SHORT COMMUNICATIONS

COMMENT ON THE PHASE TRANSITIONS OF CAESIUM AND RUBIDIUM NITRATE BELOW ROOM TEMPERATURE

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It has been reported1 that the performance of electrical measurements on anhydrous univalent nitrates, where the cation is Li+, Na+, K+, Rb+, Cs+, Ag+, Tl+, and NH4+, showed that they exhibit solid state transitions below room temperature. Samples used were formed by cooling molten p.a. grade compounds between plane electrode assemblies of silver. Anomalous dependence of the dielectric constant $\varepsilon$ and resistivity $\rho$ on temperature was claimed as evidence of a phase transition.

However, thermal analysis using a differential scanning calorimeter on both CsNO3 and RbNO3 from $-90^\circ C$ to room temperature failed to reveal any transitions. No structural change, compared to the room temperature phase, was detected when the neutron powder spectrum of CsNO3 was run at $-195^\circ C$. This evidence suggests that the anomalous electrical behaviour of these nitrates is not due to a phase transition of CsNO3 and RbNO3, but to the violent thermal history in the preparation of the electrode assemblies. The reported effects could probably be ascribed to thermal hysteresis.

The univalent nitrate (approximately 10 mg) was subject to a temperature programme in a Perkin-Elmer DSC-I, at 0.5°C/min with a sensitivity of 1 mcal s$^{-1}$ for a full scale deflection from 26°C to $-90^\circ C$. The sample was held at $-90^\circ C$ for 30 min, and rescanned back to 26°C. No exotherm or endotherm was observed. The maximum noise level was approximately 0.02 mcal s$^{-1}$ (peak to peak) and any transitions should have been observed.

Measurement of the known transitions of RbNO3 and CsNO3, under the same experimental conditions, gave:

<table>
<thead>
<tr>
<th>Phase Change</th>
<th>Temp. (lit.*) (°C)</th>
<th>Temp. (this work) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RbNO3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV $\rightarrow$ III</td>
<td>164</td>
<td>163.1(5)</td>
</tr>
<tr>
<td>III $\rightarrow$ II</td>
<td>219</td>
<td>222.2(5)</td>
</tr>
<tr>
<td>II $\rightarrow$ I</td>
<td>291</td>
<td>284.3(5)</td>
</tr>
<tr>
<td>CsNO3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II $\rightarrow$ I</td>
<td>154, 161</td>
<td>152(1)</td>
</tr>
</tbody>
</table>

Numbers in parentheses refer to the estimated standard deviation for a particular observation.

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The III $\rightarrow$ II phase change of RbNO$_3$ at 222°C was unusual. The transition occurred over a range of 5°C, probably due to the slow establishment of the thermodynamic equilibrium.

The calorimeter was calibrated before and after analytical scans by observing the melts of samples of zone-refined lead (327.4°C, 1.22 kcal mol$^{-1}$) and indium (157.0°C, 0.78 kcal mol$^{-1}$). A sample of CsNO$_3$ was contained in a vanadium can surrounded by a liquid nitrogen cryostat. This assembly was mounted on a neutron powder diffractometer installed at the Australian Atomic Energy Commission's reactor HIFAR at Lucas Heights in New South Wales.

The spectrum was run at a slow scan over 12 hr up to $2\theta = 60^\circ$, wavelength 1.083 Å. The powder spectra of both phase I and phase II have previously been recorded using this equipment. Consequently if significant structural changes had occurred, it should be detected using this technique.

Acknowledgments

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