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Raman spectroscopy of $(K,Na)NbO_3$ and $(K,Na)_{1-x}Li_xNbO_3$

H. J. Trodahl,[1,2,a)] N. Klein,[1] D. Damjanovic,[1] N. Setter,[1] B. Ludbrook,[2] D. Rytz,[3] and M. Kuball[4]
[1]*Ceramics Laboratory, Swiss Federal Institute of Technology-EPFL, Lausanne 1015, Switzerland*
[2]*MacDiarmid Institute of Advanced Materials and Nanotechnology, Victoria University, Wellington, New Zealand*
[3]*Forschungsinstitut für mineralische und metallische Werkstoffe Edelsteine/Edelmetalle (FEE), Idar-Oberstein, Germany*
[4]*Applied Spectroscopy Group, H.H. Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, United Kingdom*

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We report Raman spectroscopy in all four phases of a $(K_{0.5+\delta}Na_{0.5-\delta})NbO_3$ ($\delta \sim 0.03$) crystal and $((K_{0.5+\delta}Na_{0.5-\delta})_{1-x}Li_x)NbO_3$ for $x=0.02$ and 0.03. The phase transitions in the Li-free crystal are homogeneous and hysteretic, with no mixed-phase region between the rhombohedral and orthorhombic phases. Raman spectra in the lowest-temperature phase in the Li-doped material differ significantly from those at $x=0$ and suggest a structural phase boundary at a Li concentration of less than 2%. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3056658]

Potassium/sodium niobate $K_{1-x}Na_xNbO_3$ (KNN) has been investigated for its ferroelectric properties for decades,[1–5] but has enjoyed a renaissance as a potential alternative for $Pb(Zr_xTi_{1-x})O_3$ (PZT) in the ubiquitous applications of its strong piezoelectric response. Substitution of Li and Ta, $(K_{0.5}Na_{0.5})_{1-x}Li_xNb_{1-y}Ta_yO_3$ (KNLN for $y=0$), suggested a morphotropic phase boundary (MPB) with strong piezoelectric properties similar to PZT.[6–10] However, it is now recognized that the highest piezoelectric properties lie near a polymorphic phase transition between tetragonal and orthorhombic phases at room temperature.[11–13] It is central in this search for lead-free piezoelectrics to identify phase diagrams for promising materials and recent papers have addressed this question in KNLN and related materials through the use of Raman spectroscopy.[11,12,14–18] In particular we recently noted anomalies in the Raman spectra of KNLN that raised questions about whether the low-temperature phase transitions in KNLN are in accordance with those in KNN.[12] However, there is no report in the literature of the Raman spectra across the full set of four phases for KNN. In this letter we report full temperature-dependent Raman spectra for single-crystalline KNN and for KNLN. A comparison of the transition temperatures and spectra reveals a surprising difference in the low-temperature phases, implying an altered low-temperature crystal structure for as little as 2% Li substitution in KNN.

Extensive early studies[1–5] established that for $x<0.55$, $K_{1-x}Na_xNbO_3$ adopts the series of phases [cubic-tetragonal-orthorhombic-rhombohedral (*C-T-O-R*)] that is common to many perovskite ferroelectrics, including $KNbO_3$ (KN). The phase diagram develops smoothly from $x=0$ to 0.55, and there can be little doubt that the structural changes associated with these phases are entirely analogous to those in KN.

The KNN crystal used in the present study was grown at 1093 °C by the top seeded solution growth, cooling at 0.15 °C/h. The seed orientation was ⟨001⟩ and the crystal has a milky appearance with a high domain density. The K:Na ratio measured by inductive plasma spectroscopy–mass spectrometry was 0.59:0.41 while energy dispersive x-ray analysis gave 0.57:0.43. Both compositions are on the K rich side of the morphotropic phase boundary in the KNN phase diagram at a K:Na ratio of 45:55 ($x=0.55$).[2] A KNLN (3%) crystal was also grown, with the K:Na ratio of 45:55 ($x=0.55$), very close to the reported phase boundary to a low-temperature monoclinic phase in Li-free material.[1–5] To separate the effects of varying K:Na and Li concentration we performed Raman studies of two ceramic samples with K:Na of 50:50 and Li concentrations of 2% and 3%. The preparation and treatment of these samples has been described previously.[12]

The samples were placed in a liquid nitrogen cooled Linkam THMS600 cold/hot stage and unpolarized backscattered Raman spectra were collected with either a Renishaw InVia or a Jobin Yvon LabRam HR spectrometer using the 488 and 514 nm Ar^+ lines. The incident light was focused to a spot of about 500 nm diameter and the power was held below 1 mW, which did not significantly raise the sample temperature. Studies to lower temperatures using a liquid He flow-through cryostat confirmed the absence of phase transitions below 80 K.

Figure 1 shows typical *R*- and *O*-phase spectra at 125 K, *O*- and *T*-phase spectra at 465 K, and *T*- and *C*-phase spectra at 690 K of KNN. The hysteretic nature of these first-order transitions permits displaying spectra in adjacent phases at a common temperature. The spectra clearly signal phase changes, and the detailed phonon frequencies from multiple-line fitting are plotted as a function of temperature in Fig. 2. Frequency shifts are clear at the *R-O* and *O-T* boundaries. Across the *T-C* boundary the changes are primarily in the widths of the lines, as is clearly seen in Fig. 1(a). The trends within each phase consist primarily of mode softening with rising temperature, exactly as expected to follow from thermal expansion: Note, however, one exception: the line near 425 cm^{-1} anomalously hardens with temperature throughout the *O* phase.

Table I lists the transition temperatures measured for both heating and cooling, showing excellent agreement with transition-temperature data from the literature.[2] All of the

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[a)] Electronic mail: joe.trodahl@vuw.ac.nz.

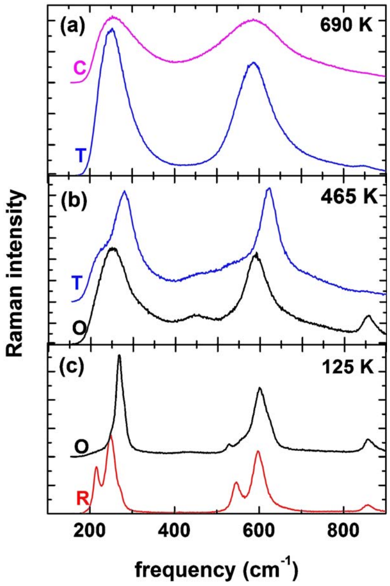

FIG. 1. (Color online) Spectral changes across the phase transitions in KNN.

transitions displayed hysteresis, with the largest (~60 K) at the *R*-*O* transition and the smallest (~5 K) at the *T*-*C* transition. Within the hysteretic temperature range the spectra were typical of the higher-temperature phase while cooling and of the lower-temperature phase while heating. There were no mixed-phase spectra at any temperature within that range, clearly signaling homogeneous transitions at the extremes of the range.

The close similarity of the KNN Raman spectra of Fig. 1 and those in KN permit a confident assignment of the features at temperatures below 500 K, based on Raman and infrared studies and vibrational calculations for the zone-center phonons in KN across all of its phases.[18–22] These zone-center assignments differ from zone-boundary internal modes proposed for some lines in KNN,[17] which could be rendered Raman active only by strong disorder. Indeed these materials are subject to disorder-induced scattering at higher temperature as will be discussed below, but the narrow lines in the *R* and *O* phases and the lower temperatures of the *T* phase are zone-center modes, as they are in KN.

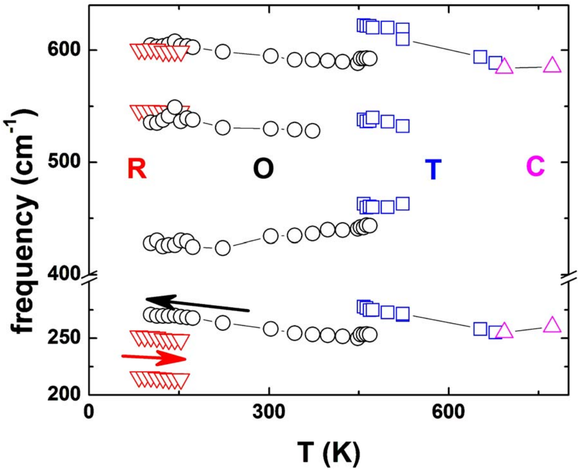

FIG. 2. (Color online) Temperature dependence of the Raman lines in KNN. Data in the *R*, *O*, *T*, *C* phases are shown as inverted red triangles, black circles, blue squares, and upright magenta triangles.

TABLE I. Transition temperatures through the phase sequence in KNN. Columns (a) and (b) were measured while the temperature is rising and falling, respectively, and column (c) is historical data.

	(a) Heating (K)	(b) Cooling (K)	(c) Ref. 2 (K)
R/*O*	158	98	127
O/*T*	470	455	473
T/*C*	690	685	680

The broad Raman bands peaking at 250 and 600 cm^{-1} in the cubic phase seen in Fig. 1(a) are a clear signal of disorder at these elevated temperatures, for Raman activity in cubic perovskites is symmetry forbidden. These features are common in the cubic phase of pervoskite ferroelectrics and they signal local static and/or dynamic disorder reminiscent of the distortions in ferroelectric phases.[23] Disorder-induced bands are also found in the spectra of the higher-temperature section of the tetragonal phase, but the discontinuous loss of intensity and increased line width of the Raman bands across the tetragonal-cubic transition seen in Fig. 2(a) signals a clear coherence-length collapse of the tetragonal distortion.

A recent x-ray diffraction (XRD) study of ceramic KNN suggested that the *O*-*R* transition is inhomogeneous, initiated by islands of rhombohedral material within an orthorhombic matrix, with the transition completed only after the islands grow to coalescence.[17] There is no evidence of any such gradual phase transition in the present data; in contrast the transition is discontinuous and complete, and shows a very large hysteresis. It is unclear whether the apparent disagreement between the studies is fundamental or merely related to the relatively small crystallites in the XRD study.

Turning next to KNLN (2%) ceramic we find phase transitions near 220 and 450 K, as we reported recently.[12] It is tempting to simply accept these as the *R*-*O* and *O*-*T* transitions as in KNN. Note, however, that the lowest-temperature transition occurs at a substantially higher temperature than the *R*-*O* transition in KNN. Furthermore the Li-concentration dependence of that transition temperature reported in Ref. 12 is very weak, and it extrapolates to 250 ± 20 K at zero Li concentration, more than 100 K higher than the *R*-*O* transition in KNN. There is thus a question as to whether the ground state in KNLN is a rhombohedral phase analogous to that in KNN. In Fig. 3 we compare the "*R*"-, *O*- and *T*-phase spectra in the two samples, seeking similarity that might support a rhombohedral assignment for the lowest-temperature phase of KNLN. The spectra in the *O* and *T* phases show no more than shifts in the frequencies of the features, while in the lowest-temperature phase there are both larger frequency shifts and a loss of a satellite on the low-frequency side of the 280 cm^{-1} line. An even more striking difference is found in the shift of the 280 cm^{-1} line in KNLN, which softens across the transition from the low-temperature to orthorhombic phases as seen clearly in Fig. 4. That softening is in disagreement with the stiffening with increasing temperature across the transition in KNN seen in Fig. 1(c). It is clear that the crystal structure of KNLN is very different from KNN, despite only 2% Li substitution.

It is significant that the Raman spectra from our KNLN (3%) ceramic and the Na-rich KNLN (3%) crystal are all but indistinguishable from the data shown in Figs. 3 and 4. We

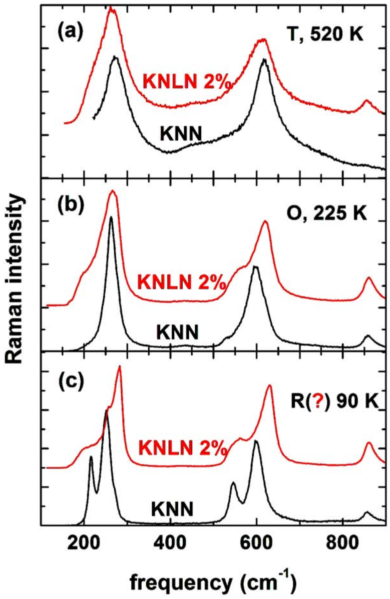

FIG. 3. (Color online) Comparison of the spectra in the three ferroelectric phases of KNN and KNLN.

draw the inference that the structures of these solid solutions are at most a weak function of the K:Na ratio across the 55:45–45:55 range, but that there is a phase transition in the ground state that occurs between 0% and 2% Li concentration.

In summary we have reported a Raman spectroscopic study through all phases of a $(K_{0.5+\delta}Na_{0.5-\delta})NbO_3$ crystal for $\delta \sim 0.05$. The spectra are similar to those reported in $KNbO_3$, with only modest shifts in the frequencies of the prominent lines, and confirm that KNN and KN adopt the same series of crystal structures through all of their ferroelectric phases.

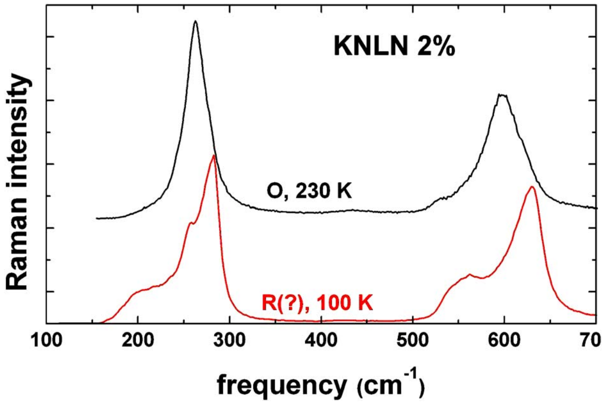

FIG. 4. (Color online) Spectra in the lowest-temperature phases in KNLN.

There is clear hysteresis at each transition, with no evidence of a mixed-phase region between the rhombohedral and orthorhombic phases of KNN. A similar close correspondence to KN is found in KNLN spectra for the tetragonal and orthorhombic phases. In contrast, we find that even a minimal 2% Li substitution leads to a lowest-temperature phase with Raman spectra that differ from the rhombohedral-phase spectra of KNN and KN. It is clear that the entire region near K:Na of 50:50 and for Li concentrations below 2% require further exploration to investigate if the phase boundary these results suggest occurs between 0 and 2% Li.

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