

In Situ High-temperature Phase Transformations in Rare Earth Niobates

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Introduction

Rare earth niobates are an interesting group of materials because of their reversible ferroelastic-to-paraelastic phase transformation. So far, these phase transformations have been studied primarily at either low temperatures (for instance in LaNbO_4) or in specimens that have been quenched after heat treatment. In this study, high-temperature phase transformations of rare earth niobates have been studied *in situ* by using synchrotron x-rays. Lattice parameters and unit cell volumes were determined. The first results on the mechanism causing the phase transformations are presented here.

$\text{A}^{3+}\text{B}^{5+}\text{O}_4$ niobates (here $\text{A} = \text{Y}$, $\text{B} = \text{Nb}$) crystallize in fergusonite-related crystal structures with a monoclinic phase (I 2/a) at room temperature, a phase transformation to tetragonal (I 41/a), and possibly a high-temperature cubic phase [1]. The phase transformation from the stable, high-temperature, tetragonal scheelite-type structure to the monoclinic fergusonite structure is easily accomplished as a distortion. Although a metastable form has been reported for the tetragonal phase (P42/nmc), which can be obtained via low-temperature crystallization in very small grains, it cannot be retrieved after heating to the tetragonal-phase field [2]. The monoclinic phase shows heavy “twinning,” which can be described as domains of two orientations of the monoclinic cell that are rotated by an angle of $\sim 93^\circ$ against each other [3]. Because of the domain structure and domain switching, “rubber-like behavior” [4] and shape memory effects were reported in LaNbO_4 ceramics [5]. By analogy, with ZrO_2 , a high-temperature cubic phase is expected, and some evidence of this phase has been detected [6].

Methods and Materials

In situ high-temperature studies were conducted by using a quadrupole furnace, which can reach up to 2000°C in air. The quadrupole furnace consists of four halogen infrared reflector lamps (OSRAM Xenophot HLX64635; 15 V, 150 W each), arranged in a water-cooled brass housing to form a “hot spot” where the common focuses of all four lamps overlap. Cylindrical samples (0.3×15 mm) of YNbO_4 were prepared by using the organic steric entrapment method developed in our laboratory [7] and studied in Debye-Scherrer geometry. Temperature calibration was achieved by using specimens that were dip-coated with Pt and MgO. The diffraction experiments were carried out at UNI-CAT beamline 33-BM at the APS over a 2θ range of 10° to 35°

(due to furnace geometry) at a step size of $0.008^\circ 2\theta$. The wavelength was calibrated with a silicon standard SRM640b (National Institute of Standards and Technology, Gaithersburg, MD). The x-ray diffraction pattern was analyzed by the Rietveld method [8].

Results

Room-temperature Monoclinic Phase

The monoclinic phase at room temperature contains domains in which two orientations of the monoclinic cell are rotated against each other around the monoclinic b-axis. This domain structure allows for accommodation of the strain in a polycrystalline sample. The monoclinic domain structure feature, in which domains are aligned around the monoclinic b-axis to accommodate strain in a polycrystalline sample, leads to anisotropic peak broadening, as shown in Fig. 1 and Fig. 2. Here the (040) monoclinic peak and structurally related peaks have narrow peak widths. The full width at half-maximum (FWHM) of these peaks are on the same order of magnitude as the peaks of the silicon standard or the mainly unstrained tetragonal phase, and it is mainly determined by instrumental parameters. Peaks that relate to lattice directions that are not parallel to the rotation axis for the domain orientations are markedly wider. From the difference in FWHM between broadened monoclinic peaks and the Si standard, the average strain in the sample

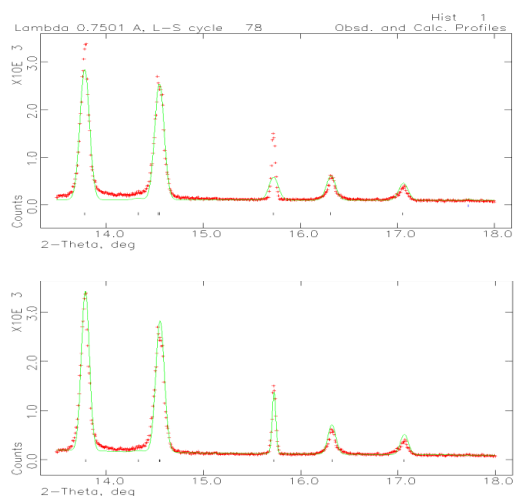


FIG. 1. Fitting of anisotropic peak broadening in monoclinic YNbO_4 .

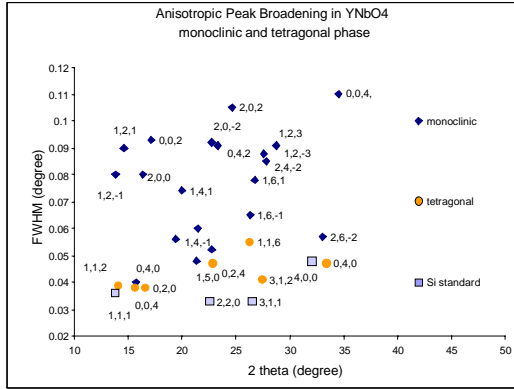


FIG. 2. FWHM of clearly defined peaks for monoclinic and tetragonal $YNbO_4$ phases compared to standard.

was estimated to be on the order of 0.3%. The anisotropic peak broadening could be fitted by using the Rietveld method with profile function 4 as introduced by Stephens [9] in General Structure Analysis System (GSAS) software [10], where the U, V, W, P, and X parameters were set to zero and only the anisotropic S parameters were used. Even in this case, the fit was good only in the region of $<18^\circ$ (R_{wp} 10.4). Attempts to fit this feature by using the Cagliotti terms could obtain R_{wp} values of only >15 .

Monoclinic-to-Tetragonal Phase Transition

The monoclinic-to-tetragonal phase transformation could be observed during intermediate-temperature experiments. The tetragonal phase started to emerge at $\sim 650^\circ\text{C}$, and by 880°C , no more monoclinic phase could be observed. This phase transformation is thought to be ferroelastic, with a spontaneous strain as the Landau order parameter for the transition. In a polycrystalline material, additional stresses that arise from the anisotropy of thermal expansion have to be taken into account. It can

also arise as a function of particle size due to the surface energy and volume relationship [11]. Each grain has its own combination of stress magnitude and stress direction; therefore, some grains can transform at a lower temperature than others, even if the transformation is displacive and of a second order. During the transition, grains that have already transformed to the tetragonal phase reduce the overall stress and/or leave behind only grains where the stress is low; this can be detected [Fig. 3(a) and 3(b)] as a slower increase in the monoclinic lattice parameter just before the phase transformation is completed for all grains. This behavior can also be observed as very wide peaks of the monoclinic phase for scans taken around the transformation temperature and is difficult to fit with the usual Rietveld method. Lattice parameters (Fig. 3) for this temperature range have been calculated from individual peak fittings.

High-temperature Cubic Phase

Further heating of $YNbO_4$ specimen close to the melting temperature shows that a high-temperature cubic phase could be detected. At this point, the specimen integrity was deteriorating, and the quality of the scans did not allow a Rietveld refinement of this phase. Scanning electron microscopy/energy dispersive spectrometry (SEM/EDS) studies of a $YNbO_4$ specimen that had been heat-treated close to the melting temperature showed the presence of a second phase around grain boundaries. EDS revealed that decomposition of the sample into yttria-rich and niobia-rich phases takes place and that the cubic phase probably consists of a solid solution of $YNbO_4$ and Y_3NbO_7 and possibly small amounts of Nb_2O_3 .

Discussion

The lattice parameters of $YNbO_4$ were determined as a function of temperature to $\sim 1400^\circ\text{C}$. The monoclinic-to-tetragonal transformation were observed *in situ*, and a

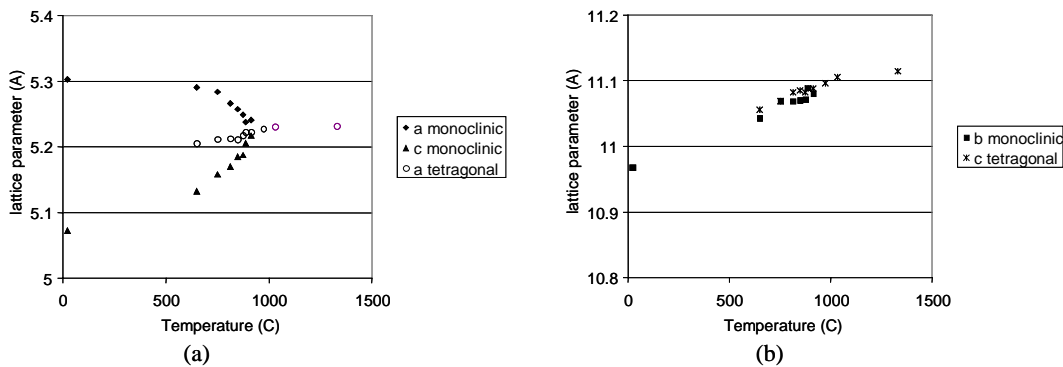


FIG. 3. Development of lattice parameters of monoclinic and tetragonal phase in $YNbO_4$.

temperature range for the existence of the two phases was measured. This was attributed to the local internal stress state experienced by each grain, which is also possibly a function of grain size. A gradual decrease in the monoclinic beta angle was noted with increasing temperature, becoming zero at $\sim 860^{\circ}\text{C}$, which is the nominal transformation temperature of YNbO_4 . From the *in situ* measurement of lattice parameters through the transformation, we concurred that the transformation is of the second-order type. The changes in lattice parameters upon cooling to room temperature indicate that a large spontaneous strain can arise in this material.

Acknowledgments

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References

[1] V. Stubican, "High temperature transitions in rare earth niobates and tantalates," *J. Am. Ceram. Soc.* **47**(2), 55-58 (1964).

[2] S.A. Mather and P.K. Davies, "Nonequilibrium phase formation in oxides prepared at low temperature: Fergusonite related phases," *J. Am. Ceram. Soc.* **78**(10), 2737-2745 (1995).

[3] S. Tsunekawa and H. Takei, "Twinning structure of ferroelastic LaNbO_4 and NdNbO_4 crystals," *Phys. Status Solidi A* **50**, 695-702 (1978).

[4] L. Jian, C.M. Huang, G. Xu, and C. Wayman, "The domain structure of LaNbO_4 in the low temperature monoclinic phase," *Mater. Lett.* **21**, 105-110 (1994).

[5] L. Jian and C. Wayman, "Compressive behavior and domain related shape memory effect in LaNbO_4 ceramics," *Mater. Lett.* **26**, 1-7 (1996).

[6] L.F. Siah, Ph.D. Thesis, University of Illinois at Urbana-Champaign, IL, 2002.

[7] W.M. Kriven, S.J. Lee, M.A. Gulgun, M.H. Nguyen, and D.K. Kim, "Synthesis of oxide powders via polymeric steric entrapment," in *Innovative Processing/Synthesis: Ceramics, Glasses, Composites III*, *Ceram. Trans.* **108**, 99-110 (2000).

[8] H.M. Rietveld, "A profile refinement method for nuclear and magnetic structures," *J. Appl. Crystallogr.* **2**, 65-71 (1969).

[9] P. Stephens, *J. Appl. Crystallogr.* **32**, 281-289 (1999).

[10] A.C. Larson and R. von Dreele, *General Structure Analysis System (GSAS)*, Los Alamos National Laboratory Report LAUR 86-748 (Los Alamos, NM, 2001).

[11] A.H. Heuer, N. Claussen, W.M. Kriven, and M. Rühle, "The stability of tetragonal zirconia particles in ceramic matrices," *J. Am. Ceram. Soc.* **65**(12), 642-650 (1982).