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Note

Thermodynamic data for some complex oxides used in electrolamp production

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INTRODUCTION

The mixed oxides Ba_2CaWO_6, $Ba_3Y_2WO_9$ and $Ba_3Y_2MoO_9$ are used in the electrolamp industry as emitters for gas-discharge light sources of high vapour pressures [1, 2]. $MgZrO_3$ is used as a high-temperature addition to emitters for high-pressure fluoroscent lamps [3].

The present paper reports research on the specific heat capacities and thermodynamic quantities of these compounds.

EXPERIMENTAL

The Ba_2CaWO_6, $Ba_3Y_2WO_9$ and $Ba_3Y_2MoO_9$ were synthesized from high-purity $BaCO_3$, $CaCO_3$, Y_2O_3, WO_3 and MoO_3 (not less than 99.99%) in corundum crucibles and air environment. $MgZrO_3$ was synthesized tribochemically by a method that we have devised.

The determination of the metal oxides in these tungsten, molybdenum and zirconium compounds was performed by complexometric titration with eriochrome black T indicator [4]; ZrO_2 was determined gravimetrically [5]. The metal oxide contents corresponded to the stoichiometry of the compounds. They were identified X-ray diffractometry performed on a TURM 61 M apparatus with Cu Kα radiation and a Ni filter for β radiation. The relative intensity of the reflections and the distances between the planes of $BaCaWO_6$ and $Ba_3Y_2WO_9$ correspond to the published X-ray diffraction patterns [2]. In the X-ray patterns of the compounds $Ba_3Y_2MoO_9$ and $MgZrO_3$, the lines corresponding to the initial carbonates

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TABLE 1

Experimental heat capacity values of Ba_2CaWO_6 in J mol^{-1} K^{-1}

T/K	C_p	T/K	C_p
400	238.32	500	256.73
420	245.02	520	260.45
440	244.51	540	258.20
460	250.24	560	273.13
480	246.52	580	267.40

and oxides were no longer apparent, which indicates that the prepared compounds are definite phases.

The molar heat capacities were determined using a Setaram differential scanning calorimeter. The samples were precisely ground and sieved (mesh 0.25 mm^2) and were placed in capsules which were inert towards the complex oxides.

Tables 1–4 list the molar heat capacities. The coefficients in the equation $C_p = a + bT + cT^{-2}$ are presented in Table 5, together with the standard entropy $S_{298.15}$ determined by the method of Kelly given in ref. 6. The temperature relations of the thermodynamic quantities (molar heat capacity C_p', entropy S, enthalpy $H_T - H_0$ and Gibb's function Φ'') are presented in Tables 6–9.

TABLE 2

Experimental heat capacity values of $Ba_3Y_2MoO_9$ in J mol^{-1} K^{-1}

T/K	C_p	T/K	C_p
400	379.41	500	402.67
420	374.89	520	404.38
440	374.22	540	401.25
460	381.50	560	405.76
480	400.91	580	399.87

TABLE 3

Experimental heat capacity values of $Ba_3Y_2WO_9$ in J mol^{-1} K^{-1}

T/K	C_p	T/K	C_p
400	449.57	480	643.80
420	498.31	520	636.52
440	567.39	550	626.14
460	578.15		

TABLE 4

Experimental heat capacity values of $MgZrO_3$ in J mol^{-1} K^{-1}

T/K	C_p	T/K	C_p
400	116.20	500	125.65
420	116.32	520	128.30
440	120.30	540	130.50
460	122.84	560	132.00
480	123.64	580	134.31

TABLE 5

Standard entropy and temperature dependence of the heat capacities of Ba_2CaWO_6, $Ba_3Y_2MoO_9$, $Ba_3Y_2WO_9$ and $MgZrO_3$

Compound	S_{298}/(J mol^{-1} K^{-1})	$C_p = a + bT + cT^{-2}$ in J mol^{-1} K^{-1}			$10^2 \frac{\delta C_p}{C_p}$
		a	b	c	
Ba_2CaWO_6	256.0	1.179×10^2	0.243	3.953×10^6	±1.40
$Ba_3Y_2MoO_9$	387.2	4.977×10^2	-8.258×10^{-2}	-1.489×10^7	±1.60
$Ba_3Y_2WO_9$	385.2	2.968×10^3	-2.933	-2.162×10^6	±1.50
$MgZrO_3$	66.0	7.603	0.102	-1.495×10^5	±0.45

TABLE 6

Thermodynamic functions of Ba_2CaWO_6: $C_p(T)$, S_T and Φ'' in J mol^{-1} K^{-1}; $H_T - H_0$ in J mol^{-1}

T/K	$C_p(T)$	S_T	$H_T - H_0$	Φ''	T/K	$C_p(T)$	S_T	$H_T - H_0$	Φ''
298	228.26	256.00	0.00	256.00	510	256.86	384.79	51080.88	284.63
300	228.44	257.53	456.70	256.01	520	258.69	389.79	53658.63	286.60
310	229.36	265.03	2745.69	256.18	530	260.56	394.74	56254.88	288.60
320	230.33	272.33	5044.11	256.57	540	262.48	399.63	58870.05	290.61
330	231.34	279.43	7352.40	257.15	550	264.44	404.46	61504.58	292.64
340	232.39	286.35	8670.99	257.91	560	266.44	409.24	64158.91	294.67
350	233.49	293.11	12000.31	258.82	570	268.48	413.98	66833.45	296.73
360	234.62	299.70	14340.79	259.86	580	270.57	418.67	69528.65	298.79
370	235.80	306.14	16692.87	261.03	590	272.70	423.31	72244.93	300.86
380	237.03	312.45	19056.97	262.30	600	274.87	427.91	74982.73	302.94
390	238.29	318.62	21433.53	263.66	610	277.09	432.47	77742.47	305.03
400	239.60	324.67	23822.98	265.11	620	279.35	437.00	80524.59	307.12
410	240.96	330.60	26225.75	266.64	630	281.65	441.48	83329.53	309.21
420	242.35	336.43	28642.26	268.23	640	283.99	445.94	86157.70	311.32
430	243.79	342.15	31072.96	269.88	650	286.38	450.36	89009.55	313.42
440	245.28	347.77	33518.27	271.59	660	288.81	454.75	91885.50	315.53
450	246.80	353.30	35978.63	273.35	670	291.29	459.11	94785.98	317.64
460	248.37	358.74	38454.47	275.14	680	293.81	463.45	97711.43	319.75
470	249.98	364.10	40946.21	276.98	690	296.37	467.75	100662.28	321.87
480	251.64	369.38	43454.29	278.85	700	298.97	472.04	103638.96	323.98
490	253.34	274.58	45979.14	280.75	710	301.62	476.30	106641.90	326.10
500	255.08	379.72	48521.19	282.68					

TABLE 7

Thermodynamic functions of $Ba_3Y_2MoO_9$: $C_p(T)$, S_T and Φ'' in $J\,mol^{-1}\,K^{-1}$; $H_T - H_0$ in $J\,mol^{-1}$

T/K	$C_p(T)$	S_T	$H_T - H_0$	Φ''	T/K	$C_p(T)$	S_T	$H_T - H_0$	Φ''
298	322.11	387.20	0.00	387.20	510	399.19	583.31	78119.82	430.13
300	323.28	389.36	645.39	387.21	520	400.50	591.07	82118.48	433.15
310	328.98	400.05	3906.87	387.45	530	401.61	598.71	86129.22	436.21
320	334.48	410.58	7224.38	388.01	540	402.50	606.23	90149.94	439.29
330	339.77	420.96	10595.83	388.85	550	403.19	613.62	94178.56	442.39
340	344.85	431.18	14019.13	389.95	560	403.66	620.89	98212.98	445.51
350	349.72	441.25	17492.19	391.27	570	403.93	628.04	102251.11	448.65
360	354.39	451.16	21012.91	392.79	580	403.99	635.06	106290.85	451.80
370	358.84	460.93	24579.19	394.50	590	403.83	641.97	110330.12	454.97
380	363.08	470.56	28188.96	396.38	600	403.47	648.75	114366.82	458.14
390	367.11	480.04	31840.10	398.40	610	402.90	655.42	118398.86	461.32
400	370.94	489.39	35530.53	400.56	620	402.12	661.96	122424.13	464.51
410	374.55	498.59	39258.16	402.84	630	401.13	668.39	126440.56	467.69
420	377.96	507.66	43020.90	405.23	640	399.93	674.70	130446.05	470.88
430	381.16	516.59	46816.64	407.71	650	398.52	680.89	134438.50	474.06
440	384.14	525.39	50643.30	410.29	660	396.91	686.96	138415.82	477.24
450	386.92	534.05	54498.79	412.94	670	395.08	692.92	142375.93	480.41
460	389.49	542.58	58381.01	415.67	680	393.04	698.75	146316.72	483.58
470	391.85	550.99	62287.87	418.46	690	390.80	704.48	150236.10	486.74
480	394.00	559.26	66217.27	421.31	700	388.34	710.08	154131.98	489.89
490	395.94	567.40	70167.13	424.20	710	385.68	715.57	158002.27	493.03
500	397.67	575.42	74135.34	427.15					

TABLE 8

Thermodynamic functions of $Ba_3Y_2WO_9$: $C_p(T)$, S_T and Φ'' in $J\,mol^{-1}\,K^{-1}$; $H_T - H_0$ in $J\,mol^{-1}$

T/K	$C_p(T)$	S_T	$H_T - H_0$	Φ''	T/K	$C_p(T)$	S_T	$H_T - H_0$	Φ''
350	55.35	95.22	1085.99	92.12	450	138.52	120.68	11390.53	95.37
360	66.97	96.95	1698.17	92.23	460	142.80	123.77	12797.77	95.95
370	77.85	98.93	2422.85	92.38	470	146.35	126.88	14244.17	96.58
380	88.00	101.15	3252.71	92.59	480	149.17	130.00	15722.40	97.24
390	97.42	103.55	4180.41	92.84	490	151.25	133.09	17225.14	97.94
400	106.10	106.13	5198.61	93.14	500	152.60	136.16	18745.05	98.67
410	114.05	108.85	6299.99	93.49	510	153.22	139.19	20274.80	99.44
420	121.27	111.69	7477.20	93.88	520	153.11	142.17	21807.04	100.23
430	127.75	114.62	8722.92	94.33	530	152.26	145.08	23334.46	101.05
440	133.50	117.62	10029.81	94.83					

TABLE 9

Thermodynamic functions of $MgZrO_3$: $C_p(T)$, S_T and Φ'' in J mol^{-1} K^{-1}; $H_T - H_0$ in J mol^{-1}

T/K	$C_p(T)$	S_T	$H_T - H_0$	Φ''	T/K	C_p(T)	S_T	$h_T - H_0$	Φ''
298	104.71	66.00	0.00	66.00	510	127.12	127.79	24590.24	79.57
300	104.93	66.70	209.64	66.00	520	128.15	130.27	25866.60	80.52
310	106.01	70.16	1264.32	66.08	530	129.19	132.72	27153.31	81.48
320	107.08	73.54	2329.76	66.26	540	130.22	135.14	28450.33	82.46
330	108.15	76.85	3405.93	66.53	550	131.25	137.54	29757.64	83.44
340	109.22	80.10	4492.82	66.88	560	132.27	139.91	31075.23	84.42
350	110.29	83.28	5590.41	67.31	570	133.30	142.26	32403.08	85.42
360	111.36	86.40	6698.67	67.79	580	134.32	144.59	33741.16	86.42
370	112.42	89.47	7817.59	68.34	590	135.34	146.90	35089.46	87.42
380	113.49	92.48	8947.15	68.93	600	136.36	149.18	36447.95	88.43
390	114.55	95.44	10087.32	69.58	610	137.37	151.44	37816.62	89.45
400	115.61	98.35	11238.10	70.26	620	138.39	153.68	39195.44	90.47
410	116.66	101.22	12399.44	70.98	630	139.40	155.91	40584.40	91.49
420	117.72	104.05	13571.35	71.73	640	140.41	158.11	41983.47	92.51
430	118.77	106.83	14753.79	72.52	650	141.42	160.29	43392.64	93.54
440	119.82	109.57	15946.75	73.33	660	142.43	162.46	44811.88	94.56
450	120.87	112.28	17150.21	74.16	670	143.43	164.61	46241.18	95.59
460	121.92	114.94	18364.14	75.02	680	144.43	166.74	47680.51	96.62
470	122.96	117.58	19588.52	75.90	690	145.43	168.86	49129.86	97.66
480	124.00	120.18	20823.35	76.79	700	146.43	170.96	50589.20	98.69
490	125.04	122.74	22068.59	77.71	710	147.43	173.04	52058.51	99.72
500	126.08	125.28	23324.22	78.63					

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