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SCIENCE DIRECT

Solid State Communications 135 (2005) 367–372

solid
state
communications

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Raman study of phase transitions in $KNbO_3$

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Received 9 February 2005; received in revised form 28 April 2005; accepted 13 May 2005 by R. Merlin

Abstract

The influence of grain size on the phase transitions of ferroelectric $KNbO_3$ was studied by micro Raman spectroscopy. It was found that the three transitions observed are not sharp for small particles (~ 50 μm), indicating that they do not behave like bulk particles. The transition temperatures depend on the size and all particles show hysteresis. From these experiments we have obtained some evidence that in small particles monodomains of the rhombohedral and orthorhombic phases coexist in a range of temperatures.

PACS: 77.80.−e; 77.80.Bh; 77.80.Dj; 77.84.Dy; 78.30.−j

Keywords: A. Ferroelectrics; D. Phase transitions; E. Inelastic light scattering

1. Introduction

Ferroelectric oxides with perovskite structure such as $BaTiO_3$ and $KNbO_3$ undergo several phase transitions with temperature. The crystallographic group ranges from low to high symmetry as the temperature increases [1]: rhombohedral, orthorhombic, tetragonal, and cubic. At room temperature $KNbO_3$ has an orthorhombic structure and $BaTiO_3$ a tetragonal structure. However, upon cooling to reach the orthorhombic phase, the $BaTiO_3$ crystal develops a large number of ferroelectric domains, while $KNbO_3$ single domain samples exist in this phase. Because of this the room temperature orthorhombic phase of $KNbO_3$ was especially investigated by neutron [2,3] and Raman [4] scattering experiments.

The structure and properties of thin ferroelectric layers are well known for exhibiting a number of deviations from those of bulk ceramics or single crystals (also referred to as size effects [5]). The formation of polydomains is favored when large $BaTiO_3$ crystals (>1 μm) undergo a phase transition from the cubic to the tetragonal phase in order to minimize the electrostatic and elastic energy. On the other hand, in small crystals (<1 μm) the formation of domains is not favored because of the higher value for the domain wall energy (due to short range interactions) in comparison with the achievable volume free energy change (where long range interactions are important) [6]. The cubic phase (non-ferroelectric) is dominant over temperatures at which the bulk particles are usually ferroelectric [7].

We have been studying the properties of a number of ferroelectric oxides with regards to adsorption of simple molecules such as H_2, CO, N_2, NO and CO_2. We have noticed that $BaTiO_3$, $KNbO_3$ and $LiNbO_3$ readily absorb CO_2 but neither H_2 nor CO or N_2. During CO_2 desorption experiments on powder of mean particle size of 50 μm, we observed CO_2 desorbing from two surface sites: desorption peaks at 140 and 300 °C with a heating rate of 20 °C/min [8,9]. The orthorhombic-to-tetragonal crystallographic transition of $KNbO_3$ observed by dielectric constant measurements occurs around 200 °C [10], just before the second peak of CO_2 desorption. We suspect that the second desorption peak is a consequence of the crystallographic transition.

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0038-1098/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ssc.2005.05.021

The spontaneous polarization of the $KNbO_3$ crystal in the tetragonal phase is larger than in the other two non centrosymmetric phases [10], and the polarization of powder is significantly depressed as a consequence of size reduction [11]. In such cases the transition between the orthorhombic and the tetragonal phases cannot be detected in dielectric measurements. This work is related to the study of the phase transitions of the ferroelectric crystal $KNbO_3$ by means of micro Raman spectroscopy. The next section describes experimental details related to the measurement techniques and the sample's characterization. The experimental results are then discussed and at the end we summarize our conclusions.

2. Experimental

Raman spectroscopy was performed with a LabRam 010 instrument from ISA using a 5.5 mW HeNe laser beam (633 nm) without a filter. The integration time for each spectrum was 40 s. The Raman microscope uses a backscattering geometry, where the incident beam is linearly polarized and the spectral detection unpolarized. The objective lens of the microscope was an Olympus Mplan 10× (numerical aperture 0.25), which provided sufficient distance between the objective and the sample. With this objective a spot size smaller than 10 μm was achieved.

The instrument includes confocal optics and this may cause a decrease in the measured peak height and an increase in the peak width if the height of the sample varies considerably within the size of the laser beam spot. Consequently, differences can appear when comparing results because large particles are usually flat and the surface can be focused well during analyses, while for small particles this might not be possible.

In order to get quantitative information from the Raman peaks, we first subtracted a baseline from the original spectrum. Then the area was evaluated integrating the curve, and the peak position was that which coincided with the vertical line, which divided the curve into two equal areas. Finally, the peak width was calculated as the distance between the lines defined in such a way that the curve between these lines has the same peak position and the integral gives half the total area.

Potassium niobate single crystals, 99.99% pure and about 1 cm in size, were grown at the University of Saarland. Powder samples with different grain sizes were obtained by crushing the crystals and all samples were expected to have a good stoichiometry. After sieving about 3 g of material through meshes of Tyler sizes 14–20, 20–50, 50–100, 100–200, and 200–325, we obtained samples with an average particle size of 1015, 551, 223, 111, and 59 μm, respectively.

To get a quantitative size distribution of the smallest particles, images were taken using a scanning electron microscope from LEO Electron Microscopy Ltd, model 1400VP. It was operated in the variable pressure mode (40 Pa) to avoid charging effects, with 12 KeV electrons, a 100 μA beam current, and a working distance of 7 mm. The largest particle was almost 100 μm in diameter and the lower bound was typically between 10 and 20 μm.

The Raman microscope was coupled to a video camera, which allowed size determination. The Raman spectrum of very large particles did not show any remarkable dependence when varying the size. For this reason we worked with a representative ∼500 μm particle and called it the large particle size (LPS). We also used the powder which has an average particle size of ∼50 μm and we refer to it as the small particle size (SPS).

We used a Linkam TMS 94 controller and THMS 600 stage to vary the sample temperature between -196 and 600 °C with a precision of ± 0.1 °C. The temperature was varied in steps of 2 °C with a heating (or cooling) rate of 10 °C/min. Before taking a spectrum the temperature was stabilized for 2 min to assure that the sample was in equilibrium with the stage.

3. Results and discussion

Fig. 1 shows the Raman spectrum of a sub-millimeter size $KNbO_3$ crystal for different temperatures. According to group theory analysis the zone center optical modes belong to the following representations:

- Cubic (space group $Pm3m$ or O_h^1): the optical phonons

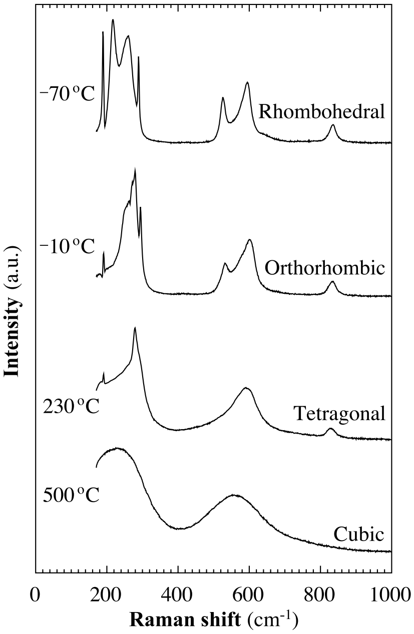

Fig. 1. Raman spectra of $KNbO_3$ in the backscattering geometry with unpolarized detection. The temperature and the corresponding crystallographic phase are indicated for each spectrum.