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Light scattering from $(K_{0.5}Na_{0.5})_{0.2}(Sr_{0.75}Ba_{0.25})_{0.9}Nb_2O_6$ with the tungsten bronze structure: An analogy with relaxor ferroelectrics

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The Brillouin and Raman scattering from a complex single crystal from the tungsten–bronze family, $(K_{0.5}Na_{0.5})_{0.2}(Sr_{0.75}Ba_{0.25})_{0.9}Nb_2O_6$ doped with Cu^{2+} (KNSBN:Cu), have been comparatively studied in a wide temperature range around the ferroelectric transition. Step-like anomalies in hypersonic velocity and damping confirm the first-order structural transition. These anomalies look like some perturbations on the high-temperature slopes of both a broad dip in sound velocity and a broad maximum in damping that develop in a wide temperature range. The acoustic behavior of KNSBN:Cu does not simply follow the Landau theory prediction valid for many ferroelectrics. Instead it resembles that of relaxors, to which the KNSBN:Cu behavior is analogous intrinsically. The total intensity of the Raman spectra as well as the intensity of separate internal and external vibrations and their width correlate with acoustic anomalies, namely there are step-like drops at the same temperature as the first-order transition and a broad range where the intensity is drastically increased. All these broad anomalies imply the existence of a wide preceding phase in respect to the relaxor ferroelectric state. Unusual properties of this preceding phase are discussed as well as the phase diagram relation to the dynamical evolution of other relaxors from the perovskite family, such as $PbMg_{1/3}Nb_{2/3}O_3$ and $Na_{1/2}Ba_{1/2}TiO_3$.
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I. INTRODUCTION

The present work is devoted to the Brillouin and Raman spectroscopy studies of a single crystal $(K_{0.5}Na_{0.5})_{0.2}(Sr_{0.75}Ba_{0.25})_{0.9}Nb_2O_6$ with copper–ion point defects (KNSBN:Cu). This complex compound has been developed as a remarkable photorefractive material.[1] KNSBN originates from the tungsten–bronze family of ferroelectrics. KNSBN has two close ancestors in this family, $Sr_xBa_{1-x}Nb_2O_6$ (SBN) and $Ba_2NaNb_5O_{15}$ (BNN).[2] K and Na additions to SBN increase the Curie temperature of materials of the KNSBN type, and also the advantage of large electro-optic coefficients of SBN remains available. The Cu^{2+} doping provides the further enhancement of the photorefractive properties of KNSBN.[1,3] From a crystallographic point of view, the KNSBN crystal occupies an intermediate position between SBN and BNN. On the one hand, there is a tendency from order to disorder in the sequence of these three compounds. BNN is a mostly ordered material, whereas SBN is rather disordered because Sr and Ba ions are distributed randomly and a one-sixth fraction of interstices remains vacant. On the other hand, the crystal structure stability changes in an opposite direction in the sequence. In spite of an obvious disorder, the SBN ferroelectric phase seems to be rather stable below the sole transition, although incommensurate superstructures have been also detected for some Sr–Ba compositions.[4] The BNN crystal seems to be very unstable and exhibits a rather unusual sequence of six phases including incommensurate structures[5] (and references therein). Even slight deviations from stoichiometry may produce some discommensurations in BNN.

Thermal stability of the KNSBN structure with the ion arrangement just between that in SBN and BNN is a matter of considerable interest for both applied and scientific approaches. However, the question about the structure stability seems to be open. According to recent Raman scattering studies,[6] some hidden transformations may occur in KNSBN below the Curie temperature, manifesting a drastic thermal change in the total intensity of the Raman modes apart from any established phase transition.

Brillouin scattering has been a sensitive method in our studies of dynamic changes in the structure of relaxor ferroelectrics from the complex perovskite family, such as $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) and $Na_{1/2}Bi_{1/2}TiO_3$ (NBT).[7–9] In NBT, the sequence of cubic-tetragonal-trigonal transformations manifests itself by sharp damping peaks. In PMN without any electric field, Brillouin scattering reveals the temperature range of the frustrated ferroelectric transition marked by a sharp peak in damping. No anomaly has been found in this range in the behavior of other characteristic values without the electric field. A definite ferroelectric transition to the trigonal phase at $T_c \approx 210$ K occurs only in an external field above the threshold value.[10] Some phenomena have been found in PMN, such as dispersion of sound velocity in a wide temperature range,[11] pseudocubic acoustic anisotropy in spite of development of ferroelectric

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properties,[12,13] and the unusual background in the Brillouin spectra with a pronounced temperature dependence[14] that evidenced the existence of a central peak in light scattering.[15] Pseudocubic behavior in combination with a drastic change in the background intensity of the Brillouin spectra by about two orders of magnitude were subsequently found in NBT.[7]

From a dielectric point of view, relaxor ferroelectrics from the perovskite family have much in common with the tungsten–bronze ferroelectrics. SBN has even been considered as a ferroelectric with the classical relaxor behavior.[2] In this respect, the Brillouin spectroscopy study of the tungsten–bronze ferroelectrics is expected to be interesting, especially in comparison with that of other relaxors. Combining the Brillouin and Raman spectra analysis, we continue our search for hidden transformations in KNSBN:Cu from the tungsten–bronze family.

II. EXPERIMENT

The KNSBN:Cu single crystal was grown by the Czochralski method. This crystal was doped with 0.04 wt % of CuO. Two rectangular samples, one with edges about 5 mm for Brillouin scattering and another one of $7\times5\times1$ mm^3 for Raman scattering, were oriented along the principal axes.

Brillouin backscattering spectra were analyzed by a five-pass Fabry-Pérot interferometer. The sample was illuminated along the fourfold axis by an argon-ion laser with $\lambda=514.5$ nm. A narrow-band ($\sim$1 Å) interference filter was used to eliminate the scattering contribution beyond the Brillouin components.

The argon laser with the same wavelength was also used as an excitation source of Raman scattering. Spectra were recorded by a triple grating spectrometer ISA Model T 64000 equipped with a liquid nitrogen cooled charge coupled device detector and with a Raman microprobe system. Both the backscattering and the right-angle geometry were used. For temperature measurements a modified Cryogenic Tech. Closed-Cycle Refrigerator Model 20 was used with a Lake-Shore DRC–84C temperature controller (accuracy of the temperature control was within about ±0.5 K). The raw Raman spectra were deconvoluted using the Jandel Peakfit software program.

III. CRYSTALLOGRAPHIC CHARACTERIZATION OF KNSBN

Let us consider in general why KNSBN occupies some intermediate position between SBN and BNN. The framework of sharing corner oxygen octahedra with the Nb ions in the center forms tetragonal ($A1$), pentagonal ($A2$), and trigonal (C) interstices in the tungsten–bronze structure.[16] Both the tetragonal and pentagonal interstices are completely occupied in BNN by the Na and Ba ions, respectively. The phase diagram for BNN shows a complicated sequence of phases, all of which below $T_c=853$ K are ferroelectric and some are incommensurate[5] (see references therein). An orthorhombic quasicommensurate phase is encountered around room temperature. This extended phase of obviously unstable characteristics, even though they are remarkable, hinders a reliable application of BNN. As one can see, ordering in the ion arrangement in the tungsten–bronze structure does not stabilize the ferroelectric phase. Unlike BNN, the amount of Sr and Ba ions in SBN is more than the pentagonal interstices could accommodate but it is not enough to occupy all of the tetragonal and pentagonal interstices. The Sr and Ba ions are distributed randomly among these two positions and one-sixth of them remain vacant. In spite of an obvious disorder in comparison with BNN, the SBN structure seems to be more stable with only one ferroelectric transition. The Curie temperature depends on the Sr–Ba composition. However, in some cases there were found incommensurate superstructures in SBN as well.[4] The ferroelectric-paraelectric transition is assumed to be tetracritical[17] and one may suppose another phase transition above T_c.[18,19] Probably, all possible structural modifications in crystals of SBN with different compositions have not been clarified yet.

The ion arrangement in KNSBN:Cu is of an intermediate type. All tetragonal and pentagonal interstices in KNSBN:Cu cannot be occupied though there are half as many vacancies as in SBN. A smaller Na ion prefers most likely the tetragonal interstices as in BNN, whereas a part of the larger K ions is expected to be found in the pentagonal interstices. Part of the Sr and Ba ions should be randomly placed in the tetragonal interstices. The smaller trigonal interstices accommodate an additive of the small Cu^{2+} ions. It seems that the crystal stability is not affected by doping concentrations under 0.1 wt %.[3] The KNSBN crystal with a close but slightly different composition, namely $(K_{0.5}Na_{0.5})_{0.4}\times(Sr_{0.75}Ba_{0.25})_{0.8}Nb_2O_6$ with a changed relation between (K,Na) and (Sr,Ba), has the Curie point at 448 K.[20,21] As in most tungsten–bronze materials,[2] the symmetry changes from $4/mmm$ above T_c to $4mm$ below T_c. Another phase transition with a strong dielectric dispersion was found at low temperature about 70 K.[22,23] That KNSBN composition had enough (K,Na) and (Sr,Ba) ions to occupy all of the tetragonal and pentagonal interstices. Slightly different composition and the appearance of vacancies reduce the Curie point in our sample of KNSBN:Cu down to 413 K.[24] Analysis of the low-frequency Raman spectra has confirmed[6,25] that the symmetry below T_c remains tetragonal in KNSBN:Cu.

IV. BRILLOUIN SCATTERING

The longitudinal acoustic phonons, whose frequency was determined by the c_{33} elastic constant, were followed in KNSBN:Cu from room temperature on heating up to 510 K. The Brillouin spectra were recorded in the backscattering geometry, so that the wave vectors of incident ($\mathbf{k}_i$) and scattered ($\mathbf{k}_s$) light as well as of phonons ($\mathbf{q}_{\mathrm{ph}}$) were parallel to the fourfold axis (c_4). Several spectra are reproduced in Fig. 1 to demonstrate a drastic change in the acoustic phonon width (δv) in the range of the ferroelectric phase transition. The other phonon parameter, Δv or the Brillouin shift from the laser line, also exhibits pronounced temperature dependence.

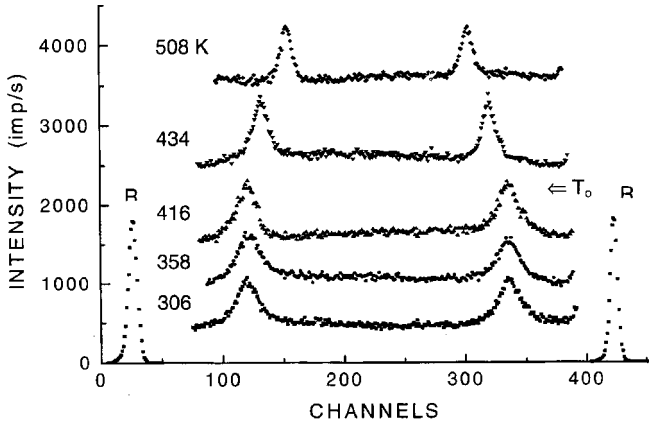

FIG. 1. Brillouin spectra of KNSBN:Cu at different temperatures. Rayleigh lines *(R)* reduced by a filter are shown for simplicity only for the spectrum at 306 K. For clarity, the spectra are shifted one from another along the *Y* axes by 500 units (306, 358, and 416 K) and by 1000 units (434 and 508 K). $T_0 \sim 420$ K is schematically shown by an arrow in order to emphasize the difference between adjacent spectra (416 and 434 K). Free spectral range (FSR) of the interferometer is 40.31 GHz so that the Brillouin doublet (Stokes and anti-Stokes lines) appears in the second order of the spectra.

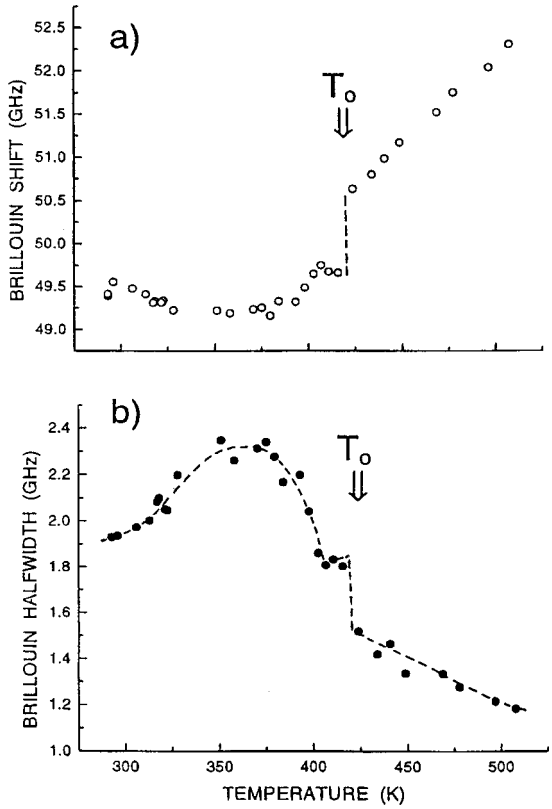

FIG. 2. The temperature dependence of the Brillouin shift (a) and the width at half maximum of Brillouin components (b). The average instrumental broadening of 0.8 GHz has not been subtracted.

The Brillouin shift and the width of the Brillouin component at half maximum for the longitudinal acoustic phonons under consideration are shown in Fig. 2 as a function of temperature. The Brillouin shift is proportional to the hypersonic velocity of phonons, whereas the width determines the damping of phonons. As one can see, in the range of the ferroelectric transition, there is a step-like anomaly in the behavior of both the sound velocity and damping. It is well known that a step-like anomaly for sound velocity is usually expected in the vicinity of a second-order ferroelectric transition if there is a specific connection between the phase transition and elastic properties, namely a coupling squared in order parameter and linear in strain, a $Q\eta^2 u$-type coupling, where Q is an electrostriction coefficient.[26,27] From this point of view, the sound velocity anomaly in KNSBN:Cu resembles the elastic behavior of many other materials with ferroelectric transitions.[28,29] However, the hypersonic damping in KNSBN:Cu exhibits a more complex behavior than the Landau–Khalatnikov maximum, which is expected in the case of $Q\eta^2 u$-type coupling. The experimental points in Fig. 2(b) show a small ''sharp'' shoulder in damping as the phase transition is approached from below, followed immediately by a step-like decrease in damping to half its previous value. On the whole, the anomalous step-like behavior of both the sound velocity and damping indicates a first-order phase transition in KNSBN:Cu.

A more important and interesting result is how these two elastic characteristics, the sound velocity and damping, are changing in a wide temperature range from 300 up to 500 K. Let us consider their behavior on cooling. The linear reduction in sound velocity in the paraelectric phase is followed by a broad dip in the ferroelectric phase. The hypersonic damping develops like a very broad peak with the maximum value at about 360 K far below the phase transition. Roughly speaking, the velocity dip and damping peak look like reflections of each other in a horizontal mirror plane. Sharp anomalies in both the sound velocity and damping in the vicinity of the phase transition appear as a slight perturbation on the high-temperature slopes of the broad dip and of the broad peak, respectively.

On the whole, the broad anomalies in sound velocity and damping are very similar to those in some relaxor ferroelectrics from the complex perovskite family, such as PMN and NBT.[7–9,13] The sharp structure of the hypersonic damping in KNSBN:Cu in the vicinity of the phase transition correlates with the ''thin'' structure of corresponding broad damping maxima in PMN and NBT mentioned above in the Introduction section. This similarity confirms a special character of some intermediate phase marked by broad elastic anomalies. Now let us consider what anomalies appear in the Raman spectra of KNSBN:Cu in the same temperature range.

V. RAMAN SCATTERING

The single crystal of KNSBN:Cu shows a set of differently polarized spectra with many lines that are rather broad and overlap one another. The diagonal (ZZ) Raman spectra taken in the backscattering geometry are depicted in Fig. 3 at five characteristic temperatures. The diagonal (ZZ) spectrum is the most intense one among all polarized spectra. The (ZZ) spectrum differs considerably from two other diagonal spectra (XX) and (YY) which are almost identical.[6,25] This important difference implies a tetragonal symmetry at room temperature in accordance with the character of the Raman tensor, namely only the $A_1(z)$ modes appear in the (ZZ) spectrum, whereas both the $A_1(z)$ and B_1 modes are present

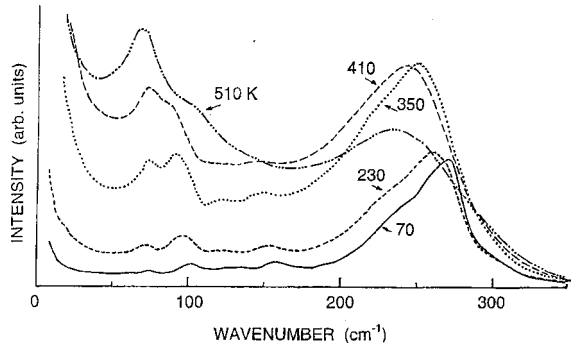

FIG. 3. Thermal evolution of the (ZZ) Raman spectra. The raw data are presented.

in the (XX) and (YY) spectra. No difference among three diagonal spectra appeared in the main ferroelectric phase of BNN around room temperature, and that result was considered as a proof of the orthorhombic structure.[5,30]

The difference between the diagonal spectra is clearly seen in the low-frequency parts of the Raman spectra, $\theta \leqslant 120\ \mathrm{cm}^{-1}$, which consist of some external lattice vibrations involving cation motions relative to the oxygen octahedron framework (Fig. 3). The framework vibrations are represented by two sets of strong Raman lines of the $A_1(z)$ symmetry around 260 and 640 cm^{-1} (Fig. 3). These groups of modes are characteristic of the tungsten–bronze structure. They were identified in BNN[30] and SBN[19] as internal modes of the NbO_6 octahedron, namely the O–Nb–O bending and Nb–O stretching vibrations. Certainly, the spectra of internal vibrations are very similar in all three materials, SBN, KNSBN:Cu, and BNN. Only the external mode analysis[6,25] evidences that the KNSBN:Cu crystal has the tetragonal structure characteristic of the tungsten–bronze-type ferroelectrics in spite of a formal similarity to BNN. The tetragonal SBN crystal exhibits spectra similar to that in KNSBN:Cu, although the low-frequency B_1 mode has not been found.[19]

However, the tetragonal character of the Raman spectra in KNSBN:Cu does not exclude the possibility of incommensurate structures. As we mentioned above, the orthorhombic symmetry of BNN manifests itself by some characteristic details in the Raman spectra, namely there are only $A_1(z)$ modes in the three diagonal spectra and the initial E modes from the tetragonal high-temperature phase split into pairs of B_1 and B_2 symmetry in the off-diagonal (XZ) and (YZ) spectra. These characteristic features remain without altering throughout the orthorhombic quasicommensurate phase as well as in both adjacent incommensurate phases at lower and higher temperatures.[5] The characteristic splitting vanishes only above the incommensurate–commensurate transition to the real tetragonal phase.[5]

Soft modes have been found by Raman scattering neither in KNSBN:Cu of the present composition nor in KNSBN crystals[21] with a close but slightly different composition mentioned above in Sec. III. The most pronounced anomaly in the Raman spectrum behavior of KNSBN:Cu at the ferroelectric phase transition could be connected with a change in the selection rules when the ferroelectric 4*mm* point group transforms into the 4/*mmm* point group with an inversion

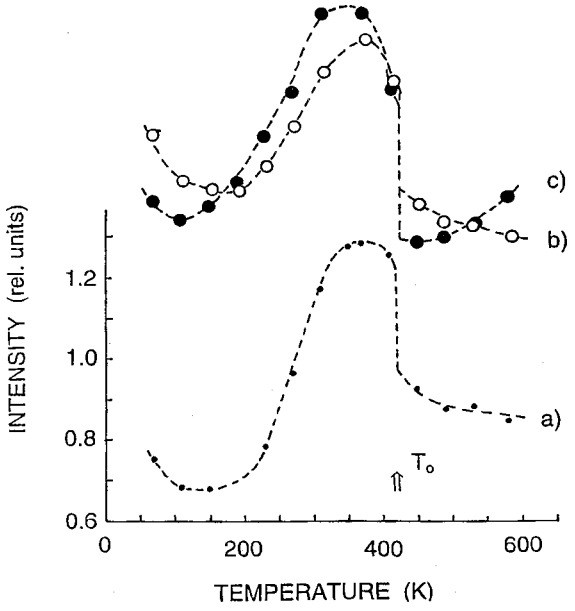

FIG. 4. The temperature dependence of mode intensity in the (ZZ) Raman spectra: (a) integrated intensity (integration in the range from 20 to 400 cm^{-1}); (b) an internal vibration at around 260 cm^{-1} (0–Nb–O bending); (c) an external vibration at about 120 cm^{-1}. The intensity scale represents an area under the corresponding curves taken after elimination of the population factor by using Eqs. (1) and (2).

center. Only about half as many modes remains Raman active in the high-temperature phase, whereas another half becomes only infrared active. This transformation implies that the total spectrum intensity is a sensitive tool to detect the ferroelectric phase transition. Comparison of the (ZZ) spectra at different temperatures (Fig. 3) shows that in fact the intensity of the broadband around 260 cm^{-1} changes drastically in the range of the transition. Moreover, this band obviously continues changing in intensity even at lower temperatures in the ferroelectric phase.

In order to obtain a correct result, we eliminated from our consideration the trivial temperature dependence of the mode intensity due to the population factor $[n(v)+1]$ that connected the scattering cross-section $S_0(v)$ with the spectral response function $S(v)$ observed experimentally

$$S(v)=S_0(v)[n(v)+1], \tag{1}$$

where the population factor was given by

$$n(v)=(e^{hv/kT}-1)^{-1}. \tag{2}$$

The thermal behavior of the scattering cross section in KNSBN:Cu was calculated in a wide temperature interval from 70 up to 580 K. The spectral intensity was integrated in the range from 20 to 400 cm^{-1} that included the most characteristic Raman spectrum of the tungsten–bronze structure, namely several external lattice modes as well as the strong internal bending modes of the NbO_6 octahedron. The intensity integration was restricted to 400 cm^{-1} because there are no Raman lines in the range from 350 to 550 cm^{-1} (Fig. 3). The lower curve (a) in Fig. 4 shows that there is an abrupt reduction in intensity at about 420 K, which could be expected, and in addition there are two unexpected anomalies in the ferroelectric phase. There is a drastic change in inten-

sity in the range 200–350 K and an anomalous reduction in intensity above a possible additional transition at about 70 K that has been found in the related KNSBN materials.[22,23] One should emphasize that the intensity change between 200 and 350 K exceeds the anomalous drop at about 420 K, although no transition has been reported in that temperature region for the KNSBN family. Thus, the Raman scattering studies give new evidence that the structure of KNSBN:Cu in the ferroelectric phase is not so stable.

VI. DISCUSSION

A. Definite structural transition at T_0

One should emphasize first of all that the anomalous point at about 420 K exhibits both hypersonic step-like anomalies (Fig. 2) and Raman intensity drop (Fig. 4). This temperature is slightly above $T_c \approx 413$ K obtained from dielectric measurements.[24] Although the relaxor-type dielectric response of KNSBN:Cu does not imply an exact and sole temperature for the Curie point, the difference seems too large to be ignored. We suppose that these two temperatures correspond to different events in the dynamical behavior of KNSBN:Cu. The first temperature, $T_0 \sim 420$ K, manifests a structural phase transition of the first order. The phase below T_0 is characterized by many anomalous properties. The dielectric response reveals the mean Curie temperature, $T_c \approx 413$ K, characteristic of relaxors. In this respect, the evolution of KNSBN:Cu correlates with the behavior of NBT that is a relaxor from the pervoskite family. The cubic-tetragonal ferroelastic transition of the first order is positively detected by acoustic anomalies, such as a sharp maximum in hypersonic damping and a small step in velocity[7,9,31] without any anomaly in the dielectric response. The broad dielectric maximum in NBT[32] appears at a lower temperature ($T \sim 640$ K) just in the intertransition range between the cubic-tetragonal transition ($T_{c1} \sim 820$ K) and the next transition in the sequence, the tetragonal-trigonal transition ($T_{c2} \sim 590$ K).

B. Acoustic anomalies of the ''relaxor type''

The similarity between KNSBN:Cu and some perovskite-type relaxors is emphasized by the broad acoustic anomalies, which are much alike in KNSBN:Cu (Fig. 2) and in both NBT and PMN.[8,9] Broad anomalies for both the hypersonic velocity and damping in NBT are centered in the intertransition region ($T_{\max} \sim 675$ K) and extend beyond transitions at T_{c1} and T_{c2}. This acoustic anomaly in the intertransition region was attributed to fluctuations of two coupled order parameters.[7] The dielectric response of NBT (Ref. 32 and references therein) is very close to that predicted for a two phase transition sequence with coupled order parameters.[33] This model with competing interactions[33] may also explain the broad intermediate phase in NBT with such a special characteristic as double hysteresis loops observed in the range near the low-temperature boundary. As one can see, the preceding phase in NBT (in relation to the relaxor ferroelectric state) is very broad and includes, in addition, an enigmatic range near the low-temperature boundary. Alternatively, this range may actually be another phase, between the tetragonal ferroelastic and trigonal ferroelectric phases. This phase exhibits some very unusual properties including the most clearly expressed double hysteresis loops. This phase has been considered as an antiferroelectric phase for a long time (Refs. 34 and 35 and references therein), although structural methods, such as x-ray[36] and neutron scattering studies,[37] and recent dielectric measurements[38] deny the existence of any antiferroelectric phase. In any case, the preceding phase (or phases) with some unusual properties does really exist in NBT, and it plays a key role in the evolution to the ferroelectric state. The preceding phase becomes ''softer'' for sound propagation, namely the sound velocity reduces, whereas the sound damping increases considerably. As one can see, KNSBN:Cu exhibits a similar phase with very broad acoustic anomalies of the same type.

The broad acoustic anomalies in sound velocity and damping in PMN and NBT are almost alike (Fig. 5 in Ref. 9). The principal difference is that NBT possesses the proven sequence of cubic-tetragonal-trigonal transformations,[35–39] whereas PMN evolves to the ferroelectric state without any macroscopic structural change.[40] However, a definite ferroelectric transition occurs in PMN in an external electric field.[10] Being frustrated in normal conditions without an external field, this transition manifests itself in a sharp fluctuation damping maximum at about 210 K in Brillouin scattering.[8,9] Returning to the related results in KNSBN:Cu, one can emphasize that the acoustic anomalies measured by Brillouin scattering correlate with hidden changes in the structure of relaxors, even if a ferroelectric transition is frustrated.

As we know, on the one hand the broad acoustic anomalies, found recently in PMN and NBT[7–9] and now in KNSBN:Cu, have no analogs among any other materials. On the other hand, the preceding phase with double hysteresis loops has been found in a number of complex perovskite materials, such as $PbCo_{1/2}W_{1/2}O_3$ (PCW),[41,42] $PbYb_{1/2}Ta_{1/2}O_3$,[43] and $PbSc_{1/2}Ta_{1/2}O_3$ (PST).[44] The transmission electron microscopy study of PCW evidences a complicated evolution to the ferroelectric state through an ''antiferroelectric incommensurate'' phase.[45] That study has found a direct interaction between the ''antiferroelectric domains'' and the incommensurate structure that implies a significant effect of pinning in the behavior of most physical values. Transmission electron microscopy has also revealed a modulated antiferroelectric state in the preceding phase of PST with an ordinary diffuse ferroelectric phase transition.[46] Returning to KNSBN:Cu, one can hope for advanced microstructural studies in the nearest future.

C. An exceptional change in intensity of the optical modes

Let us consider the behavior of Raman modes of KNSBN:Cu in the range of the broad acoustic anomalies. One may explain in principle the step-like increase in intensity of the Raman modes at T_0 [Fig. 4, the (a) curve] by flare-up below T_0 of the former infrared modes in Raman scattering after the upper centrosymmetric phase transforms to the lower phase without a center of symmetry. However, the total increase by 50% seems too large and, as one can see

(Fig. 3), the increase concerns not the separate parts of the spectrum where the infrared modes may be flaring up, but almost all parts of the spectrum. The intensity of flaring up modes is a measure of the structure change at a phase transition. The structure distortions at the ferroelectric transitions, especially of the second order, are usually very small,[2] so that even the first-order transition in KNSBN:Cu cannot explain an increase of 50%. It is interesting to compare how the mode intensity changes in KNSBN:Cu and SBN, which also possesses a ferroelectric transition between two tetragonal symmetries, $4/mmm \rightarrow 4mm$. The mode intensity behavior around T_c in SBN with $x=0.61$ (SBN:61) is available.[19] The data discussed below are corrected according to Eqs. (1) and (2) in order to eliminate the population factor effect. In contrast with KNSBN:Cu, the total intensity in SBN:61 changes at T_c only a little, about 1.03 times. However, this effect seems to be enough to detect the ferroelectric phase transition near 338 K and assume an additional one near 393 K with almost the same change in intensity, about 1.05.[19] One can make two conclusions. First, Raman scattering is rather sensitive to some changes in the tungsten–bronze structure. The possibility of another phase transition in the SBN family has been suggested earlier,[16] just at 408 K for SBN with $x=0.72$. Second, the contribution of the infrared modes flaring up in the Raman spectra below T_c is insignificant, as it should be at small structural distortions. Another result on SBN:61 seems to be more interesting, especially in comparison with KNSBN:Cu. The intensity of the internal vibrations around 630–640 cm^{-1} is unaffected by both the ferroelectric and additional transitions. The same behavior is assumed for the 250–260 cm^{-1} band. Subtracting the unchanged intensities of these two intense bands from the total intensity, one can obtain a marked change for the remaining low-frequency part of the spectrum, about 1.44 at T_c and 1.25 at the next possible transition. These two are the only anomalies in the thermal behavior of the Raman spectra of SBN that have been reported.[19]

The behavior of the Raman spectra of KNSBN:Cu contrasts in several respects with that of SBN:61 considered above. The effect for total intensity is large, about 1.5 [Fig. 4, the (a) curve]. The intensity of the 260 cm^{-1} band of internal vibrations changes drastically [Fig. 4, the (b) curve] as well as the intensity of external vibrations in the low-frequency spectrum. The behavior of a mode at about 120 cm^{-1} is shown in Fig. 4, the (c) curve as an example. Another important difference is that the total intensity as well as the intensity of the separate modes continues increasing after a jump at T_0. The maximum value is reached at lower temperatures, about 350–370 K. This additional increase is about as great as the jump increase, or a little less in some cases. In this respect, the anomalous behavior of the Raman mode intensity correlates clearly with the broad acoustic anomalies. At further cooling to about 200 K, the largest anomaly develops in the intensity behavior. The total intensity as well as the intensity of separate modes corresponding to both the external and internal vibrations reduces almost two times on average. On the whole, there is a broad range in KNSBN:Cu from about 200 K up to T_0, which is character

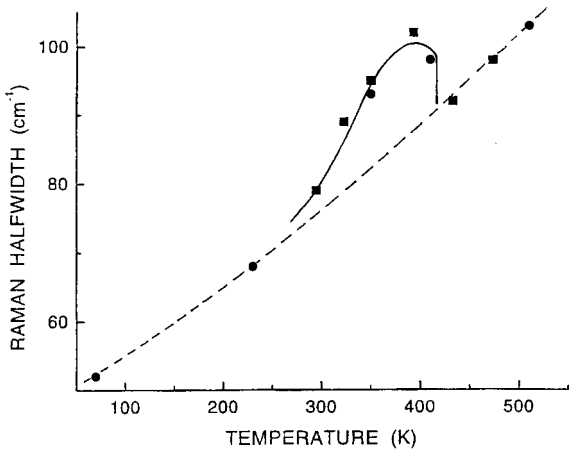

FIG. 5. The temperature dependence of an effective mode width taken at half maximum of the complex band around 260 cm^{-1}. The dashed line shows an extrapolated monotonic behavior determined by the experimental data beyond the anomalous range where the solid line is merely a guide for the eye.

ized by a dynamical change in the Raman mode intensities. As far as we know, no anomalies of this type have been reported for any ferroelectrics.

D. Dynamical mode broadening

The anomalous evolution of intensity does not mean a change of the spectra as a whole. Figure 3 shows clearly that a broad band around 260 cm^{-1}, which is structureless above T_0, becomes asymmetric below with a structure developing suddenly along the low-frequency slope. The most pronounced structure, which is also characterized by the broadest bandwidth, appears in the range of the largest intensity. Reduction in intensity below 300 K is followed by narrowing of both the structure and the width owing to shrinking the low-frequency slope of the band. In order to characterize this process, we measured an effective total width of the 260 cm^{-1} band at different temperatures. The result in Fig. 5 shows a monotonic increase of the effective width in a wide temperature range plus an anomalous additional broadening in the enigmatic phase. A drop in the effective width at T_0 finishes the anomaly and returns the width to an extrapolated monotonic dependence. The width drop at T_0 emphasizes a similarity between all anomalous properties considered above: hypersonic velocity and damping as well as intensity of the Raman mode. Almost all modes in the Raman spectra of KNSBN:Cu exhibit dynamical broadening in the enigmatic phase under consideration. A similar dynamical broadening around the singlet A_{1g} mode has been clearly demonstrated in the Raman spectra of PST.[47] The pronounced structure around a clearly singlet structureless mode in PST (at higher temperatures) was accompanied by both a width broadening and an intensity increase. These effects were found in the PST relaxor in the preceding phase above the so-called diffuse ferroelectric phase transition.

No evidence of a change in the crystal structure of KNSBN:Cu just below the ferroelectric transition has been published. However, both Brillouin and Raman scattering revealed an anomalous broad phase with nontrivial properties.

By analogy with other relaxors like PMN or PST,[9,47] one can suppose that the complex structure and broadening of modes in KNSBN:Cu are mostly connected with a breakdown in the wave vector selection rules, so some symmetry points along the corresponding optical phonon branches in the Brillouin zone contribute to the Raman scattering around the initial modes in the zone center. The low-frequency slope of the Raman modes is affected the most because the dispersion in the Brillouin zone usually reduces the phonon frequencies along the optical branches. Even a weak effect in the selection rules breaking may result in substantial contributions to the initial mode intensities because the density of phonon states in the special points of the Brillouin zone is considerably higher than at the zone center. One should distinguish the present dynamical broadening from a disorder effect. Disordering in the ion distribution leads to the relaxation of translational symmetry. One also expects the relaxation of inversion symmetry for disordered systems. The loss of translational and inversion symmetry allows us to see in Raman scattering some contributions from the Brillouin zone as well as some infrared and silent modes. Significant effects of this type due to the mixed nature of materials were found and analyzed in many crystals, perhaps first in the complex perovskite $KTa_{1-x}Nb_xO_3$.[48] Disordering leads to static broadening of some modes. One may expect to find the static effect in KNSBN:Cu above T_0 and below 200 K; however, by analogy with relaxors from the perovskite family, the contribution due to static disorder appears to be insignificant.

We considered a mechanism of dynamical broadening of some initially existent modes in the anomalous phase of KNSBN:Cu analogous to that in other relaxor ferroelectrics, PMN and PST. Some additional modes may appear also due to relaxation of inversion symmetry if the anomalous phase is really a preceding phase in the evolution to the ferroelectric state of a relaxor type. In this respect, there is a close analogy with such complex systems as $KTaO_3$ with off-center Li and Nb ions at low concentrations[49,50] where the appearance of normally forbidden modes, namely infrared-active and silent modes, has been explained by precursor effects. The precursor order is initiated by polar microregions, which are formed at relatively high temperatures above the ferroelectric transition. Unfortunately, the rich and complex Raman spectrum of KNSBN:Cu consists of broad and overlapping bands at temperatures above T_0, especially in the range of internal vibrations. Therefore, it is difficult if even possible to make real and justified fitting by the phonon functions in order to follow the behavior of separate modes on cooling. The possible appearance of some contributions from the Brillouin zone does not allow us to use a usual phonon fitting below T_0. Any physically justified fitting is impossible at present because the dispersion of optical phonon branches in the Brillouin zone as well as the density of states are unknown for KNSBN materials. We have been compelled to confine ourselves to a qualitative analysis of the Raman mode behavior. For example, we calculated an effective width and an effective intensity of a group of modes around 260 cm^{-1} (Figs. 4 and 5).

VII. CONCLUSIONS

The complex evolution of KNSBN:Cu to the ferroelectric state has been revealed by light scattering experiments. No soft mode has been found in Raman scattering. However, some other characteristics, such as mode intensity, evidence the complex dynamic evolution that includes the first-order structural transition followed by a broad anomalous phase. The behavior of the longitudinal acoustic phonons in Brillouin scattering does not show any normal coupling with a possible but ''unseen'' soft mode. Their behavior confirms the first-order transition and reveals an anomalous phase below in agreement with Raman scattering.

We assume that an anomalous phase in KNSBN:Cu should be considered as the preceding phase in respect to the relaxor ferroelectric state. The preceding phase is characterized by high sound damping, reduction of sound velocity, and breaking down in the selection rules for Raman scattering. The mode analysis implies that the translational symmetry is dynamically distorted in this phase. The broad anomalies in KNSBN:Cu obtained from Brillouin and Raman scattering resemble unusual features in the behavior of other relaxors, such as NBT, PMN, and PST from the perovskite family. KNSBN:Cu is distinguished from others by a strong combination of different features in one crystal. In this respect KNSBN:Cu has no analogs among any materials studied.

The anomalous phase in NBT, PMN, and PST plays the role of a preceding phase in respect to the relaxor ferroelectric state.[7–9,32,44] A model with competing interactions[33,44] seems to be very fruitful in the explanation of some unusual properties of the preceding phase. The problem is that a real interaction between ferroelectric and ferroelastic ordering has been confirmed only in NBT.[37] In PMN, even the ferroelectric transition is frustrated under normal conditions.[10,40] Unlike NBT, this frustration may hide the competing interaction with another (nonferroelectric) phase of unknown nature. The microstructure of the preceding phase in relaxors is not quite clear, although some incommensurate features have been noticed in PST[46] and PCW.[45] Returning to KNSBN:Cu, one can assume that an incommensurate structure is quite possible, especially taking into account some energy competition between the commensurate and incommensurate structures in the thermal evolution.[51] Further structural studies are needed.

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