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Tu, C.-S., I. G. Siny, and V. H. Schmidt. " Brillouin Scattering in Na 1/2 Bi 1/2 TiO 3 ." Ferroelectrics 152, no. 1 (February 1994): 403–408. doi:10.1080/00150199408017654.

Brillouin Scattering in $Na_{1/2}Bi_{1/2}TiO_3$

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(Received August 9, 1993)

Abstact Measurements of Brillouin scattering in single crystal $Na_{1/2}Bi_{1/2}TiO_3$ are reported from 50 to 900 K which covers a cubic-tetragonal-trigonal succession of phase transitions, ending in a ferroelectric state. An extended dip in the hypersonic sound velocity and an extended maximum in the hypersonic damping were found with the extreme in the intertransition region. These anomalies are connected with a response of mixed fluctuations. The Brillouin spectra background confirms the existence of a central peak in light scattering whose intensity increases drastically in the same intertransition region.

INTRODUCTION

In this report we present the first results of Brillouin scattering measurements in $Na_{1/2}Bi_{1/2}TiO_3$(NBT) single crystals. This complex compound has a perovskite-type structure ABO_3 with two unlike valence cations Na^+ and Bi^{+3} distributed in the A-positions. In this respect NBT has a close relation to the large family of $AB'_x B''_{1-x} O_3$ compounds including relaxor ferroelectrics. The recent increasing interest in relaxor ferroelectric behavior has raised the question of phase transition dynamics also. NBT seems to be a suitable candidate for such a study. Neutron scattering confirmed a sequence of transformations (cubic-tetragonal-trigonal) to a final ferroelectric state at T < 450 K[1] (and references herein). The neutron studies indicated that the phase transition is driven by soft modes.

However, a simple soft mode concept is not valid in this case. Even in neutron experiments so-called softening of some modes at the M and R points of the Brillouin zone were not obtained directly but from analysis of the integrated scattered intensities. Raman scattering measurements also did not reveal any ordinary soft modes[2,3] but instead a strong, broad central peak[3] that seems to play a determining role in the phase transition dynamics. It is known from a long study of $Gd_2(MoO_4)_3$ that acoustic anomalies can help to reconstruct the soft mode dynamics in spite of the existence of overdamped modes or central peaks[4-6]. In order to reveal the phase transition dynamics from the acoustic anomalies, we started Brillouin scattering measurements in NBT.

EXPERIMENTAL RESULTS AND DISCUSSION

In our experiments the Brillouin spectra were obtained in the backscattering geometry. In order to reduce low-frequency scattering due to the central peak and the Raman signal from the low-lying F_{2g} mode we used a narrow-band (1 Å) interference filter. A cubic sample with edges about 5mm was illuminated along [001] direction by an argon laser with λ=514.5 nm, so the longitudinal phonons with wave vectors along the same direction were studied. Scattered light was analyzed by a Burleigh five-pass Fabry-Perot interferometer. The laser power was kept at ~50 mW to avoid local heating. For T < 298 K, a Leybold RGD-210 cold head was used for temperature control. Above room temperature an oven was used with a LakeShore PT-103 platinum resistance thermometer that was calibrated for high temperature. The error of temperature reading was about ±0.1 K. The sample was heated from ~46 up to ~903 K by steps and the data were collected automatically.

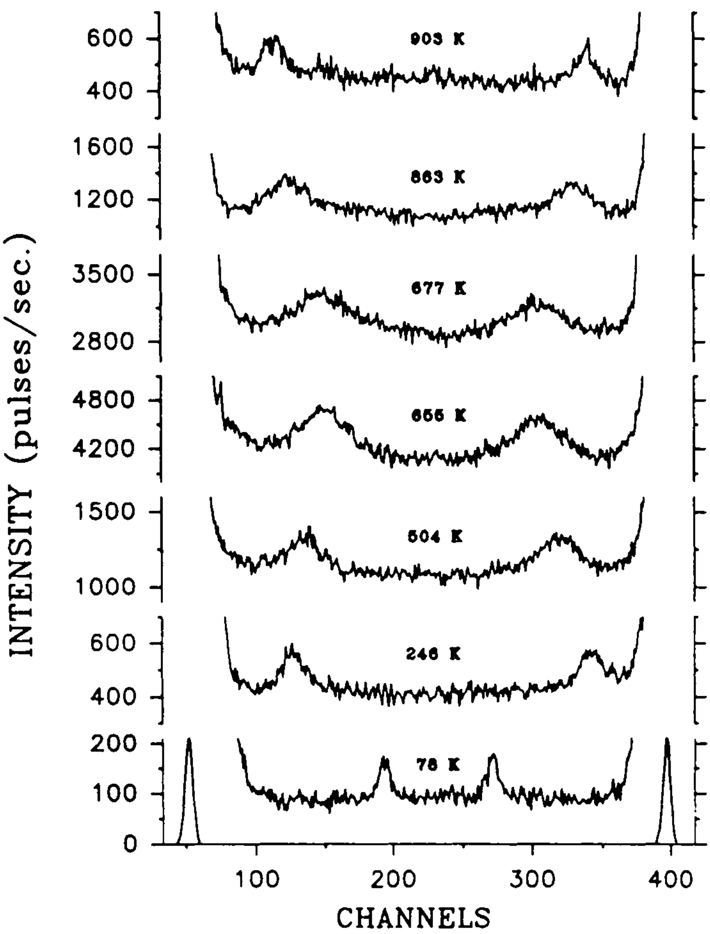

FIGURE 1 Brillouin spectra of NBT at different temperatures.

Fig. 1 illustrates qualitatively the changes in the Brillouin spectra obtained at different temperatures. The free spectral ranges of the interferometer are 30.20 GHz for all spectra at T > 235 K and 34.60 GHz for the spectrum at the bottom of Fig. 1 at T = 78 K so that the Brillouin doublet in NBT appears in the second order with respect to the Rayleigh line. As seen from the spectra, the position and especially the width of the Brillouin components are strongly temperature dependent. Fig. 1 also shows that the background in the Brillouin spectra changes drastically and has the largest value at ~ 650 K which exceeds many times the peak intensity of the Brillouin doublet. Qualitatively, the same behavior was found from comparisons of the background intensity and the central peak intensity from Raman scattering[3]. Strong background due to existence of a central peak in light scattered from NBT was the main origin of the data spreads in the vicinity of anomalies in the behavior of Brillouin shift and linewidth. Let us consider these anomalies now.

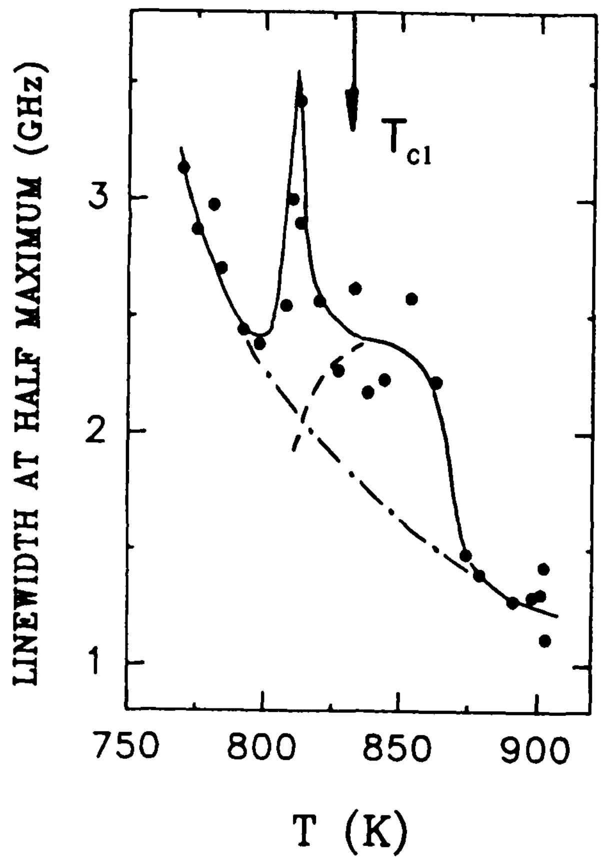

FIGURE 2 Damping of the longitudinal acoustic phonons vs. temperature in the vicinity of the cubic-tetragonal phase transition.

Both the Brillouin shift (or the hypersonic sound velocity) and Brillouin linewidth (or the hypersonic phonon damping) exhibit some anomalies in the vicinity of the first phase transition from a cubic to tetragonal phase at T_{c1}.~835 K. An increase of damping begins far above T_{c1} in the cubic paraphase (Fig. 2) and can be connected with the contribution of fluctuations in a full accord with increasing critical phenomena in neutron and Raman scattering [1,3] nearly in the same temperature region. We tried to reveal qualitatively the critical fluctuation contribution to damping by the dashed curve in Fig. 2.

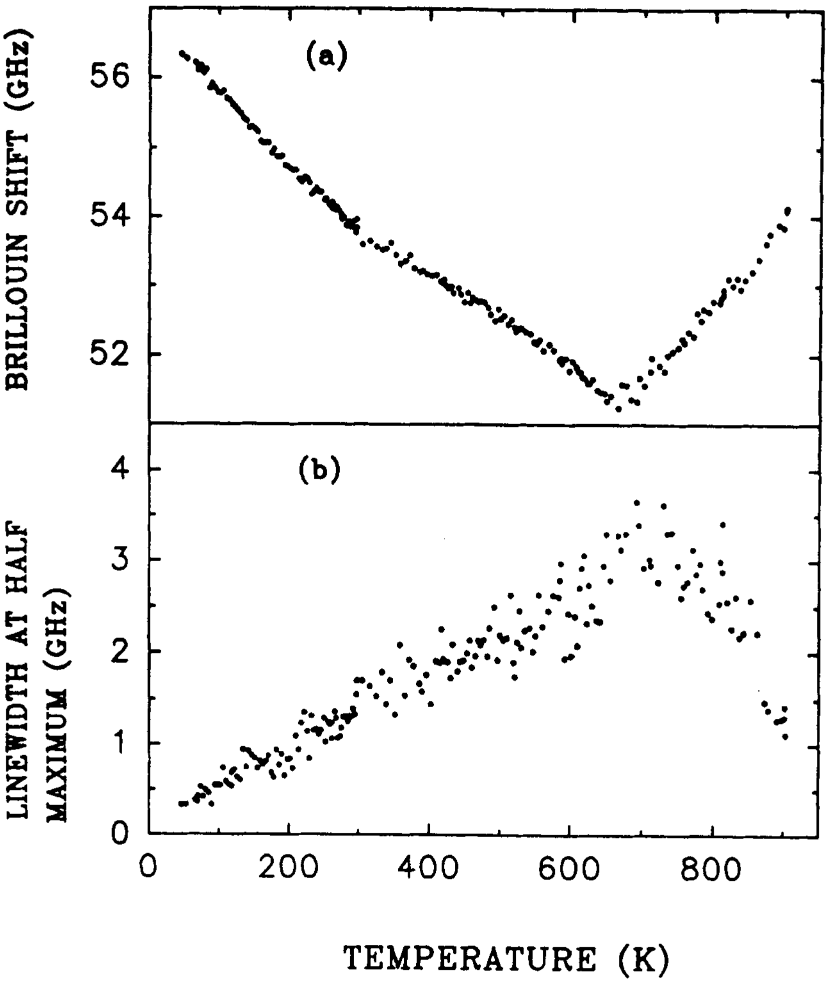

FIGURE 3 Temperature dependence of the Brillouin shift (a) and damping (b) for longitudinal phonons along [001] from 46 to 903 K.

Besides this, there is a "splash" of additional damping in the tetragonal phase close to T_{c1}. This latter peak is connected with the usual Landau-Khalatnikov maximum in damping but now it is shifted into the tetragonal phase due to dispersion. One can expect such a peak for longitudinal acoustic phonons to appear according to a η^2u-type coupling, squared in order parameter and linear in strain.

However, such traditional analysis can not describe all of this complicated situation in NBT. First, the fluctuation contribution to damping in the vicinity of T_{c1} is of the same order of magnitude and even exceeds the relaxation portion describing by the most effective η^2u-coupling from the Landau expansion. This comparison shows that there is a critical region for the order parameter dynamics in NBT in the vicinity of T_{c1}.

This implies an inescapable mixing of the order parameter and fluctuation contribution as was found for critical ultrasonic attenuation at the liquid helium λ-point[7]. Probably, in the case of T_{c1} in NBT a limit situation occurs when the two contributions can be still separated.

Second, the anomalies considered above seem to be small perturbations against the background of another increased damping process . We illustrate this fact by the broken curve in Fig. 2. On the whole, we found an extended dip in sound velocity and an extended damping peak (Fig. 3). It is difficult to find an perturbation connected with the second phase transition from the tetragonal to trigonal phase at T_{c2}. It is obvious that a linear superposition of two even critical anomalies at T_{c1} and T_{c2} can not explain the hypersonic damping behavior in NBT.

We suppose that a very important analogy exists between complex perovskites like NBT and some disordered systems like proton glasses[8]. This analogy implies a total response of mixed fluctuations with the wave vectors different from those characteristic of the T_{c1} and T_{c2} phase transitions. This competing process may therefore be expected to generate anomalies in the behavior of hypersonic sound velocity and damping just between two phase transitions but not in the vicinity of every transition point. Large fluctuation contributions provide critical behavior of NBT and prevent us from observing relaxation contributions of the order parameters.

CONCLUSION

The existence of a phase transformation sequence is characteristic of many crystals with the initial perovskite-type structure[9]. As a rule, different properties exhibit anomalies at phase transitions in agreement with that point in spite of the significant fluctuation contributions. As far as we know, no one has shown acoustic anomalies to be shifted to an intertransition region. Our experimental data have emphasized correlated anomalies in the behavior of different values: in the sound velocity and damping as well as in the background intensity, the latter being simply connected with a central peak in light scattering.

The authors would like to express sincere thanks to T.V. Kruzina for single crystal growth and to Prof. George F. Tuthill for helpful discussions. This work was supported in part by NSF Grant DMR-9017429 and an NRC-CAST Grant.

REFERENCES

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1. S.V. Vakhrushev, B.E. Kvyatkovsky, R.S. Malysheva, N.M. Okuneva, E.L. Plachenova and P.P. Symikov, Kristallografiya 34, 154 (1989) [Sov. Phys.Crystallogr. 34, 89 (1989)].
2. M.S. Zhang, J.R. Scott and J.A. Zvirgzds, Ferroelectrics Lett. 6, 147 (1986).
3. I.G. Siny, T.A. Smirnova and T.V. Kruzina, Fiz. Tverd. Tela 33, 110 (1991) [Sov. Phys. Solid State 33, 61 (1991)]; Ferroelectrics 124, 207 (1991).
4. W. Yao, H.Z. Cummins and R.H. Bruce, Phys. Rev. B 24, 424 (1981).
5. P.A. Fleury, K.B. Lyons and R.S. Katiyar, Phys. Rev. B 26, 6397 (1982).
6. I.G. Siny, Ferroelectrics 112, 73 (1990).
7. R.A. Ferrell and J.K. Bhattacharjee, Phys. Rev. B 23, 2434 (1981).
8. P. Xhonneux, E. Courtens and H. Grim, Phys. Rev. B 38, 9331 (1988).
9. M.E. Lines and A.M. Glass, **Principles and Applications of Ferroelectrics and Related Materials** (Clarendon Press, Oxford, 1977).