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

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

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X-ray diffractometry measurements were made as a function of temperature on a series of polycrystalline $\text{LaV}_x\text{Nb}_{1-x}\text{O}_4$ compounds ($0 < x \leq 0.3$) to determine the effect of V substitutions on the temperature of the monoclinic/tetragonal 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 ($\text{I4}_1/\text{a}$) to monoclinic fergusonite ($\text{I2}/\text{c}$) transformation, from 770°K in LaNbO_4 to approximately 215°K for $\text{LaV}_{0.25}\text{Nb}_{0.75}\text{O}_4$ (the solubility limit is close to $x = 0.35$). The transformation is displacive, of second order, involving two coupled order parameters. Heat capacity measurements on $\text{LaV}_{0.25}\text{Nb}_{0.75}\text{O}_4$ showed that the specific heat anomaly at the transformation point is extremely small. It is concluded that the two polymorphic forms of $\text{LaV}_x\text{Nb}_{1-x}\text{O}_4$ 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 substances 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 substitutional 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

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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 $\text{LaV}_x\text{Nb}_{1-x}\text{O}_4$ ($0 < x \leq 0.3$). 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°K in pure LaNbO_4 (2)] involves two coupled order parameters ($a-c$) and ($\beta-90$) 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°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°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 $\pm 3^\circ\text{K}$, as measured by either a platinum thermometer or a copper-constantan thermocouple. The

widths of the (004) and (008) lines, unsplit by the transformation, 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 $\text{LaV}_{0.25}\text{Nb}_{0.75}\text{O}_4$ 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 polycrystalline 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 $\text{LaV}_{0.25}\text{Nb}_{0.75}\text{O}_4$ 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 displacive 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 $(\beta-90)$ would vary as $(T_c - T)^\alpha$ with $\alpha = 0.50$ over some temperature range near T_c . Thus a plot of the square of the order parameters versus temperature would yield straight lines extrapolating to zero at T_c . Figure 2, showing typical plots of this type, indicates that the transformation point is strongly dependent on the level of V substitution. 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 $\text{LaV}_x\text{Nb}_{1-x}\text{O}_4$ system. The transformation should occur at ambient temperature and pressure at the approximate composition, $\text{LaV}_{0.22}\text{Nb}_{0.78}\text{O}_4$.

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 $< 64 \mu\text{m}$). 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 sufficiently small, the combined effects of surface energy and specific volume favor the retention of the high temperature tetragonal structure over the monoclinic form. The applicability of this concept to the $\text{LaV}_x\text{Nb}_{1-x}\text{O}_4$ transformation is under study in this Laboratory.

Figure 1B shows the temperature dependence of c_p for $\text{LaV}_{0.25}\text{Nb}_{0.75}\text{O}_4$ over a temperature range bracketing the transformation 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 $0.05 \text{ J/g at. K at } 215^\circ\text{K}$. 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 temperature in the $\text{LaV}_x\text{Nb}_{1-x}\text{O}_4$ 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 stability. 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.

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