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# New thermodynamic data for $CoTiO_3$, $NiTiO_3$ and $CoCO_3$ based on low-temperature calorimetric measurements

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## Abstract

The low-temperature heat capacities of nickel titanate ($NiTiO_3$), cobalt titanate ($CoTiO_3$), and cobalt carbonate ($CoCO_3$) were measured between 2 and 300 K, and thermochemical functions were derived from the results. Our new data show previously unknown low-temperature lambda-shaped heat capacity anomalies peaking at 37 K for $CoTiO_3$ and 26 K for $NiTiO_3$. From our data we calculate standard molar entropies (298.15 K) for $NiTiO_3$ of 90.9 ± 0.7 J $mol^{-1}$ $K^{-1}$ and for $CoTiO_3$ of 94.4 ± 0.8 J $mol^{-1}$ $K^{-1}$. For $CoCO_3$, we find only a small broad heat capacity anomaly, peaking at about 31 K. From our data, we suggest a new standard entropy (298.15 K) for $CoCO_3$ of 88.9 ± 0.7 J $mol^{-1}$ $K^{-1}$.

## Background

Nickel titanate ($NiTiO_3$) and cobalt titanate ($CoTiO_3$) belong to an important group of ilmenite-type transition metal bearing phases with a number of interesting magnetic and electric properties [1-5]. They are also important for technical applications due to their catalytic properties [6-8]. $CoCO_3$ is a phase with interesting magnetic properties, which has not been studied in detail [9-12]. Structures, phase relations and physical properties of these phases are well documented [5,9,13-21], there is, however, a lack of low-temperature calorimetric data and associated third-law entropies. Other transition metal bearing oxide phases have recently been shown to exhibit large, hitherto unknown low-temperature heat capacity anomalies [22-31] and the aim of this paper is to investigate low-temperature heat capacities for $NiTiO_3$, $CoTiO_3$, and $CoCO_3$. To our knowledge, for $NiTiO_3$, $CoTiO_3$, there are no reported low-temperature $C_P$ data published in the literature, and the only data for $CoCO_3$ date back to the 1960s.

## Experimental

### Samples

Heat capacity measurements were performed on synthetic polycrystalline $NiTiO_3$, $CoTiO_3$, and $CoCO_3$ samples. The $NiTiO_3$ and $CoTiO_3$ sample used in our study were synthesized from equimolar mixtures of CoO (Merck, 99.999% purity), NiO (Merck, 99.999% purity) and $TiO_2$ (Merck, 99.99% purity). The $TiO_2$ powder was previously fired at 1,000°C for 12 h to release any absorbed water or hydroxide. The oxides were mixed under acetone in an agate mortar and pestle for 15 min and subsequently pressed into several high density pellets of 3 mm diameter. $CoCO_3$ was purchased from Alfa Aesar (99.5% purity, metals based). X-ray diffraction indicated $CoCO_3$ only, with cell parameters of a = 4.662 ± 0.002 and c = 14.955 ± 0.005 Å. The $NiTiO_3$ and $CoTiO_3$ pellets were placed in a vertical drop furnace in a small, hand-crafted basket made of platinum wire, were fired in air at 1,150°C for 24 h, then slowly cooled to 1,000°C for 24 h, and further cooled to 900°C and held for another 24 h. The samples were then rapidly drop-quenched in distilled water and dried at 110°C for 1 h. X-ray diffraction indicated $CoTiO_3$ and $NiTiO_3$ only, no impurities or other unreacted oxides were detected. Our synthetic $CoTiO_3$ had cell parameters of a = 5.029 ± 0.004 and c = 13.79 ± 0.02 Å and the $NiTiO_3$ sample had cell parameters of a = 5.061 ± 0.006 and c = 13.91 ± 0.08 Å which compares well with previous results [1].

### Low-temperature calorimetry

The heat capacities were measured with a commercially available low temperature Quantum Design Physical Properties Measurement System (PPMS) at the University of Münster. The heat capacities were

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measured using the heat pulse method, measuring the response of the calorimeter to a heat pulse, which is evaluated as a function of time [32]. The accuracy of the method has been tested by several groups [33,34] who found that the PPMS is capable of reproducing heat capacities of reference materials to better than 1% at T > 100 K and around 3-5% at T < 100 K. We have performed further tests using the Münster PPMS, coming to the identical conclusions. Our measurements on synthetic $Al_2O_3$ (NIST SRM-720, [35]) are depicted in Figure 1. The data show that we reproduce the heat capacity of SRM-720 to better than 1% (with an average of 0.4%) at temperatures higher than 90 K, and around 4% at T < 90 K. Overall, the standard entropy of NIST SRM-720 corundum was reproduced with our calorimeter within 0.8%, a value which is used to estimate the overall uncertainty of our calculated standard entropy values.

For the actual measurements, the sample pellets were fixed onto a pre-calibrated sample holder using Apiezon N-Grease. To compensate for the heat capacity and anomalies caused by the grease [36], addenda measurements were first performed without the sample. These heat capacity values were then subtracted from the sample measurement. Heat capacities were measured from below 5 to 303 K in increments that varied between 0.5 and 20 K at the highest temperatures (Figure 1; Tables 1, 2 and 3).

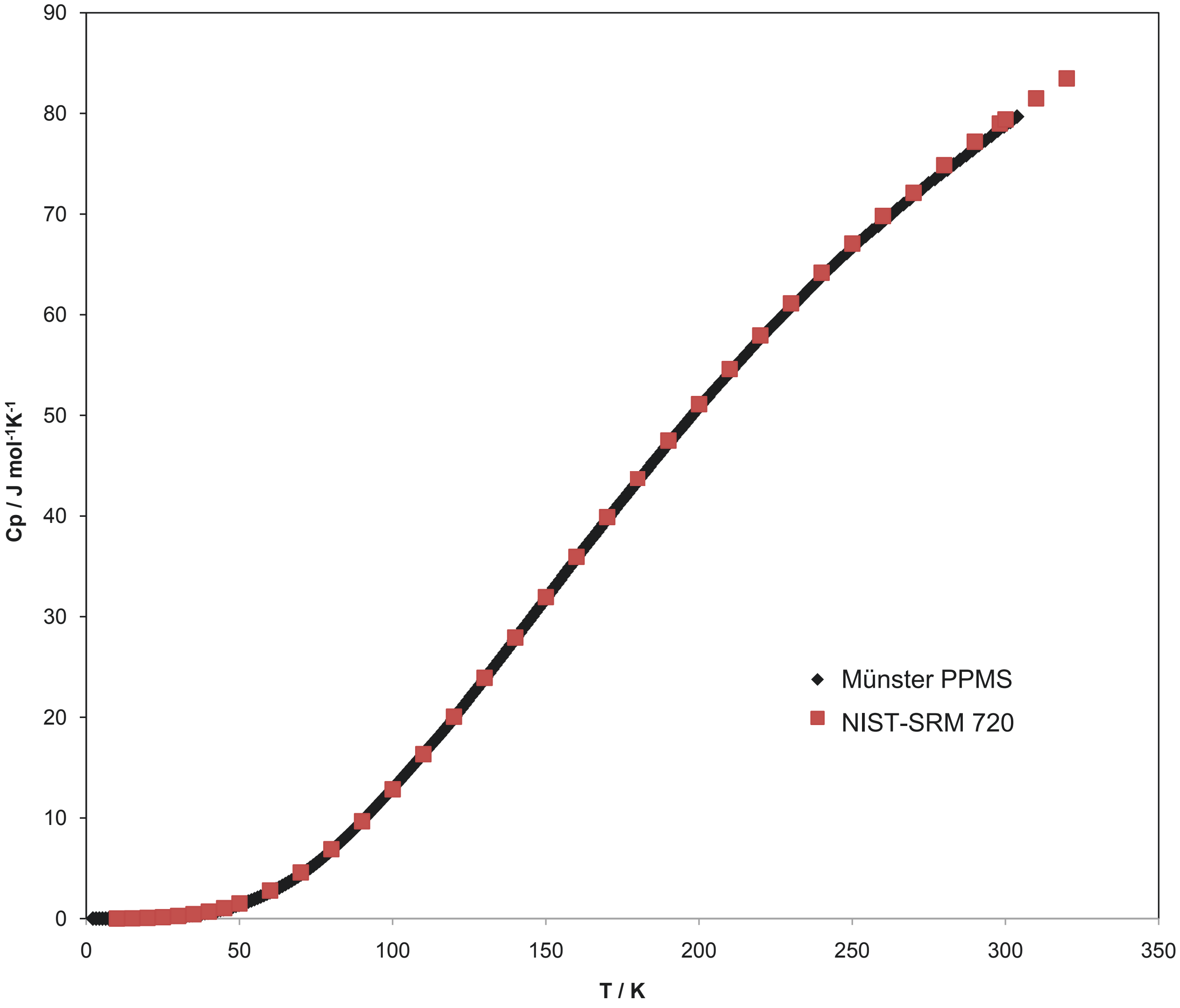

**Figure 1** Comparison of published heat capacities of NIST SRM-720 (Ditmars et al. 1982) with PPMS measurements done at Münster University.

**Table 1 Experimental Molar Heat Capacities for $NiTiO_3$**

| T K | Cp J mol$^{-1}$ K$^{-1}$ | T K | Cp J mol$^{-1}$ K$^{-1}$ | T K | Cp J mol$^{-1}$ K$^{-1}$ | T K | Cp J mol$^{-1}$ K$^{-1}$ | T K | Cp J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| 2.70 | 0.02 | 51.0 | 7.45 | 163.1 | 59.1 | 274.7 | 88.7 | 21.0 | 15.2 |
| 3.24 | 0.05 | 53.0 | 8.21 | 165.1 | 59.9 | 276.7 | 89.1 | 21.6 | 16.6 |
| 3.78 | 0.09 | 55.0 | 9.01 | 167.2 | 60.6 | 278.7 | 89.4 | 22.1 | 18.6 |
| 4.32 | 0.18 | 57.1 | 9.81 | 169.2 | 61.3 | 280.7 | 89.8 | 22.6 | 13.9 |
| 4.84 | 0.29 | 59.1 | 10.6 | 171.2 | 62.0 | 282.7 | 90.0 | 23.0 | 6.4 |
| 5.37 | 0.45 | 61.2 | 11.5 | 173.3 | 62.8 | 284.8 | 90.3 | 23.6 | 4.8 |
| 5.90 | 0.65 | 63.2 | 12.3 | 175.3 | 63.5 | 286.8 | 90.6 | 24.1 | 4.0 |
| 6.43 | 0.88 | 65.3 | 13.2 | 177.3 | 64.3 | 288.8 | 91.0 | 24.6 | 3.5 |
| 6.95 | 1.15 | 67.3 | 14.2 | 179.3 | 64.9 | 290.9 | 91.3 | 25.2 | 3.2 |
| 7.45 | 1.44 | 69.4 | 15.1 | 181.4 | 65.6 | 292.9 | 91.6 | 25.7 | 3.0 |
| 7.98 | 1.77 | 71.4 | 16.1 | 183.4 | 66.3 | 294.9 | 91.9 | 26.2 | 2.8 |
| 8.20 | 1.91 | 73.4 | 17.1 | 185.4 | 66.9 | 296.9 | 92.1 | 26.7 | 2.7 |
| 9.20 | 2.60 | 75.5 | 18.2 | 187.4 | 67.7 | 299.0 | 92.4 | 27.3 | 2.6 |
| 10.2 | 3.35 | 77.5 | 19.2 | 189.5 | 68.3 | 301.0 | 92.5 | 27.8 | 2.5 |
| 11.2 | 4.14 | 79.6 | 20.3 | 191.5 | 69.0 | 303.1 | 92.7 | 28.3 | 2.5 |
| 12.2 | 4.97 | 81.6 | 21.4 | 193.5 | 69.6 | | | 28.8 | 2.5 |
| 13.2 | 5.84 | 83.6 | 22.5 | 195.6 | 70.3 | Series 2 | | 29.3 | 2.5 |
| 14.2 | 6.72 | 85.7 | 23.6 | 197.6 | 70.9 | T | Cp | 29.9 | 2.5 |
| 15.2 | 7.72 | 87.7 | 24.7 | 199.6 | 71.6 | K | J mol$^{-1}$ K$^{-1}$ | 30.4 | 2.5 |
| 16.2 | 8.70 | 89.8 | 25.7 | 201.7 | 72.2 | 2.17 | 0.010 | 30.9 | 2.5 |
| 17.2 | 9.76 | 91.8 | 26.8 | 203.7 | 72.8 | 2.70 | 0.023 | 31.4 | 2.6 |
| 18.2 | 10.91 | 93.8 | 27.9 | 205.7 | 73.3 | 3.24 | 0.048 | 32.0 | 2.6 |
| 19.2 | 12.17 | 95.9 | 29.0 | 207.8 | 73.9 | 3.78 | 0.094 | 32.5 | 2.7 |
| 20.2 | 13.69 | 97.9 | 30.0 | 209.8 | 74.5 | 4.32 | 0.18 | 33.0 | 2.7 |
| 21.2 | 15.61 | 100.0 | 31.0 | 211.8 | 75.1 | 4.84 | 0.29 | 33.5 | 2.8 |
| 22.1 | 19.00 | 102.0 | 32.0 | 213.9 | 75.7 | 5.37 | 0.45 | 34.0 | 2.9 |
| 23.1 | 5.92 | 104.0 | 33.0 | 215.9 | 76.3 | 5.90 | 0.65 | 34.5 | 3.0 |
| 24.1 | 4.04 | 106.1 | 33.9 | 217.9 | 76.8 | 6.43 | 0.88 | 35.1 | 3.0 |
| 25.1 | 3.25 | 108.1 | 34.9 | 219.9 | 77.4 | 7.0 | 1.2 | 35.6 | 3.1 |
| 26.1 | 2.84 | 110.1 | 35.9 | 222.0 | 77.9 | 7.5 | 1.4 | 36.1 | 3.2 |
| 27.1 | 2.62 | 112.2 | 36.8 | 224.0 | 78.4 | 8.0 | 1.8 | 36.6 | 3.3 |
| 28.1 | 2.50 | 114.2 | 37.7 | 226.0 | 78.9 | 8.5 | 2.1 | 37.1 | 3.4 |
| 29.1 | 2.46 | 116.3 | 38.6 | 228.0 | 79.4 | 9.0 | 2.5 | 37.7 | 3.5 |
| 30.1 | 2.48 | 118.3 | 39.5 | 230.1 | 79.9 | 9.5 | 2.9 | 38.2 | 3.7 |
| 31.1 | 2.53 | 120.3 | 40.5 | 232.1 | 80.3 | 10.1 | 3.3 | 38.7 | 3.8 |
| 32.1 | 2.62 | 122.4 | 41.4 | 234.1 | 80.8 | 10.6 | 3.6 | 39.2 | 3.9 |
| 33.1 | 2.74 | 124.4 | 42.4 | 236.2 | 81.3 | 11.1 | 4.1 | 39.7 | 4.0 |
| 34.0 | 2.87 | 126.5 | 43.4 | 238.2 | 81.8 | 11.6 | 4.5 | 40.3 | 4.1 |
| 35.0 | 3.03 | 128.5 | 44.3 | 240.2 | 82.3 | 12.2 | 5.0 | 40.8 | 4.2 |
| 36.0 | 3.21 | 130.5 | 45.3 | 242.3 | 82.8 | 12.7 | 5.4 | | |
| 37.0 | 3.40 | 132.6 | 46.1 | 244.3 | 83.2 | 13.2 | 5.9 | | |
| 38.0 | 3.61 | 134.6 | 47.1 | 246.3 | 83.6 | 13.7 | 6.3 | | |
| 39.0 | 3.83 | 136.6 | 48.0 | 248.4 | 84.0 | 14.3 | 6.8 | | |
| 40.0 | 4.05 | 138.7 | 48.9 | 250.4 | 84.4 | 14.8 | 7.3 | | |
| 41.0 | 4.30 | 140.7 | 49.8 | 252.4 | 84.8 | 15.3 | 7.8 | | |
| 42.0 | 4.56 | 142.7 | 50.7 | 254.4 | 85.2 | 15.8 | 8.3 | | |
| 43.0 | 4.85 | 144.8 | 51.6 | 256.5 | 85.6 | 16.3 | 8.9 | | |
| 44.0 | 5.15 | 146.8 | 52.4 | 258.5 | 85.9 | 16.9 | 9.4 | | |
| 45.0 | 5.46 | 148.8 | 53.3 | 260.5 | 86.3 | 17.4 | 10.0 | | |
| 46.0 | 5.77 | 150.9 | 54.2 | 262.6 | 86.7 | 17.9 | 10.6 | | |

**Table 1 Experimental Molar Heat Capacities for $NiTiO_3$** *(Continued)*

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 47.0 | 6.09 | 152.9 | 55.0 | 264.6 | 87.0 | 18.4 | 11.2 |
| 48.0 | 6.41 | 155.0 | 55.9 | 266.6 | 87.4 | 18.9 | 11.8 |
| 49.0 | 6.74 | 157.0 | 56.7 | 268.6 | 87.7 | 19.5 | 12.6 |
| 49.9 | 7.08 | 159.0 | 57.5 | 270.6 | 88.0 | 20.0 | 13.3 |
| 50.9 | 7.47 | 161.1 | 58.3 | 272.6 | 88.4 | 20.5 | 14.2 |

**Table 2 Experimental Molar Heat Capacities for $CoTiO_3$**

| $\frac{T}{\mathrm{K}}$ | $\frac{C_P}{\mathrm{J\,mol^{-1}K^{-1}}}$ | $\frac{T}{\mathrm{K}}$ | $\frac{C_P}{\mathrm{J\,mol^{-1}K^{-1}}}$ | $\frac{T}{\mathrm{K}}$ | $\frac{C_P}{\mathrm{J\,mol^{-1}K^{-1}}}$ | $\frac{T}{\mathrm{K}}$ | $\frac{C_P}{\mathrm{J\,mol^{-1}K^{-1}}}$ | $\frac{T}{\mathrm{K}}$ | $\frac{C_P}{\mathrm{J\,mol^{-1}K^{-1}}}$ | $\frac{T}{\mathrm{K}}$ | $\frac{C_P}{\mathrm{J\,mol^{-1}K^{-1}}}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2.17 | 0.002 | 95.0 | 34.89 | 127.2 | 49.74 | 155.3 | 61.01 | 8.15 | 0.093 | 46.7 | 9.6 |
| 3.92 | 0.006 | 96.7 | 35.78 | 127.7 | 49.95 | 155.8 | 61.22 | 9.14 | 0.15 | 47.2 | 9.8 |
| 5.65 | 0.022 | 98.3 | 36.62 | 128.2 | 50.17 | 156.3 | 61.40 | 10.12 | 0.22 | 47.8 | 10.0 |
| 7.34 | 0.065 | 100.0 | 37.42 | 128.7 | 50.37 | 156.8 | 61.56 | 11.1 | 0.31 | 48.3 | 10.1 |
| 9.04 | 0.131 | 101.6 | 38.00 | 129.3 | 50.62 | 157.3 | 61.79 | 12.1 | 0.43 | 48.8 | 10.3 |
| 10.8 | 0.286 | 101.7 | 38.25 | 129.8 | 50.85 | 157.8 | 61.92 | 13.1 | 0.58 | 49.3 | 10.5 |
| 12.4 | 0.491 | 102.2 | 38.49 | 130.3 | 51.07 | 158.3 | 62.13 | 14.1 | 0.75 | 49.8 | 10.7 |
| 14.2 | 0.774 | 102.7 | 38.73 | 130.8 | 51.24 | 158.9 | 62.31 | 15.1 | 0.95 | 50.3 | 10.9 |
| 15.8 | 1.14 | 103.2 | 39.01 | 131.3 | 51.46 | 159.4 | 62.47 | 16.0 | 1.17 | 50.9 | 11.1 |
| 17.5 | 1.59 | 103.7 | 39.22 | 131.8 | 51.70 | 159.9 | 62.67 | 17.0 | 1.42 | 51.4 | 11.4 |
| 19.2 | 2.11 | 104.2 | 39.47 | 132.3 | 51.89 | 160.4 | 62.85 | 18.0 | 1.70 | 51.9 | 11.6 |
| 20.9 | 2.73 | 104.8 | 39.73 | 132.8 | 52.12 | 160.9 | 63.01 | 19.0 | 2.01 | 52.4 | 11.8 |
| 22.6 | 3.44 | 105.3 | 39.95 | 133.3 | 52.35 | 161.4 | 63.20 | 20.0 | 2.35 | 52.9 | 12.0 |
| 24.3 | 4.23 | 105.8 | 40.18 | 133.8 | 52.58 | 161.9 | 63.33 | 20.9 | 2.71 | 53.4 | 12.3 |
| 26.0 | 5.11 | 106.3 | 40.45 | 134.3 | 52.80 | 162.4 | 63.34 | 21.9 | 3.11 | 53.9 | 12.5 |
| 27.7 | 6.11 | 106.8 | 40.69 | 134.9 | 52.96 | 162.4 | 63.46 | 22.9 | 3.55 | 54.5 | 12.7 |
| 29.3 | 7.18 | 107.3 | 40.91 | 135.4 | 53.19 | 167.3 | 65.01 | 23.9 | 4.02 | 55.0 | 13.0 |
| 31.0 | 8.38 | 107.8 | 41.17 | 135.9 | 53.42 | 172.2 | 66.53 | 24.9 | 4.49 | 55.5 | 13.2 |
| 32.7 | 9.77 | 108.3 | 41.38 | 136.4 | 53.61 | 177.0 | 68.01 | 25.8 | 5.00 | 56.0 | 13.5 |
| 34.4 | 11.32 | 108.8 | 41.63 | 136.9 | 53.83 | 181.9 | 69.38 | 26.8 | 5.54 | 56.5 | 13.7 |
| 36.1 | 13.20 | 109.3 | 41.86 | 137.4 | 54.11 | 186.8 | 70.68 | 27.8 | 6.11 | 57.0 | 14.0 |
| 37.6 | 14.08 | 109.9 | 42.07 | 137.9 | 54.30 | 191.6 | 72.00 | 28.8 | 6.77 | 57.6 | 14.2 |
| 39.4 | 10.69 | 110.4 | 42.32 | 138.4 | 54.48 | 196.5 | 73.31 | 29.7 | 7.38 | 58.1 | 14.5 |
| 41.1 | 9.24 | 110.9 | 42.52 | 138.9 | 54.73 | 201.4 | 74.40 | 30.6 | 7.82 | 58.6 | 14.7 |
| 42.8 | 8.97 | 111.4 | 42.75 | 139.5 | 54.88 | 206.2 | 75.52 | 30.7 | 8.12 | 59.1 | 14.9 |
| 44.5 | 9.13 | 111.9 | 42.96 | 140.0 | 55.10 | 211.1 | 76.59 | 31.2 | 8.50 | 59.6 | 15.2 |
| 46.2 | 9.51 | 112.4 | 43.16 | 140.5 | 55.34 | 216.0 | 77.77 | 31.8 | 8.91 | 60.1 | 15.4 |
| 47.9 | 10.02 | 112.9 | 43.41 | 141.0 | 55.54 | 220.8 | 78.73 | 32.3 | 9.33 | 60.6 | 15.7 |
| 49.6 | 10.64 | 113.4 | 43.58 | 141.5 | 55.76 | 225.7 | 79.58 | 32.8 | 9.75 | 61.2 | 15.9 |
| 51.3 | 11.31 | 113.9 | 43.77 | 142.0 | 55.97 | 230.5 | 80.34 | 33.3 | 10.2 | | |
| 52.9 | 12.05 | 114.5 | 43.99 | 142.5 | 56.16 | 235.4 | 81.07 | 33.8 | 10.7 | | |
| 54.6 | 12.84 | 115.0 | 44.20 | 143.0 | 56.35 | 240.3 | 81.96 | 34.3 | 11.2 | | |
| 56.3 | 13.62 | 115.5 | 44.44 | 143.5 | 56.51 | 245.2 | 82.62 | 34.8 | 11.7 | | |
| 58.0 | 14.43 | 116.0 | 44.67 | 144.0 | 56.73 | 250.0 | 83.15 | 35.4 | 12.3 | | |
| 59.7 | 15.21 | 116.5 | 44.89 | 144.6 | 56.95 | 254.9 | 83.70 | 35.9 | 13.0 | | |
| 61.4 | 16.04 | 117.0 | 45.14 | 145.1 | 57.15 | 259.8 | 84.11 | 36.4 | 13.8 | | |
| 63.0 | 16.88 | 117.5 | 45.35 | 145.6 | 57.36 | 264.6 | 84.53 | 36.9 | 14.5 | | |
| 64.7 | 17.75 | 118.0 | 45.59 | 146.1 | 57.55 | 269.4 | 85.05 | 37.4 | 14.6 | | |
| 66.4 | 18.62 | 118.5 | 45.79 | 146.6 | 57.71 | 274.3 | 85.48 | 37.9 | 13.8 | | |
| 68.1 | 19.51 | 119.1 | 46.06 | 147.1 | 57.93 | 279.1 | 85.82 | 38.4 | 12.6 | | |
| 69.8 | 20.41 | 119.6 | 46.26 | 147.6 | 58.11 | 284.0 | 86.18 | 38.9 | 11.5 | | |
| 71.5 | 21.33 | 120.1 | 46.49 | 148.1 | 58.31 | 288.8 | 86.29 | 39.4 | 10.7 | | |

**Table 2 Experimental Molar Heat Capacities for $CoTiO_3$** *(Continued)*

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 73.1 | 22.33 | 120.6 | 46.74 | 148.6 | 58.52 | 293.7 | 86.52 | 40.0 | 10.0 |
| 74.8 | 23.30 | 121.1 | 46.99 | 149.2 | 58.75 | 298.6 | 86.80 | 40.5 | 9.6 |
| 76.5 | 24.26 | 121.6 | 47.21 | 149.7 | 58.92 | 304.3 | 90.15 | 41.0 | 9.3 |
| 78.2 | 25.27 | 122.1 | 47.45 | 150.2 | 59.13 | | | 41.5 | 9.1 |
| 79.9 | 26.29 | 122.6 | 47.70 | 150.7 | 59.31 | Series 2 | | 42.1 | 9.0 |
| 81.5 | 27.25 | 123.1 | 47.93 | 151.2 | 59.51 | T | Cp | 42.6 | 9.0 |
| 83.2 | 28.24 | 123.6 | 48.14 | 151.7 | 59.69 | K | J $mol^{-1}K^{-1}$ | 43.1 | 9.0 |
| 84.9 | 29.21 | 124.2 | 48.41 | 152.2 | 59.88 | 2.24 | 0.0018 | 43.6 | 9.0 |
| 86.6 | 30.21 | 124.7 | 48.62 | 152.7 | 60.06 | 3.19 | 0.0034 | 44.1 | 9.1 |
| 88.3 | 31.13 | 125.2 | 48.88 | 153.2 | 60.24 | 4.20 | 0.0085 | 44.7 | 9.2 |
| 89.9 | 32.06 | 125.7 | 49.07 | 153.7 | 60.44 | 5.20 | 0.0164 | 45.2 | 9.3 |
| 91.6 | 33.05 | 126.2 | 49.30 | 154.3 | 60.65 | 6.19 | 0.0285 | 45.7 | 9.4 |
| 93.3 | 33.99 | 126.7 | 49.49 | 154.8 | 60.86 | 7.21 | 0.0572 | 46.2 | 9.5 |

**Table 3 Experimental Molar Heat Capacities for $CoCO_3$**

| T<br>K | Cp<br>J $mol^{-1}K^{-1}$ | T<br>K | Cp<br>J $mol^{-1}K^{-1}$ | T<br>K | Cp<br>J $mol^{-1}K^{-1}$ | T<br>K | Cp<br>J $mol^{-1}K^{-1}$ |
|---|---|---|---|---|---|---|---|
| 2.21 | 0.02 | 24.8 | 3.23 | 47.3 | 10.17 | 282.8 | 82.56 |
| 2.60 | 0.03 | 25.2 | 3.28 | 47.7 | 10.35 | 287.9 | 83.26 |
| 3.01 | 0.04 | 25.6 | 3.34 | 48.1 | 10.54 | 293.0 | 83.84 |
| 3.43 | 0.06 | 26.0 | 3.39 | 48.5 | 10.72 | 298.1 | 84.79 |
| 3.86 | 0.08 | 26.4 | 3.45 | 48.9 | 10.90 | 304.0 | 86.19 |
| 4.27 | 0.11 | 26.8 | 3.52 | 49.3 | 11.08 | | |
| 4.68 | 0.15 | 27.2 | 3.58 | 49.7 | 11.29 | | |
| 5.10 | 0.19 | 27.7 | 3.68 | 50.1 | 11.47 | | |
| 5.51 | 0.24 | 28.1 | 3.77 | 50.5 | 11.66 | | |
| 5.92 | 0.33 | 28.5 | 3.84 | 50.8 | 11.67 | | |
| 6.34 | 0.39 | 28.9 | 3.92 | 51.0 | 11.93 | | |
| 6.75 | 0.45 | 29.3 | 4.00 | 56.1 | 14.51 | | |
| 7.18 | 0.52 | 29.7 | 4.09 | 61.3 | 17.03 | | |
| 7.54 | 0.58 | 30.1 | 4.20 | 66.5 | 19.66 | | |
| 7.95 | 0.73 | 30.5 | 4.31 | 71.7 | 22.30 | | |
| 8.35 | 0.81 | 30.9 | 4.39 | 76.8 | 25.28 | | |
| 8.76 | 0.90 | 31.3 | 4.48 | 82.0 | 28.12 | | |
| 9.17 | 0.99 | 31.8 | 4.57 | 87.2 | 30.85 | | |
| 9.58 | 1.08 | 32.2 | 4.68 | 92.3 | 33.40 | | |
| 9.99 | 1.30 | 32.6 | 4.80 | 97.5 | 35.82 | | |
| 10.4 | 1.41 | 33.0 | 4.92 | 102.7 | 37.95 | | |
| 10.8 | 1.53 | 33.4 | 5.01 | 107.8 | 39.99 | | |
| 11.2 | 1.64 | 33.8 | 5.14 | 113.0 | 41.75 | | |
| 11.6 | 1.90 | 34.2 | 5.26 | 118.2 | 43.56 | | |
| 12.0 | 2.06 | 34.6 | 5.40 | 123.3 | 45.43 | | |
| 12.5 | 2.20 | 35.0 | 5.50 | 128.5 | 47.20 | | |
| 12.9 | 2.50 | 35.4 | 5.59 | 133.6 | 48.95 | | |
| 13.3 | 2.66 | 35.8 | 5.71 | 138.8 | 50.65 | | |
| 13.7 | 2.83 | 36.2 | 5.83 | 144.0 | 52.24 | | |
| 14.1 | 3.15 | 36.7 | 6.00 | 149.1 | 53.85 | | |
| 14.5 | 3.26 | 37.0 | 6.13 | 154.3 | 55.46 | | |
| 14.9 | 3.22 | 37.5 | 6.25 | 159.5 | 56.93 | | |
| 15.3 | 3.05 | 37.9 | 6.40 | 164.6 | 58.27 | | |
| 15.7 | 2.91 | 38.3 | 6.57 | 169.8 | 59.60 | | |

**Table 3 Experimental Molar Heat Capacities for $CoCO_3$** *(Continued)*

| | | | | | |
|---|---|---|---|---|---|
| 16.1 | 2.82 | 38.7 | 6.68 | 174.9 | 60.84 |
| 16.6 | 2.76 | 39.1 | 6.79 | 180.1 | 62.22 |
| 17.0 | 2.71 | 39.5 | 6.94 | 185.2 | 63.43 |
| 17.4 | 2.69 | 39.9 | 7.11 | 190.3 | 64.64 |
| 17.8 | 2.67 | 40.3 | 7.25 | 195.5 | 65.84 |
| 18.2 | 2.66 | 40.7 | 7.39 | 200.6 | 66.91 |
| 18.6 | 2.66 | 41.1 | 7.55 | 205.8 | 68.13 |
| 19.0 | 2.67 | 41.5 | 7.72 | 210.9 | 69.25 |
| 19.4 | 2.67 | 42.0 | 7.88 | 216.1 | 70.36 |
| 19.8 | 2.69 | 42.4 | 8.05 | 221.2 | 71.34 |
| 20.3 | 2.77 | 42.8 | 8.23 | 226.4 | 72.16 |
| 20.7 | 2.80 | 43.2 | 8.40 | 231.5 | 73.25 |
| 21.1 | 2.82 | 43.6 | 8.57 | 236.6 | 74.31 |
| 21.5 | 2.85 | 44.0 | 8.74 | 241.8 | 75.37 |
| 21.9 | 2.88 | 44.4 | 8.90 | 247.0 | 76.42 |
| 22.3 | 2.91 | 44.8 | 9.10 | 252.1 | 77.36 |
| 22.7 | 2.96 | 45.2 | 9.26 | 257.2 | 78.22 |
| 23.1 | 3.00 | 45.6 | 9.42 | 262.4 | 79.16 |
| 23.5 | 3.03 | 46.1 | 9.62 | 267.5 | 80.16 |
| 24.0 | 3.09 | 46.5 | 9.80 | 272.6 | 81.02 |
| 24.4 | 3.18 | 46.9 | 9.98 | 277.7 | 81.90 |

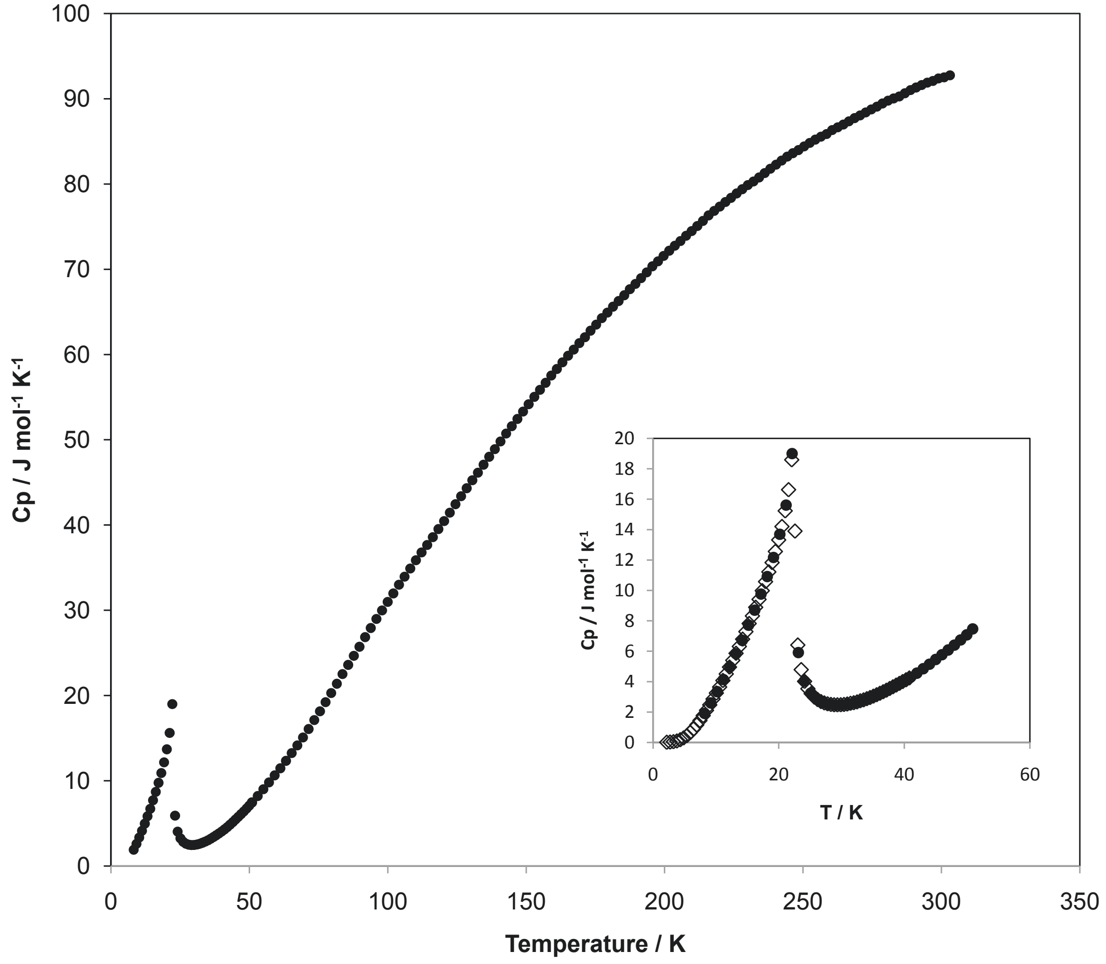

**Figure 2 Low-temperature heat capacity data for $NiTiO_3$**. The insert shows results from two scans done at low temperatures.

## Results and Discussion

The experimental values for the low-temperature heat capacity of $NiTiO_3$, $CoTiO_3$ and $CoCO_3$ are compiled in Tables 1, 2 and 3.

Figures 2, 3, and 4 depict the heat capacity of $NiTiO_3$, $CoTiO_3$ and $CoCO_3$ as a function of temperature. The data for $NiTiO_3$ and $CoTiO_3$ were recorded in two scans, the first one ranging from about 1.5 to about 60 K, the other scan continuously up to room temperature. Figures 2 and 3 show excellent agreement between the two separate measurements. The data for $CoCO_3$ were collected in only one scan, as only a broad low-temperature anomaly was found (Figure 4).

The standard entropies at 298.15 K ($S_{298}$) were calculated from the $C_P$ data (using a $T^3$ extrapolation to 0 K) and resulted in $S_{298}$ = 90.9 ± 0.7 J $mol^{-1}$ $K^{-1}$ for $NiTiO_3$, 94.4 ± 0.8 J $mol^{-1}$ $K^{-1}$ for $CoTiO_3$ and 88.9 ± 0.7 J $mol^{-1}$ $K^{-1}$ for $CoCO_3$ (Tables 4, 5 and 6). Our data for $S_{298}$ are

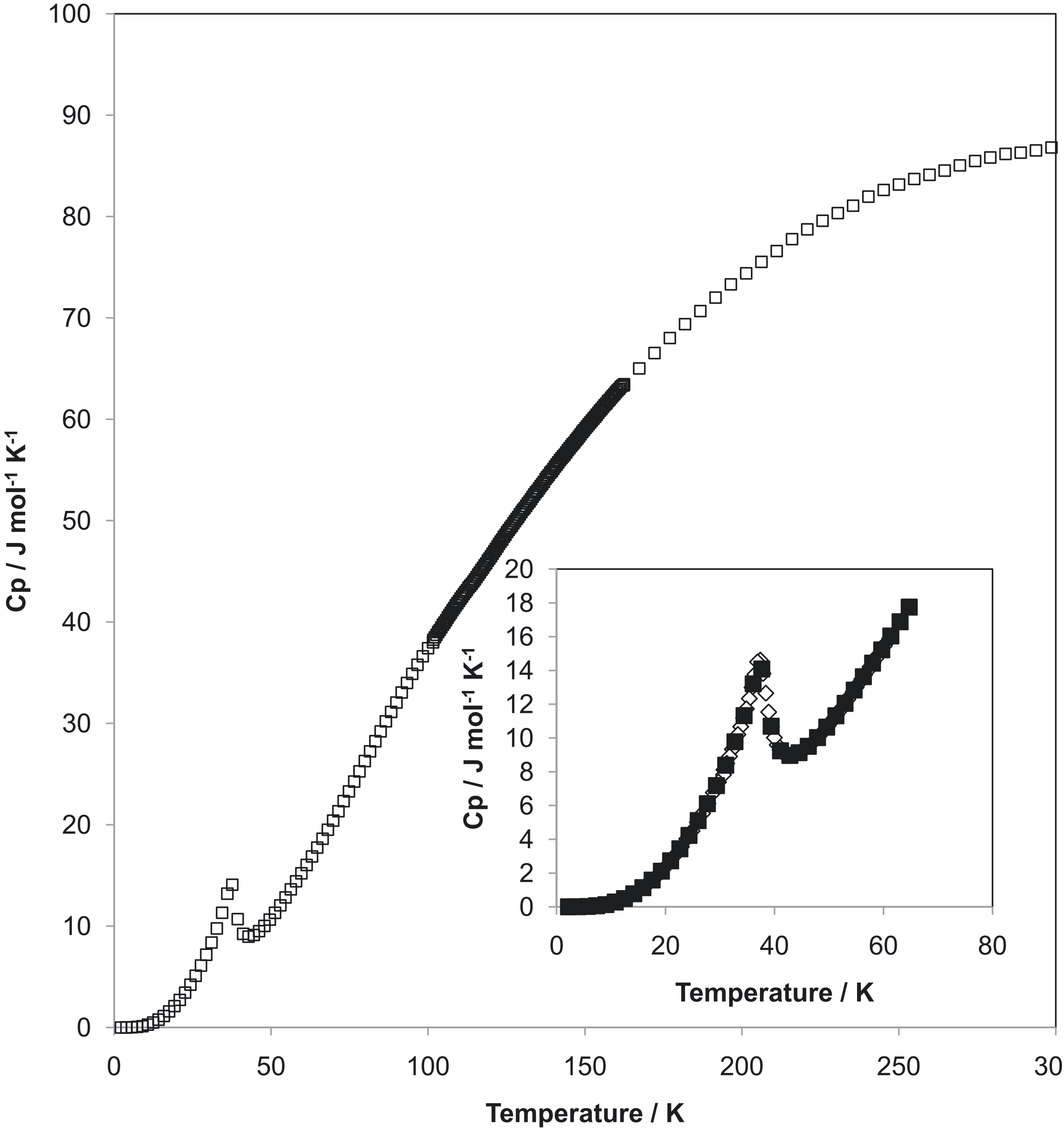

**Figure 3 Low-temperature heat capacity data for $CoTiO_3$**. The insert shows results from two scans done at low temperatures.

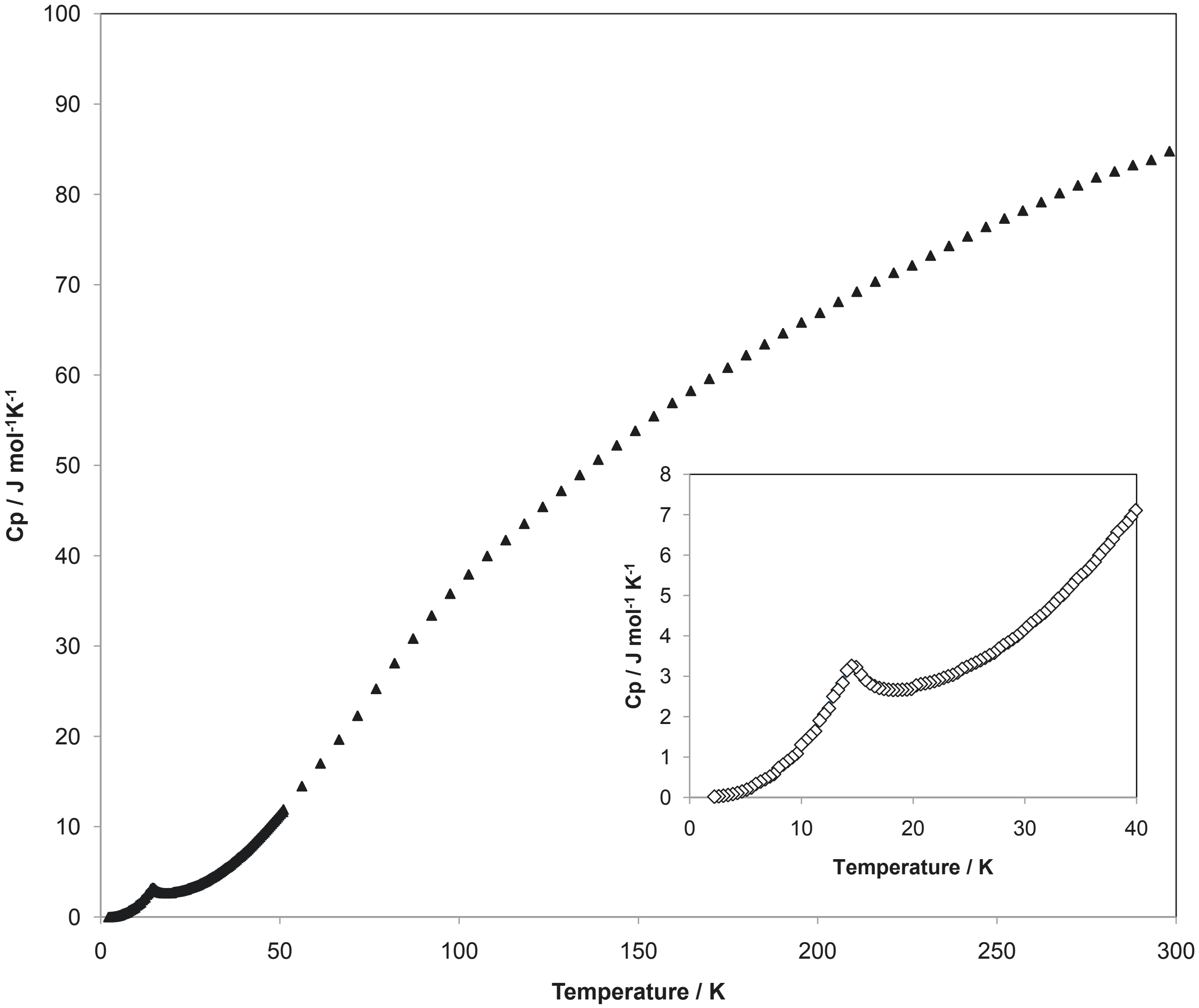

**Figure 4** Low-temperature heat capacity data for $CoCO_3$.

**Table 4 Thermodynamic properties at selected temperatures for $NiTiO_3$**

| T<br>K | Cp<br>$J\ mol^{-1}K^{-1}$ | Cp/T<br>$J\ mol^{-1}\ K^{-2}$ | S (T)<br>$J\ mol^{-1}\ K^{-1}$ |
|---|---|---|---|
| 300 | 92.4 | 0.308 | 91.5 |
| 298.15 | 92.3 | 0.309 | 90.9 |
| 290 | 91.2 | 0.314 | 88.4 |
| 280 | 89.7 | 0.320 | 85.2 |
| 270 | 87.9 | 0.326 | 82.0 |
| 260 | 86.2 | 0.332 | 78.7 |
| 250 | 84.3 | 0.337 | 75.3 |
| 240 | 82.2 | 0.343 | 71.9 |
| 230 | 79.9 | 0.347 | 68.5 |
| 220 | 77.4 | 0.352 | 65.0 |
| 210 | 74.5 | 0.355 | 61.4 |
| 200 | 71.7 | 0.358 | 57.9 |
| 190 | 68.5 | 0.360 | 54.3 |

**Table 4 Thermodynamic properties at selected temperatures for NiTiO$_3$** *(Continued)*

| | | | |
|---|---|---|---|
| 180 | 65.1 | 0.362 | 50.7 |
| 170 | 61.6 | 0.362 | 47.1 |
| 160 | 57.9 | 0.362 | 43.4 |
| 150 | 53.8 | 0.359 | 39.8 |
| 140 | 49.5 | 0.354 | 36.3 |
| 130 | 45.0 | 0.346 | 32.8 |
| 120 | 40.3 | 0.336 | 29.3 |
| 110 | 35.8 | 0.325 | 26.0 |
| 100 | 31.0 | 0.310 | 22.9 |
| 90 | 25.9 | 0.287 | 19.9 |
| 80 | 20.5 | 0.257 | 17.1 |
| 70 | 15.4 | 0.220 | 14.8 |
| 60 | 11.0 | 0.183 | 12.7 |
| 50 | 7.11 | 0.142 | 11.1 |
| 40 | 4.05 | 0.101 | 9.89 |
| 30 | 2.48 | 0.083 | 9.01 |
| 20 | 13.4 | 0.672 | 6.03 |
| 15 | 7.53 | 0.502 | 3.13 |
| 10 | 3.20 | 0.320 | 1.05 |
| 5 | 4.15 | 0.830 | 0.080 |

**Table 5 Thermodynamic properties at selected temperatures for CoTiO$_3$**

| T K | Cp J mol$^{-1}$K$^{-1}$ | Cp/T J mol$^{-1}$ K$^{-2}$ | S (T) J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|
| 300 | 87.6 | 0.292 | 95.0 |
| 298.15 | 86.8 | 0.291 | 94.4 |
| 290 | 86.3 | 0.298 | 92.0 |
| 280 | 85.9 | 0.307 | 89.0 |
| 270 | 85.1 | 0.315 | 85.9 |
| 260 | 84.1 | 0.324 | 82.7 |
| 250 | 83.1 | 0.333 | 79.4 |
| 240 | 81.9 | 0.341 | 76.1 |
| 230 | 80.3 | 0.349 | 72.6 |
| 220 | 78.6 | 0.357 | 69.1 |
| 210 | 76.3 | 0.364 | 65.5 |
| 200 | 74.1 | 0.370 | 61.8 |
| 190 | 71.6 | 0.377 | 58.1 |
| 180 | 68.9 | 0.383 | 54.3 |
| 170 | 65.9 | 0.387 | 50.4 |
| 160 | 62.7 | 0.392 | 46.5 |
| 150 | 59.1 | 0.394 | 42.6 |
| 140 | 55.1 | 0.394 | 38.7 |
| 130 | 51.0 | 0.392 | 34.7 |
| 120 | 46.5 | 0.387 | 30.8 |
| 110 | 42.1 | 0.383 | 27.0 |
| 100 | 37.4 | 0.374 | 23.2 |
| 90 | 32.1 | 0.357 | 19.5 |
| 80 | 26.4 | 0.330 | 16.1 |
| 70 | 20.5 | 0.293 | 13.0 |
| 60 | 15.4 | 0.256 | 10.2 |
| 50 | 10.8 | 0.216 | 7.86 |

**Table 5 Thermodynamic properties at selected temperatures for $CoTiO_3$** *(Continued)*

| | | | |
|---|---|---|---|
| 40 | 10.2 | 0.254 | 5.71 |
| 30 | 7.65 | 0.255 | 2.56 |
| 20 | 2.39 | 0.120 | 0.72 |
| 15 | 0.96 | 0.064 | 0.26 |
| 10 | 0.22 | 0.022 | 0.058 |
| 5 | 0.02 | 0.003 | 0.006 |

compared to previous results in Table 7. For $CoCO_3$, our new data agree very well with more than 40 year old data [37]. However, our measured entropies do not agree well with estimated values [38], probably due to the fact that low temperature heat capacity anomalies occur in $NiTiO_3$ and $CoTiO_3$.

Our data for $NiTiO_3$ show that a lambda-shaped low-temperature heat capacity anomaly occurs at around 26 K (Figure 2), coinciding with the antiferromagnetic transition [15,16,39]. In a similar fashion, $CoTiO_3$ exhibits a low-temperature heat capacity anomaly peaking at 37 K, which is in excellent agreement with the old structural and magnetic data [18,40]. In contrast, $CoCO_3$ shows only a broad

**Table 6 Thermodynamic properties at selected temperatures for $CoCO_3$**

| T K | Cp J mol$^{-1}$K$^{-1}$ | Cp/T J mol$^{-1}$ K$^{-2}$ | S (T) J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|
| 300 | 85.2 | 0.284 | 89.4 |
| 298.15 | 84.8 | 0.284 | 88.9 |
| 290 | 83.5 | 0.288 | 86.6 |
| 280 | 82.2 | 0.294 | 83.7 |
| 270 | 80.6 | 0.298 | 80.7 |
| 260 | 78.7 | 0.303 | 77.7 |
| 250 | 77.0 | 0.308 | 74.7 |
| 240 | 75.0 | 0.312 | 71.6 |
| 230 | 72.9 | 0.317 | 68.4 |
| 220 | 71.1 | 0.323 | 65.2 |
| 210 | 69.0 | 0.329 | 61.9 |
| 200 | 66.8 | 0.334 | 58.6 |
| 190 | 64.6 | 0.340 | 55.3 |
| 180 | 62.2 | 0.346 | 51.8 |
| 170 | 59.7 | 0.351 | 48.4 |
| 160 | 57.1 | 0.357 | 44.8 |
| 150 | 54.1 | 0.361 | 41.2 |
| 140 | 51.0 | 0.364 | 37.6 |
| 130 | 47.7 | 0.367 | 33.9 |
| 120 | 44.2 | 0.369 | 30.3 |
| 110 | 40.7 | 0.370 | 26.6 |
| 100 | 36.9 | 0.369 | 22.9 |
| 90 | 32.2 | 0.358 | 19.2 |
| 80 | 27.0 | 0.338 | 15.7 |
| 70 | 21.4 | 0.306 | 12.5 |
| 60 | 16.4 | 0.273 | 9.62 |
| 50 | 11.4 | 0.228 | 7.09 |
| 40 | 7.14 | 0.178 | 5.06 |
| 30 | 4.17 | 0.139 | 3.49 |
| 20 | 2.72 | 0.136 | 2.16 |
| 15 | 3.18 | 0.212 | 1.37 |
| 10 | 1.31 | 0.131 | 0.46 |
| 5 | 0.18 | 0.036 | 0.062 |

**Table 7 Comparison of our data with previous results**

| $NiTiO_3$ | $CoTiO_3$ | $CoCO_3$ | reference |
|---|---|---|---|
| S (298.15) J $mol^{-1}K^{-1}$ | S (298.15) J $mol^{-1}K^{-1}$ | S (298.15) J $mol^{-1}K^{-1}$ | |
| 90.9(0.7) | 94.4(0.8) | 88.9(0.7) | this study |
| 80.1(3.7) | 96.9* | | [38] |
| | | 88.7(1.7) | [37] |

Uncertainties given in brackets. * Note that the value for $S_{298}$ for $CoTiO_3$ reported in [38] did not contain uncertainties.

anomaly peaking at around 31 K (Figure 4), which may be caused by the transition to an antiferromagnetic state [9,11,12]. Our data agree well with a recent study [11] which found that the weak antiferromagnets (Co, Ni)$CO_3$ exhibit magnetic ordering temperatures of well below 40 K. Whilst our data indicate a transition temperature of 31 K, the older magnetic susceptibility data [10] gave a transition temperature of 18 K. The reason for the discrepancy is unknown.

## Conclusions

We present new low-temperature calorimetric data for the ilmenite-type oxides $NiTiO_3$ and $CoTiO_3$, and for the weak antiferromagnet $CoCO_3$. Our data show that all three phases show low-temperature heat capacity anomalies peaking between 20 and 40 K. The calorimetric data are used to calculate standard molar entropies (298.15 K), which are, due to the low-temperature anomalies, significantly higher than those previously anticipated.

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**Authors' contributions**
SK drafted the manuscript, synthesized the samples, and performed the data analysis. ME and WH carried out the calorimetric measurements and participated in the design of the experiments and helped to draft the manuscript. RP, AR, CHW participated in the experimental design and coordination and helped to draft the manuscript. All authors read and approved the final manuscript.

**Competing interests**
The authors declare that they have no competing interests.

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