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Neutron scattering study of the relaxor ferroelectric $K_{1-x}Li_xTaO_3$

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ABSTRACT

Neutron scattering experiments using triple axis spectrometers have been performed for the relaxor ferroelectric materials $K_{1-x}Li_xTaO_3$ (x=0.05, 0.10) in order to study the behavior of the zone-center (ZC) transverse-optic (TO) phonon mode (ferroelectric mode). A major contrast between the x=0.05 and 0.10 samples is the ferroelectric transition-observed only for the latter material at T_C=115 K on warming and as detected by dielectric measurements and neutron diffraction. The ZC TO mode for x=0.05 shows monotonic softening with decreasing temperature down to 10 K, whereas the x=0.10 sample shows a phonon component below T_C which hardens with decreasing temperature in addition to a phonon mode which behaves similarly to that of the x=0.05 sample. This suggests a phase separation of the x=0.10 sample into ferroelectric and relaxor states below T_C, possibly originating from a percolative nature of the ferroelectric state.

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1. Introduction

Relaxor ferroelectric materials show a diffusive ferroelectric transition that can be characterized by a large broad peak in the temperature dependence of the dielectric permittivity, feature that has attracted a significant amount of attention for industrial applications. Such behavior of relaxors is now widely believed to arise from the relaxational nature of randomly oriented polarized nanoregions (PNRs). Among the various relaxor materials, the $K_{1-x}Li_xTaO_3$ (KLT) system exhibits rich dielectric properties via changes in the Li concentration x. The undoped compound $KTaO_3$ is an incipient ferroelectric material that never undergoes a ferroelectric transition [1], in spite of the markedly softened zone-center (ZC) transverse-optic (TO) mode [2]. A doped Li^+ ion in this system occupies an off-centered position due to the small lithium ionic radius, resulting in a large dipole moment and a precursor to the PNR formation. Thus, at low Li concentrations, $x<0.04$, the system shows relaxor behavior. With further doping, it is known that the system shows a ferroelectric transition. However, the ground state of this system is currently not well understood.

Lattice dynamics, such as the ZC TO ferroelectric mode, should give important insights into the basic nature of the ferroelectric transition in KLT. Although the lattice dynamics in KLT have been studied extensively by Raman scattering [3–5], neutron scattering studies are sparse [6–8]. In this paper, we report the results of neutron inelastic scattering experiments on KTL with x=0.05 and 0.10 in order to study the ZC TO phonon properties.

2. Experimental details

The KLT crystals with x=0.05 and 0.10 in the present study were grown by the slow-cooling method. The neutron inelastic scattering measurements were performed at the TAS-1 and TAS-2 triple axis spectrometers installed at the JRR3M research reactor at JAEA, Tokai. For both spectrometers, a fixed final neutron energy of E_f=14.7 meV was utilized and pyrolytic graphite filters were used to eliminate higher order neutrons. Collimation sets of 40′-40′-80′-open for TAS-1 and Guide(15′)-80-80-open for TAS-2 were used.

The crystals were characterized by both dielectric measurements and neutron diffraction. The dielectric measurements indicate that the well-defined ferroelectric transition exists only in the x=0.10 sample at T_C=115 K on heating, and the x=0.05 sample remains in the relaxor state down to 10 K. The transition for x=0.10 is further confirmed by a sudden decrease of the nuclear Bragg width and intensity at T_C on heating-as measured by neutron diffraction [9]. Such behavior is absent in the x=0.05 sample, and thus, there is no ferroelectric transition in the x=0.05 sample.

We note that the x=0.05 crystal contains an unintended Ca impurity at a level of ~15 ppm. This small amount of impurity has no significant influence on the Li dipole relaxations as well as the lattice dynamics of the host lattice [8]. However, we cannot rule

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out the possibility that the ferroelectric transition in the x=0.05 sample is affected by the additional quenched disorder by the Ca impurity.

3. Neutron scattering results

Figs. 1 and 2 show peak profiles of the ZC TO phonon for x=0.05 and 0.10, respectively, measured at **Q**=(2 0 0) at various temperatures for the zero field cooling process. For x=0.05 (no ferroelectric transition), the phonon profile has a single peak at all temperatures and the peak position decreases monotonically with decreasing temperature. On the other hand, the ZC TO phonon of the x=0.10 sample, which has a ferroelectric transition at T_C=115 K, shows a "two-peak" structure below T_C—where one mode clearly hardens with decreasing temperature. At the lowest temperature, the "two-peak" structure is unclear.

All profiles were analyzed by being fit to the following Lorentzian function convoluted with an instrumental resolution:

$$S(q,E) = (n(E)+1)\chi''(q,E) \tag{1}$$

$$\chi''(q,E) = \frac{I}{(E-E_{ph}(q))^2+\Gamma} - \frac{I}{(E+E_{ph}(q))^2+\Gamma} \tag{2}$$

where E is the neutron energy transfer, $n(E)=1/(e^{E/kT}-1)$ is the Bose factor, E_{ph} is the phonon energy, and Γ is the half width at half maximum of the phonon peak. We have assumed the following phonon dispersion

$$E_{ph}^2(q) = E_0^2 + (Cq)^2 \tag{3}$$

where E_0 is the phonon energy at the ZC. A constant C is determined to be 40.3 meV^2 Å^2 after the dispersion at room temperature. (C shows small dependence on temperature. However, it does not affect the fitting results of the low temperature data.) Those profiles of x=0.10 showing the two-peak structure are fit with two Lorentzians. The results of these fits are shown by solid lines in Figs. 1 and 2.

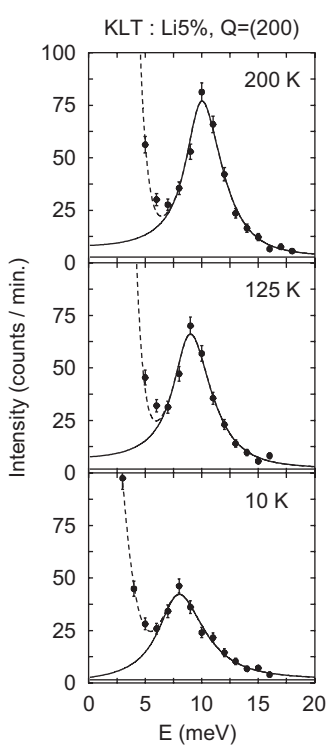

Fig. 1. The zone-center transverse-optic phonon profiles of $K_{1.95}Li_{0.05}TaO_3$ at 200, 125 and 10 K. All profiles are measured at Q=(2, 0, 0) using the TAS-1 triple axis instrument. The solid and dotted curves are results of fits to a resolution-convoluted Lorentzian function.

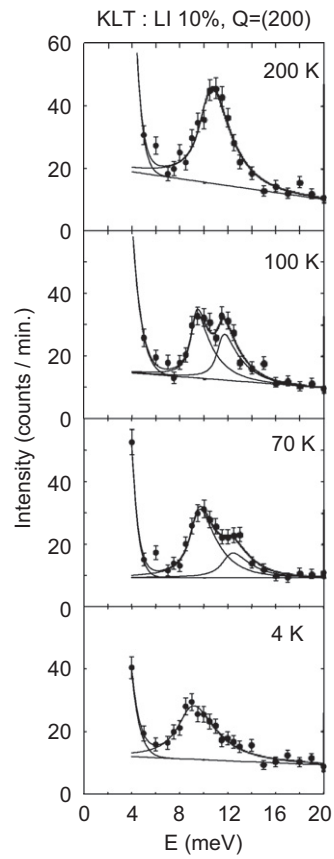

Fig. 2. The zone-center transverse-optic phonon profiles of $K_{1.90}Li_{0.10}TaO_3$ at 200, 100, 70 and 4 K. All profiles are measured at Q=(2, 0, 0) using the TAS-2 triple axis instrument. The solid lines are results of fits to a resolution-convoluted Lorentzian function.

E_0^2 obtained from the fits is summarized in Fig. 3 as a function of temperature. E_0^2 for x=0.05 decreases linearly with decreasing temperature and saturates at very low temperature. E_0^2 for x=0.10 also decreases linearly with decreasing temperature for $T>T_C$, while one component increases linearly with decreasing temperature below $T<T_C$. Nevertheless, the other mode behaves very similar to that of the x=0.05 sample.

4. Discussion

We have shown that the ZC TO mode in the x=0.10 sample splits below T_C. Similar observations have been reported from Raman [3–5] and Neutron [6] results for samples with different Li concentrations that have the ferroelectric transition. In the previous studies, this split has been accounted for in terms of tetragonal asymmetry in the ferroelectric state, based on the assumption that the ferroelectric transition occurs in a bulk region of the sample. In this case, one would expect a hardening of the both modes below T_C. Our study of the detailed temperature dependence revealed that one mode does not harden but behaves similarly to that of the relaxor, i.e., x=0.05 sample.

Dielectric measurements of the x=0.10 sample indicate that there is a relaxation of the Li ions even below T_C [9]. Also, neutron diffraction studies show that, although the diffuse scattering around the nuclear Bragg peaks exhibits a critical scattering

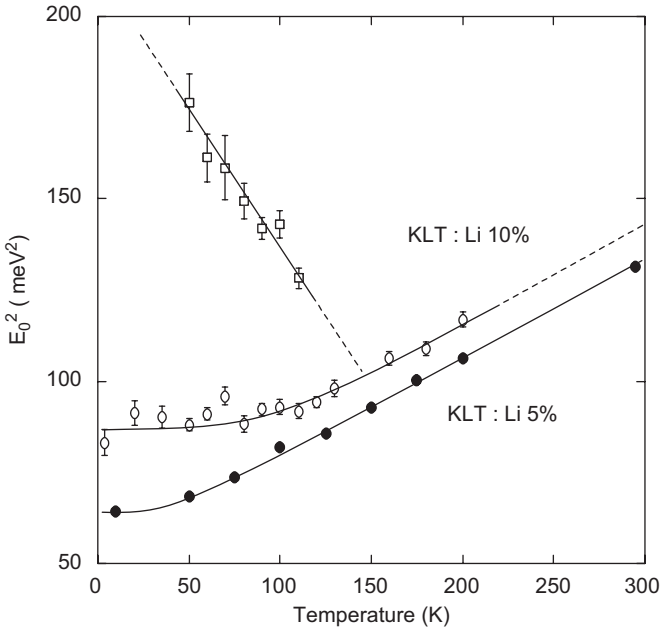

Fig. 3. Temperature dependence of the squared phonon energy of the zone-center transverse-optic mode for $K_{1.95}Li_{0.05}TaO_3$ (closed symbols) and $K_{1.90}Li_{0.10}TaO_3$ (open symbols).

nature: that is, the diffuse intensity has a sharp maximum at T_C, there is a vestige of the diffuse scattering even at 4 K [9].

These facts suggest that the entire system is not in the ferroelectric state below T_C, but is separated into the ferroelectric and relaxor phases. We believe that this is due to the percolative nature of the ferroelectric state in KLT where the ferroelectric macrodomains are formed only vicinity of the doped Li atoms. In this scenario, we still should see two ZC modes from the ferroelectric phase, but this split in energy could be too small to be detected in the present study due to the very small tetragonal asymmetry. The energy difference should increase with decreasing temperature, which might be the reason why the two-peak structure is unclear at the lowest temperature where the higher energy mode has a large energy width.

In summary, we have studied the ZC TO phonon in the KLT with x=0.05 and 0.10 where the former is a relaxor at all temperatures and the latter shows a ferroelectric transition at T_C=115 K. We have observed a splitting of the mode for x=0.10 below T_C, which suggests a phase separation below T_C into the ferroelectric and relaxor states.

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