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Letter

X-Ray study of the thermal expansion anisotropy in neodymium vanadate

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Abstract

The thermal expansivity of zircon-type neodymium vanadate ($NdVO_4$) was studied using the X-ray powder diffraction method in the temperature range 301–691 K. The thermal expansion is anisotropic, having a larger expansion coefficient along the c-axis than along the a-axis ($\alpha_c > \alpha_a$). The mean values of α_a and α_c, evaluated in the temperature range 301–691 K are found to be 3.74×10^{-6} K^{-1} and 10.57×10^{-6} K^{-1}, respectively. The temperature variation of α_c is unusual, for it decreases with increasing temperature.

Keywords: Thermal expansion; Neodymium vanadate; X-ray powder diffraction.

1. Introduction

Neodymium vanadate belongs to the class of rare earth compounds represented by the general formula RMO_4 (where R is trivalent rare earth metal including scandium and yttrium and M is a pentavalent metal such as vanadium, arsenic or phosphorus) crystallizing in the tetragonal zircon structure with space group $I4_1/amd$ [1,2]. The study of its physical properties at various temperatures is of great interest because of its potential use in various technological applications [3–6]. However, no information is available about the lattice thermal behaviour of this compound. Since these studies are of great importance to a large number of problems involving lattice vibrations and unharmonic effects in solids, we have studied the lattice thermal expansivity of $NdVO_4$ as part of a general program of X-ray investigations on zircon-type rare earth vanadates undertaken in this laboratory [7,8]. In this paper, the temperature dependence of the lattice parameters and the linear thermal expansion coefficients of $NdVO_4$ are reported.

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2. Experimental details

The $NdVO_4$ sample was grown from $Pb_2V_2O_7$ flux by a slow cooling method. The preparation and purity analysis are as detailed in Refs. [9,10]. The crystalline sample of $NdVO_4$ was crushed to powder and sieved through a 325 mesh. The specimen for the X-ray diffraction study was prepared by filling the powder into a thin-walled quartz capillary of diameter 0.5 mm. Measurements of the diffraction lines were made using a Unicam 190 mm high temperature powder camera and Co Kα radiation. The experimental set-up and the sample preparation details are the same as those in Ref. [11]. Four pairs of reflections $(712)\alpha_1,\alpha_2$, $(316)\alpha_1,\alpha_2$, $(703)\alpha_1,\alpha_2$ and $(732)\alpha_1,\alpha_2$ recorded in the Bragg diffraction angle region from 65° to 75° were investigated at different temperatures ranging from 301 to 691 K. They were processed by the least-squares method [12] to give the values of lattice parameters a and c at different temperatures. Measurements and calculations were performed several times and the average deviation of the individual values from the mean value was taken as the error in the lattice parameters. The standard error was found to be 0.00002 nm in the a parameter and 0.00008 nm in the c parameter. The details of computational procedure

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followed in evaluating the lattice parameters and the coefficient of thermal expansion and standard errors in these parameters are described elsewhere [13,14].

3. Results and discussion

The lattice parameters a and c and axial ratio c/a of $NdVO_4$ at 301 K, obtained in the present study are listed in Table 1 along with the values reported by the earlier investigators. The values of a, c and c/a of $NdVO_4$ obtained in the present study are in good agreement with those reported by Wycoff [1]. Fig. 1 shows the variation of the lattice parameters a and c with temperature. The temperature dependence of a and c can be represented by the following expressions obtained by least squares fitting of the observed lattice parameter data.

Table 1
Comparison of room temperature lattice parameters of $NdVO_4$

Source	Lattice parameters		c/a
	a (nm)	c (nm)	
[2]	0.73315	0.64359	0.8778
[1]	0.73290	0.64360	0.8781
Present study	0.73337 ±0.00002	0.64363 ±0.00008	0.8776

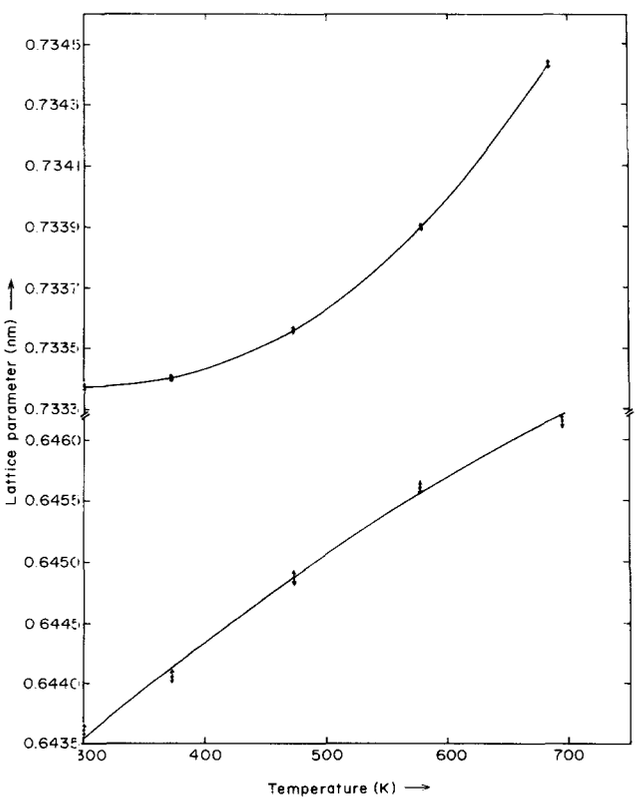

Fig. 1. Temperature variation of lattice parameters a and c of $NdVO_4$.

$$a(\text{nm}) = 0.73409 - 4.655\times10^{-6}T + 7.458\times10^{-9}T^2 \quad (1)$$

standard error of estimate = 0.000015 nm

and

$$c(\text{nm}) = 0.64071 + 1.056\times10^{-5}T - 3.786\times10^{-9}T^2 \quad (2)$$

standard error of estimate = 0.00013 nm

where T is the temperature in kelvin. It can be seen that both the parameters increase non-linearly with increasing temperature.

The thermal expansion coefficients α_a and α_c of the lattice parameters a and c, respectively were evaluated from the standard formula

$$x_i^T = x_i^{To}[1 + \alpha_i^T(T - T_o)]$$

where x_i^T is the lattice parameter a or c measured at a temperature T and x_i^{To} is the lattice parameter at room temperature T_o. Fig. 2 shows the variation of α_a and α_c with temperature. The value of α_a increases with increasing temperature, whereas α_c decreases. Both the parameters vary linearly with temperature. The mean values of α_a and α_c in the temperature range studied were found to be 3.74×10^{-6} K^{-1} and 10.57×10^{-6} K^{-1}, respectively.

The thermal expansion behaviour of $NdVO_4$ is anisotropic, having a larger mean coefficient of thermal expansion along the c-axis than along the a-axis ($\alpha_c > \alpha_a$). This thermal behaviour is similar to that observed in its iso-structural compounds $DyVO_4$, YVO_4 and $GdVO_4$ including zircon [15–17]. The value of α_a decreases from 12.87×10^{-6} K^{-1} at 301 K to 8.13×10^{-6} K^{-1} at 691 K. A similar thermal expansion behaviour was observed in some zircon type compounds YVO_4 [17] and $GdVO_4$ [16] (Table 2). The studies on physical properties of these compounds at elevated temperatures are scarce and therefore no convincing explanation can

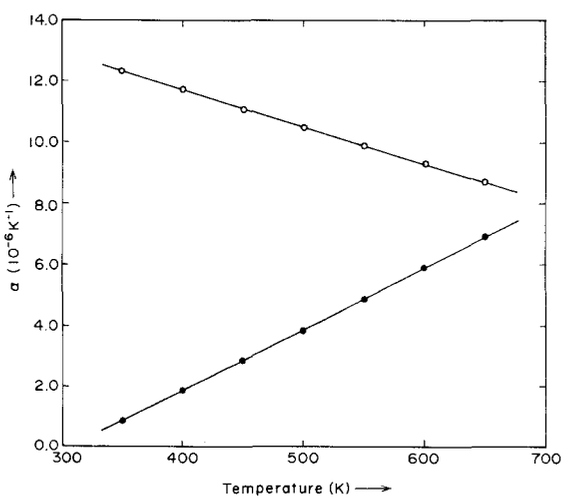

Fig. 2. Temperature variation of the coefficients of thermal expansion of $NdVO_4$, α_a (●), α_c (○).

Table 2
Comparison of coefficients of thermal expansion of some RVO_4 compounds

Parameter (10^{-6} K^{-1})	$GdVO_4$ [a]		YVO_4 [b]		$NdVO_4$ [c]	
	300 K	809 K	300 K	809 K	300 K	691 K
α_a	2.05	2.26	1.01	5.22	0.16	7.87
α_c	11.62	6.38	8.28	6.16	12.87	8.13

[a] [15].
[b] [16].
[c] Present study.

be given at present for their unusual thermal expansion behaviour. In this connection, it will be interesting to determine the crystal structure of these compounds at different high temperatures, which may throw some light on their thermal expansion behaviour.

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