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Effect of hydroxyl group on global and local structures of hydrothermally grown $KNbO_3$ nanorods

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ABSTRACT

We report the annealing temperature dependence of global and local structures of hydrothermally grown $KNbO_3$ nanorods. With increasing annealing temperature, the amount of hydroxyl groups in the $KNbO_3$ nanorods decreased and finally disappeared at about 800 °C. Morphology of the nanorods seemed not to change significantly, however, X-ray intensity ratio between (0 2 2) and (2 0 0) planes, i.e., I_{022}/I_{200}, increased with decreasing lattice hydroxyl group contents. This result could be attributed to the fact that the hydroxyl groups were desorbed more effectively along the [0 1 1] direction than in other directions due to the elongated nanorod along the [0 1 1] direction. The frequencies of external and bending modes, besides stretching mode, showed red-shift with decreasing lattice hydroxyl group contents. This result implied that the lattice hydroxyl groups existed as interstitial defects near K ions.

1. Introduction

Ferroelectric nanostructures, such as nanoparticles, nanowires and nanorods, have drawn considerable interest due to their scientific as well as technological importance [1–3]. The size effect inherent in ferroelectric nanostructures can modify the magnitude and direction of spontaneous electric polarization, the Curie temperature and the crystal structure of their ferroelectric bulk counterparts [4,5]. A spontaneous electric polarization and large piezoelectricity inherent in ferroelectric nanostructures can be utilized for ultra-high density non-volatile memory, nano piezoelectric actuator and transducer device applications [6,7]. Among the ferroelectric nanocrystals, $KNbO_3$ nanorods have recently become one of the most important materials due additionally to their non-toxicity [8–10].

Until now, hydrothermal method has been frequently used for the synthesis of $KNbO_3$ based nanostructures [11,12]. Due to the dehydrolysis nature of the hydrothermal process, hydroxyl groups could remain inside and on the surface of the nanocrystals. The remaining hydroxyl groups could act as defects [13]; which affect global and local structures, and ferroelectric properties of the $KNbO_3$ based nanocrystals. Therefore, it is important to understand the characteristics of the hydroxyl group, such as amount and position, in $KNbO_3$ based nanostructures.

In this paper, we investigated the effect of hydroxyl group on global and local structures of hydrothermally grown $KNbO_3$ nanorods. With increasing annealing temperature, the amount of hydroxyl groups systematically decreased and then finally disappeared at about 800 °C. By analyzing the global and local structures obtained from high-resolution X-ray diffraction and Raman scattering measurements, we will discuss the amount, position and nature of hydroxyl defects in the hydrothermally grown $KNbO_3$ nanorods.

2. Experimental

$KNbO_3$ nanorods were synthesized by using a hydrothermal method [14]. The as-grown nanorods were annealed at selected temperatures for 12 h in air. Hereafter, we call the as-grown $KNbO_3$ as 'KNO-AG' and the annealed $KNbO_3$ at selected temperatures as 'KNO-temperature'.

Global structure and morphology of the KNO nanorods were characterized by using a high-resolution X-ray diffractometer (HR-XRD) with Cu Kα radiation and a field emission scanning electron microscopy (FESEM), respectively. Hydroxyl groups in the KNO nanorods were characterized by using thermogravimetric (TG) analysis and Fourier transform infrared (FTIR) spectroscopy measurements. For FTIR spectroscopy measurement, the nanorods were mixed with KBr powder and dried at 120 °C for 12 h. Micro Raman scattering measurement was used to characterize local structure of the KNO nanorods. The nanorods were excited by the 488 nm line of a DPSS laser, and focused to 1 μm by using a microscope objective lens (×100). The power of the excitation laser was about 1.5 mW to avoid laser heating.

3. Results and discussion

TG and FTIR spectroscopy measurements show that the amount of hydroxyl groups in the KNO nanorods decreased with increasing

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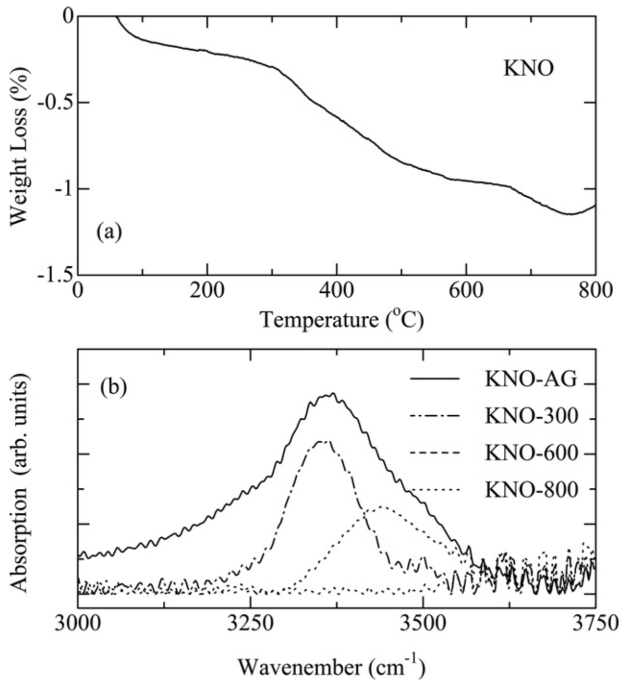

Fig. 1. (a) Thermogravimetry and (b) Fourier transform infrared absorption spectra of the KNO nanorods.

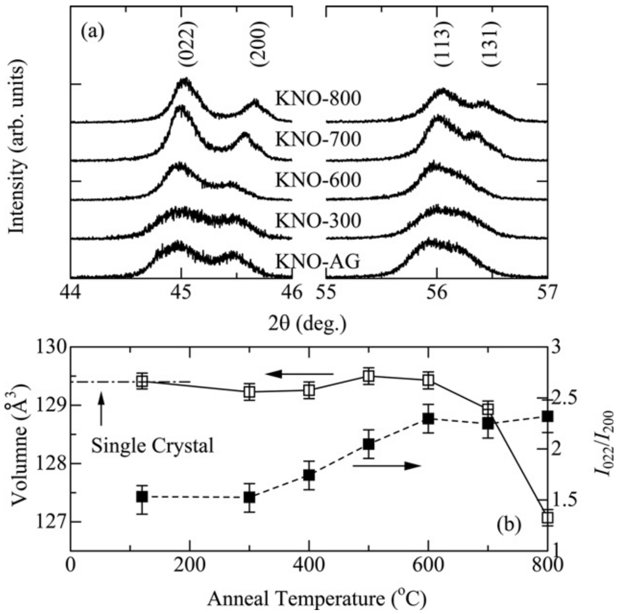

Fig. 2. (a) XRD patterns of the KNO nanorods near $2\theta = 45^\circ$ (left) and 56° (right). (b) Annealing temperature dependence of volume (open squares), and intensity ratio between (0 2 2) and (2 0 0) planes, i.e., I_{022}/I_{200} (solid squares). In (b), the dash-dot line represents the volume of a KNO single crystal.

annealing temperature and finally disappeared at about 800 °C. Fig. 1(a) shows TG result of the KNO nanorods. The total weight loss of about 1.1%, up to 800 °C, seems to occur through three different mechanisms. A gradual weight loss occurs over a wide temperature range from 50 to 600 °C, while a sudden loss occurs in a narrow temperature range from 300 to 400 °C. The former and the latter weight loss may be attributed to the desorption of surface-adsorbed and lattice hydroxyl groups, respectively. Wada et al. reported similar TG results in hydrothermally grown $BaTiO_3$ nanoparticles [15]. Based on the particle size dependence in a TG analysis, they showed that the amount of surface-adsorbed hydroxyl groups increased with decreasing particle size while that of lattice hydroxyl groups remained nearly the same irrespective of particle size. Another sudden weight loss occurs in a narrow temperature range, i.e., at about 700 °C. Since K ion is reported to evaporate near 800 °C in bulk KNO [16], we attribute the third weight loss in the KNO nanorods to the volatilization of K ion.

Fig. 1(b) shows absorption spectra of the annealed KNO nanorods near the stretching mode of hydroxyl group. To completely remove interference due to absorbed H_2O, we measured the absorption spectra in vacuum just after drying the nanorod. The KNO-AG shows a broad and strong absorption spectrum. On the other hand, the KNO-300 clearly shows two absorption peaks centered at about 3350 and 3500 cm^{-1}. With a further increase in annealing temperature, for example, the KNO-600 shows an absorption peak centered at about 3450 cm^{-1} and the KNO-800 shows negligible absorption. (The absorption spectra of KNO-700 are nearly the same as those of KNO-800.) It is well known that the absorption spectra due to surface-adsorbed hydroxyl groups are quite broad because the absorption occurred at many surface sites, and those due to lattice hydroxyl groups are narrow and located at about 3500 cm^{-1} [15,17]. Based on these facts and the results shown in Fig. 1(a), the absorption peak of surface-adsorbed hydroxyl groups should become narrower and show a frequency shift with increasing annealing temperature, as shown in Fig. 1(b). The absorption peak of lattice hydroxyl groups should start to decrease above 300 °C with negligible frequency shift. In KNO-300, the absorption of lattice hydroxyl groups is quite obvious. In KNO-AG and KNO-600, on the other hand, the absorptions of lattice hydroxyl groups are not obvious due to the broad spectrum and the higher-frequency shifted spectrum originated from the surface-adsorbed hydroxyl groups. However, we believe that the absorption of lattice hydroxyl groups decreases with annealing temperature and nearly disappears above 600 °C.

Global structural properties of the KNO nanorods seem to follow the evolution of hydroxyl groups and K ion with annealing temperature. In Fig. 2(a), we show XRD patterns of the annealed KNO nanorods near the (0 2 2) and (2 0 0) planes, i.e., $2\theta = 45^\circ$ (left), and near the (1 1 3) and (1 3 1) planes, i.e., $2\theta = 56^\circ$ (right). To precisely determine the structural parameters, we scanned 2θ angles with a very high resolution of 0.002°. In the wide XRD patterns, we did not observe secondary phases in the annealed KNO nanorods (not shown). With increasing annealing temperature, especially above 300 °C, i.e., the temperature at which lattice hydroxyl group starts to desorb, all peaks become narrow. At 700 °C, i.e., the temperature near which K ion starts to volatilize, the peak positions abruptly shift to higher angles.

In Fig. 2(b), we show annealing temperature dependences of volume (open squares) and the intensity ratio between the (0 2 2) and (2 0 0) planes, i.e., I_{022}/I_{200} (solid squares). Since hydroxyl groups could result in an increase in lattice constants [13], we expected a shrink in volume upon the desorption of the lattice hydroxyl groups. Probably due to the small amount of hydroxyl groups in our KNO-AG, however, the volume of the annealed KNO does not change significantly. On the other hand, the volume of KNO sharply shrinks above 600 °C, probably due to the volatilization of K ion as has been observed in K-deficient KNO single crystals [18]. While there is little change in volume below 600 °C, the intensity ratio I_{022}/I_{200} remains the same below 300 °C but starts to increase above 300 °C, at which temperature the lattice hydroxyl groups start to desorb. We notice that the KNO-AG grows along [0 1 1] direction and its zone axis is parallel to [1 0 0] direction [11,14]. We think that the increase in I_{022}/I_{200} might be related to the morphology of the nanorods. The desorption of the lattice hydroxyl group occurs at the whole nanorods, which results in more