TRANSFORMATION CHARACTERISTICS OF LaV$_x$Nb$_{1-x}$O$_4$ COMPOUNDS*

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FINAL

Revised June 1983

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X-ray diffractometry measurements were made as a function
of temperature on a series of polycrystalline $LaV_xNb_{1-x}O_4$
compounds ($0 < x \lesssim 0.3$) to determine the effect of V
substitutions on the temperature of the monoclinic/tetra-
gonal transformation. The purpose was to provide basic
information relating to crystal lattice stability in ABO_4
compounds that are either candidates or are appropriate
models for candidate materials for hosting nuclear-waste
ions. Partial substitution of V^{5+} on the Nb^{5+} site
significantly lowers the tetragonal scheelite ($I4_1/a$) to
monoclinic fergusonite ($I2/c$) transformation, from 770°K
in $LaNbO_4$ to approximately 215° K for $LaV_{0.25}Nb_{0.75}O_4$
(the solubility limit is close to x = 0.35). The trans-
formation is displacive, of second order, involving two
coupled order parameters. Heat capacity measurements on
$LaV_{0.25}Nb_{0.75}O_4$ showed that the specific heat anamoly at
the transformation point is extremely small. It is con-
cluded that the two polymorphic forms of $LaV_xNb_{1-x}O_4$ have
very nearly the same free energies over a substantial
range of temperature below the transformation.

The need for high chemical and physical stability in the sub-
stances that will hold nuclear waste ions in an immobilized
state has stimulated extensive materials research. In support
of the candidacy of the cation-linked tetrahedral compounds
having the monazite, scheelite or zircon crystal structure,
studies have sought to determine the extent to which various
elements occurring in the waste can occupy stable substitu-
tional positions on the host lattice sites. See, for example,
(1).
　These ABO_4 compounds, although they have high thermodynamic
stability, have a pronounced tendency toward polymorphism, the
rationale for which is incompletely formulated (2-3). There is

only a modest amount of information, principally on $BiVO_4$ and to a lesser extent on $LaNbO_4$, concerning the transformation mechanism and origin (4-7).

The present work, the initial phase of a basic transformation and lattice dynamics study of relevant oxides, focuses on compounds in the system $LaV_xNb_{1-x}O_4$ ($0 < x \lesssim 0.3$). This choice is based on the following factors:

(1) There is considerable existing information on the host compound, $LaNbO_4$; (2) The substitution of V for Nb provides a simple (and hopefully interpretable) cation replacement on the tetrahedral site; (3) Preliminary studies in this Laboratory have shown that the V substitution has a significant effect on transformation temperature. The transformation from the high temperature tetragonal scheelite ($I4_1/a$) structure to the low temperature monoclinic fergusonite ($I2/c$) structure [$770^{\circ}K$ in pure $LaNbO_4$ (2)] involves two coupled order parameters (a-c) and (β-90) which describe the deformation of the base of the scheelite unit cell from a square to a parallelogram.

Materials Preparation

Polycrystalline samples having densities about 80% of their theoretical values were prepared from 99.9+% pure powders of La_2O_3, V_2O_5 and Nb_2O_5 by repetitive sintering, grinding, mixing and resintering of pellets at $1700^{\circ}K$ in oxygen gas at one atm pressure. The La_2O_3 was obtained by decomposition of lanthanum oxalate, and care was maintained to perform all the preparation steps as far as possible under an inert atmosphere. In some cases this procedure was followed by a hot isostatic pressing (HIP) treatment of the sintered and crushed pellets at the same temperature in hermetically sealed capsules in argon gas at 2000 atm pressure. The HIP treatment produced samples with densities within 3% of theoretical values, and with an average grain diameter of approximately 20 µm. As will be discussed, the transformation characteristics of the compounds were influenced by the sample preparation process. Compositions of the conventionally-sintered samples were checked by scanning electron microscopy; the compositions of the HIP-treated samples are nominal.

Experimental Methods

X-ray diffractometry was performed, by methods described in a companion paper (8), between 80 and $600^{\circ}K$ at ambient pressure on thin solid wafers cut from the prepared samples. Mounted with high temperature cement on relatively massive metal backing plates, these wafers could be maintained at temperatures constant to within $\pm 3^{\circ}K$, as measured by either a platinum thermometer or a copper-constantan thermocouple. The

widths of the (004) and (008) lines, unsplit by the transfor-
mation, provided assurance of the chemical homogeneity of the
samples; the full width at half maximum (FWHM) of these
reflections did not significantly exceed the FWHM of a standard
material and the instrumental resolution, thus indicating that
the experimental observations could be associated with
discrete, uniform V-ion substitutions [See also (8)]. Lattice
parameters were determined by a least-squares procedure based
on d-spacings derived from ten to twenty reflections.

The specific heat at constant pressure, c_p, of the HIP-
treated sample with nominal composition $LaV_{0.25}Nb_{0.75}O_4$ was
measured over the temperature range 4-400°K by the heat pulse
method in a calorimeter that incorporates a feedback system to
regulate the temperature of concentric radiation shields
surrounding the sample (9). The c_p values are accurate to
within 1%, as determined by calibration runs using a poly-
crystalline copper sample and a sapphire single crystal sample.

Results

The upper part of Figure 1 shows the collapse of the monoclinic
a and c lattice parameters to become the tetragonal a parameter
of $LaV_{0.25}Nb_{0.75}O_4$ as temperature is increased. This data is
typical of HIP-treated samples, and the transformation, which
occurs at 215 ± 1 K for this composition (see below), is dis-
placive and of higher order than first. Similar results have
been reported for $LaNbO_4$ (12). If the transformation can be
described in a mean-field model, we would anticipate that the
order parameters (a-c) and (β-90) would vary as $(T_t-T)^\alpha$ with
α = 0.50 over some temperature range near T_t. Thus a plot of
the square of the order parameters versus temperature would
yield straight lines extrapolating to zero at T_t. Figure 2,
showing typical plots of this type, indicates that the trans-
formation point is strongly dependent on the level of V substi-
tution. Careful, repetitive measurements made with rising and
falling temperature, and after varying times at constant
temperature, show that the transformation has no observable
hysteresis and no measurable induction period. The upper part
of Figure 3 shows the transformation temperature as a function
of composition. By analogy with the upper part of Figure 1,
the lower portion of Figure 3 shows the collapse of the room-
temperature monoclinic lattice parameters a and c as a function
of composition in the $LaV_xNb_{1-x}O_4$ system. The transformation
should occur at ambient temperature and pressure at the
approximate composition, $LaV_{0.22}Nb_{0.78}O_4$.

The samples prepared without the HIP treatment showed
substantially the same transformation behavior as the HIP-
treated material, with one notable exception: The monoclinic
and tetragonal forms were seen to coexist over at least a 100 K
temperature range in all vanadium-substituted samples that did

not receive a post-sinter HIP treatment and also in HIP-treated
samples that were subsequently reground and examined in the
powdered condition (particle size < 64 μm). Faint tetragonal
reflections could be observed at low temperatures, and these
reflections increased in intensity with increasing temperature,
merging indistinguishably with the coalescing monoclinic
reflections at the transformation point. Both the intensities
and the 2θ positions of these tetragonal reflections varied
smoothly and reproducibly on cycling through the transformation
with no evidence of hysteresis. Additionally, no time-
dependent effects on the relative intensities or 2θ positions
of the two phases were observed. As there is no evidence, X-
ray or otherwise, of chemical inhomogeneity in any of the
samples, it is tempting to associate this anomaly with a
constrained phase transformation, which has been connected to
the metastable retention of tetragonal ZrO_2 at room temperature
(11-12). It is postulated that when ZrO_2 grains are suffi-
ciently small, the combined effects of surface energy and
specific volume favor the retention of the high temperature
tetragonal structure over the monoclinic form. The applica-
bility of this concept to the $LaV_xNb_{1-x}O_4$ transformation is
under study in this Laboratory.

Figure 1B shows the temperature dependence of c_p for
$LaV_{0.25}Nb_{0.75}O_4$ over a temperature range bracketing the trans-
formation point. There is no discernable latent heat at the
transformation point, thus confirming the X-ray observations
that the order of the transformation is higher than first. It
is also evident that the specific heat anomaly, which
accompanies a higher order transformation, is exceedingly
small, not greater than 0.05 J/g at. K at 215°K. The absence
of a discernable specific heat anomaly at the transformation
point, taken together with the observed coexistence of the two
phases, indicates that there is little difference between the
free energies of the two polymorphic forms over a substantial
range of temperature below the transformation.

Discussion

The work reported here shows that the transformation tempera-
ture in the $LaV_xNb_{1-x}O_4$ system is significantly affected by the
simple, partial substitution of one 5+ ion for another at the
center of the tetrahedron. This effect is connected closely to
the dynamical characteristics of the crystal lattice. A study
involving inelastic neutron scattering, heat capacity and Raman
scattering is under way in this Laboratory to clarify these
aspects of the problem.

With reference to the candidacy of generically-related
crystalline materials to host and immobilize nuclear waste
ions, these results prompt several comments regarding stabi-
lity. Displacive transformations, as observed here, represent

relatively small distortional changes in structure that are not likely to produce physically disruptive effects such as would accompany first order, reconstructive transformations involving nucleation and growth of another phase. This is a positive consideration as regards long term physical integrity of the material. On the other hand, the occurrence of a composition-sensitive, and possibly strain-sensitive, displacive transformation, linking polymorphic forms with very small differences in structure and free energy, may reflect conditions favorable to the occurrence of the metamict state. Since these conditions will probably occur in the waste storage environment, where there will be diverse and time-variant ion substitutions, the connection to a tendency toward metamict behavior should be clarified.

Acknowledgements

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