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Note

The temperature relations of the thermodynamic quantities of Ca, Sr, Ba, and Pb zirconates

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INTRODUCTION

The mixed oxides of zirconium $MZrO_3$ (where M is Ca^{2+}, Sr^{2+}, Ba^{2+} or Pb^{2+}) are used in industry as modifiers of titanates and serve as ceramic components in electrical devices. Lead zirconate, in combination with lead titanate, forms an important class of commercially manufactured ferroelectrical material [1, 2]. The zirconates of calcium, strontium and barium are used in the electrolamp industry as emitters, or are components of complex emitters in the production of gas-discharging sources of light with low and high vapour pressure [3–7].

The present article reports the study of the specific heat capacities and thermodynamic quantities of these compounds.

EXPERIMENTAL

The syntheses of $CaZrO_3$, $SrZrO_3$, $BaZrO_3$ and $PbZrO_3$ were performed using high-purity $CaCO_3$, $SrCO_3$, $BaCO_3$, PbO and ZrO_2 (not less than 99.99%) in corundum crucibles and air environment.

The determination of the metal oxides in the complex oxides was performed by complexometric titration with eriochrome black T indicator [8], and gravimetrically for ZrO_2 [9]. The contents of the metal oxides correspond to the stiochiometry of the compounds. They were identified by X-ray diffractometry using 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 the X-ray patterns of $CaZrO_3$, $BaZrO_3$, $SrZrO_3$ and $PbZrO_3$ are those expected from the literature [10]. The molar heat capacities were determined using a Setaram differential scanning

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TABLE 1

Experimental heat capacity values of $CaZrO_3$ in J mol^{-1} K^{-1}

T/K	C_p	T/K	C_p
400	614.33	500	712.10
420	649.90	520	715.38
440	676.10	540	739.00
460	693.48	560	735.78
480	691.98	580	749.29

calorimeter. The samples were precisely ground and sieved (mesh 0.25 mm^2) and were placed in capsules that were inert towards the complex oxides.

Tables 1–4 give the molar heat capacities C_p. The C_p of $PbZrO_3$ was determined only up to 480 K: at higher temperatures the course of its C_p curve shows a sharp change which is probably due to its transformation to the high temperature modification.

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 Kumok [11]. The temperature relations of the thermodynamic quantities (molar heat capacity C_p, entropy S, enthalpy $H_T - H_0$, and Gibb's funtion Φ'') are presented in Tables 6–9.

TABLE 2

Experimental heat capacity values of $SrZrO_3$ in J mol^{-1} K^{-1}

T/K	C_p	T/K	C_p
400	854.76	500	905.20
420	872.00	520	907.91
440	877.44	540	937.80
460	897.94	560	967.42
480	892.06	580	996.74

TABLE 3

Experimental heat capacity values of $BaZrO_3$ in J mol^{-1} K^{-1}

T/K	C_p	T/K	C_p
400	601.13	500	688.26
420	618.72	520	708.62
440	644.17	540	731.88
460	661.18	560	736.98
480	677.03	680	759.42

TABLE 4

Experimental heat capacity values of $PbZrO_3$ in J mol^{-1} K^{-1}

T/K	C_p	T/K	C_p
400	294.50	460	318.86
420	308.72	480	313.94
440	318.57		

TABLE 5

Standard entropy and temperature dependence of the heat capacities of $CaZrO_3$, $SrZrO_3$, $BaZrO_3$ and $PbZrO_3$

Compound	S_{298} in J mol^{-1} K^{-1}	$C_p = a + bT + cT^{-2}$ in J mol^{-1} K^{-1}			
		a	b	c	$(\delta C_p/C_p) \times 10^2$
$CaZrO_3$	89.1	1.095×10^3	−0.319	-5.546×10^7	±0.93
$SrZrO_3$	106.2	-1.626×10^2	1.695	5.599×10^7	±1.00
$BaZrO_3$	121.0	4.311×10^2	0.629	-1.303×10^7	±0.50
$PbZrO_3$	119.7	1.845×10^3	−2.244	-1.045×10^8	±0.23

TABLE 6

Thermodynamic functions of $CaZrO_3$: $C_p(T)$, 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	471.87	89.10	0.00	89.10	510	719.54	414.76	130847.89	158.15
300	475.42	92.27	947.29	89.11	520	724.81	428.79	138097.12	163.22
310	492.82	108.14	5788.95	89.47	530	729.50	442.64	145369.18	168.36
320	509.64	124.06	10801.73	90.30	540	733.62	456.31	152685.30	173.56
330	525.89	139.99	15979.84	91.56	550	737.16	469.81	160039.69	178.83
340	541.55	155.92	21317.52	93.22	560	740.12	483.12	167426.59	184.14
350	556.64	171.84	26808.99	95.24	570	742.51	496.24	174840.22	189.50
360	571.16	187.73	32448.47	97.59	580	744.31	509.17	182274.81	194.90
370	585.09	203.57	38230.18	100.24	590	745.54	521.91	189724.57	200.34
380	598.45	219.35	44148.36	103.17	600	746.19	534.44	197183.74	205.80
390	611.23	235.06	50197.22	106.35	610	746.27	546.78	204646.53	211.29
400	623.43	250.69	56371.00	109.76	620	745.76	558.91	212107.18	216.80
410	635.06	266.23	62663.91	113.39	630	744.68	570.83	219559.91	222.33
420	646.10	281.66	69070.18	117.21	640	743.03	582.55	226998.93	227.86
430	656.57	296.99	75584.04	121.21	650	740.79	594.05	234418.49	233.41
440	666.46	312.20	82199.70	125.38	660	737.98	605.34	241812.79	238.96
450	675.78	327.28	88911.40	129.70	670	734.58	616.41	249176.07	244.51
460	684.52	342.23	95713.36	134.16	680	730.62	627.27	256502.55	250.06
470	692.68	357.04	102599.80	138.74	690	726.07	637.90	263786.46	255.60
480	700.26	371.71	109564.95	143.45	700	720.95	648.31	271022.01	261.14
490	707.26	386.22	116603.03	148.25	710	715.24	658.50	278203.44	266.66
500	713.69	400.57	123708.27	153.16					

TABLE 7

Thermodynamic functions of $SrZrO_3$: $C_p(T)$, 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	894.07	106.20	0.00	106.20	510	914.75	577.83	186277.64	212.68
300	892.81	112.18	1786.88	106.22	520	923.42	595.68	195417.93	219.88
310	886.92	141.35	10684.94	106.89	530	932.79	613.36	204698.43	227.13
320	881.72	169.43	19527.56	108.40	540	942.85	630.89	214076.08	234.45
330	877.22	196.49	28321.67	110.67	550	953.61	648.28	223557.82	241.82
340	873.41	222.62	37074.20	113.58	560	965.06	665.57	233150.58	249.23
350	870.29	247.89	45792.10	117.06	570	977.20	682.76	242861.30	256.68
360	867.87	272.37	54482.30	121.03	580	990.04	699.86	252696.91	264.18
370	866.14	296.12	63151.73	125.44	590	1003.57	716.90	262664.36	271.71
380	865.10	319.21	71807.33	130.24	600	1017.79	733.88	272770.57	279.27
390	864.76	341.67	80456.04	135.38	610	1032.71	750.83	283022.48	286.86
400	865.11	363.57	89104.79	140.81	620	1048.32	767.75	293427.03	294.48
410	866.15	384.94	97760.52	146.50	630	1064.62	784.65	303991.16	302.13
420	867.89	405.83	106430.16	152.43	640	1081.62	801.55	314721.79	309.80
430	870.32	426.28	115120.66	158.56	650	1099.31	818.46	325625.88	317.49
440	873.45	446.33	123838.95	164.87	660	1117.70	835.38	336710.35	325.21
450	877.27	466.00	132591.95	171.35	670	1136.78	852.33	347982.14	332.95
460	881.78	485.33	141386.62	177.96	680	1156.55	869.31	359448.18	340.71
470	886.99	504.34	150299.89	184.71	690	1177.01	886.35	371115.42	348.50
480	892.89	523.08	159128.69	191.56	700	1198.17	903.43	382990.78	356.30
490	899.48	541.56	168089.95	198.52	710	1220.03	920.58	395081.21	364.13
500	906.77	559.80	177120.63	205.56					

TABLE 8

Thermodynamic functions of $BaZrO_3$: $C_p(T)$, 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	494.38	121.00	0.00	121.00	510	701.95	440.15	127893.06	189.38
300	496.63	124.31	991.01	121.01	520	710.23	453.86	134954.10	194.33
310	507.77	140.78	6013.10	121.38	530	718.38	467.47	142097.26	199.36
320	518.77	157.08	11145.89	122.24	540	726.38	480.97	149321.16	204.45
330	529.64	173.21	16388.04	123.55	550	734.25	494.37	156624.46	209.60
340	540.37	189.18	21738.17	125.24	560	741.99	507.67	164005.78	214.80
350	550.96	204.99	27194.94	127.29	570	749.59	520.87	171463.76	220.06
360	561.42	220.66	32756.97	129.67	580	757.05	533.97	178997.05	225.36
370	571.74	236.19	38422.90	132.34	590	764.37	546.98	186604.28	230.70
380	581.93	251.57	44191.37	135.28	600	771.56	559.88	194284.09	236.09
390	591.98	266.81	50061.02	138.45	610	778.62	572.70	202035.11	241.49
400	601.89	281.93	56030.49	141.85	620	785.54	585.41	209855.99	246.94
410	611.67	296.91	62098.41	145.45	630	792.32	598.04	217745.36	252.41
420	621.31	311.77	68263.43	149.23	640	798.96	610.57	225701.86	257.91
430	630.82	326.50	74524.17	153.19	650	805.47	623.00	233724.13	263.43
440	640.18	341.11	80879.29	157.29	660	811.84	635.35	241810.81	268.97
450	649.42	355.60	87327.42	161.54	670	818.08	647.61	249960.53	274.53
460	658.51	369.97	93867.19	165.91	680	824.18	659.77	258171.93	280.11
470	667.47	384.23	100497.24	170.41	690	830.14	671.85	266443.66	285.70
480	676.30	398.37	107216.22	175.01	700	835.97	683.83	274774.34	291.30
490	684.99	412.41	114022.75	179.71	710	841.66	695.73	283162.63	296.91
500	693.54	426.33	120915.49	184.50					

TABLE 9

Thermodynamic functions of $PbZrO_3$: $C_p(T)$, 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''
298	110.78	119.70	0.00	119.70
300	116.08	120.46	226.87	119.70
310	141.59	124.69	1516.64	119.79
320	165.39	129.56	3052.93	120.02
330	187.48	134.99	4818.66	120.39
340	207.86	140.90	6796.75	120.91
350	226.53	147.20	8970.14	121.57
360	243.50	153.82	11321.73	122.37
370	258.76	160.70	13834.44	123.31
380	272.31	167.79	16491.21	124.39
390	284.15	175.02	19274.95	125.59
400	294.29	182.34	22168.58	126.92
410	302.72	189.72	25155.03	128.36
420	309.44	197.10	28217.21	129.91
430	314.45	204.44	31338.05	131.56
440	317.75	211.71	34500.47	133.30
450	319.35	218.87	37687.39	135.12
460	319.24	225.89	40881.73	137.02
470	317.42	232.74	44066.41	138.98
480	313.89	239.39	47224.35	141.00

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