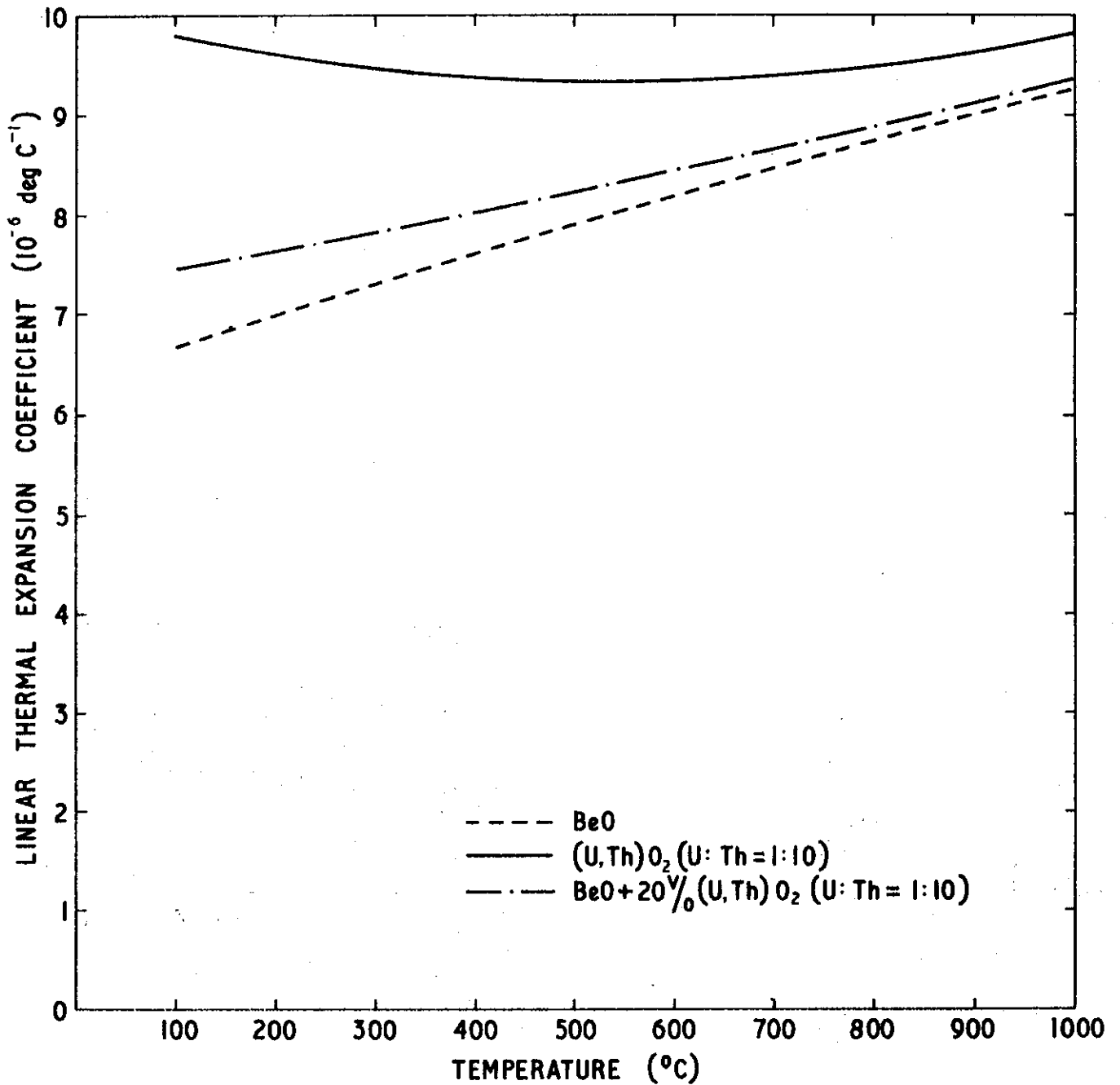


FIGURE 4. MEAN COEFFICIENTS OF LINEAR THERMAL EXPANSION OF BeO, (U,Th)O<sub>2</sub> AND BeO + 20 VOL. PER CENT (U,Th)O<sub>2</sub> FOR TEMPERATURE RANGE 20 - T°C v. TEMPERATURE 'T'