PHASE ANALYSIS OF SOME VANADIUM OXIDES BY DIFFERENTIAL SCANNING CALORIMETRY

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Abstract

Phase transitions in Magneli type phases in V-O system were investigated by DSC. The phases with generic formula \( V_nO_{2n-1} \) showed only one phase transition but those expressed by \( V_nO_{2n-2} \) exhibited two phase changes.

Introduction

The existence of different phases of vanadium oxides with general formula \( V_nO_{2n-1} \) (\( 3 \leq n \leq 8 \)) called Magneli phases was first revealed by Anderson [1]. They undergo phase transition showing structural order-disorder phenomena at critical temperature except \( V_7O_{13} \). A considerable literature has been built up on this Magneli phases [2-4]. The studies were extended for the preparation and thermal characterization of the composition \( V_nO_{2n-2} \) (\( n=5,7,9,11 \)) where \( n \) is the odd number and these compositions are in between compositions of Magneli phases.

Experimental

The compositions like \( V_5O_8, V_9O_{16} \) and \( V_{11}O_{20} \) were attempted except \( V_7O_{12} \). These compositions were prepared by the method reported for Magneli phases [4,5] by taking the appropriate molar ratio of \( V_2O_5 \) and \( V_2O_3 \). The mixture is homogenized with acetone, pelletised and then fired in an evacuated (10\(^{-5}\) torr) quartz ampoule, initially at 873K for two days and then at 1173K for four to five days respectively. Examination of x-ray powder diffraction data could not confirm their monophasic or biphasic character. For examples \( V_5O_{16} \) could show some peaks of \( V_4O_7 \) and \( V_3O_9 \) in the powder x-ray pattern. Similarly \( V_5O_8 \) could reflect some biphasic character of \( V_2O_3 \) and \( V_3O_5 \), also in \( V_{11}O_{20} \) could find the biphasic nature of \( V_5O_9 \) and \( V_6O_{11} \) respectively.

The DSC scans were recorded on a Perkin Elmer DSC-2 model; the rate of heating/cooling was \( 10^0K/min \) and the temperature range was between 120 to 500K. DSC-scan were recorded for two to three samples several times to see the reproducibility.
Results and Discussion

Results of the DSC-scans have been summarized in the table 1 along with some of the Magnéli phases which are already reported [4,5] elsewhere.

**TABLE - 1**
Summary of the DSC scans of vanadium oxides

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Phase Transition while heating (K)</th>
<th>Phase Transition while cooling (K)</th>
<th>Phases observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>V$_2$O$_3$</td>
<td>158</td>
<td>150</td>
<td>V$_2$O$_3$</td>
</tr>
<tr>
<td>V$_3$O$_5$</td>
<td>425</td>
<td>420</td>
<td>V$_3$O$_4$</td>
</tr>
<tr>
<td>V$_4$O$_7$</td>
<td>239</td>
<td>230</td>
<td>V$_4$O$_7$</td>
</tr>
<tr>
<td>V$_5$O$_9$</td>
<td>130</td>
<td>124</td>
<td>V$_5$O$_9$</td>
</tr>
<tr>
<td>V$<em>6$O$</em>{11}$</td>
<td>162</td>
<td>154</td>
<td>V$<em>6$O$</em>{11}$</td>
</tr>
<tr>
<td>V$<em>7$O$</em>{16}$</td>
<td>130 &amp; 425</td>
<td>150 &amp; 420</td>
<td>V$_2$O$_3$ &amp; V$_3$O$_5$</td>
</tr>
<tr>
<td>V$<em>9$O$</em>{16}$</td>
<td>130 &amp; 239</td>
<td>124 &amp; 230</td>
<td>V$_4$O$_7$ &amp; V$_5$O$_9$</td>
</tr>
<tr>
<td>V$<em>{11}$O$</em>{20}$</td>
<td>130 &amp; 162</td>
<td>124 &amp; 154</td>
<td>V$_5$O$_9$ &amp; V$<em>6$O$</em>{11}$</td>
</tr>
</tbody>
</table>

It is clear from the above table that Magnéli phases V$_{2n}$O$_{2n-1}$ (n = 3 to 6) form monophasic compounds with one phase transition of which details have been reported elsewhere [4,5,6]. But the compositions V$_{2n-2}$O$_{2n-1}$ (n = 5, 7, 9, 11) like V$_5$O$_8$, V$_7$O$_{16}$ and V$_{11}$O$_{20}$ showed biphasic character, for example the compositions V$_9$O$_{16}$ gave two phase transitions one at 130°K that corresponding to V$_5$O$_9$ and other at 239°K that of V$_4$O$_7$ respectively, hence the compositions is a mixture of V$_4$O$_7$ and V$_5$O$_9$. The enthalpy values at two different phase transitions are low compared to monophasic compounds, also in other compositions. In the case of V$_{11}$O$_{20}$ which gave two phase transition one at 130°K corresponding to V$_5$O$_9$, gave very low value of enthalphy compared to 162°K phase transition that corresponding to V$_6$O$_{11}$, thereby indicating the predominant character of V$_6$O$_{11}$ in the composition.

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It may be concluded that $V_{n\times2n-2}^{\text{2n}}(n=5,7,9,11)$ type composition give biphasic character of Magneli phases. The formation of monophasic different vanadium oxides depends on the Stoichiometry of reactants to give a particular crystalline structure. But when it is altered, the reaction mixture fails to give monophasic product and on the contrary gives two different crystalline structures resulting in biphasic character as in the case of $V_{n\times2n-2}^{\text{2n}}(n=5,7,9,11)$ compositions. This is confirmed by Differential Scanning Calorimetry.

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References