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THERMODYNAMIC PROPERTIES OF COMPOUNDS OF ALKALINE EARTH ELEMENTS WITH OTHER FISSION PRODUCTS

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ABSTRACT

The alkaline earth fission products barium and strontium can combine with other major fission product elements such as Mo, Ce and Zr in a mixed oxide fuel pin of a fast breeder reactor to form compounds such as molybdates, cerates and zirconates. In order to understand the condition of their formation in the fuel pin basic thermodynamic data on these compounds applicable to the relevant temperature range are required. In this work enthalpy increments of $BaMoO_4$, $BaCeO_3$ and $(Ba,Sr)ZrO_3$ were determined relative to room temperature using a high temperature differential calorimeter. The experimentally measured enthalpy data covered the temperature range of 985–1750 K. From these enthalpy values other thermodynamic functions such as heat capacities, entropies and free energy functions were generated using C^0_{p298} and S^0_{298} values of the compounds available in the literature. The free energies of formation of these compounds and the equilibrium barium partial pressures for the formation reactions have been computed in the temperature range of 500–2000 K and in the oxygen potential range of -376.56 kJ mol^{-1} to -502.08 kJ mol^{-1}.

INTRODUCTION

When reactor fuel is subjected to high burn-up, a number of fission products are generated in significant quantities. For example, when a mixed oxide fuel is burned in a fast breeder reactor to 10 at.% burn-up, molybdenum, zirconium, barium, strontium and rare earths are produced to the extent of 2.06, 2.02, 0.65 and 0.39 at.% respectively [1]. The chemical nature of these fission products depends on several factors such as the prevailing temperature, solubility of the fission products in the fuel matrix, oxygen potentials etc. Zirconates, molybdates and cerates of barium and strontium are compounds that can be formed in the fuel at high temperatures. In order to predict their formation under specific conditions that may occur at different locations in the fuel pin, we require their high temperature thermodynamic properties. Experimental data on these systems are, however, sparse.

We have reported earlier [2] studies on thermodynamic data of barium and strontium zirconates. In this paper, we describe the measurements on

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barium molybdate, barium cerate and the mixed zirconate of barium and strontium. $(Ba,Sr)ZrO_3$ is known to form a separate phase in irradiated fast reactor oxide fuels [3].

EXPERIMENTAL

Sample preparation

The molybdates and cerates of barium, namely $BaMoO_4$ and $BaCeO_3$, were prepared by heating pellets containing appropriate quantities of $BaCO_3$ with MoO_3 and CeO_2 respectively at 1373 K in air. The preparation of $(Ba,Sr)ZrO_3$ solid solution was carried out by heating a mixture containing the carbonates of barium and strontium with zirconia at 1373 K in air. The X-ray diffraction patterns of the compounds confirmed the formation of perovskite $BaCeO_3$ and $(Ba,Sr)ZrO_3$ and tetragonal $BaMoO_4$.

Calorimeter and method of measurement

In this study, a high temperature differential calorimeter (model HT-1500 of M/s. SETARAM, France) was used for the enthalpy increment measurements. The calorimeter and the details of the experimental measurements have been described elsewhere [2].

The sample, in the form of a pellet, is dropped into the sample crucible maintained at the selected temperature and the heat flow between the sample and the reference crucible is recorded. This signal is compared with that of a standard material which is measured immediately before and after the sample.

RESULTS

Data treatment

The ratio of the heat flows corresponding to sample and standard (α-Al_2O_3) was obtained by making measurements in the sequence standard–sample–standard. Using these ratios and the known enthalpy increment data of the standard, the $H_T^0 - H_{298}^0$ values of the sample at the experimental temperatures were computed.

The $H_T^0 - H_{298}^0$ values thus obtained at different temperatures were fitted by the weighted least-squares method to obtain linear expressions in temperature. The fit was subjected to the following constraints: (1) $H_T^0 - H_{298}^0 = 0$ at 298 K, (2) $C_p^0 = C_{p298}^0$ (literature value) at 298 K. Standard error for this fit is computed using the expression:

$$\text{Standard error} = \left(\frac{\sum (\text{residual})^2}{\text{No. of observations} - \text{No. of coefficients}} \right)^{1/2}$$

$BaMoO_4$

The $H_T^0 - H_{298}^0$ values for $BaMoO_4$ were measured in the temperature range 986–1732 K. These were fitted to the following expression:

$$H_T^0 - H_{298}^0 = 129.3933T + 16.8144 \times 10^{-3}T^2 + 14.662 \times 10^5 T^{-1}$$
$$- 44990.96 \text{ J mol}^{-1} (298\text{–}1732 \text{ K})$$

The standard error of this fit was 3.1%.

Other thermodynamic functions were derived from the above expression using C_{p298}^0 and S_{298}^0 values taken from the literature [4,5]. Table 1 shows all these functions listed as a function of temperature.

$BaCeO_3$

The measurements on this system were carried out between 1065 and 1725 K. The data were fitted to obtain the following expression:

$$H_T^0 - H_{298}^0 = 120.8973T + 6.5056 \times 10^{-3}T^2 + 12.1336 \times 10^5 T^{-1}$$
$$- 40693.49 \text{ J mol}^{-1} (298\text{–}1725 \text{ K})$$

TABLE 1

Thermodynamic functions of $BaMoO_4$

Temperature (K)	$H_T^0 - H_{298}^0$ measured (J mol^{-1})	$H_T^0 - H_{298}^0$ from fit (J mol^{-1})	Temperature (K)	$H_T^0 - H_{298}^0$ (J mol^{-1})	C_p^0 (J K^{-1} mol^{-1})	S_T^0 (J K^{-1} mol^{-1})	$-(G_T^0 - H_{298}^0)/T$ (J K^{-1} mol^{-1})
986	97141	100425	298	0	122.93	144.35	144.35
1033	105561	108034	300	228	123.19	145.11	144.35
1079	116984	115559	400	13122	133.68	182.13	149.33
1124	118098	122995	500	26842	140.34	212.72	159.03
1224	135504	139775	600	41142	145.50	238.78	170.21
1256	143011	145220	700	55918	149.94	261.55	181.67
1277	146463	148812	800	71118	154.00	281.83	192.94
1304	148942	153454	900	86712	157.85	300.20	203.85
1346	156848	160725	1000	102683	161.56	317.02	214.34
1388	161763	168057	1100	119020	165.17	332.59	224.39
1427	175463	174920	1200	135339	168.73	347.12	234.02
1454	179210	179703	1300	152764	172.24	360.76	243.25
1495	190374	187013	1400	170163	175.72	373.65	252.11
1536	193023	194382	1500	187909	179.12	385.89	260.62
1591	211264	204357	1600	206000	182.63	397.57	268.82
1633	221145	212045	1700	224434	186.05	408.74	276.73
1669	233338	218683	1800	243210	189.47	419.48	284.36
1732	233903	230405					

TABLE 2

Thermodynamic functions of $BaCeO_3$

Temperature (K)	$H_T^0 - H_{298}^0$ measured (J mol^{-1})	$H_T^0 - H_{298}^0$ from fit (J mol^{-1})	Temperature (K)	$H_T^0 - H_{298}^0$ (J mol^{-1})	C_p^0 (J K^{-1} mol^{-1})	S_T^0 (J K^{-1} mol^{-1})	$-(G_T^0 - H_{298}^0)/T$ (J K^{-1} mol^{-1})
1063	94531	96313	298	0	111.13	131.80	131.80
1108	104989	102343	300	206	111.32	132.48	131.80
1156	113136	108807	400	11740	118.52	165.62	136.20
1201	116266	114898	500	23808	122.55	192.53	144.91
1242	120906	120473	600	36209	125.33	215.13	154.78
1265	124587	123611	700	48856	127.53	234.62	164.83
1291	127886	127168	800	61705	129.41	251.78	174.64
1334	134037	133070	900	74732	131.11	267.12	184.08
1381	139486	139552	1000	87923	132.70	281.01	193.09
1423	143574	145370	1100	101269	134.21	293.73	201.67
1460	150243	150575	1200	114763	135.67	305.47	209.84
1507	154401	157679	1300	128401	137.09	316.39	217.62
1547	158056	162688	1400	142181	138.49	326.60	225.64
1600	164003	170155	1500	156099	139.88	336.20	232.14
1644	171986	176383	1600	170155	141.24	345.28	238.93
1685	178794	182210	1700	184347	142.59	353.88	245.44
1725	186286	187916	1800	198674	143.94	362.07	251.69

The standard error for this fit was found to be 2.6%. The measured values of $H_T^0 - H_{298}^0$ along with the fitted values and the derived thermodynamic properties C_{pT}^0, S_T^0 and $-(G_T^0 - H_{298}^0)/T$ are given in Table 2 as functions of temperature.

As there are no reported values of C_{p298}^0 or S_{298}^0 for $BaCeO_3$, estimates were made by adding the corresponding values [6] of the component oxides.

(Ba,Sr)ZrO₃

Measurement on this solid solution covered the temperature range of 1033–1743 K. The smoothed enthalpy values are given by the expression:

$$H_T^0 - H_{298}^0 = 116.26859T + 6.6138 \times 10^{-3}T^2 + 15.7009 \times 10^5 T^{-1}$$
$$-40519.49 \text{ J mol}^{-1} (298\text{–}1743 \text{ K}).$$

The standard error of this fit is computed to be 1.1%. For this compound too, no C_{p298}^0 or S_{298}^0 data are available. $(Ba,Sr)ZrO_3$ may be considered as an ideal solid solution of $BaZrO_3$ and $SrZrO_3$ for which C_{p298}^0 and S_{298}^0 data are reported from low temperature studies [7]. Therefore, C_{p298}^0 and S_{298}^0 for $(Ba,Sr)ZrO_3$ were taken as the average of those values reported for $BaZrO_3$ and $SrZrO_3$. Table 3 gives thermodynamic functions of this compound

TABLE 3

Thermodynamic functions of $(Ba,Sr)ZrO_3$

Temperature (K)	$H_T^0 - H_{298}^0$ measured (J mol^{-1})	$H_T^0 - H_{298}^0$ from fit (J mol^{-1})	Temperature (K)	$H_T^0 - H_{298}^0$ (J mol^{-1})	C_p^0 (J K^{-1} mol^{-1})	S_T^0 (J K^{-1} mol^{-1})	$-(G_T^0 - H_{298}^0)/T$ (J K^{-1} mol^{-1})
1034	89419	88292	298	0	102.35	119.87	119.87
1078	96569	93960	300	190	102.79	120.51	119.87
1125	100352	100049	400	10971	111.75	151.46	124.03
1170	103735	105910	500	22408	116.60	176.96	132.15
1214	112216	111671	600	34239	119.84	198.52	141.46
1259	117883	117593	700	46352	122.32	217.19	150.98
1302	124151	123280	800	58691	124.40	233.66	160.30
1345	130170	128994	900	71224	126.24	248.43	169.28
1389	135328	134868	1000	83933	127.93	261.81	177.88
1432	138811	140636	1100	96806	129.52	274.08	186.08
1473	144547	146160	1200	109835	131.05	285.42	193.89
1518	150287	152251	1300	123015	132.54	295.96	201.34
1570	158825	159325	1400	136341	133.98	305.84	208.46
1609	165380	164655	1500	149811	135.41	315.13	215.26
1649	171038	170144	1600	163423	136.82	323.92	221.78
1686	176380	175241	1700	177175	138.21	332.26	228.03
1743	183229	183131	1800	191065	139.59	340.19	234.04

derived from the measured enthalpy increments and the estimated values of C_{p298}^0 and S_{298}^0.

DISCUSSION

Heat capacity

Prior to this study the only thermodynamic data available on $BaMoO_4$ was that reported by Barin and Knacke [6]. They quoted Kubaschewski [8] as their source. It appears from Kubaschewski and Alcock [5], that these values could have been derived from the e.m.f. cell measurements of Rezukhina and Zharkova [4]. The enthalpy values reported in this work agree within ±2% with those given by Barin and Knacke. Our C_p values are slightly higher because the C_{p298}^0 value used (122.93 J K^{-1} mol^{-1}) [4] is higher than the one used by Barin and Knacke (114.64 J K^{-1} mol^{-1}).

Figure 1 shows the heat capacity as a function of temperature, for $BaMoO_4$, $BaCeO_3$ and $(Ba,Sr)ZrO_3$ solid solution. The high temperature data thus obtained could not be extrapolated to the lower temperatures as no measurements have been reported for these compounds at low temperatures. In fact there is no information in the literature on the heat capacities of these compounds at any temperature. It is clear from Fig. 1 that in the

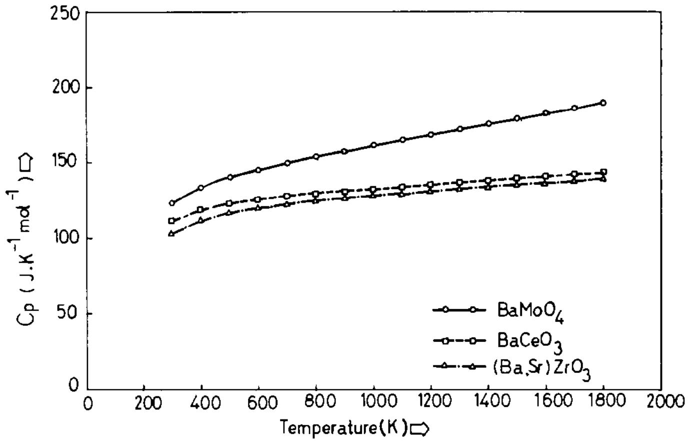

Fig. 1. Heat capacities of barium compounds.

entire temperature range the C_p of $BaMoO_4$ is higher than that of $BaCeO_3$ which is slightly higher than that of $(Ba,Sr)ZrO_3$.

Free energies of formation—ΔG_T^0

Using the free energy functions of $BaMoO_4$, $BaCeO_3$ and $(Ba,Sr)ZrO_3$ from the present study and the free energy functions of BaO(s), MoO_3(s), CeO_2(s), $BaZrO_3$(s) and $SrZrO_3$(s) from the literature [2,6,9], the change in free energy functions $\Delta(G_T^0 - H_{298}^0)/T$ were calculated for the following reactions.

$$BaO(s) + MoO_3(s) \rightleftharpoons BaMoO_4(s) \tag{1}$$

$$BaO(s) + CeO_2(s) \rightleftharpoons BaCeO_3(s) \tag{2}$$

$$1/2BaZrO_3(s) + 1/2SrZrO_3(s) \rightleftharpoons (Ba,Sr)ZrO_3(s) \tag{3}$$

Then substituting ΔH_{298}^0 values from the literature [8,10–12] the ΔG_T^0 values have been calculated. Table 4 shows the ΔG_T^0 values at 1000 K.

TABLE 4

Free energies of formation of $BaMoO_4$, $BaCeO_3$ and $(Ba,Sr)ZrO_3$ at 1000 K

No.	Reaction	ΔG_T^0 kJ mol^{-1}
1.	$BaO(s) + MoO_3(s) \rightleftharpoons BaMoO_4(s)$	−245.446
2.	$BaO(s) + CeO_2(s) \rightleftharpoons BaCeO_3(s)$	−49.308
3.	$1/2BaZrO_3(s) + 1/2SrZrO_3(s) \rightleftharpoons (Ba,Sr)ZrO_3(s)$	−1771.907

TABLE 5

Equilibrium partial pressure of barium at $T = 1000$ K

No.	Reaction	Equilibrium partial pressure of Ba (atm) at $\Delta\bar{G}_{O_2}$ of				O'Hare et al. [12] -418.4 (kJ mol^{-1})
	-376.56 (kJ mol^{-1})	-418.4 (kJ mol^{-1})	-460.24 (kJ mol^{-1})	-502.08 (kJ mol^{-1})		
1.	$Ba(g) + Zr(s) + 3/2O_2(g) \rightleftharpoons BaZrO_3(s)$	2.332×10^{-53}	4.560×10^{-50}	8.620×10^{-47}	1.640×10^{-43}	1.48×10^{-49}
2.	$Ba(g) + ZrO_2(s) + 1/2O_2(g) \rightleftharpoons BaZrO_3(s)$	1.816×10^{-25}	1.57×10^{-24}	2.78×10^{-23}	3.45×10^{-22}	4.836×10^{-24}
3.	$Ba(g) + Mo(s) + 2O_2(g) \rightleftharpoons BaMoO_4(s)$	3.779×10^{-28}	8.89×10^{-24}	2.092×10^{-19}	4.923×10^{-15}	4.93×10^{-23}
4.	$Ba(g) + MoO_3(s) + 1/2O_2(g) \rightleftharpoons BaMoO_4(s)$	6.565×10^{-32}	8.131×10^{-32}	1.007×10^{-29}	1.247×10^{-28}	–
5.	$Ba(g) + MoO_2(s) + O_2(g) \rightleftharpoons BaMoO_4(s)$	2.554×10^{-26}	3.917×10^{-24}	6.009×10^{-22}	9.217×10^{-20}	–
6.	$Ba(g) + Ce(s) + 3/2O_2(g) \rightleftharpoons BaCeO_3(s)$	2.192×10^{-48}	4.163×10^{-45}	7.909×10^{-42}	1.503×10^{-38}	–
7.	$Ba(g) + CeO_2(s) + 1/2O_2(g) \rightleftharpoons BaCeO_3(s)$	6.867×10^{-22}	8.505×10^{-21}	1.053×10^{-19}	1.305×10^{-18}	–
8.	$1/2Ba(g) + 1/2SrO(s) + ZrO_2(s) \rightleftharpoons (Ba_{0.5}Sr_{0.5})ZrO_3(s)$	2.603×10^{-54}	4.882×10^{-54}	9.159×10^{-54}	1.718×10^{-53}	–

Equilibrium barium pressures

Equilibrium barium pressures were calculated for the following reactions in the temperature range 500–2000 K and in the oxygen potential range -376.56 to -502.08 kJ mol^{-1}

$BaZrO_3$: $Ba(g) + Zr(s) + 3/2O_2(g) \rightleftharpoons BaZrO_3(s)$ (4)

$Ba(g) + ZrO_2(s) + 1/2O_2(g) \rightleftharpoons BaZrO_3(s)$ (5)

$BaMoO_4$: $Ba(g) + Mo(s) + 2O_2(g) \rightleftharpoons BaMoO_4(s)$ (6)

$Ba(g) + MoO_3(s) + 1/2O_2(g) \rightleftharpoons BaMoO_4(s)$ (7)

$Ba(g) + MoO_2(s) + O_2(g) \rightleftharpoons BaMoO_4(s)$ (8)

$BaCeO_3$: $Ba(g) + Ce(s) + 3/2O_2(g) \rightleftharpoons BaCeO_3(s)$ (9)

$Ba(g) + CeO_2(s) + 1/2O_2(g) \rightleftharpoons BaCeO_3(s)$ (10)

$(Ba,Sr)ZrO_3$: $1/2Ba(g) + 1/2SrO(s) + ZrO_2(s) + 1/4O_2(g)$
$\rightleftharpoons (Ba_{0.5}Sr_{0.5})ZrO_3(s)$ (11)

O'Hare et al. [13] computed the equilibrium barium partial pressures at 1000 K and at an oxygen potential of -418.4 kJ mol^{-1} for the reactions (4), (5) and (6). We have calculated the barium partial pressures using the change in free energy functions $\Delta(G_T^0 - H_{298}^0)/T$ computed from the present data and ΔH_{298}^0 from the literature [8,10–13]. For calculation of $\Delta(G_T^0 - H_{298}^0)/T$ the free energy functions of $BaMoO_4$, $BaCeO_3$ and $(Ba,Sr)ZrO_3$ from the present data and the free energy functions of Ba(g), Zr(s), $ZrO_2(s)$, Mo(s), $MoO_3(s)$, Ce(s), $CeO_2(s)$, SrO(s) and $O_2(g)$ from the literature [6,9,14] were used.

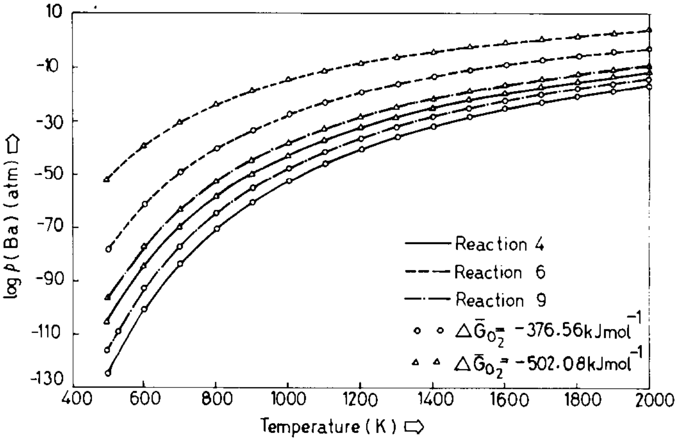

Fig. 2. Equilibrium barium partial pressures of $BaZrO_3$, $BaMoO_4$ and $BaCeO_3$ formed from their elements.

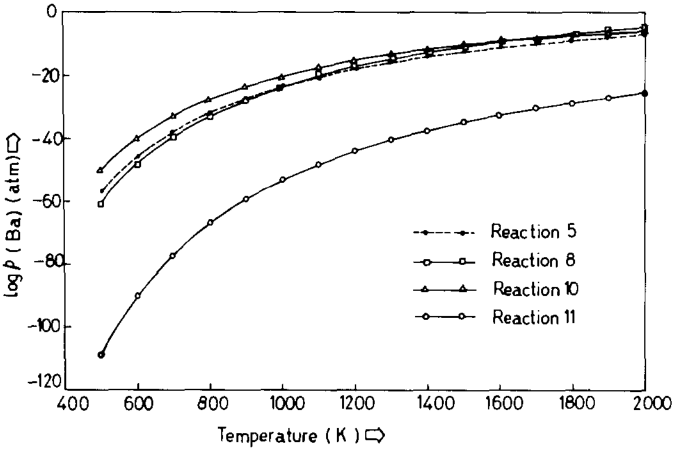

Fig. 3. Equilibrium barium partial pressures of $BaZrO_3$, $BaMoO_4$, $BaCeO_3$ and $(Ba,Sr)ZrO_3$ formed from oxides at $\Delta\overline{G}_{O_2} = -418.4$ kJ mol^{-1}.

The barium partial pressure values thus calculated at 1000 K are shown in Table 5. The present values at an oxygen potential of -418.4 kJ mol^{-1} are marginally lower than the values of O'Hare et al. [12] for reactions (4), (5) and (6). This is because O'Hare et al. have computed the barium pressures assuming that ΔH_T^0 and ΔS_T^0 values for the reactions (4), (5), (6) do not vary with temperature above 298 K.

Figure 2 shows the variation of barium pressures as a function of temperature and oxygen potential for reactions (4), (6) and (9). Figures 3 and 4 show the variation of barium pressures as a function of temperature

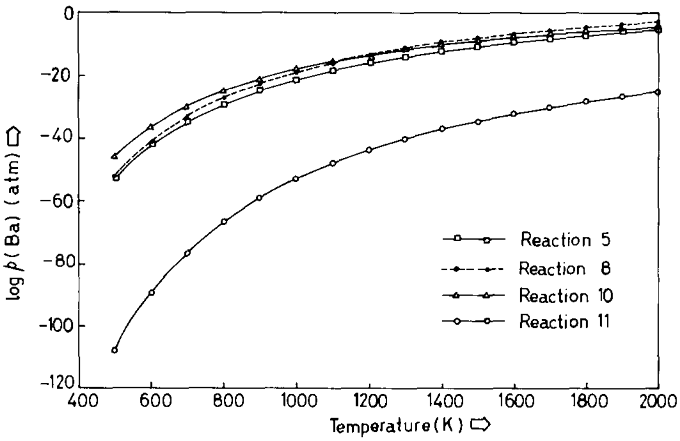

Fig. 4. Equilibrium barium partial pressures of $BaZrO_3$, $BaMoO_4$, $BaCeO_3$ and $(Ba,Sr)ZrO_3$ formed from oxides at $\Delta\overline{G}_{O_2} = -502.08$ kJ mol^{-1}.

and oxygen potential for reactions (5), (8), (10) and (11) at oxygen potentials -418.4 kJ mol^{-1} and -502.08 kJ mol^{-1} respectively.

It is clear from these figures that equilibrium barium pressures are lower when the reaction equilibria involve the metal phase. For equilibria involving the oxide phases of zirconium and molybdenum, the partial pressure of barium is lowest in the case where a mixed zirconate is formed.

CONCLUSIONS

$BaMoO_4$, $BaCeO_3$ and $(Ba,Sr)ZrO_3$ are the barium compounds likely to be formed in an irradiated fast reactor oxide fuel as a result of interaction between barium and the fission products, Mo, Ce, Sr and Zr. They form a part of what is known as a separate "grey phase".

So far no experimental heat capacity data has been published for these compounds. This work provides the only experimental data for the thermodynamic functions of these compounds in the temperature range 1000–1700 K. Under the conditions of oxygen potential and temperature prevailing at a given point in the fuel, the barium pressure depends on the fission product phase (such as Mo, MoO_2, Zr, ZrO_2 etc.) with which the ternary oxide is in equilibrium. For example, if Ba(g) is in equilibrium with ZrO_2 and SrO, the formation of $(Ba,Sr)ZrO_3$ will be favoured. In fact, it would appear that formation of any of the compounds mentioned is thermodynamically possible and could be determined by the physical proximity of the reactants (to one another) and the chemical state of Zr and Mo.

It must be remembered, however, that conditions vary from point to point in the fuel pin. A detailed evaluation of the alkaline earth compounds calls for an understanding of the chemical state of Zr, Mo and Ce in the fuel at different locations. A model taking all these factors into account is being attempted in our laboratory.

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REFERENCES

1 J.R. Findlay, Behaviour and Chemical State of Irradiated Ceramic Fuels, IAEA-PL-463/2 (1974).
2 K. Nagarajan, R. Saha, R. Babu and C.K. Mathews, Thermochim. Acta, 90 (1985) 297.

3 M. Koizumi, M. Satoh and K. Noro, J. Nucl. Mater., 51 (1974) 90.
4 T.N. Rezukhina and L.A. Zharkova, Zhur. Fiz. Khim., 32 (1958) 2233.
5 O. Kubaschewski and C.B. Alcock, Metallurgical Thermochemistry, Pergamon, London, 1979.
6 I. Barin and O. Knacke, Thermochemical Properties of Inorganic Substances, Springer-Verlag, Berlin, 1973.
7 E.G. King and W.W. Weller, US Bur. Mines. Rep. Invest., 5571 (1960) 3.
8 O. Kubaschewski, Thermodynamic Data of Binary Oxides, DCS Rep. 71 NPL, London.
9 D.R. Stull and H. Prophet, JANAF Thermochemical Tables NSRDS-NBS-37, US Department of Commerce, Washington, DC, 1970.
10 P.A.G. O'Hare, J. Chem. Thermodyn., 6 (1974) 425.
11 S. Aronson, J. Nucl. Mater., 107 (1982) 343.
12 A.S. L'Vova and N.N. Feodosev, Russ. J. Phys. Chem., 38 (1964) 14.
13 P.A.G. O'Hare, J. Boerio and H.R. Hoekstra, J. Chem. Thermodyn., 8 (1976) 845.
14 R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley and D.D. Wagman, Selected Values of Thermodynamic Properties of the Elements, American Society for Metals, OH, 1973.