**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.

A$^3$B$^5+$O$_4$ niobates (here A = Y, B = 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 ~93° 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 2$\theta$ range of 10° to 35° (due to furnace geometry) at a step size of 0.008° 2$\theta$. The wavelength was calibrated with a silicon standard SRM640b (National Institute of Standards and Technology, Gaithersberg, 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 poly-crystalline 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...
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.

**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 ~650°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 YNbO₄ 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 YNbO₄ 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 YNbO₄ and Y₂NbO₇ and possibly small amounts of Nb₂O₅.

**Discussion**

The lattice parameters of YNbO₄ were determined as a function of temperature to ~1400°C. The monoclinic-to-tetragonal transformation were observed in situ, and a
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 ~860°C, which is the nominal transformation temperature of YNbO₄. 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.

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References