JOURNAL OF SOLID STATE CHEMISTRY 59, 95–102 (1985)

Composition Dependence of Lattice Parameters in $A\mathrm{Nb}_{1-x}\mathrm{V}_x\mathrm{O}_4$ Systems Where A = Ce, Nd*

A. T. ALDRED

Materials Science and Technology Division, Argonne National Laboratory, Argonne, Illinois 60439

Received October 15, 1984; in revised form January 9, 1985

The room-temperature lattice parameters of a series of $\mathrm{CeNb}_{1-x}\mathrm{V}_x\mathrm{O}_4$ and $\mathrm{NdNb}_{1-x}\mathrm{V}_x\mathrm{O}_4$ compounds ($0 \leq x \leq 1$) have been measured. Substitution of vanadium for niobium in both CeNbO_4 and NdNbO_4 drives the structure from monoclinic (fergusonite type) to tetragonal (scheelite type) at $x = 0.296$ and 0.346, respectively. In both systems, there is an expansion of the long-axis dimension of the fergusonite structure as x increases, despite the fact that vanadium is a smaller ion than niobium. This leads to an anomalous variation of the unit cell volume with concentration. The composition dependence of the strain parameters, which are a measure of the relative distortion of the monoclinic lattice, is found to fit a Landau mean-field model, thus demonstrating a thermodynamic correspondence between composition and temperature.

I. Introduction

In the course of some studies (*1, 2*) to examine the effect of isovalent B site substitutions on the phase stability of $A^{3+}B^{5+}\mathrm{O}_4$ compounds, where A is a lanthanide element and B is either P, V, or Nb, it was discovered (*3*) that gradual replacement of the niobium by vanadium in LaNbO_4 leads to the stabilization of the high-temperature tetragonal form of LaNbO_4 at room temperature with vanadium concentrations in excess of 22 at.%. Further, this substitution of a smaller V for a larger Nb ion led to an increase in the unit cell volume in the monoclinic phase arising from a dramatic increase in the long axis dimension. To study the systematics of this effect further, and to examine the phase stability of $A\mathrm{Nb}_{1-x}\mathrm{V}_x\mathrm{O}_4$ compounds within the context of the structure-field map concept of Muller and Roy (*4*), samples have been prepared and examined by room-temperature X-ray diffraction in several other series where A is a rare earth. In the present paper, some X-ray results are reported for the $\mathrm{CeNb}_{1-x}\mathrm{V}_x\mathrm{O}_4$ and $\mathrm{NdNb}_{1-x}\mathrm{V}_x\mathrm{O}_4$ systems. In both cases it is possible to stabilize the tetragonal high-temperature phase at room temperature with sufficient V substitutions. Such a result had also been alluded to in the Ce-based series by Roth *et al.* (*5*).

The pure rare-earth niobates crystallize in the tetragonal scheelite structure ($I4_1/a$, C_{4h}^6) at high temperatures (*6, 7*), and transform, on cooling, to the monoclinic fergusonite structure ($I2/a$, C_{2h}^6). The transformation temperature T_c increases from ~770 K in LaNbO_4 to ~1070 K in GdNbO_4 and

---

* Work supported by the U.S. Department of Energy. The U.S. Government's right to retain a nonexclusive royalty-free license in and to the copyright covering this paper, for governmental purposes, is acknowledged.

0022-4596/85 $3.00

then remains constant as A varies along the rare-earth series (*6, 7*). The second-order transformation is displacive and involves the shearing of the square base of the tetragonal unit cell to become a parallelogram with unequal sides in the monoclinic unit cell via a linear combination of two homogeneous strains, one of which leads to the edge lengths becoming unequal and the other to the deviation of the monoclinic angle from 90°. The effect of temperature on these strain parameters has already been analyzed in the $LaNb_{1-x}V_xO_4$ system (*8*) in terms of a Landau mean-field model. Additionally, Raman scattering measurements (*8*) have shown that a key effect of V subsubstitutions is to soften an interlayer force constant between nearest neighbor (Nb,VO_4) tetrahedra which may, in turn, be responsible for the remarkable expansion of the long-axis dimension as the V concentration increases. Because of the analogy between the effect of V substitutions and an increase in temperature, the Landau model has been applied to the concentration dependence of the strain parameters at room temperature in the present paper.

II. Experimental

Samples were prepared by repetitive dry sintering under pure O_2 with starting materials at least 99.9% pure as described in Ref. (*3*). The neodymium oxide was pretreated at 700°C to remove any moisture and reconvert it to Nd_2O_3 as determined by X-ray analysis; cerium was in the form of CeO_2. After a minimum of three heat treatments, with the final annealing temperature at 1700 K, powder samples were examined by X-ray diffractometry to ensure complete reaction, chemical homogeneity, and a lack of impurity phases. Selected samples were also examined by scanning electron microscopy to check overall compositions and the relative amounts of phases in two-phase samples. In agreement with the pseudobinary designation $ANb_{1-x}V_xO_4$, no more than two phases were found as x varied from 0 to 1. To check that V is substituting for Nb in the compounds, the intensities of the eight strongest X-ray lines were monitored as a function of composition and compared with calculated intensities based on V occupying the same site as Nb in both the fergusonite and scheelite structures. In all cases, good agreement was found between observed and calculated intensities. Lattice parameters were obtained by standard Debye–Scherrer film pattern techniques with Cr$K\alpha$ radiation and least-squares analysis (*9*). The lattice parameters of pure $CeNbO_4$ and $NdNbO_4$ reported, together with values for the other rare-earth niobates, elsewhere (*10*) are consistent with both Ce and Nd being present as trivalent ions.

III. Results

As in the case of the corresponding La series, vanadium shows extensive solubility in both $CeNb_{1-x}V_xO_4$ and $NdNb_{1-x}V_xO_4$ compounds. The effect of V substitutions, as noted earlier, is to stabilize the tetragonal high-temperature form of the pure niobate, but at higher x than in the case of the corresponding La-based compounds. Beyond $x \simeq 0.40$, the single-phase tetragonal form is no longer stable and a two-phase region is observed up to $x \simeq 0.97$ for both series. In this region the scheelite structure coexists with the tetragonal zircon structure characteristic of either $CeVO_4$ or Nd VO_4. The compositions of the phase boundaries were determined by estimating the relative amounts of the zircon and scheelite phases in two-phase samples on the basis of both the SEM results and the relative intensities of principal reflections of each structure in the diffraction pattern. The lever rule was then applied in a least-squares manner. Lattice parameters of both phases in this two-phase region were invariant with composition, as expected.

The room-temperature lattice parameters for the cerium series of compounds $CeNb_{1-x}V_xO_4$ are given in Table I. The values of the unit cell dimensions in the fergusonite and scheelite phases are plotted versus V concentration x in Fig. 1. All lattice dimensions denoted by a subscript M are for the monoclinic fergusonite structure and those denoted by a subscript T are for the tetragonal scheelite structure throughout the paper. The data points at highest x, indicated by the asterisk in Table I, represent values obtained for a two-phase sample with $x = 0.5$ but listed in Table I and plotted in Fig. 1 at the phase boundary composition determined as described earlier. A comparison with Fig. 1 of Ref. (*3*) shows the same qualitative behavior, namely, a smooth merging of the basal dimensions of the monoclinic unit cell to become the edge of the tetragonal unit cell as x increases, and a dramatic increase in the long-axis dimension as x increases, with a change in slope on going from the monoclinic to the tetragonal structure. Before proceeding to the results for the neodymium series, it should be noted that the lattice parameters of the zircon structure in vanadium-rich samples (bottom of Table I) show a small increase from the value for pure $CeVO_4$, consistent with limited solu-

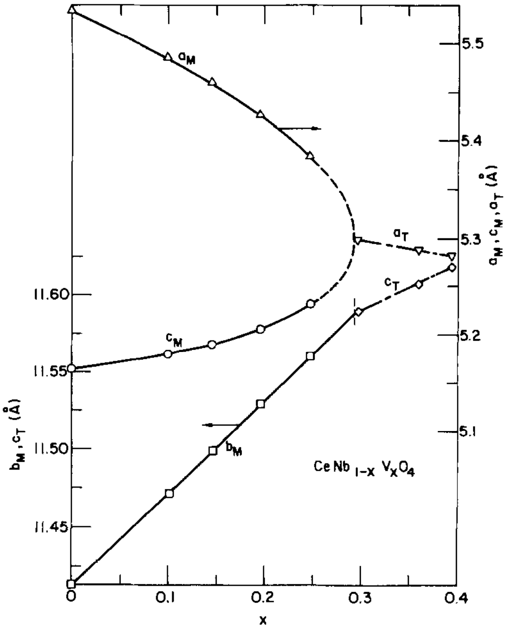

FIG. 1. Composition dependence of the monoclinic unit cell parameters a_M, b_M, and c_M and the corresponding tetragonal parameters a_T and c_T in the $CeNb_{1-x}V_xO_4$ system.

TABLE I

ROOM-TEMPERATURE (296 K) LATTICE PARAMETERS OF $CeNb_{1-x}V_xO_4$ COMPOUNDS

x	Structure	a (Å)	b (Å)	c (Å)	β (deg)
0.0	F[a]	5.5362(3)[b]	11.4126(4)	5.1637(3)	94.542(4)
0.102		5.4867(10)	11.4717(14)	5.1790(9)	93.586(6)
0.148		5.4606(12)	11.4991(18)	5.1892(10)	93.103(5)
0.198		5.4274(6)	11.5291(12)	5.2050(6)	92.498(6)
0.250		5.3845(8)	11.5607(14)	5.2311(12)	91.698(8)
0.300	S	5.2988(4)		11.5901(8)	
0.363		5.2882(4)		11.6078(10)	
0.398*[c]		5.2820(4)		11.6191(9)	
0.975*	Z	7.4042(5)		6.5054(4)	
1.0		7.4013(4)		6.4980(3)	

[a] F = fergusonite (mono.), S = scheelite (tet.), Z = zircon (tet.).

[b] Numbers in parentheses represent statistical uncertainties in least significant figure(s) as yielded by least-squares fit.

[c] Compositions marked with asterisks represent phase-boundary compositions (see text).

TABLE II

ROOM-TEMPERATURE (296 K) LATTICE PARAMETERS OF $NdNb_{1-x}V_xO_4$ COMPOUNDS

x	Structure	a (Å)	b (Å)	c (Å)	β (deg)
0.0	F[a]	5.4687(3)[b]	11.2811(5)	5.1466(3)	94.528(4)
0.130		5.4212(4)	11.3427(15)	5.1577(4)	93.474(5)
0.215		5.3809(6)	11.3821(9)	5.1731(5)	92.640(5)
0.241		5.3669(3)	11.3948(7)	5.1799(5)	92.363(4)
0.306		5.3213(4)	11.4273(7)	5.2050(4)	91.434(4)
0.321		5.3070(10)	11.4350(20)	5.2140(10)	91.112(10)
0.350	S	5.2560(8)		11.4472(16)	
0.375*[c]		5.2518(14)		11.4538(16)	
0.972*	Z	7.3330(5)		6.4443(8)	
1.0		7.3315(2)		6.4359(4)	

[a] F = fergusonite (mono.), S = scheelite (tet.), Z = zircon (tet.).

[b] Numbers in parentheses represent statistical uncertainties in least significant figure(s) as yielded by least-squares fit.

[c] Compositions marked with asterisks represent phase-boundary compositions (see text).

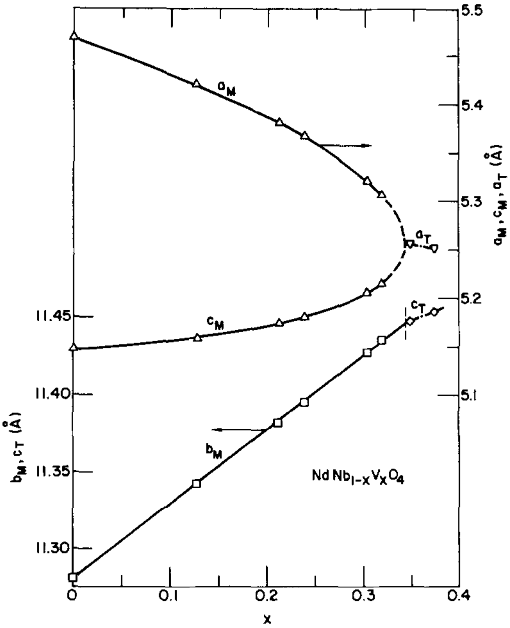

FIG. 2. Composition dependence of the monoclinic unit cell parameters a_M, b_M, and c_M and the corresponding tetragonal parameters a_T and c_T in the Nd $Nb_{1-x}V_xO_4$ system.

bility of the larger Nb ion (for V) in the zircon structure of $CeVO_4$.

The corresponding lattice parameters for the $NdNb_{1-x}V_xO_4$ compounds are given in Table II and the unit cell dimensions are plotted versus V composition in Fig. 2. The qualitative similarities between Figs. 1 and 2 are evident. Because the transformation to the tetragonal structure occurs at higher x in the neodymium series, as compared to the La and Ce series, whereas the total single-phase region is about the same, the composition range of stability of the tetragonal scheelite structure in the neodymium series is very narrow at room temperature. Results for analogous series with heavier rare earths, to be reported separately, show that the tetragonal scheelite structure cannot be maintained at room temperature. Again note that there is limited solubility of Nb in $NdVO_4$, with a small expansion of the unit cell.

IV. Discussion

To assess the systematic effects of V substitution on the lattice dimensions of rare-earth niobates, Fig. 3 (lower) shows a comparison of the concentration dependence of the basal unit cell area [$A_M^{1/2} = (ac \sin \beta)^{1/2}$, $A_T^{1/2} = a_T$] for the three series with A = La, Ce, or Nd. In the upper part of Fig. 3, the corresponding cell volumes V are plotted (note that to maintain linear dimensions $V^{1/3}$ is used, and also there are separate but incrementally equivalent scales for each series of compounds). The results for the La series represent values already reported in Ref. (*3*), together with new data for samples prepared subsequent to the initial investigation and used in other studies (*8*). The effect of vanadium substitutions is to shrink the cell dimensions within the plane perpendicular to the long axis, as expected on the basis that V^{5+} is a smaller ion than Nb^{5+} (for fourfold coordination, $r_V = 0.495$ Å, and $r_{Nb} = 0.62$ Å) (*11*).

The rate of decrease is greater in the tetragonal structure than in the monoclinic structure. At the same time, because of the weakening of the intertetrahedral force constants between adjacent pairs of planes noted earlier, there is a dramatic increase in the long-axis dimension as x increases, although the slope again becomes less positive in the tetragonal structure. The combination leads to a unit cell volume that expands as x increases in the monoclinic structure for the La series, and is almost constant with x in the Ce and Nd series. In all cases there is a contraction of the cell volume as x increases in the tetragonal structure. To quantify these results, linear least-squares analysis has been performed on the composition dependence of the various cell parameters, and the results are summarized as the initial slopes of the various plots in Table III. There is a decrease of ~25% in both db_M/dx and dc_T/dx on going from La to Ce to Nd although in all cases

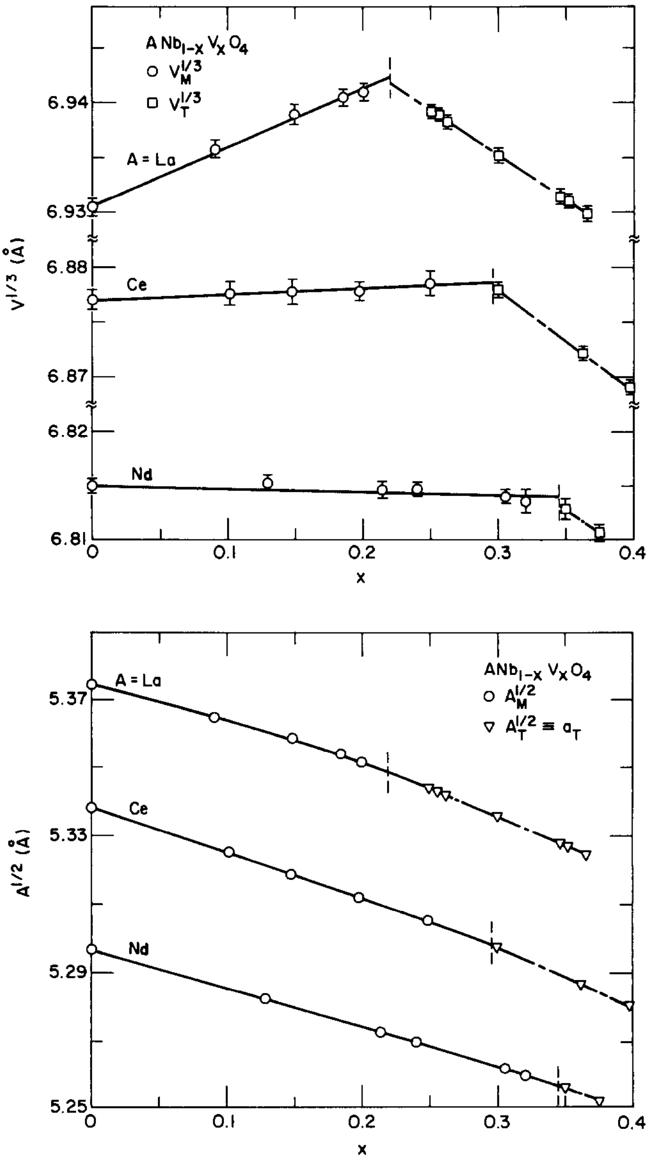

FIG. 3. (Lower) Composition dependence of the square root of the area of the base of the unit cell in both the monoclinic fergusonite and tetragonal scheelite structures for $A\mathrm{Nb}_{1-x}\mathrm{V}_x\mathrm{O}_4$ compounds where A = La, Ce, and Nd. (Upper) Composition dependence of the cube root of the unit cell volume in both the monoclinic fergusonite and tetragonal scheelite structures for $A\mathrm{Nb}_{1-x}\mathrm{V}_x\mathrm{O}_4$ compounds where A = La, Ce, and Nd.

db_{M}/dx is a factor of two larger than dc_{T}/dx. On the other hand, both $dA_{\mathrm{M}}^{1/2}/dx$ and $dA_{\mathrm{T}}^{1/2}/dx$ are essentially independent of the A partner although, again, $dA_{\mathrm{T}}^{1/2}/dx$ is more negative than $dA_{\mathrm{M}}^{1/2}/dx$. The differences in the composition dependences of the cell volume thus arise primarily from the effects on the long-axis dimension.

The variation of the basal unit cell dimensions as x increases (Figs. 1 and 2) is remi-

TABLE III

COMPOSITION DEPENDENCE OF LATTICE PARAMETERS IN $ANb_{1-x}V_xO_4$ SYSTEMS WHERE A = La, Ce, AND Nd

A	db_M/dx	dc_T/dx	$dA_M^{1/2}/dx$	da_T/dx	$dV_M^{1/3}/dx$	$dV_T^{1/3}/dx$
La	+0.745(3)[a]	+0.322(3)	−0.108(2)	−0.166(1)	+0.055(1)	−0.080(1)
Ce	+0.590(2)	+0.294(5)	−0.129(1)	−0.171(5)	+0.006(1)	−0.090(5)
Nd	+0.477(3)	~+0.26	−0.114(2)	~−0.17	−0.003(1)	~−0.09

[a] Numbers in parentheses represent statistical uncertainties of least-squares fits.

niscent of the behavior as temperature increases at constant x (*8*). By analogy, the composition dependence of a_M and c_M (Figs. 1 and 2) can be treated in terms of the Landau model of phase transformations. The Gibbs free energy G may be written as a Taylor series expansion in terms of a strain parameter η which is a measure of the distortion of the low-symmetry monoclinic structure from the high-symmetry tetragonal structure:

$$G = G_0 + A\eta^2 + B\eta^4 + \dots \quad (1)$$

In the present case, η represents a linear combination of two strains $(e_1 - e_2)$ and e_6 (*12*). From the definitions of these strains (*13*), it is straightforward to show that the first distorts the square base of the tetragonal unit cell to a rectangle with edges a and c and the second to a parallelogram with $\beta \neq 90°$. In dimensionless notation, we may write

$$(e_1 - e_2) = (a - c)/(ac)^{1/2}, \quad (2a)$$

$$e_6 = \cos(\pi - \beta). \quad (2b)$$

In the usual Landau approach, it is assumed that the higher-order terms have negligible temperature/composition dependence and that A in Eq. (1) may be linearized around the critical temperature/composition, i.e., $A = A'\,(T - T_c)$ or $A = A'\,(x - x_c)$ where x_c represents the critical vanadium concentration at which the system is driven tetragonal, in the present case, at room temperature (296 K). Minimization of Eq. (1) leads to $\eta^2 = -A/2B$, and because η is a linear combination of $(e_1 - e_2)$ and e_6, we would expect that

$$(e_1 - e_2)^2 = p_1(x_c - x), \quad (3a)$$

$$e_6^2 = p_2(x_c - x), \quad (3b)$$

where p_1 and p_2 are positive constants.

To test this concept, values of $e_1 - e_2$ and

TABLE IV

RESULTS OF LEAST-SQUARES FITS OF COMPOSITION DEPENDENCE OF STRAIN PARAMETERS $(e_1 - e_2)$ AND e_6 TO EQ. (4) FOR $ANb_{1-x}V_xO_4$ SYSTEMS WITH A = La, Ce, OR Nd

A	x_c	p_1	q_1	p_2	q_2	T_c[a] (K)
La	0.2191(4)[b]	0.0229(3)	−0.0085(15)	0.0205(3)	+0.0128(13)	770
Ce	0.2966(5)	0.0184(1)	−0.0070(5)	0.0183(1)	+0.0101(4)	850
Nd	0.3455(5)	0.0127(1)	−0.0059(4)	0.0153(1)	+0.0084(3)	1010

[a] From Refs. (*6, 7*).

[b] Numbers in parentheses represent statistical uncertainties from least-squares fits.

e_6 have been calculated by means of Eq. (2) for each of the $ANb_{1-x}V_xO_4$ series based on A = La, Ce, and Nd, and are plotted as $(e_1 - e_2)^2$ and e_6^2 vs x in Fig. 4. Although both parameters appear to go to zero at the same x and Eq. (3) represents a reasonable first approximation, linear behavior is not observed over extended composition ranges. This is not surprising when one considers the correspondence between vanadium substitutions and temperature. Addition of 10 at.% V ($x = 0.1$) depresses T_c in the La $Nb_{1-x}V_xO_4$ system by ~230 K. Thus the composition ranges in Fig. 4 correspond to temperature ranges much broader than those over which the simple linearization represented by Eq. (3) is expected to be adequate. Accordingly, Eq. (3) was expanded to the next order:

$$(e_1 - e_2)^2 = p_1(x_c - x) + q_1(x_c - x)^2, \quad (4a)$$

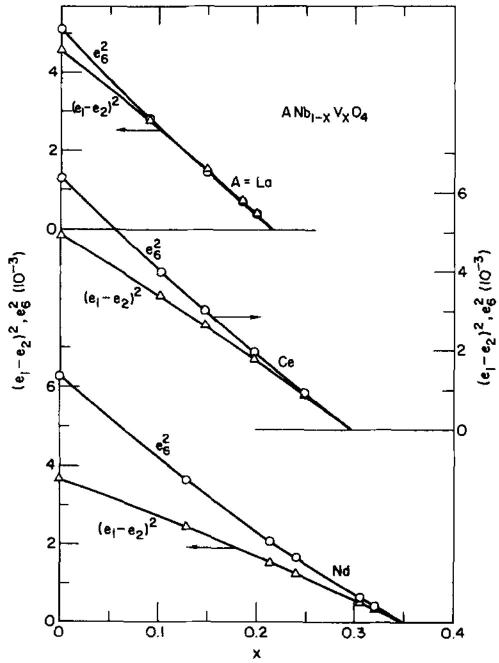

FIG. 4. Composition dependence of the strain parameters $(e_1 - e_2)$ and e_6 [Eq. (2)] for the monoclinic fergusonite structure in $ANb_{1-x}V_xO_4$ compounds where A = La, Ce, and Nd.

$$e_6^2 = p_2(x_c - x) + q_2(x_c - x)^2 \ . \ . \ . \ , \quad (4b)$$

and the data in Fig. 4 were least-squares analyzed to Eq. (4) with x_c, p_1, q_1, p_2, and q_2 treated as disposable parameters. The results of this analysis are shown as the solid lines in Fig. 4 (and also the upper portions of Figs. 1 and 2), and the parameters are given in Table IV together with reported (*6, 7*) transformation temperatures for the pure niobates. The increase in x_c as the rare-earth partner goes from La to Ce to Nd is a reflection of the increase in T_c in the corresponding pure rare-earth niobates. On the other hand, the remaining least-squares parameters in Table IV decrease in magnitude as the rare-earth partner changes from La to Ce to Nd. The higher-order coefficient for $(e_1 - e_2)$, i.e., q_1, is consistently negative, whereas the higher-order coefficient for e_6, i.e., q_2, is consistently positive.

In summary, the response of the monoclinic fergusonite cell of the rare-earth niobates $LaNbO_4$, $CeNbO_4$, and $NdNbO_4$ to systematic substitutions of vanadium for niobium has been studied. A striking expansion of the long-axis dimension with V substitutions is observed which leads to anomalous behavior of the unit cell volume. The composition dependence of the strain parameters associated with the transformation of the monoclinic fergusonite structure to the tetragonal scheelite structure has been shown to be consistent with the Landau model of phase transformations, thus demonstrating a thermodynamic correspondence between T and x.

Acknowledgments

The author would like to thank J. W. Downey for experimental assistance and S.-K. Chan for helpful discussions concerning the Landau model.

References

1. A. T. ALDRED, *ACS Symp. Ser.* **246**, 305 (1984).

2. A. T. ALDRED, *Mater. Lett.* **3**, 37 (1984).
3. A. T. ALDRED, *Mater. Lett.* **1**, 197 (1983).
4. O. MULLER AND R. ROY, "Crystal Chemistry of Non-Metallic Materials," Vol. 4, "The Major Ternary Structural Families," Springer-Verlag, New York, 1974.
5. R. S. ROTH, T. NEGAS, H. S. PARKER, D. B. MINOR, AND C. JONES, *Mater. Res. Bull.* **12**, 173 (1977).
6. K. A. GINGERICH AND H. E. BAIR, *Adv. X-Ray Anal.* **7**, 22 (1964).
7. V. S. STUBICAN, *J. Amer. Ceram. Soc.* **47**, 55 (1964).
8. A. T. ALDRED, S.-K. CHAN, M. H. GRIMSDITCH, AND M. V. NEVITT, *Mater. Res. Soc. Symp. Proc.* **24**, 81 (1984).
9. M. H. MUELLER, L. HEATON, AND K. T. MILLER, *Acta Crystallogr.* **13**, 828 (1960).
10. A. T. ALDRED, *Acta Crystallogr. B* **40**, 569 (1984).
11. R. D. SHANNON, *Acta Crystallogr. A* **32**, 751 (1976).
12. N. BOCCARA, *Ann. Phys.* **47**, 40 (1968).
13. See, e.g., C. H. KITTEL, "Introduction to Solid State Physics," 2nd ed., p. 85, Wiley, New York, 1960.