Specific Heat Measurement of Cubic Sodium Tungsten Bronzes from 200 To 800°K

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Specific heats of three cubic sodium tungsten bronze samples (Na_xWO₃) with x values of 0.485, 0.698, and 0.794 were measured from 200 to 800°K. Specific heats per gram-atom of three samples at the same temperature were equal within experimental error regardless of the difference of the composition and those at 700°K showed the Dulong–Petit value. λ -Type specific heat anomalies were observed around 400°K, showing the existence of a second-order phase transition. The transition temperature increases as the sodium content of the sample increases, and a linear relationship between enthalpy change of the transition and the transition temperature was observed. The entropy increments of the transition were obtained as 0.79, 0.84, and 0.90 J/mole·K for Na_{0.485}WO₃, Na_{0.698}WO₃, and Na_{0.794}WO₃, respectively. It is supposed that the entropy increment of the transition is caused by the increase in the number of slightly displaced atoms with respect to the ideal perovskite position.

1. Introduction

The cubic sodium tungsten bronzes have chemical formula Na_xWO₃, the with 0.4 < x < 1.0, and are characterized by the perovskite structure. The properties of these compounds are of interest not only because they are metallic compounds of high electric and thermal conductivity (1, 2), but also because they are nonstoichiometric compounds of metal-oxygen systems. In the nonstoichiometric compounds, the difference in stoichiometry usually has little influence on the specific heat value; however, when phase transition occurs, as in the case of $Ni_{1-x}Se(3)$, $Fe_{1-x}Se(4)$ and $U_4O_{9-y}(5)$, the enthalpy and entropy changes of the phase transition depend on nonstoichiometry.

The existence of the phase transition above room temperature in the cubic sodium tungsten bronze has been suggested by the following results. Optical measurements (6)have shown the presence of a birefringent phase over a wide temperature range from

Copyright © 1975 by Academic Press, Inc. All rights of reproduction in any form reserved. Printed in Great Britain about 270 to about 420°K, depending on the sodium content of the sample. Anomalies have been observed above room temperature in the coefficient of thermal expansion (7), 23 Na spin-phonon relaxation rate (8), and electrical conductivity (9). DSC measurement (9) has found the change of thermal property near 420°K, and an abrupt decrease of thermal conductivity (10) has been observed between 400 and 500°K.

Gerstein et al. (11) have measured the specific heat of $Na_{0.679}WO_3$ in the range 15 to 300°K by an adiabatic calorimeter. Taylor and Weller (9) have reported the specific heat of $Na_{0.8}WO_3$ in the range 330 to 770°K by using DSC apparatus; however, their data are not precise enough because of the use of DSC apparatus.

In this paper, we have measured the specific heat of three tungsten bronzes, $Na_{0.485}WO_3$, $Na_{0.698}WO_3$, and $Na_{0.794}WO_3$, in the range 200 to 800°K, and discussed the phase transition of nonstoichiometric sodium tungsten bronzes.

2. Experimental

2.1. Sample Preparation

 Na_xWO_3 samples were prepared as described by Brown and Banks (12). Na_2WO_4 , WO_3 , and W powder of chemical pure grade with no further purification were uniformly mixed in proper ratios, sealed in an evacuated quartz tube and kept at 700°C for 150 hr. Products were crushed into fine powder and annealed at 600°C for 150 hr.

Sodium concentration of the samples was determined by the measurement of the lattice parameter of X-ray diffraction using the known relation (12) between the lattice parameter and the sodium concentration. The composition of samples was determined to be $Na_{0.485}WO_3$, $Na_{0.698}WO_3$, and $Na_{0.794}WO_3$.

2.2. Specific Heat Measurement

Specific heat of Na_xWO_3 has been measured by the adiabatic scanning calorimeter (13); in this calorimeter the power supplied to the sample was measured continuously, where heating rate was controlled to be constant regardless of the kind and amount of the sample.

Heating rate was chosen as 2° K/min, and the measurement was carried out between 200 and 800°K under nitrogen gas of about 10 Torr. The heating rate control and adiabatic control were usually maintained to within $\pm 0.01^{\circ}$ K/min and $\pm 0.03^{\circ}$ K, respectively. The Na_xWO₃ sample was sealed in a quartz vessel filled with helium gas at about 250 Torr. The sample amount used was 12.246 g for Na_{0.485}WO₃, 11.371 g for Na_{0.698}WO₃, and 13.185 g for Na_{0.794}WO₃.

3. Results and Discussion

Specific heats measured for $Na_{0.485}WO_3$, $Na_{0.698}WO_3$, and $Na_{0.794}WO_3$ are listed in Table I and are shown in Fig. 1, where the results for $Na_{0.679}WO_3$ by Gerstein et al. (11) and those for $Na_{0.8}WO_3$ by Taylor and Weller (9) are also shown for comparison. The precision of the specific heat measurement

TABLE I SPECIFIC HEAT OF Na_xWO₃

	Specific heat (J/mole · K)					
	Na0.485WO3	Na _{0.698} WO ₃	Na _{0.794} WO ₃			
<i>T</i> (°K)	(MW;243.01) (MW;247.90)	(MW; 250.11)			
200	71.2	75.4	79.2			
205	72.4	76.4	80.2			
210	73.7	77.8	81.3			
215	74.8	78.7	82.3			
220	75.8	80.0	83.2			
225	76.5	81.0	84.2			
230	77.6	81.9	85.1			
235	78.4	82.8	86.2			
240	79.5	83.8	87.3			
245	80.6	84.7	88.2			
250	81.5	85.5	89.1			
255	82.1	86.2	90.2			
260	83.1	87.2	91.2			
265	84.3	88.3	92.2			
270	84.9	89.4	92.8			
275	85.6	90.0	93.7			
280	86.6	90.8	94.5			
285	87.2	91.4	95.1			
290	87.7	91.8	95.7			
295	88.3	92.3	96.0			
300	89.0	93.1	97.2			
305	89.8	93.8	97.7			
310	90.3	94.5	98.2			
315	90.9	95.3	98.5			
320	91.3	95.7	99.0			
325	91.9	96.2	99.4			
330	92.1	96.4	99.8			
335	92.5	96.9	100.2			
340	93.2	97.3	100.8			
345	93.6	97.5	101.1			
350	94.1	98.2	101.6			
355	94.2	98.8	102.1			
360	94.5	99.3	102.5			
365	95.0	99.7	102.7			
370	95.3	100.2	103.7			
375	95.7	100.8	103.9			
380	96.5	101.2	104.1			
385	97.1	101.5	104.6			
390	97.9	102.0	105.1			
395	98.7	102.7	105.3			
400	98.4	103.4	105.7			
405	98.0	104.2	106.6			
410	97.6	104.6	107.0			
415	97.8	103.9	107.7			
420	98.3	103.7	108.7			
425	98.6	103.5	109.6			
430	99.1	103.6	110.5			

TABLE I-(continued)

Nature 243.01) (MW; 247.90) (MW; 250.01) T(K) Nature 243.01) (MW; 247.90) (MW; 250.01) 435 99.7 103.8 111.3 680 112.1 117.3 120.1 440 100.1 104.4 110.3 685 112.1 117.3 120.1 445 100.2 104.7 110.2 690 112.4 117.6 120.2 460 101.5 105.9 110.1 705 112.4 117.6 120.2 465 101.7 106.6 110.7 715 113.3 117.9 120.6 475 102.6 107.0 110.8 720 113.3 117.8 120.9 480 103.4 107.7 111.2 730 113.9 117.8 120.9 490 103.6 107.9 111.1 735 114.2 118.1 121.2 500 104.2 108.2 112.5 750 114.6 118.5 121.9 501 104.3 108.5 112.5 <th></th> <th colspan="3">Specific heat (J/mole·K)</th> <th>·</th> <th colspan="3">Specific hest (J/mole·K)</th>		Specific heat (J/mole·K)			·	Specific hest (J/mole·K)		
435 99.7 103.8 111.3 680 112.1 117.0 120.0 445 100.2 104.7 110.2 690 112.4 117.3 120.1 455 101.0 105.4 110.0 695 112.4 117.6 120.2 455 101.0 105.4 110.0 700 112.4 117.6 120.2 460 101.7 106.2 110.4 710 113.3 117.9 120.6 470 102.1 106.6 110.7 715 113.3 117.8 120.9 485 103.4 107.7 111.2 725 113.3 117.8 120.9 490 103.6 107.9 111.1 735 114.2 118.1 121.2 495 103.8 108.1 112.0 740 114.4 118.6 121.2 495 103.6 107.9 111.1 735 114.2 118.1 121.2 500 104.3 108.5 112.5 750 114.6 118.5 121.6 50	$T^{\circ}(\mathbf{K})$	Na _{0.485} WO ₃ (MW; 243.01)	Na _{0.698} WO ₃ (MW;247.90)	Na _{0.794} WO ₃ (MW;250.11)	<i>T</i> (°K)	Na _{0.485} WO ₃ (MW; 243.01) (Na _{0.698} WO ₃ MW; 247.90)	Na _{0.794} WO ₃ (MW; 250.11)
440100.1104.4110.8685112.1117.3120.1445100.2104.7110.2690112.4117.6120.2455101.0105.4110.0700112.4117.6120.2460101.5105.9110.1705112.8117.7120.4465101.7106.6110.7715113.3117.9120.5470102.1106.6110.7715113.3117.9120.5470102.6107.0110.8720113.3117.8120.7480102.7107.2111.2725113.3117.8120.8485103.4107.7111.2730113.9117.9120.9490103.6107.9111.1735114.4118.6121.5500104.2108.2112.5740114.4118.6121.6505104.3108.5112.5750114.6118.5121.9510104.7108.9113.1765114.8119.0122.4520105.3109.9113.7765114.8119.1122.1535105.9110.2114.0770114.9118.9122.3535105.9110.5114.4780115.0119.6123.1540106.6110.5114.4780115.0119.6123.1555107.5115.3	435	99.7	103.8	111.3	680	112.1	117.0	120.0
445100.2104.7110.2690112.4117.3120.1450100.7105.1110.0695112.4117.6120.2455101.0105.9110.1705112.8117.7120.5460101.5105.9110.1705112.8117.7120.5470102.1106.6110.7715113.3117.9120.5475102.6107.0110.8720113.3117.8120.7480102.7107.2111.2730113.9117.9120.9485103.4107.7111.2730113.9117.9120.9490103.6107.9111.1735114.4118.6121.5500104.2108.2112.5750114.4118.6121.9510104.7108.9112.8755114.7118.7122.0510104.7108.9112.8755114.4118.0122.4510105.3100.2113.8775114.4118.9122.4513105.5110.2114.0770114.9119.1122.5515105.5110.2114.4780115.0119.6123.0545106.6113.2115.9115.0119.6123.1555107.6111.9115.117.6115.2119.6123.1565107.6111.9115.1<	440	100.1	104.4	110.8	685	112.1	117.3	120.1
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455 101.0 105.4 110.0 700 112.4 117.6 120.4 460 101.5 105.9 110.1 705 112.8 117.7 120.4 465 101.7 106.2 110.4 710 113.3 117.9 120.5 470 102.1 106.6 110.7 715 113.3 117.9 120.6 475 102.6 107.0 110.8 720 113.3 117.8 120.7 485 103.4 107.7 111.2 730 113.9 117.9 120.9 490 103.6 107.9 111.1 735 114.4 118.6 121.2 500 104.2 108.2 112.5 745 114.4 118.5 121.9 510 104.3 108.5 112.5 750 114.4 118.5 121.9 510 104.7 108.9 112.5 755 114.4 118.1 122.1 525 105.5 110.2 113.8 775 114.4 118.9 122.3 5	450	100.7	105.1	110.0	695	112.4	117.6	120.2
460 101.5 105.9 110.1 705 112.8 117.7 120.4 465 101.7 106.6 110.4 710 113.3 117.9 120.5 470 102.1 106.6 110.7 715 113.3 117.9 120.6 475 102.6 107.0 110.8 720 113.3 117.8 120.6 480 102.7 107.2 111.2 730 113.9 117.9 120.9 485 103.4 107.7 111.2 730 113.9 117.8 120.9 495 103.8 108.1 112.0 740 114.4 118.1 121.5 500 104.3 108.5 112.5 750 114.6 118.5 121.6 510 104.7 108.9 113.7 765 114.8 119.0 122.4 525 105.5 110.2 113.8 775 114.9 118.9 122.4 535 105.9 110.5 114.4 780 115.0 119.6 123.0 5	455	101.0	105.4	110.0	700	112.4	117.6	120.2
465 101.7 106.2 110.4 710 113.3 117.9 120.5 470 102.1 106.6 110.7 715 113.3 117.9 120.6 475 102.6 107.0 110.8 720 113.3 117.8 120.6 485 103.4 107.7 111.2 725 113.3 117.9 120.9 490 103.6 107.7 111.1 735 114.2 118.1 121.2 495 103.8 108.1 112.0 740 114.4 118.5 121.6 500 104.2 108.2 112.5 750 114.4 118.5 121.6 505 104.3 108.9 112.8 755 114.4 118.0 122.0 515 105.0 109.1 113.7 765 114.4 118.9 122.3 520 105.5 110.2 113.8 775 114.9 119.1 122.5 535 105.9 110.2 113.8 775 114.4 119.6 123.0 5	460	101.5	105.9	110.1	705	112.8	117.7	120.4
470102.1106.6110.7715113.3117.9120.6475102.6107.0110.8720113.3117.8120.7480102.7107.2111.2725113.3117.8120.9490103.6107.9111.1735114.2118.1121.2495103.8108.1112.0740114.4118.6121.5500104.2108.2112.5745114.5118.5121.9510104.7108.9112.8755114.7118.7122.0510104.7108.5112.5750114.4118.6121.4525105.0109.1113.1760114.8119.0122.4525105.5110.2113.8775114.9119.1122.5530105.9110.5114.4780115.0119.6123.0540106.1110.5114.4785115.0119.6123.1555107.6111.3114.8795115.2119.9123.2555107.6111.3116.2500115.2119.9123.2555100.7114.5117.7600115.2119.9123.2555107.6111.3116.4507050500600555110.3115.9115.4115.0115.2119.9123.2560107.6111.3 <td>465</td> <td>101.7</td> <td>106.2</td> <td>110.4</td> <td>710</td> <td>113.3</td> <td>117.9</td> <td>120.5</td>	465	101.7	106.2	110.4	710	113.3	117.9	120.5
475102.6107.0110.8720113.3117.8120.7480102.7107.2111.2730113.3117.8120.8485103.4107.7111.2730113.9117.9120.9490103.6107.9111.1735114.2118.1121.2495103.8108.1112.0740114.4118.6121.5500104.2108.5112.5745114.5118.5121.6505104.3108.5112.8755114.7118.7122.0515105.0109.1113.1760114.8119.0122.4520105.3109.9113.7765114.8119.1122.5530105.7110.2114.0770114.9118.9122.3531105.9110.5114.1780115.0119.6123.1540106.6110.5114.4785115.0119.6123.1550106.9111.3114.8795115.2119.9123.2555107.6111.3115.915.115.2119.9123.2555107.6111.2116.1200400400, 400, 400, 400, 400, 400, 400, 400,	470	102.1	106.6	110.7	715	113.3	117.9	120.6
480 102.7 107.2 111.2 725 113.3 117.8 120.8 485 103.4 107.7 111.2 730 113.9 117.9 120.9 490 103.6 107.9 111.1 735 114.2 118.1 121.2 495 103.8 108.1 112.0 740 114.4 118.6 121.5 500 104.2 108.2 112.5 755 114.6 118.5 121.6 510 104.7 108.9 112.8 755 114.7 118.7 122.0 510 105.0 109.1 113.1 760 114.8 119.1 122.1 520 105.3 109.9 113.7 765 114.8 119.1 122.3 530 105.7 110.2 113.8 775 114.9 118.9 122.3 540 106.6 110.5 114.4 785 115.0 119.6 123.2 550 107.6 111.3 115.0 800 115.2 119.9 123.2 5	475	102.6	107.0	110.8	720	113.3	117.8	120.7
485 103.4 107.7 111.2 730 113.9 117.9 120.9 490 103.6 107.9 111.1 735 114.2 118.1 121.2 495 103.8 108.1 112.0 740 114.4 118.6 121.5 500 104.3 108.5 112.5 745 114.5 118.5 121.6 510 104.7 108.9 112.8 755 114.7 118.7 122.0 515 105.0 109.1 113.1 760 114.8 119.0 122.4 520 105.3 109.9 113.7 765 114.8 119.1 122.5 530 105.7 110.2 113.8 775 114.9 119.1 122.5 535 105.9 110.5 114.1 780 115.0 119.6 123.0 545 106.6 110.9 114.7 790 115.2 119.6 123.1 550 107.2 111.3 114.8 795 115.2 119.9 123.2 5	480	102.7	107.2	111.2	725	113.3	117.8	120.8
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495103.8108.1112.0740114.4118.6121.5500104.2108.2112.5745114.5118.5121.6505104.3108.5112.8755114.6118.5121.9510104.7108.9112.8755114.4118.7122.0515105.0109.1113.1760114.8119.0122.4520105.3109.9113.7765114.8119.1122.1531105.7110.2113.8775114.9119.1122.5535105.9110.5114.4785115.0119.6123.1540106.1110.5114.4785115.0119.6123.1550106.9111.3114.8795115.2119.6123.1550106.9111.3114.8795115.2119.9123.2555107.2111.3115.9800115.2119.9123.2555107.6111.9115.1116.2910.9913.7116.1600109.1113.8116.2910.9910.8910.4910.1565100.3115.1117.1910.9910.4910.4615110.3115.2117.7910.9910.4910.4616110.5115.4118.290.090.090.0615110.3115.9118.690.090.0 <td>490</td> <td>103.6</td> <td>107.9</td> <td>111 1</td> <td>735</td> <td>114.2</td> <td>118.1</td> <td>121.2</td>	490	103.6	107.9	111 1	735	114.2	118.1	121.2
500 104.2 108.2 112.5 745 114.5 118.5 121.6 500 104.3 108.5 112.5 750 114.6 118.5 121.6 510 104.7 108.9 112.8 755 114.7 118.7 122.0 515 105.0 109.1 113.1 760 114.8 119.0 122.4 520 105.5 110.2 113.8 775 114.9 118.9 122.3 530 105.7 110.2 113.8 775 114.9 119.1 122.5 535 105.9 110.5 114.1 780 115.0 119.6 123.1 540 106.6 110.9 114.7 790 115.2 119.6 123.1 550 106.6 110.9 114.8 795 115.2 119.9 123.2 560 107.5 111.3 116.2 119.9 123.2 585 108.6 113.2 115.9 116.2 119.9 123.2 585 109.1 113.8 <td< td=""><td>495</td><td>103.8</td><td>108.1</td><td>112.0</td><td>740</td><td>114.4</td><td>118.6</td><td>121.5</td></td<>	495	103.8	108.1	112.0	740	114.4	118.6	121.5
505 104.3 108.5 112.5 750 114.6 118.5 121.9 510 104.7 108.9 112.8 755 114.7 118.7 122.1 515 105.0 109.1 113.1 760 114.8 119.0 122.4 520 105.5 110.2 114.0 770 114.9 118.9 122.3 530 105.7 110.2 113.8 775 114.9 119.0 122.3 530 105.7 110.2 113.8 775 114.9 119.6 123.0 540 106.6 110.9 114.4 785 115.0 119.6 123.1 543 106.6 110.9 114.7 790 115.2 119.9 123.2 555 107.6 111.3 115.0 115.2 119.9 123.2 560 107.6 111.9 115.1 115.2 119.9 123.2 580 108.4 113.5 116.2 117.7 113.8 116.2 115.0 115.2 117.7	500	103.0	108.1	112.5	745	114.5	118.5	121.6
350 104.7 108.9 112.8 755 114.7 118.7 122.0 510 105.0 109.1 113.1 760 114.8 119.0 122.4 520 105.3 109.9 113.7 765 114.8 119.1 122.1 525 105.5 110.2 114.0 770 114.9 119.1 122.5 530 105.7 110.2 113.8 775 114.9 119.6 123.0 543 106.6 110.9 114.7 780 115.0 119.6 123.1 550 106.9 111.3 114.8 795 115.2 119.6 123.1 550 106.9 111.3 114.8 795 115.2 119.9 123.2 555 107.2 111.3 115.0 119.6 123.1 560 107.5 111.9 115.1 116.2 119.9 123.2 575 108.2 112.8 115.9 16.2 110.5 116.2 110.5 116.4 110.5 10.6 10.5	505	104.2	108.5	112.5	750	114.6	118.5	121.9
10 106.7 106.7 112.8 112.8 112.8 112.8 112.8 112.8 112.8 112.8 112.8 112.8 112.8 112.1 113.1 113.1 113.1 113.1 113.1 113.1 113.1 113.1 1	510	104.5	108.9	112.5	755	114.7	118.7	122.0
510105.0105.1115.1755114.8119.1122.1520105.3100.2114.0770114.9118.9122.3530105.7110.2113.8775114.9118.9122.3535105.9110.5114.1780115.0119.6123.0540106.1110.5114.4785115.0119.6123.1545106.6110.9114.7790115.2119.6123.1550106.9111.3114.8795115.2119.9123.2555107.2111.3115.0800115.2119.9123.2555107.6111.9115.1115.2119.9123.2555107.6111.9115.1115.2119.9123.2555107.6111.9115.1115.9115.2119.9123.2555108.6113.2115.9115.2119.9123.2595109.0113.7116.15100.5114.2116.8605109.5114.2116.85510.3115.2117.7630110.4115.9118.6115.0117.5100640110.8115.8118.416.7119.7and Na _{0.794} WO ₃ with the results of Na _{0.465} WO _{3.} Na _{0.695} WO655111.3116.3118.9FIG. 1. Specific heats of Na _{0.465} WO _{3.9} Na _{0.695} WO665111.2	515	104.7	100.9	112.0	760	114.8	119.0	122.4
250105.3105.9113.7775114.9118.9122.3530105.7110.2113.8775114.9119.6123.0530105.7110.5114.1780115.0119.6123.1531105.9110.5114.4785115.0119.6123.1545106.6110.9114.7790115.2119.6123.1550106.9111.3114.8795115.2119.9123.2555107.2111.3115.0800115.2119.9123.2560107.5111.5114.9115.1115.2119.9123.2560107.6111.9115.1115.9115.2119.9123.2575108.2112.8115.9115.2119.9123.2585108.6113.2115.9116.2120tworkNa.488 WO3595109.0113.7116.115.9116.2120tworkNa.488 WO3565109.5114.2116.817.5100115.4118.2600109.1113.8116.415.3100115.4118.2610109.7114.5117.7116.3116.3118.9625110.3115.4118.2100116.419.2660111.2116.4119.2FIG. 1. Specific heats of Na.0.485 WO3, Na.0.699 WO665111.5116.7119.8 <td>520</td> <td>105.0</td> <td>109.1</td> <td>113.1</td> <td>765</td> <td>114.8</td> <td>1191</td> <td>122.1</td>	520	105.0	109.1	113.1	765	114.8	1191	122.1
525 105.7 110.2 114.0 715 114.9 119.1 122.5 530 105.7 110.2 113.8 775 114.9 119.1 122.5 535 105.9 110.5 114.4 785 115.0 119.6 123.0 540 106.1 110.5 114.4 785 115.0 119.6 123.1 545 106.6 110.9 114.7 790 115.2 119.9 123.2 555 107.2 111.3 114.8 795 115.2 119.9 123.2 560 107.5 111.5 114.9 115.2 119.9 123.2 565 107.6 111.9 115.1 115.2 119.9 123.2 575 108.2 112.8 115.8 116.2 (1) 118.9 116.2 (2) (3) (3) (3) (3) (3) (3) (3) (3) (4) (4) (4) (4) (4)	520	105.5	110.2	113.7	770	114.9	118.9	122.3
530 110.5. 110.5 114.1 780 115.0 119.6 123.0 535 105.9 110.5 114.4 785 115.0 119.6 123.0 540 106.6 110.9 114.7 790 115.2 119.6 123.0 545 106.6 110.9 114.7 790 115.2 119.6 123.0 555 107.2 111.3 114.8 795 115.2 119.9 123.2 560 107.5 111.5 114.9 800 115.2 119.9 123.2 565 107.6 111.9 115.1 119.9 123.2 575 108.2 112.8 115.9 115.2 119.9 123.2 585 108.6 113.2 115.9 115.4 115.9 116.2 115.0 115.4 116.4 10.4 10.5 114.5 116.4 10.5 10.4 115.3 117.7 10.5 114.5 117.7 10.5 114.5 116.3 118.9 10.4 115.3 117.5 10.5 115.4 <td>525</td> <td>105.5</td> <td>110.2</td> <td>114.0</td> <td>775</td> <td>114.9</td> <td>119.1</td> <td>122.5</td>	525	105.5	110.2	114.0	775	114.9	119.1	122.5
533 105.9 110.5 114.4 785 115.0 119.6 123.1 540 106.6 110.9 114.4 785 115.0 119.6 123.1 545 106.6 110.9 114.7 790 115.2 119.6 123.1 550 106.9 111.3 114.8 795 115.2 119.9 123.2 555 107.2 111.3 115.0 800 115.2 119.9 123.2 560 107.5 111.5 114.9	530	105.7	110.2	113.8	780	115.0	119.6	122.5
540106.1110.5114.4105115.0115.0115.0115.0545106.6110.9114.7790115.2119.6123.1550106.9111.3114.8795115.2119.9123.2555107.2111.3115.0800115.2119.9123.2560107.5111.5114.9115.1114.9115.2119.9123.2560107.5111.5114.9115.1115.9115.2119.9123.2570107.9112.4115.9115.8116.9123.1Na_e.48 WO3585108.6113.2115.9116.1 $\nabla_{0.68}$ WO3Na_e.98 WO313.5590108.8113.7116.1 $\nabla_{0.66}$ WO3Na_e.98 WO313.5600109.1113.8116.4 $\nabla_{0.66}$ Na_e.97 WO312.2615110.1115.0117.510.0Na_e.97 WO312.2625110.3115.1117.610.0115.3116.7635110.5115.4118.210.0118.611.2640110.8115.8118.6118.911.4665111.2116.7119.7and Na _{0.794} WO3 with the results of Na _{0.698} WO3, Na _{0.698} WO665111.2116.7119.8Gerstein et al. and these of Na _{0.8} WO3, by Taylor670111.8116.7119.8Gerstein et al. and these of Na _{0.8} WO3 by Taylor <td>535</td> <td>105.9</td> <td>110.5</td> <td>114.1</td> <td>785</td> <td>115.0</td> <td>119.6</td> <td>123.0</td>	535	105.9	110.5	114.1	785	115.0	119.6	123.0
545106.6110.9114.7790113.2119.0123.1550106.9111.3114.8795115.2119.9123.2555107.2111.3115.0800115.2119.9123.2560107.5111.5114.9115.1119.9123.2565107.6111.9115.1119.9123.2575108.2112.8115.9	540	106.1	110.5	114.4	700	115.0	119.0	123.1
550106.9111.3114.8793113.2119.9123.2555107.2111.3115.0800115.2119.9123.2560107.5111.5114.9800115.2119.9123.2565107.6111.9115.1114.9 (15.2) 119.9123.2575108.2112.8115.9 (-1) this work $Na_{a.489}W0_3$ (-2) this work $Na_{a.489}W0_3$ 585108.6113.2115.9 (-2) this work $Na_{a.490}W0_3$ (-3) 590108.8113.5116.2 (-2) this work $Na_{a.489}W0_3$ (-3) 595109.0113.7116.1 (-2) this work $Na_{a.490}W0_3$ (-3) 600109.1113.8116.4 (-2) this work $Na_{a.490}W0_3$ (-3) 615110.1115.0117.5 (-2) this work $Na_{a.879}W0_3$ (-3) 616109.7114.5117.1 (-1) this work $Na_{a.879}W0_3$ (-1) this615110.3115.2117.7 (-1) this (-1) this (-1) this (-1) this616110.3115.2117.7 (-1) this (-1) this (-1) this635110.3115.9118.6 (-1) this (-1) this640110.8115.8118.6 (-1) this (-1) this655111.3116.3118.9 (-1) this (-1) this660111.2116.4119.2	545	106.6	110.9	114.7	790	115.2	119.0	123.1
555 107.2 111.3 115.0 600 113.2 119.9 123.2 560 107.5 111.5 114.9 575 107.6 111.9 115.1 570 107.9 112.4 115.9 575 108.2 112.8 115.8 580 108.4 113.0 115.9 585 108.6 113.2 115.9 590 108.8 113.5 116.2 595 109.0 113.7 116.1 600 109.1 113.8 116.4 605 109.5 114.2 116.8 616 109.7 114.5 117.1 615 110.1 115.2 117.7 630 110.4 115.9 118.6 640 110.8 115.8 118.4 645 111.0 115.9 118.6 655 111.3 116.3 118.9 660 111.2 116.4 119.2 Fig. 1. Specific heats of $Na_{0.485}WO_3$, $Na_{0.698}WO_3$ 665 111.5 116.7 119.7 and $Na_{0.794}WO_3$ with the results of $Na_{0.679}WO_3$ 670 111.8 116.7 119.7 670 111.8 116.7 119.8 670 111.8 116.7 119.8 670 111.8 116.7 119.8 670 111.8 116.7 119.8 670 111.8 116.7 119.8 670 111.8 116.7 119.8 670 <td>550</td> <td>106.9</td> <td>111.3</td> <td>114.8</td> <td>195</td> <td>115.2</td> <td>119.9</td> <td>123.2</td>	550	106.9	111.3	114.8	195	115.2	119.9	123.2
560 107.5 111.5 114.9 565 107.6 111.9 115.1 570 107.9 112.4 115.9 575 108.2 112.8 115.9 580 108.4 113.0 115.9 585 108.6 113.2 115.9 590 108.8 113.7 116.1 600 109.1 113.8 116.4 605 109.5 114.2 116.8 616 109.7 114.5 117.1 615 110.1 115.0 117.5 620 110.3 115.1 117.6 630 110.4 115.3 117.7 630 110.4 115.3 117.7 630 110.3 115.4 118.2 640 110.8 115.8 118.4 6445 111.0 115.9 118.6 655 111.3 116.3 118.9 660 111.2 116.4 119.2 FiG. 1. Specific heats of Na _{0.485} WO ₃ , Na _{0.6598} WO ₃ 665 11	555	107.2	111.3	115.0	800	115.2	119.9	123.2
565107.6111.9115.1570107.9112.4115.9575108.2112.8115.8580108.4113.0115.9585108.6113.2115.9590108.8113.5116.2595109.0113.7116.1600109.1113.8116.4605109.5114.2116.8610109.7114.5117.1615110.1115.0117.5620110.3115.2117.7630110.4115.3640110.8115.8655111.1116.1660111.2116.4655111.3116.3660111.2116.4660111.2116.4675112.3116.770111.8116.770113.8116.770113.8116.7710116.8710116.8711.0115.9711.0116.7711.0116.7711.0116.7711.1116.7711.2116.8711.3116.7711.4116.7711.8116.7711.8116.7711.9711.9711.0116.8711.0116.8711.0116.8711.0116.8711.0711.8711.0711.9711.0711.97	560	107.5	111.5	114.9		·		
570107.9112.4115.9575108.2112.8115.8580108.4113.0115.9585108.6113.2115.9590108.8113.5116.2595109.0113.7116.1600109.1113.8116.4605109.5114.2116.8610109.7114.5117.1615110.1115.0117.5620110.3115.1117.6635110.5115.4118.2640110.8115.8118.4645111.0115.9118.6650111.1116.3118.9660111.2116.4119.2665111.5116.7119.7670111.8116.7119.770111.8116.7119.8675112.3116.8110.9116.8119.2	565	107.6	111.9	115.1	ſ			
575108.2112.8115.8580108.4113.0115.9585108.6113.2115.9590108.8113.5116.2595109.0113.7116.1600109.1113.8116.4605109.5114.2116.8610109.7114.5117.1615110.1115.0117.5620110.3115.1117.6635110.5115.4118.2640110.8115.9635111.0115.9640110.8115.9655111.3116.3660111.2116.4660111.2116.4660111.2116.4660111.2116.4665111.5116.7670111.8116.770111.8116.770111.8116.770111.8116.770111.8116.770111.8116.771116.971116.971116.971116.871116.971116.971116.871116.771119.772116.873116.974116.975112.376119.976119.976119.9	570	107.9	112.4	115.9		111 ALLE WORK		
580108.4113.0115.9585108.6113.2115.9590108.8113.5116.2595109.0113.7116.1600109.1113.8116.4605109.5114.2116.8610109.7114.5117.1615110.1115.0117.5620110.3115.1117.6635110.5115.4118.2640110.8115.8118.4645111.0115.9118.6655111.3116.3118.9660111.2116.4119.2665111.5116.7119.7670111.8116.7119.7and Na _{0.794} WO ₃ with the results of Na _{0.679} WO675112.3116.7675112.3116.7675112.3116.7675112.3116.7675112.3116.7675112.3116.7675112.3116.7675112.3116.77011.8116.771119.971116.9119.071116.971116.971116.971116.971116.971116.972116.874116.975112.376119.976119.9	575	108.2	112.8	115.8			Na	
585108.6113.2115.9590108.8113.5116.2595109.0113.7116.1600109.1113.8116.4605109.5114.2116.8610109.7114.5117.1615110.1115.0117.5620110.3115.1117.6625110.3115.2117.7630110.4115.3117.9635110.5115.4118.2640110.8115.8650111.1116.1655111.3116.3660111.2116.4660111.2116.4665111.5116.7675111.8116.7670111.8116.7675112.3116.9675112.3116.7675112.3116.7675112.3116.7675112.3116.77011.8116.771119.8Gerstein et al. and thcs2 of Na _{0.8} WO ₃ by Taylor	580	108.4	113.0	115.9			No. WO.	
590108.8113.5116.2595109.0113.7116.1600109.1113.8116.4605109.5114.2116.8610109.7114.5117.1615110.1115.0117.5620110.3115.1117.6625110.3115.2117.7630110.4115.3117.9635110.5115.4118.2640110.8115.9118.6650111.1116.1118.7655111.3116.3118.9660111.2116.4119.2665111.5116.7119.7and Na _{0.794} WO ₃ with the results of Na _{0.679} WO670111.8116.7112.3116.9119.8Gerstein et al. and thcs2 of Na _{0.8} WO ₃ by Taylor	585	108.6	113.2	115.9		Taylor and Weller	No. WO.	(2)
595109.0113.7116.1600109.1113.8116.4605109.5114.2116.8610109.7114.5117.1615110.1115.0117.5620110.3115.1117.6625110.3115.2117.7630110.4115.3117.9635110.5115.4118.2640110.8115.9118.6650111.1116.1118.7655111.3116.3118.9660111.2116.4119.2665111.5116.7119.7670111.8116.7119.8670111.8116.7119.8670112.3116.9119.970111.8116.7119.870111.8116.7119.870111.8116.771119.8116.971116.9119.9	590	108.8	113.5	116.2	😧 120	- 000 Gerstein etal.	Na. 679 WO3	(2) -
600109.1113.8116.4E605109.5114.2116.8610109.7114.5117.1615110.1115.0117.5620110.3115.1117.6625110.3115.2117.7630110.4115.3117.9635110.5115.4118.2640110.8115.9118.6650111.1116.1118.7655111.3116.3118.9660111.2116.4119.2665111.5116.7119.7665111.8116.7119.8670111.8116.7119.8675112.3116.9119.970111.8116.7675112.3116.8675112.3116.7675112.3116.7675112.3116.7675112.3116.8675112.3675112.3675112.370111.870116.871119.871719.87271.2374719.875112.375112.376112.876116.876112.376116.876117.376116.876117.376116.876117.376119.87	595	109.0	113.7	116.1	ō			(1)
605 109.5 114.2 116.8 $\overline{2}_{00}$ 610 109.7 114.5 117.1 615 110.1 115.0 117.5 620 110.3 115.1 117.6 625 110.3 115.2 117.7 630 110.4 115.3 117.9 635 110.5 115.4 118.2 640 110.8 115.8 118.4 645 111.0 115.9 118.6 650 111.1 116.3 118.9 660 111.2 116.4 119.2 665 111.5 116.7 119.7 665 111.8 116.7 119.7 675 112.3 116.7 119.8 670 111.8 116.7 119.8 670 111.8 116.7 119.8 675 112.3 116.9 119.9 W_{0} Works W_{0} with the results of Na _{0.679} WO 675 112.3 116.9 119.9	600	109.1	113.8	116.4	Ĕ,		\sim	
610109.7114.5117.1 G_{100} 615110.1115.0117.5620110.3115.1117.6625110.3115.2117.7630110.4115.3117.9635110.5115.4118.2640110.8115.9118.6650111.1116.1118.7655111.3116.3118.9660111.2116.4119.2665111.5116.7119.7665111.8116.7119.7670111.8116.7119.8671112.3116.8672112.3116.8673112.3116.7674112.3116.8675112.3116.7675112.3116.7675112.3116.7675112.3116.8675112.3675112.3675112.3	605	109.5	114.2	116.8	2			
615 110.1 115.0 117.5 620 110.3 115.1 117.6 625 110.3 115.2 117.7 630 110.4 115.3 117.9 635 110.5 115.4 118.2 640 110.8 115.8 118.4 645 111.0 115.9 118.6 650 111.1 116.1 118.7 655 111.3 116.3 118.9 660 111.2 116.4 119.2 Fig. 1. Specific heats of Na _{0.485} WO ₃ , Na _{0.698} WO 665 111.5 116.7 119.7 and Na _{0.794} WO ₃ with the results of Na _{0.679} WO 670 111.8 116.7 119.8 Gerstein et al. and thcs2 of Na _{0.8} WO ₃ by Taylor 675 112.3 116.8 110.9 Wollward	610	109.7	114.5	117.1	ت 100	. //	*/	-
620 110.3 115.1 117.6 625 110.3 115.2 117.7 630 110.4 115.3 117.9 635 110.5 115.4 118.2 640 110.8 115.8 118.4 645 111.0 115.9 118.6 650 111.1 116.1 118.7 655 111.3 116.3 118.9 660 111.2 116.4 119.2 FIG. 1. Specific heats of $Na_{0.485}WO_3$, $Na_{0.698}WO_3$ 665 111.5 116.7 119.7 and $Na_{0.794}WO_3$ with the results of $Na_{0.679}WO_3$ 670 111.8 116.7 119.8 Gerstein et al. and thcs2 of $Na_{0.8}WO_3$ by Taylor 675 112.3 116.9 110.9 W_0 Worlder	615	110.1	115.0	117.5		115	<	
625110.3115.2117.7630110.4115.3117.9635110.5115.4118.2640110.8115.8118.4645111.0115.9118.6650111.1116.1118.7655111.3116.3118.9660111.2116.4119.2665111.5116.7119.7670111.8116.7119.8675112.3116.7119.8675112.3116.7675112.3116.7675112.3116.7675112.3676111.8770111.8770112.8770112.3770116.9770116.9770117.8770116.8770116.8770116.8770116.8770116.8770116.9770117.8770116.9770117.8770117.8770117.8770117.8770117.8770117.8770117.8770117.8770117.8770116.8770117.8770117.8770117.8770117.8770117.8770117.8770117.8770117.8 <td< td=""><td>620</td><td>110.3</td><td>115.1</td><td>117.6</td><td></td><td>61</td><td></td><td></td></td<>	620	110.3	115.1	117.6		61		
630 110.4 115.3 117.9 80^{-1} 80^{-1	625	110.3	115.2	117.7	(/\$/		<u> </u>
635 110.5 115.4 118.2 640 110.8 115.8 118.4 645 111.0 115.9 118.6 650 111.1 116.1 118.7 655 111.3 116.3 118.9 660 111.2 116.4 119.2 665 111.5 116.7 119.7 665 111.8 116.7 119.8 670 111.8 116.7 119.8 675 112.3 116.7 119.8 675 112.3 116.7 119.8 675 112.3 116.7 119.8 675 112.3 116.7 119.8	630	110.4	115.3	117.9	80	_ /\$/)
640 110.8 115.8 118.4 9^{7} 645 111.0 115.9 118.6 200 400 600 800 650 111.1 116.1 118.7 $T(K)$ $T(K)$ 655 111.3 116.3 118.9 $T(K)$ 660 $T(K)$ 660 111.2 116.4 119.2 FIG. 1. Specific heats of Na _{0.485} WO ₃ , Na _{0.698} WO 665 111.5 116.7 119.7 and Na _{0.794} WO ₃ with the results of Na _{0.679} WO 670 111.8 116.7 119.8 Gerstein et al. and thcse of Na _{0.8} WO ₃ by Taylor 675 112.3 116.8 110.9 Wolling	635	110.5	115.4	118.2		6/		1
645 111.0 115.9 118.6 650 111.1 116.1 118.7 655 111.3 116.3 118.9 660 111.2 116.4 119.2 FIG. 1. Specific heats of Na _{0.485} WO ₃ , Na _{0.698} W 665 111.5 116.7 119.7 and Na _{0.794} WO ₃ with the results of Na _{0.679} WO 670 111.8 116.7 119.8 Gerstein et al. and thcse of Na _{0.8} WO ₃ by Taylor 675 112.3 116.8 110.0 Wolling	640	110.8	115.8	118.4		%		
650 111.1 116.1 118.7 $7 (K)$ 655 111.3 116.3 118.9 $T(K)$ 660 111.2 116.4 119.2 FIG. 1. Specific heats of $Na_{0.485}WO_3$, $Na_{0.698}W$ 665 111.5 116.7 119.7 and $Na_{0.794}WO_3$ with the results of $Na_{0.679}WO$ 670 111.8 116.7 119.8 Gerstein et al. and thcse of $Na_{0.8}WO_3$ by Taylor 675 112.3 116.8 110.9 $W_{0.1107}$	645	111.0	115.9	118.6				.
655 111.3 116.3 118.9 660 111.2 116.4 119.2 FIG. 1. Specific heats of $Na_{0.485}WO_3$, $Na_{0.698}W$ 665 111.5 116.7 119.7 and $Na_{0.794}WO_3$ with the results of $Na_{0.679}WO$ 670 111.8 116.7 119.8 Gerstein et al. and thcse of $Na_{0.8}WO_3$ by Taylor 675 112.3 116.8 110.9 Wolling	650	111.1	116.1	118.7	·	200 40	0 600	800
660 111.2 116.4 119.2 FIG. 1. Specific heats of Na _{0.485} WO ₃ , Na _{0.698} W 665 111.5 116.7 119.7 and Na _{0.794} WO ₃ with the results of Na _{0.679} WC 670 111.8 116.7 119.8 Gerstein et al. and thcse of Na _{0.8} WO ₃ by Taylor 675 112.3 116.7 119.8 Gerstein et al. and thcse of Na _{0.8} WO ₃ by Taylor	655	111.1	116 3	118 0			т(К)	
665 111.5 116.7 119.7 and Na _{0.794} WO ₃ with the results of Na _{0.679} WC 670 111.8 116.7 119.8 Gerstein et al. and thcse of Na _{0.8} WO ₃ by Taylor 675 112.3 116.7 119.8 Gerstein et al. and thcse of Na _{0.8} WO ₃ by Taylor	660	111.5	116.5	119.2	FIG	1. Specific heats c	of Na ₀ WO	a. Nao conWO
111.8 116.7 119.8 110.9 $110.$	665	111 5	1167	110.7	and Na	with th	e results of	Na
775 117.0 116.7 117.0 Generative at an treast of $14a_{0.8}$ (0.3 by Taylor	670	111.5	116.7	119.7	Gerstei	n et al and these	of Nac WO	hv Tavlor at
013 114.3 110.0 117.7 Weller	675	112.3	116.8	119.9	Weller		0. I 100,8 11 02	, <i>.,</i> 10,101 di

is within ± 1 %. Data by Gerstein et al. are in good agreement with our results, taking into consideration the small difference of the sodium content of samples, but results by Taylor and Weller measured by DSC may contain large error at higher temperatures.

As discussed in previous papers (5, 13), in dynamic calorimeters a temperature difference is produced in the sample and a so-called scanning error is produced. The scanning error was corrected by shifting the sample temperature by about 3°K in this experiment according to the carlier method (5, 13).

Specific heats of Na_xWO₃ per gram-atom (per 1/(4 + x) mole) at temperatures 200, 500, 600, 700, and 800°K, which have nothing to do with the phase transition, are given in

TABLE II

Specific Heat of Na_xWO₃ per Gram-Atom (1/(4 + x) mole)

<i>Т</i> (°К)	Specific heat $(J/g-atom \cdot K)$				
	Na _{0.485} WO ₃	Na _{0.698} WO ₃	Na _{0.794} WO ₃		
200	15.88	16.05	16.52		
500	23.23	23.03	23.47		
600	24.33	24.22	24.28		
700	25.06	25.03	25.07		
800	25.69	25.52	25.70		



FIG. 2. Transition temperatures of Na_xWO_3 against the sodium content of sample.

Table II. Specific heats per gram-atom at each temperature are the same within experimental error, except for the case of 200°K, regardless of the difference in composition among the samples. Above the Debye temperature, which Gerstein et al. (11) have determined to be 450°K for Na_{0.679}WO₃, specific heats per gram-atom approach the Dulong–Petit value of 24.95 J/g-atom K, and those at 700°K correspond to the Dulong–Petit value.

A λ -type specific heat anomaly of Na_xWO₃, as seen in Fig. 1, begins around 250°K and peaks around 400°K, depending on the sodium content of the sample; this shows the occurrence of a second-order phase transition. The peak temperature (T_k) of the phase transition against the sodium content of the sample is shown in Fig. 2; the previous data reported in the literature are also shown for comparison. In Fig. 2 the data of T_h show considerable scatter, which may be ascribed to the differences in sample preparation and the method of measurement. The data of T_h obtained by this work are in good agreement with those by Ingold and DeVries by the optical measurement (6). T_1 shown in Fig. 2 obtained by Ingold and DeVries (6) represents the temperature at which birefringent patterns begin to appear, and this corresponds to the temperature at which the specific heat curve begins to rise, as seen in Fig. 1.

In the measurement of ²³Na spin-phonon relaxation rate in Na_xWO₃ (8) some peaks are overlapped, perhaps showing the existence of some corresponding relaxation mechanisms. But these effects may not clearly contribute to the specific heat curve.

To obtain the enthalpy and entropy changes due to the phase transition, the baseline of the specific heat curve for each sample of Na_xWO_3 is determined by the least-squares method, using the data in the range from 200 to 240°K and from 420 to 550°K (dependent on the sodium content of the sample) which have nothing to do with the specific heat anomaly, so as to fit the equation

$$C_n = a + bT - cT^{-2}.$$

By using the baseline thus determined, enthalpy and entropy increments for the

TABLE III

Enthalpy and Entropy Increment; and the transition Temperature for the λ -Type Transition in Na_xWO₃

	ΔH (J/mole)	ΔS (J/mole · K)	T_h (°K)
Na _{0.485} WO ₃	263 ± 9	0.79 ± 0.03	395
Na0.698WO3	289 ± 11	0.84 ± 0.04	410
Na _{0.794} WO ₃	332 ± 12	0.90 ± 0.04	435

transition are obtained and are given in Table III, where the transition temperature T_h is also given.

 T_h tends to increase as ΔH increases, and RT_h is plotted against ΔH as shown in Fig. 3, where good linearity is observed. This indicates that thermal energy necessary to cause the phase transition is related to the enthalpy change as the result of the transition. Similar behavior is seen in the phase transition of some nonstoichiometric compounds such as U_4O_{9-y} (5). The fact that T_h and enthalpy increments increase as the sodium content of the sample increases may indicate that the crystal structure becomes more stable as the sodium content increases.

Ingold et al. (6) supposed that before the transition the low temperature phase was distorted cubic (tetragonal) and the high temperature phase became cubic after the transition, judging from the analogy of the optical behavior with the phase transition of



FIG. 3. Transition temperatures multiplied by gas constant against the enthalpy increments for the transition.

BaTiO₃. The positive entropy change as shown in Table III may indicate that the crystal structure in the high temperature phase is more irregular than that in the low temperature phase. Atoji and Rundle (14) have found from the neutron diffraction study of Na_xWO₃ in the low temperature phase that oxygen atoms are slightly displaced with respect to the ideal perovskite structure, although the crystal structure differs little from the regular perovskite structure. It is supposed that the entropy change relates to the change of the number of such displaced oxygen atoms.

Although the detail of the phase transition of Na_xWO₃ has not been clear, the entropy change obtained in this study may be explainable by this supposition qualitatively. The positive entropy change indicates that the number of displaced atoms in the high temperature phase is more than that in the low temperature phase. This is supported by the fact (10) that the thermal conductivity in the high temperature phase is lower than that in the low temperature phase because the phonon scattering is increased in the high temperature phase by the increase of displaced atoms.

The fact that entropy increments increase as the sodium content of the sample increases is interpreted to mean that the number of displaced atoms from the ideal perovskite structure increases as the sodium content increases. This interpretation is also supported by the observation (10) that the decrease of the thermal conductivity of $Na_{0.804}WO_3$ during the transition is larger than that of $Na_{0.513}WO_3$.

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