Thermal expansion of Ni₃V₂O₈ and its anisotropy in the temperature range 299(3)-1323(8) K

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Introduction

Metal orthovanadates with general formula $(A_3V_2O_8$ where A is divalent metal-ion like Mg, Mn, Co, Ni and Zn) are important due to their potential applications in energy storage devices and as a photcatalyst [1-2]. Ni₃V₂O₈ (a = 5.936 Å, b = 11.420 Å, c = 8.240 Å [3]) one of metal orthovanadates is an important multiferroic material that crystallize in orthorhombic crystal structure with *Cmca* space group (Z=8) [4]. Coordination polyhedrons A⁺², V⁵ are octahedrons and tetrahedron formed by oxygen atoms, respectively [5]. Thermal behavior of Zn₃V₂O₈ was studied by Tabero et al. [6]. In this work we study high temperature behavior of the structure of Ni₃V₂O₈ as function of temperature (*T*) and gain insight into structural features that may be useful in understanding physical properties of such material.

Experiment

 $Ni_3V_2O_8$ 5g sample was made in one step. NiO and V_2O_5 powders were weighted in stoichiometric ratio of 3:1. And then carefully crushed in agate mortar to obtain fine and homogeneous powder and from this powder pellets (13 mm diameter) were made using uniaxial press. The pellets were then heated in air at 800 °C for 12 hrs in a covered alumina crucible. The measurement at high temperature (299(3)-1323(8) K) were performed using Anton Paar High Temperature Oven chamber (model HTK 1200N) using flat sample holder configuration. The lattice parameters and structure are refined by employing the Rietveld method using XRD data for whole temperature range.





Table. 1. Comparing mean TEC $\alpha(a,b,c)$ Ni₃V₂O₈ and Zn₃V₂O₈ at temperature range of 299-873K.

Sample	α _a MK ⁻¹	α _b MK⁻¹	α _c MK⁻¹
Ni ₃ V ₂ O ₈	11.615	7.519	8.656
Zn ₃ V ₂ O ₈ [6]	27.0	13.4	13.2

Fig. 6 Temperature dependence of Ni-O and V-O bond lengths of $\rm Ni_3V_2O_8$

Summary

- The phase analysis of $Ni_3V_2O_8$ has shown that as expected sample crystalize in *Cmca* group having pseudo two-dimensional Kagome-staircase type structure.
- X-Ray diffraction studies of $Ni_3V_2O_8$ shows that there is no impurity phase present for whole temperature range (299(3)-1323(8) K).
- Due to heating, there is variation in lattice parameters with more expansion in 'a' (5.932-6.020 Å) than in 'b' (11.385-11.488 Å) and 'c' (8.239-8.326 Å) (1.5, 0.9 and 1.1%, respectively). The increase in lattice parameters *a*,*b*,*c* and *v* are 1.46%, 0.92%, 1.07% and 2.55%. The mean TEC ($\alpha_a, \alpha_b, \alpha_c$) values of Ni₃V₂O₈ for temperature range (299-1323) K) are 14.19 MK⁻¹, 8.59 MK⁻¹ and 10.02 MK⁻¹ so there is an expansion anisotropy, the strongest expansion is in 'a' direction. The TEC shows expansion anisotropy with more expansion in a-direction and follow order $\alpha_a > \alpha_c > \alpha_b$. The increase in average interatomic distance for Ni(1)-O is 1.14%, Ni(2)-O is 1.54% and for V-O is just 0.23% due high rigidity of V-O bond. After comparing the structure of different orthovanadates at room temperature we see high spin metal are involved in metal orthovanadates formation and the axial ratios shows weak tendency to decrease with increase of ionic volume.



Fig. 4. Comparison of temperature dependence of lattice parameters and volume of $Ni_3V_2O_8$ and $Zn_3V_2O_8$.

Fig. 2. Rietveld refinement for $Ni_3V_2O_8$ at 1323K



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