

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_9O_{16} could show some peaks of V_4O_7 and V_5O_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 recorder on a Perkin Elmer DSC-2 model; the rate of heating/cooling was $10^\circ\text{K}/\text{min}$ 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 I along with some of the Magneli phases which are already reported [4,5] elsewhere.

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Summary of the DSC scans of vanadium oxides

Compositions	Phase Transition while heating (K)	Phase Transition while cooling (K)	Phases observed
V_2O_3	158	150	V_2O_3
V_3O_5	425	420	V_3O_4
V_4O_7	239	230	V_4O_7
V_5O_9	130	124	V_5O_9
V_6O_{11}	162	154	V_6O_{11}
V_5O_8	158 & 425	150 & 420	V_2O_3 & V_3O_5
V_9O_{16}	130 & 239	124 & 230	V_4O_7 & V_5O_9
$V_{11}O_{20}$	130 & 162	124 & 154	V_5O_9 & V_6O_{11}

It is clear from the above table that Magneli phases V_nO_{2n-1} ($n = 3$ to 6) form monophasic compounds with one phase transition of which details have been reported else where [4,5,6]. But the compositions V_nO_{2n-2} ($n=5,7,9,11$) like V_5O_8 , V_9O_{16} and $V_{11}O_{20}$ showed biphasic character, for example the compositions V_9O_{16} gave two phase transitions one at $130^\circ K$ that corresponding to V_5O_9 and other at $239^\circ K$ that of V_4O_7 respectively, hence the compositions is a mixture of V_4O_7 and V_5O_9 . The enthalphy 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 $130K$ corresponding to V_5O_9 , gave very low value of enthalphy compared to $162^\circ K$ phase transition that corresponding to V_6O_{11} , thereby indicating the predominant character of V_6O_{11} in the composition.

It may be concluded that V_nO_{2n-2} ($n=5,7,9,11$) 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_nO_{2n-2} ($n=5,7,9,11$) compositions. This is confirmed by Differential Scanning Calorimetry.

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References

1. Anderson, G. (1954) Acta. Chem. Scand. 8, 1599
2. Honiz, J.M. and Van Zandt L.L. (1975), Ann. Rev. Mater. Sci. 5, 255.
3. Andrew, V.N. and Chudnoskii, F.A. (1974), Inzh. Fiz. Zh. 28, 844
4. Salker, A.V., Mirza, E.B., Deshpande, V.V. and Keer, H.V. (1984), Phys. Stat. Solidi (a) 84, K105.
5. Salker, A.V., Keer, H.V., Mirza, E.B. and Deshpande, V.V. (1985), J. Solid State Chem., 60, 135.