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# Heat Capacity Measurement of Cubic Lithium Tungsten Bronzes from 200 to 800°K

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Heat capacities of three cubic lithium tungsten bronze samples ($Li_xWO_3$) with $x$ values of 0.363, 0.437, and 0.478 were measured from 200 to 800°K. Heat capacities per gram-atom at the same temperature of $Li_{0.363}WO_3$ and $Li_{0.437}WO_3$ were equal within experimental error and also equal to those of $Na_{0.485}WO_3$, $Na_{0.698}WO_3$, and $Na_{0.794}WO_3$, regardless of the difference of the composition. $\lambda$-type heat capacity anomalies were observed around 330, 460, and 590°K in $Li_{0.363}WO_3$ and around 330 and 460°K in $Li_{0.437}WO_3$ and $Li_{0.478}WO_3$, showing the existence of second-order phase transitions. The entropy increments of the transitions were obtained as 1.36, 0.45, and 1.68 J mole$^{-1}$ K$^{-1}$ for $Li_{0.363}WO_3$, 1.09 and 0.59 J mole$^{-1}$ K$^{-1}$ for $Li_{0.437}WO_3$, and 1.42 and 0.50 J mole$^{-1}$ K$^{-1}$ for $Li_{0.478}WO_3$.

The cubic lithium tungsten bronzes, $Li_xWO_3$, are nonstoichiometric compounds with $0.25 < x < 0.50$ (*1*) and they have perovskite structure and metallic properties. In the previous paper (*2*), heat capacity of $Na_xWO_3$ for various $x$ values was measured and $\lambda$-type heat capacity anomalies were observed around 400°K. It was found that the transition temperatures and enthalpy and entropy increments for the transition are changed with $x$ values.

$Li_xWO_3$ samples were prepared in a manner similar to that described in the previous paper (*2*). $Li_2WO_4$, $WO_3$, and W powder were mixed in the proper ratios, sealed in an evacuated quartz tube, and kept at 900°C for 150 hr. The products were crushed into a fine powder and annealed at 900°C for 150 hr. The lithium concentration of the samples was determined by the measurement of the lattice parameter of X-ray diffraction using the relation between the lattice parameter and the lithium concentration (*3*):

$$a_0 = 3.785 - 0.134x.$$

The heat capacity of $Li_xWO_3$ has been measured by the adiabatic scanning calorimeter (*4*) and conditions for the measurement were the same as in the previous paper (*2*). The sample amount used was 20.310 g for $Li_{0.363}WO_3$, 20.648 g for $Li_{0.437}WO_3$, and 20.240 g for $Li_{0.478}WO_3$.

The heat capacities measured for the three samples are listed in Table I and are shown in Fig. 1. The precision of the heat capacity measurement is within $\pm 1\%$. As described in previous papers (*2, 4*), the scanning error was corrected by shifting the sample temperature by about 3°K for the heating rate, 2°K min$^{-1}$ in this experiment.

The heat capacities of $Li_xWO_3$ and $Na_xWO_3$ per gram-atom (per $1(4 + x)$ mole) at 700 and 800°K, which have nothing to do with the anomaly, are given in Table II. Heat capacities per gram-atom are the same within experimental error, except for the case of $Li_{0.478}WO_3$, regardless of the differences in composition among the samples. Heat capacities per gram-atom of $Li_{0.478}WO_3$ are greater than those of the others by about $2\%$. The reason for this is not clear.

As seen in Fig. 1, three heat capacity anomalies are observed around 330, 460, and 590°K in $Li_{0.363}WO_3$, and two anomalies

TABLE I

HEAT CAPACITY OF $Li_xWO_3$

| T (°K) | $C_p$ (J mole$^{-1}$ K$^{-1}$) | | |
|---|---|---|---|
| | $Li_{0.363}WO_3$ | $Li_{0.437}WO_3$ | $Li_{0.478}WO_3$ |
| 200 | 61.8 | 64.2 | 67.4 |
| 205 | 63.4 | 65.8 | 69.3 |
| 210 | 65.0 | 67.2 | 71.2 |
| 215 | 66.3 | 68.5 | 72.5 |
| 220 | 67.4 | 69.8 | 74.2 |
| 225 | 68.4 | 71.0 | 75.0 |
| 230 | 69.5 | 72.2 | 76.4 |
| 235 | 70.9 | 73.4 | 77.9 |
| 240 | 72.0 | 74.6 | 78.8 |
| 245 | 73.2 | 75.6 | 79.8 |
| 250 | 74.6 | 76.5 | 80.8 |
| 255 | 75.7 | 77.5 | 81.5 |
| 260 | 76.4 | 78.6 | 82.1 |
| 265 | 77.5 | 79.6 | 83.5 |
| 270 | 78.6 | 80.6 | 84.6 |
| 275 | 79.9 | 82.0 | 86.0 |
| 280 | 80.6 | 82.6 | 87.0 |
| 285 | 81.8 | 83.5 | 88.0 |
| 290 | 83.0 | 84.5 | 88.8 |
| 295 | 84.2 | 85.9 | 90.0 |
| 300 | 85.4 | 87.0 | 91.1 |
| 305 | 86.4 | 88.3 | 92.5 |
| 310 | 87.2 | 89.9 | 93.9 |
| 315 | 88.1 | 91.5 | 95.1 |
| 320 | 88.4 | 92.3 | 96.0 |
| 325 | 89.0 | 93.0 | 96.9 |
| 330 | 89.1 | 93.5 | 96.9 |
| 335 | 89.7 | 94.1 | 96.8 |
| 340 | 89.5 | 94.2 | 96.7 |
| 345 | 89.8 | 94.6 | 96.7 |
| 350 | 90.7 | 95.1 | 96.7 |
| 355 | 90.7 | 95.6 | 97.1 |
| 360 | 91.2 | 96.0 | 97.2 |
| 365 | 91.5 | 95.8 | 97.3 |
| 370 | 91.7 | 95.9 | 97.4 |
| 375 | 92.2 | 96.0 | 97.9 |
| 380 | 92.0 | 95.9 | 98.4 |
| 385 | 92.2 | 96.0 | 98.4 |
| 390 | 91.8 | 95.9 | 98.2 |
| 395 | 92.8 | 96.6 | 98.4 |
| 400 | 93.5 | 97.2 | 99.3 |
| 405 | 94.1 | 97.5 | 99.8 |
| 410 | 94.9 | 98.5 | 100.1 |
| 415 | 95.5 | 98.9 | 100.7 |
| 420 | 96.1 | 99.2 | 101.7 |
| 425 | 96.2 | 99.7 | 101.5 |
| 430 | 97.1 | 100.0 | 102.2 |

TABLE I (*continued*)

| T (°K) | $C_p$ (J mole$^{-1}$ K$^{-1}$) | | |
|---|---|---|---|
| | $Li_{0.363}WO_3$ | $Li_{0.437}WO_3$ | $Li_{0.478}WO_3$ |
| 435 | 98.4 | 101.2 | 103.5 |
| 440 | 98.9 | 101.6 | 103.9 |
| 445 | 99.5 | 102.4 | 104.6 |
| 450 | 100.1 | 103.1 | 104.9 |
| 455 | 100.5 | 103.4 | 105.3 |
| 460 | 101.2 | 104.1 | 106.1 |
| 465 | 101.9 | 104.2 | 106.5 |
| 470 | 102.2 | 104.4 | 107.0 |
| 475 | 102.3 | 104.7 | 107.3 |
| 480 | 102.6 | 104.7 | 107.6 |
| 485 | 102.8 | 105.2 | 107.6 |
| 490 | 103.9 | 105.3 | 108.0 |
| 495 | 104.2 | 105.6 | 108.1 |
| 500 | 104.3 | 105.9 | 108.2 |
| 505 | 104.9 | 106.0 | 108.8 |
| 510 | 105.4 | 106.2 | 109.0 |
| 515 | 105.6 | 106.3 | 108.7 |
| 520 | 106.3 | 107.1 | 109.8 |
| 525 | 106.6 | 107.0 | 109.7 |
| 530 | 107.0 | 107.1 | 110.0 |
| 535 | 107.5 | 107.1 | 110.0 |
| 540 | 107.5 | 107.1 | 109.9 |
| 545 | 108.0 | 107.4 | 110.7 |
| 550 | 108.4 | 107.5 | 110.8 |
| 555 | 109.0 | 107.8 | 110.9 |
| 560 | 109.8 | 108.1 | 111.6 |
| 565 | 110.6 | 108.4 | 111.7 |
| 570 | 112.0 | 109.2 | 111.9 |
| 575 | 112.6 | 108.8 | 112.2 |
| 580 | 114.1 | 109.6 | 112.7 |
| 585 | 115.3 | 109.6 | 112.7 |
| 590 | 116.3 | 110.0 | 112.9 |
| 595 | 115.6 | 109.7 | 113.2 |
| 600 | 114.1 | 109.9 | 113.5 |
| 605 | 110.1 | 110.1 | 113.7 |
| 610 | 107.7 | 110.3 | 114.0 |
| 615 | 107.2 | 111.0 | 114.4 |
| 620 | 107.6 | 111.0 | 114.6 |
| 625 | 107.8 | 110.7 | 114.6 |
| 630 | 108.2 | 111.1 | 114.8 |
| 635 | 107.8 | 111.3 | 114.8 |
| 640 | 108.6 | 111.7 | 114.9 |
| 645 | 108.5 | 111.8 | 115.0 |
| 650 | 108.3 | 111.9 | 114.8 |
| 655 | 108.3 | 111.8 | 114.8 |
| 660 | 108.4 | 111.4 | 114.9 |
| 665 | 109.0 | 111.5 | 115.4 |
| 670 | 109.0 | 111.9 | 115.2 |
| 675 | 109.6 | 112.3 | 115.6 |

TABLE I (*continued*)

| T (°K) | $C_p$ (J mole$^{-1}$ K$^{-1}$) | | |
|---|---|---|---|
| | $Li_{0.363}WO_3$ | $Li_{0.437}WO_3$ | $Li_{0.478}WO_3$ |
| 680 | 109.2 | 112.5 | 115.6 |
| 685 | 109.2 | 112.2 | 116.1 |
| 690 | 109.4 | 112.8 | 116.3 |
| 695 | 109.5 | 112.7 | 115.8 |
| 700 | 110.6 | 112.4 | 116.3 |
| 705 | 110.4 | 112.8 | 116.1 |
| 710 | 110.7 | 113.1 | 116.4 |
| 715 | 110.4 | 113.0 | 116.6 |
| 720 | 110.4 | 113.5 | 116.9 |
| 725 | 110.8 | 113.4 | 117.4 |
| 730 | 110.9 | 113.7 | 117.0 |
| 735 | 111.9 | 114.4 | 117.6 |
| 740 | 111.4 | 114.1 | 117.7 |
| 745 | 111.6 | 114.2 | 117.8 |
| 750 | 111.6 | 114.3 | 118.2 |
| 755 | 111.4 | 114.5 | 118.0 |
| 760 | 111.6 | 114.6 | 118.4 |
| 765 | 111.8 | 114.7 | 118.4 |
| 770 | 111.8 | 114.9 | 118.7 |
| 775 | 111.8 | 114.8 | 118.6 |
| 780 | 112.4 | 115.0 | 118.8 |
| 785 | 112.0 | 114.9 | 119.0 |
| 790 | 112.4 | 115.0 | 118.8 |
| 795 | 112.6 | 115.1 | 119.1 |
| 800 | 112.3 | 115.2 | 119.2 |
| 805 | 112.7 | 115.4 | 119.4 |

around 330 and 460°K in $Li_{0.437}WO_3$ and $Li_{0.478}WO_3$, showing the second-order phase transitions. The baselines of the heat capacity curve were determined so as to join to one another in smooth lines across the whole temperature range and the enthalpy and entropy increments were calculated and are given in Table III.

Shanks *et al.* (*5*) measured the electrical resistivity of cubic lithium tungsten bronzes,

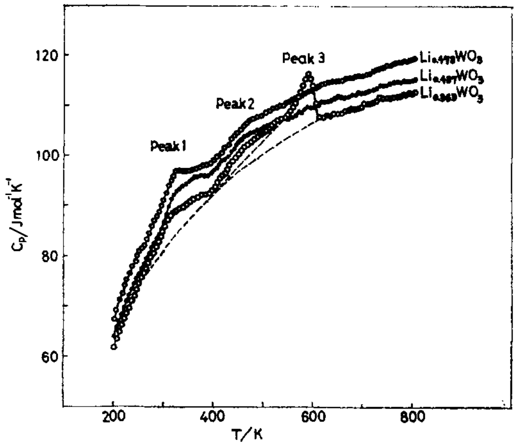


FIG. 1. Heat capacities of $Li_{0.363}WO_3$, $Li_{0.427}WO_3$, and $Li_{0.478}WO_3$.

$Li_{0.280}WO_3$ and $Li_{0.345}WO_3$, in the range 100 to 750°K. They found, in the case of $Li_{0.280}WO_3$, an increase in the slope of the electrical resistivity against temperature around 320°K and a rapid decrease in electrical resistivity around 600°K, but, in the case of $Li_{0.345}WO_3$, they found one anomaly in resistivity around 320°K.

Temperatures at which anomalies in electrical resistivity in $Li_{0.280}WO_3$ occur, 330 and 600°K, correspond to those at which heat capacity anomalies are observed in $Li_{0.363}WO_3$, 320 and 590°K. In the case of $Na_{0.8}WO_3$, Taylor and Weller (*6*) observed an increase in the slope of electrical resistivity against temperature similar to that in $Li_{0.280}WO_3$ around 320°K, and this increase in $Na_xWO_3$ was assumed to be caused by the increase in the number of slightly displaced atoms with respect to the ideal perovskite position (*2*). It may be concluded, therefore, that the heat capacity anomaly observed

TABLE II

HEAT CAPACITY OF $Li_xWO_3$ AND $Na_xWO_3$ PER GRAM-ATOM ($1/(4 + x)$ Mole)

| T (°K) | $C_p$ (J mole$^{-1}$ K$^{-1}$) | | | | | |
|---|---|---|---|---|---|---|
| | $Li_{0.363}WO_3$ | $Li_{0.478}WO_3$ | $Li_{0.478}WO_3$ | $Na_{0.485}WO_3$ | $Na_{0.698}WO_3$ | $Na_{0.794}WO_3$ |
| 700 | 25.34 | 25.33 | 25.97 | 25.06 | 25.03 | 25.07 |
| 800 | 25.74 | 25.96 | 26.62 | 25.69 | 25.52 | 26.62 |

TABLE III

ENTHALPY AND ENTROPY INCREMENTS FOR THE $\lambda$-TYPE TRANSITIONS IN $Li_xWO_3$

| | | $Li_{0.363}WO_3$ | $Li_{0.437}WO_3$ | $Li_{0.478}WO_3$ |
|---|---|---|---|---|
| Peak 1 | H (J mole$^{-1}$) | $433 \pm 9$ | $357 \pm 12$ | $449 \pm 12$ |
| | $S$ (J mole$^{-1}$ K$^{-1}$) | $1.36 \pm 0.03$ | $1.09 \pm 0.04$ | $1.42 \pm 0.04$ |
| Peak 2 | H (J mole$^{-1}$) | $211 \pm 10$ | $272 \pm 12$ | $236 \pm 10$ |
| | $S$ (J mole$^{-1}$ K$^{-1}$) | $0.45 \pm 0.03$ | $0.59 \pm 0.03$ | $0.50 \pm 0.03$ |
| Peak 3 | $H$ (J mole$^{-1}$) | $882 \pm 11$ | | |
| | $S$ (J mole$^{-1}$ K$^{-1}$) | $1.68 \pm 0.03$ | | |

around 330°K in $Li_{0.363}WO_3$ occurs in the same mechanism as the phase transition in $Na_xWO_3$.

The large anomalous peak observed around 590°K in $Li_{0.363}WO_3$ may correspond to the rapid decrease in electrical resistivity in $Li_{0.280}WO_3$. X-ray diffraction of the quenched sample from 750°K showed the same pattern as those measured at the room temperatures, showing no change in the main cubic structure during the transition. As was suggested by Shanks *et al.* (*5*), the order–disorder process of lithium atoms may be considered for the interpretation of this phase transition. The entropy change for the transition is calculated in the zeroth approximation for this order–disorder process as

$$\Delta S = -R(0.363 \ln 0.363 + 0.637 \ln 0.637) = 5.45 \text{ J mole}^{-1} \text{ K}^{-1}.$$

This value, however, is quite large compared with the observed one, 1.68 J mole$^{-1}$ K$^{-1}$, indicating that this cannot be interpreted as such a simple process.

The origins of heat capacity anomalies observed around 330 and 460°K in $Li_{0.437}WO_3$ and $Li_{0.478}WO_3$ are also not clear, and further investigations such as neutron diffraction, thermal conductivity, and NMR spin-lattice relaxation rate should be performed.

## References


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