

TABLE II

Wavelength (nm)	V_i (V)	V_λ (V)
White light	0.460	0.120
370	0.106	0.020
410	0.341	0.117
440	0.335	0.100

two fields of different origins would thus be

$$E_R = E_i \pm E_\lambda.$$

In our case $E_\lambda < E_i$ and the photocurrent depends on the magnitude and shape of E_i . Therefore, depending on the sign of the spontaneous polarization with respect to E_i , whose sign is fixed, the shape of the current will be normal if $\text{sign } E_i = \text{sign } E_\lambda$ and anomalous if $\text{sign } E_i \neq \text{sign } E_\lambda$. This is also the behaviour in non-doped ceramic SBN samples [3].

Light next to ultraviolet produces a fixed sign strong internal electric field E_i in ferroelectric SBN, due to space charge accumulated near the surface, of the order of 10^4 V cm^{-1} . It is possible to follow the build-up of this field studying the shape of photocurrents as a function of time and to verify that the change in sign of the stationary part is not due to photocommutation but to the influence of E_i .

In non-doped samples, the internal field is

higher than the photovoltaic field, and there is an anomalous photocurrent. The origins of these two fields are different; the former is due to space charge, and the latter to charge transfer and charges in spontaneous polarization.

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Thermal expansion of dysprosium vanadate

The rare earth vanadates with a chemical formula RVO_4 , where R is a trivalent rare earth ion, crystallize with the tetragonal zircon structure (space group $I4_1/amd$). At low temperatures, some of these crystals exhibit cooperative Jahn–Teller phase transitions from tetragonal to orthorhombic symmetry, Cooke *et al.* [1]. As a part of a general programme of X-ray investigation of zircon type compounds, the authors have studied the thermal expansion of dysprosium vanadate at high temperatures. In this communication, the precision lattice parameters and the coefficients of thermal expansion of dysprosium vanadate determined at various high temperatures are presented.

The sample used in the present study was kindly made available by Dr Wendl, Fakultät für Physik, Universität Karlsruhe, West Germany. The specimen used in the investigation was prepared by placing the sample in a thin walled quartz capillary tube. X-ray diffraction patterns were recorded at various temperatures in the temperature range 30 to 604°C, using $\text{CuK}\alpha$ radiation. The temperature could be held constant within about 2°C using a voltage stabilizer and a variac. The details of the experimental arrangement have been described in an earlier publication by Krishna Rao *et al.* [2]. The least squares method of Cohen [3] was adopted in evaluating the precision lattice parameters. The lattice parameters at different temperatures were deter-

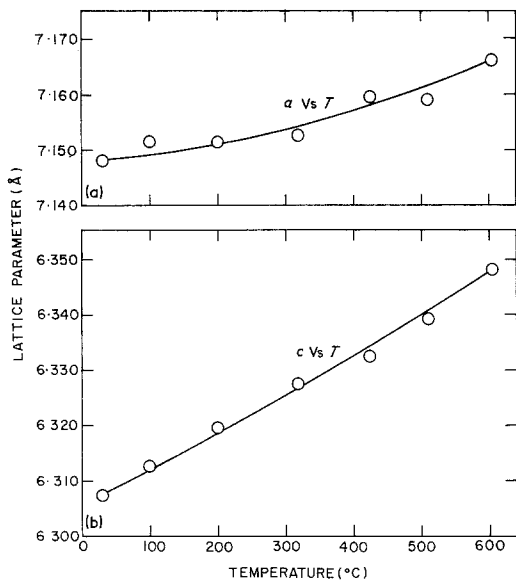


Figure 1 (a) Lattice parameter *a* against temperature and (b) lattice parameter *c* against temperature.

mined from the diffraction lines $(6.4.4)_{\alpha_1}$, $(6.4.4)_{\alpha_2}$, $(7.5.2)_{\alpha_1}$, $(7.5.2)_{\alpha_2}$, $(5.3.6)_{\alpha_1}$ and $(5.3.6)_{\alpha_2}$ recorded in the Bragg angle region of 66 to 76° C. Independent measurements and calculations were made on several films and the average of the deviations of the individual values from their mean was taken as the error in the lattice parameter. This error was found to be 0.0004 Å for the *a* parameter and 0.0003 Å for the *c* parameter. The coefficients of thermal expansion at various temperatures were evaluated

TABLE I Lattice parameters of DyVO₄ at various temperatures

Temperature (° C)	<i>a</i> (Å)	<i>c</i> (Å)
30	7.1483	6.3075
100	7.1516	6.3128
200	7.1516	6.3196
318	7.1527	6.3276
424	7.1598	6.3325
510	7.1590	6.3392
604	7.1660	6.3483

from the lattice parameter against temperature data by a graphical method described in an earlier paper [4].

The lattice parameters determined at various temperatures are given in Table I and are shown graphically in Fig. 1. It can be seen that both the lattice parameters vary non-linearly with increasing temperature.

The temperature variation of the coefficients of thermal expansion, both perpendicular (α_{\perp}) and parallel (α_{\parallel}) to the principal axis (*c*-axis) can be represented by the following equations.

$$\alpha_{\perp T} = 1.3141 \times 10^{-6} + 7.8640 \times 10^{-9} T + 4.0529 \times 10^{-12} T^2$$

$$\alpha_{\parallel T} = 9.7366 \times 10^{-6} + 5.2748 \times 10^{-9} T - 8.5019 \times 10^{-13} T^2.$$

The mean coefficients of thermal expansion over the temperature range studied are as follows

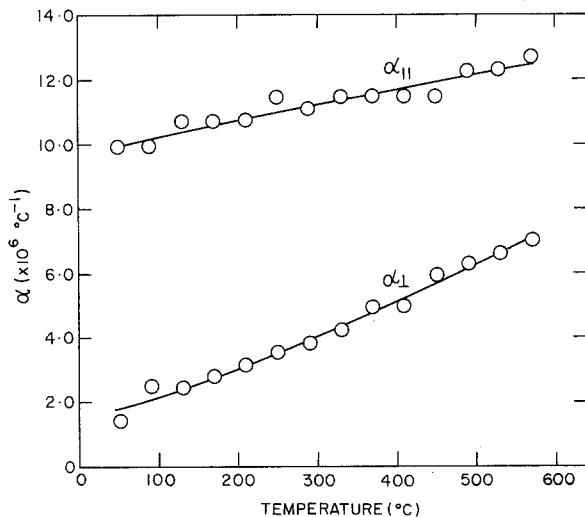


Figure 2 Variation of the coefficient of thermal expansion with temperature.

TABLE II

Compound	$\alpha_{\perp}(\times 10^6)$	$\alpha_{\parallel}(\times 10^6)$	$\beta(\times 10^6)$
Zircon [6]	3.47	4.36	10.79
DyVO ₄ (Present study)	1.33	9.89	12.54

$$\alpha_{(30-604^{\circ}\text{C})} = 4.30 \times 10^{-6} (^{\circ}\text{C})^{-1}$$

$$\alpha_{(30-604^{\circ}\text{C})} = 11.26 \times 10^{-6} (^{\circ}\text{C})^{-1}$$

The variation of the coefficient of thermal expansion with temperature is shown graphically in Fig. 2.

The lattice parameters ($a = 7.1483 \pm 0.0004 \text{ \AA}$, $c = 6.3075 \pm 0.0003 \text{ \AA}$) of DyVO₄ obtained by us at 30° C are in agreement with the parameters at 25° C ($a = 7.1434 \text{ \AA}$, $c = 6.3130 \text{ \AA}$) reported by Swanson and Tatge [5].

The coefficients of thermal expansion reported by Worlton *et al.* [6] in the case of zircon are given in Table II along with the present data. Although $\alpha_{\parallel} > \alpha_{\perp}$ in both cases, the anisotropy is more marked in the case of DyVO₄. From Table II, it is clear that the coefficient of volume expansion (β) is almost the same for both compounds.

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Dipole ordering in dilute solutions of ferroelectrics in antiferroelectric materials*

Antiferroelectric materials such as PbZrO₃ and NaNbO₃ form solid solutions over the entire range of compositions with ferroelectrics such as PbTiO₃ and KNbO₃ that involve either cationic or anionic substitution. The solid solutions exhibit different kinds of dipole ordering depending on the composition. The antiferroelectric states of PbZrO₃, NaNbO₃ and such materials appear to be generally unstable with respect to such alteration in composition [1, 2]. Thus, for x greater than 0.10,

PbZr_{1-x}Ti_xO₃ (PZT) is ferroelectric [3], a behaviour also shown by Na_{1-x}K_xNbO₃ (PSN) [4]. Compositions of PZT and PbHf_{1-x}Ti_xO₃ (PHT) close to $x = 0$, are antiferroelectric upto the paraelectric transition temperature [2, 5]; the nature of ordering in PSN around $x = 0.01$ is, however, not clear [4]. It has been considered interesting to investigate dilute solutions of ferroelectrics in antiferroelectric materials such as PHT, PZT and PSN with a view to understanding the nature of dipole ordering in the interface region between the antiferroelectric ($x \approx 0$) and ferroelectric ($x \geq 0.1$) phases. This interface

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