Dynamical Properties of the Relaxor Ferroelectric $0.71Pb(Ni_{1/3}Nb_{2/3})O_3$-$0.29PbTiO_3$ Probed by Brillouin and Raman Scattering

Shinya Tsukada, Yuji Ike, Jun Kano, Seiji Kojima, *Member, IEEE*, Tadashi Sekiya, Yoshiro Shimojo, and Ruiping Wang

Abstract—Structural phase transitions in relaxor ferroelectric materials remain to be one of the most puzzling issues in materials science. In the present work, we have investigated relaxational and vibrational properties of a relaxor ferroelectric $0.71Pb(Ni_{1/3}Nb_{2/3})O_3$-$0.29PbTiO_3$ single crystal by means of inelastic light scattering measurements. Analysis based on the spectra has shown anomalous behaviors at Burns' temperature T_d, freezing temperature T_f, those are related to a development of polar nanoregions (PNRs). The PNR must play a key role in the relaxor nature, and obtained results provide new insights into the relaxational dynamics in the PNRs and into how they develop below T_f.

I. INTRODUCTION

RESEARCH on structural phase transitions in relaxor ferroelectrics has undergone in the fundamental understanding of the structural and physical properties. The characteristic properties of them are believed to be attributed to reorientational polar species composed of clusters having several nanometers (polar nanoregion or PNR). Therefore, on the nanometer scale, the relaxor ferroelectrics are inhomogeneous [1], [2].

At high temperatures, the relaxor ferroelectrics show a nonpolar paraelectric phase, which is similar to a paraelectric phase of normal ferroelectrics. Upon cooling, it transforms into an ergodic relaxor state in which the PNRs appear. This transformation at the temperature so-called Burn's temperature T_d is not considered as a structural-phase transition because it is not accompanied by any change of the crystal structure on the macro- and mesoscopic scales [3]. Nevertheless, the PNRs affect the behavior of the crystal drastically, giving rise to the unique physical properties. For this reason, the state at $T < T_d$ often is considered as a new phase different from the paraelectric phase. Close to T_d, the PNRs appear, and their dynamics of the dipole moments slow down enormously on cooling. Then the PNRs freeze into a nonergodic (i.e., ferroelectric

S. Tsukada, Y. Ike, J. Kano, and S. Kojima are with the Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan (e-mail: s-tsukada@ims.tsukuba.ac.jp).

S. Tsukada and Y. Ike also are with the Japan Society for the Promotion of Science, Chiyoda, Tokyo 102-8471, Japan.

T. Sekiya, Y. Shimojo, and R. Wang are with the National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8568, Japan.

state) and their volume becomes larger below, an enough low temperature T_f [4].

Consequently, understanding of temperature development of the PNRs is essential to manifest the mechanism of the structural phase transitions in the relaxor ferroelectrics. In this paper, we used the methods of Brillouin spectroscopy and Raman spectroscopy to investigate them in a relaxor ferroelectric $0.71Pb(Ni_{1/3}Nb_{2/3})O_3$-$0.29PbTiO_3$ (0.71PNN-0.29PT) single crystal through interactions between the relaxation and the light, the vibration and the light. The composition of 0.71PNN-0.29PT is near the morphotropic phase boundary ($x \sim 0.33$), which is one of the most technologically important regions because of their rich applications such as medical imaging, telecommunication, and ultrasonic devices using its huge piezoelectric and dielectric constants [5], [6].

II. EXPERIMENTAL

The single crystal of 0.71PNN-0.29PT with light green color was grown by the flux method [7]. The concrete composition of the sample was determined by the comparison of maximum temperature T_m ($\sim$309 K: 1 kHz) in the real part of the dielectric constant with data by several researchers [5], [8]. Each surface was perpendicular to $[100]_c$ of the pseudo-cubic orientations that were confirmed by x-ray diffraction.

Light scattering at low-frequency range (0.5 cm^{-1} $\sim$15 cm^{-1}) was measured by a high-contrast 3+3-pass tandem Fabry-Perot interferometer (JRS Scientific Instruments, Zwillikon, Switzerland) combined with an optical microscope (BH-2, Olympus, Tokyo, Japan). A diode-pumped solid-state laser (DPSS, Coherent, Santa Clara, CA) with a single frequency operation at 532 nm with 100 mW was used together with a custom built micro-optical system and photon counting system. A narrow interference filter also was used to suppress higher orders of interferences [8]. Two frequency ranges were measured; free spectral range of 2.5 cm^{-1} for scanning range of 2 cm^{-1} and 20 cm^{-1} for 16.7 cm^{-1}, respectively, to discuss the central peak in the broad frequency range.

Higher frequency range (10 cm^{-1} $\sim$1000 cm^{-1}) was measured by a triple-grating spectrometer of additive dispersion (T64000, Jobin Yvon, Edison, NJ) with a resolution of 3 cm^{-1}. A diode-pumped, solid-state laser (Torus,
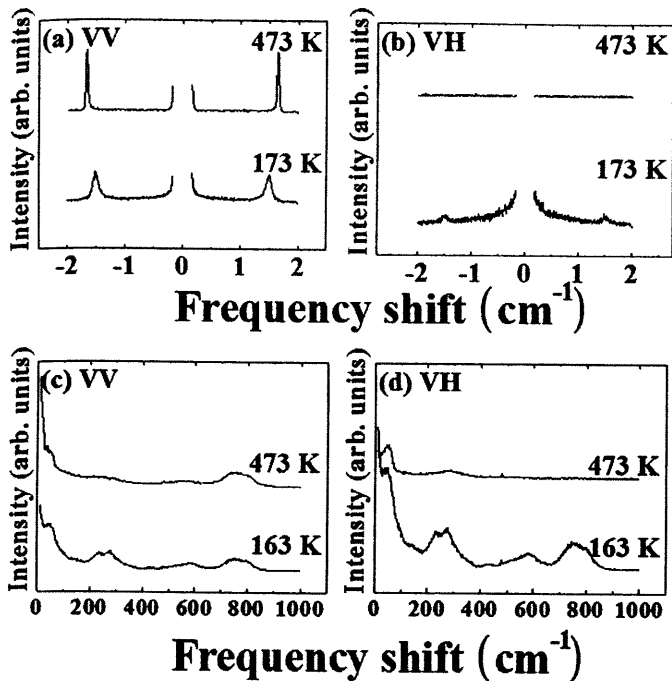
Fig. 1. Light scattering spectra at two temperatures. The spectra of (a) and (b) were observed by a Fabry-Perot interferometer. (c) and (d) were observed by a grating spectrometer. VV and VH denote polarized and depolarized scattering, respectively. Two peaks at 1~2 cm^{-1} frequency shift in (a) are Brillouin scattering, which is attributed to the longitudinal acoustic phonon. Peaks at non-0 cm^{-1} in (c) and (d) are Raman scattering, which is attributed to the optical phonons. Broad central peaks are seen in several spectra at 0 cm^{-1} frequency shift.

Laser Quantum, Cheshire, UK) with a single-frequency operation at 532 nm with < 100 mW was used. The scattered light was detected by the photon-counting technique with a photo multiplier tube.

For the temperature variation in the light-scattering measurements, the sample was put inside a cryostat cell (THMS600, LINKAM, Tadworth, UK) with a stability of 1 K. The sample also was annealed at more than 800 K before measurements. The scattered light was collected on [100]$_c$-plate at $a(cb)\bar{a}$ (Vertical to Horizontal or VH) and $a(bb)\bar{a}$ (Vertical to Vertical or VV) scattering geometries in which the elastic scattering at the former geometry is relatively weak.

III. RESULTS AND DISCUSSION

Light-scattering spectra of low and high frequency ranges are shown in Fig. 1. They indicate the features of the relaxor ferroelectrics in Raman scattering, Brillouin scattering, Rayleigh scattering, and a central peak. Raman scattering is known as the scattering due to long wavelength optical phonons in condensed matter (10–3000 cm^{-1}). Brillouin scattering is the light scattering by long wavelength acoustic phonons in condensed matter (0.05–2 cm^{-1}). Rayleigh scattering occurs by the nonpropagating fluctuations in matter, and Rayleigh wing is a tail

of central peak that corresponds to anisotropic reorientation motion of dipole moments.

A. Raman Scattering

Figs. 1(c) and (d) show Raman spectra at two temperatures on a [100]$_c$-plate with VV and VH scattering geometries. Our Raman spectra are very similar to those in previous study on other relaxor ferroelectrics [9]–[11]. Even above T_f (~280 K), two strong lines at 50 and 760 cm^{-1} exist, that reflect the positional disorder of Pb and the PNRs, respectively. On cooling from a high temperature, each line becomes intense but still broad compared with normal ferroelectrics because of the characteristic disorder of the relaxor ferroelectrics. A central peak also is seen in Figs. 1(c) and (d). The Raman spectra obtained in Figs. 1(c) and (d) were fitted by a narrow Lorentzian-type central peak and damped harmonic oscillation for all the phonons without any coupling [9].

Group theoretical analysis of the Raman peaks based on its point group symmetry is difficult because of the lowering of the local symmetry induced by Pb and the PNRs [9], [11]. The intensity of Raman spectra at high temperatures could be explained based on the consideration of the temperature variation of averaged size of the PNRs. Below T_d (620 K), the PNRs can exist [3], [12]. The energy for the switching of dipole moments in the PNRs is approximately proportional to its volume. Between T_d and T_f, the PNRs are so small that their energy is compatible to or smaller than $k_B T$. Thus, its direction of dipole moments is easily changed by thermal agitation.

A dominant feature is the band at 760 cm^{-1}, which has been assigned to Nb-O-Ni, Nb-O-Nb, and Ni-O-Ni stretching modes, i.e., it indicates the existence of the PNRs [9], [10]. It shows marked temperature and polarization dependences as shown in Fig. 2. Above T_f, the peak is seen in the VV spectra [Fig. 2(a)]; no peak is in the VH spectra [Fig. 2(b)]. Below T_f, then, the peak also appears in the VH spectra and becomes intense. To understand the temperature behavior of this peak, the depolarization ratio of this peak is shown in Fig. 3. It increases gradually on cooling from T_f. It must indicate the gradual growing of the correlation length on cooling below T_f, because the interaction among the PNRs becomes strong below T_f. It is consistent with the behavior of the quasielastic scattering in the neutron scattering spectra, in which size of the PNRs were investigated [4]. So we have considered this behavior is originated from the evolution of ferroelectric ordering.

B. Brillouin Scattering

Figs. 1(a) and (b) show Brillouin spectra at two temperatures on a [100]$_c$-plate with VV and VH scattering geometries. No transverse acoustic mode was found at the VV scattering geometry as shown in Fig. 1(a). The small Brillouin component in VH spectra at 173 K must be attributed to the leakage of the VV scattering. Not only Brillouin component but also central peak was observed
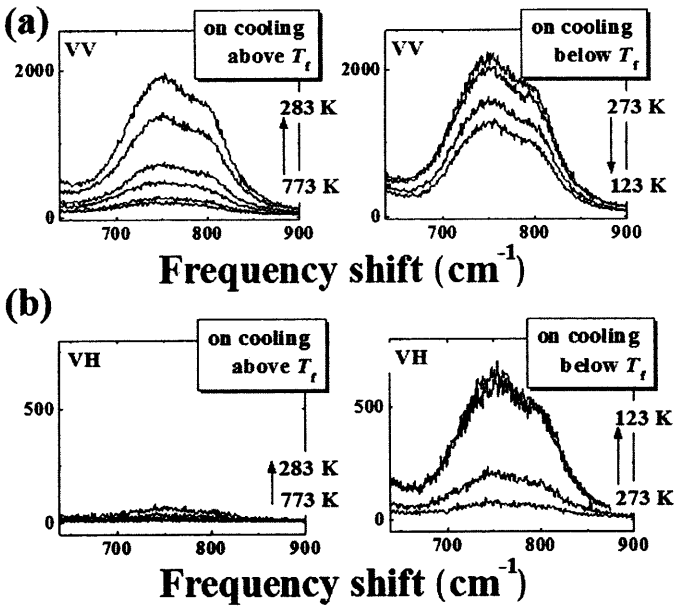
Fig. 2. Temperature dependence of Raman peaks around 760 cm^{-1} at (a) VV and (b) VH scattering geometries. The spectra above T_f were measured at 773 K, 673 K, 573 K, 473 K, 373 K, and 283 K. The spectra below T_f were measured at 273 K, 243 K, 183 K, and 123 K.
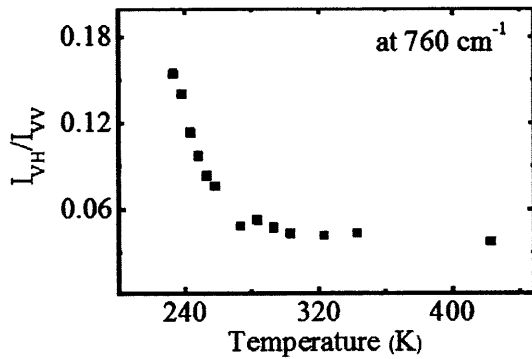

Fig. 3. Depolarization ratio versus temperature for the peaks around 760 cm^{-1}, which was obtained by analyzing the spectra in Fig. 2. The depolarization ratio increases on cooling below $T_f \sim 280$ K.

in both scattering geometries. On cooling from 773 K, the central component began to appear, the full width at half maximum (FWHM) and the intensity also depends on temperature. In order to analyze the observed Brillouin spectra in Fig. 1(a), we decomposed them using a multiple peak fitting procedure. The Brillouin component was fitted by a Lorentzian function convoluted by a Gaussian function to subtract an instrumental broadening. Here the width of Gaussian function was fixed as an instrumental broadening.

Frequency shift of a Brillouin peak, which is very sensitive to the structure, shows two anomalies in the temperature dependence as indicated in Fig. 4(a). The anomaly at 620 K was attributed to the formation of the PNRs (T_d) and that at 280 K to the macroscopic structural change (T_f). Abrupt changes that are found in normal ferroelectrics were smeared because of the fluctuation of
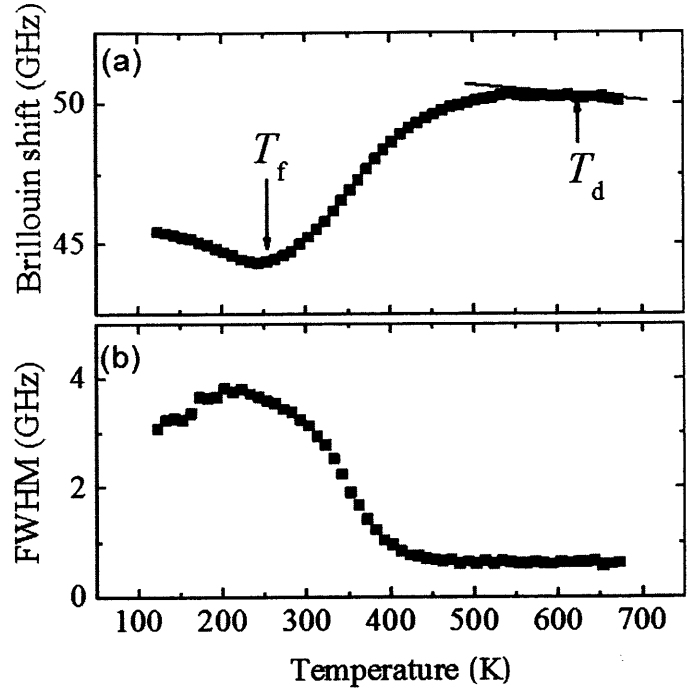

Fig. 4. Temperature dependences of Brillouin shift (a) and FWHM (b). T_d denotes Burn's temperature from which the linear temperature dependence of Brillouin shift deviates. T_f denotes the freezing temperature.

an order parameter induced by the PNRs. Fig. 4(b) shows the temperature dependence of FWHM. Compared with Brillouin shift, no anomaly was found around T_d. Around T_f, FWHM have a broad peak.

C. Central Peak

It is attributed to the thermally activated fast relaxation in the PNRs [13]–[15]. We measured the central peak in the broad frequency range combining a Fabry-Perot interferometer and a grating spectrometer. It was found that the central peak cannot be reproduced by a single Lorentzian peak. In other words, non-Debye relaxation process exists in the dynamical properties of the PNRs. To reproduce the obtained central peak, we used two Lorentzian peaks, assuming two-step relaxation. Then, it was well-fitted. We consider the different time scale of each relaxation process and suggest that one relaxation process corresponds to 180° switching of the dipole moments in the PNRs, and the other one corresponds non-180° (71° or 109°) switching in them. In these switching processes of the dipole moment, the rate of 180° switching is faster than the rate of non-180° switching, because some strain should be induced with the non-180° switching. Therefore, the slower relaxation process (the narrow Lorentzian peak) can correspond to the non-180° switching process accompanied with the change of strain. The faster relaxation process (the broader Lorentzian peak) can correspond to the 180° switching free from any change of strain. Detailed discussions on the relaxation time and its intensity related to the PNRs were made in our previous paper [16].

IV. CONCLUSIONS

Light scattering from the relaxor ferroelectric 0.71PNN-0.29PT was measured with a broad frequency range and we discussed the correlation between its dynamical properties and microstructures.

The obtained spectra consist of three components, Raman scattering, Brillouin scattering, and a central peak. In the Raman scattering measurement, all the peaks have been broad and no soft mode has been observed. This is due to the disorder in the lattice, and the breaking of translational symmetry. The disorder affects the intensity of Raman spectrum, and we discussed the depolarization ratio of the peak at 760 cm^{-1} attributed to the appearance of the PNRs. Frequency shift and width of Brillouin scattering are very sensitive to the structure of a sample, and two anomalies were found. The anomaly at 620 K is attributed to the formation of the PNRs, and that at 280 K to the macroscopic structural change. The central peak is attributed to the thermally activated fast relaxation of dipole moments in the PNRs. We suggested the two-step relaxations to explain the temperature behavior of the central peak.

REFERENCES

[1] A. A. Bokov and Z.-G. Ye, "Recent progress in relaxor ferroelectrics with perovskite structure," *J. Mater. Sci.*, vol. 41, pp. 31–62, Feb. 2006.

[2] Z.-G. Ye, "Relaxor ferroelectric complex perovskites: Structure, properties and phase transitions," *Key Eng. Mater.*, vol. 155, pp. 81–122, Sep. 1998.

[3] G. Burns and F. H. Dacol, "Glassy polarization behavior in ferroelectric compounds $Pb(Mg_{1/3}Nb_{2/3})O_3$ and $Pb(Zn_{1/3}Nb_{2/3})O_3$," *Solid State Commun.*, vol. 48, pp. 853–856, Dec. 1983.

[4] G. Xu, G. Shirane, J. R. D. Copley, and P. M. Gehring, "Neutron elastic diffuse scattering study of $Pb(Mg_{1/3}Nb_{2/3})O_3$," *Phys. Rev. B*, vol. 69, art. no. 64112, Feb. 2004.

[5] C. Lei, K. Chen, X. Zhang, and J. Wang, "Study of the structure and dielectric relaxation behavior of $Pb(Ni_{1/3}Nb_{2/3})$-$PbTiO_3$ ferroelectric ceramics," *Solid State Commun.*, vol. 123, pp. 445–450, Jul. 2002.

[6] S.-E. Park and T. R. Shrout, "Ultrahigh strain and piezoelectric behavior in relaxor based ferroelectric single crystals," *J. Appl. Phys.*, vol. 82, pp. 1804–1811, Aug. 1997.

[7] T. Sekiya, K. Kusumoto, H. J. Hwang, J. P. Reyes, J. P. Chaminade, and J. Ravez, "Flux growth and properties of $Pb(Ni_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ single crystals," *J. Korea. Phys. Soc.*, vol. 32, pp. S1201–S1203, Feb. 1998.

[8] J. Gapinski, W. Steffen, A. Patkowski, A. P. Sokolov, A. Kisliuk, U. Buchenau, M. Russina, F. Mezei, and H. Schober, "Spectrum of fast dynamics in glass forming liquids: Does the 'knee' exist?," *J. Chem. Phys.*, vol. 110, pp. 2312–2315, Feb. 1999.

[9] J. Toulouse, F. Jang, O. Svitelskiy, W. Chen, and Z.-G. Ye, "Temperature evolution of the relaxor dynamics in $Pb(Zn_{1/3}Nb_{2/3})O_3$: A critical Raman analysis," *Phys. Rev. B*, vol. 72, art. no. 184106, Nov. 2005.

[10] O. Svitelskiy, J. Toulouse, G. Yong, and Z.-G. Ye, "Polarized Raman study of the phonon dynamics in $Pb(Mg_{1/3}Nb_{2/3})O_3$ crystal," *Phys. Rev. B*, vol. 68, art. no. 104107, Sep. 2003.

[11] F. M. Jang and S. Kojima, "Raman scattering of 0.91 $Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.09PbTiO_3$ relaxor ferroelectric single crystals," *Jpn. J. Appl. Phys.*, vol. 38, pp. 5128–5132, Sep. 1999.

[12] S. Tsukada, Y. Ike, J. Kano, T. Sekiya, Y. Shimojo, R. Wang, and S. Kojima, "Diffuse phase transition of $0.8Pb(Ni_{1/3}Nb_{1/3})O_3$-$0.2PbTiO_3$ single crystals studied by micro-Brillouin scattering," *Ferroelectrics*, vol. 346, pp. 37–42, Mar. 2007.

[13] I. G. Siny, S. G. Lushnikov, and R. S. Katiyar, "Central peak in light scattering from the relaxor ferroelectric $Pb(Mg_{1/3}Nb_{2/3})O_3$," *Phys. Rev. B*, vol. 56, pp. 7962–7966, Oct. 1997.

[14] F. M. Jang and S. Kojima, "Relaxation mode in $0.65Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.35PbTiO_3$ relaxor single crystals studied by micro-Brillouin scattering," *Phys. Rev. B*, vol. 62, pp. 8572–8575, Oct. 2000.

[15] Y. Nakata, Y. Tsujimi, K. Katsuraya, M. Iwata, and T. Yagi, "Dynamical slowing down of polar nanoregion in relaxor-based ferroelectric $0.89Pb(Zn_{2/3}Nb_{1/3})O_3$-$0.11PbTiO_3$," *Appl. Phys. Lett.*, vol. 89, art. no. 22903, Jul. 2006.

[16] S. Tsukada, Y. Ike, J. Kano, T. Sekiya, Y. Shimojo, R. Wang, and S. Kojima, "Broadband inelastic light scattering of a relaxor ferroelectric $0.71Pb(Ni_{1/3}Nb_{2/3})O_3$-$0.29PbTiO_3$," *Appl. Phys. Lett.*, vol. 89, art. no. 212903, Nov. 2006.
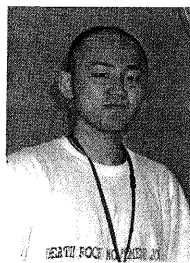
Shinya Tsukada was born in Ibaraki, Japan, on May 6, 1982. He received B.Eng. and M.Eng. degrees in the Department of Pure and Applied Sciences at the University of Tsukuba, Japan in 2005 and 2007, respectively. He is enrolled in a doctoral program at the University of Tsukuba as a JSPS Research Fellow from 2007. His major field of study is condensed matter physics.

He won a poster award at The 5th Asian Meeting on Ferroelectrics in 2006 and a young scientist award at The 8th Russia/CIS/Baltic/Japan Symposium on Ferroelectricity in 2006.

Yuji Ike was born in Fukuoka, Japan, on February 28, 1981. He received B.Eng. and M.Eng. degrees in the Department of Pure and Applied Sciences at the University of Tsukuba, Japan in 2003 and 2005, respectively. He is enrolled in a doctoral program at the University of Tsukuba as a JSPS Research Fellow from 2006.

His major field of study is condensed matter physics. He won a young scientist award at The 27th Symposium on Ultrasonic Electronics in 2006.
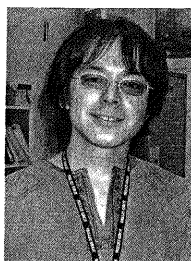
Jun Kano was born in Aichi, Japan, on November 18, 1975. He received a B.S. degree in the Department of Mathematics and a Sc.D. degree in the Department of Physics, Hokkaido University, Japan, in 1999 and 2004, respectively. He was a research associate under Prof. Seiji Kojima at the Graduate School of Pure and Applied Sciences, University of Tsukuba, Japan, during 2004–2007.

Presently he is working as an assistant professor at the same group.

Seiji Kojima (M'07) was born in Tokyo, Japan, on April 22, 1951. He received B.S. and Sc.D. degrees in the Department of Physics, University of Tokyo, Japan, in 1974 and 1979, respectively. He joined the Institute of Solid State Physics, University of Tokyo as a JSPS PD Fellow in 1979. In 1980 he joined the Institute of Applied Physics, University of Tsukuba as a research associate and is now a professor in the Institute of Materials Science, University of Tsukuba.

     His major field of study is condensed matter physics. Prof. Kojima was the Chairman of the Organizing Committee of the 8th Russia/CIS/Baltic/Japan symposium on ferroelectricity, Tsukuba, May, 2006. He is a member of the editorial board of the international journal, *Materials Science*.
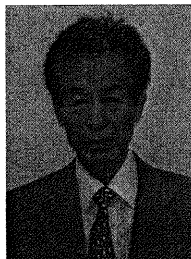
Tadashi Sekiya was born in Nagano, Japan, on April 9, 1943. He received the Eng.D. degree at Tokyo Institute of Technology, Japan, in 1988. He has addressed the development of high performance ferroelectric ceramics and piezoelectric ceramics at the National Institute of Advanced Industrial Science and Technology (AIST) at Tsukuba, Japan. His recent research interests lie in the field of medical devices using piezoelectric materials.

Yoshiro Shimojo was born in Gifu, Japan, on April 11, 1970. He received a M.Chem. degree in Interdisciplinary Graduate School of Engineering Sciences at Kyushu University, Japan, in 1996. He is a researcher at the National Institute of Advanced Industrial Science and Technology (AIST) at Tsukuba, Japan.

Ruiping Wang was born in Anhui, P. R. China, on September 11, 1962. She received a Ph.D. degree in material sciences and engineering at Tokyo Institute of Technology, Japan, in 2000.

     She is a research scientist at the National Institute of Advanced Industrial Science and Technology (AIST) at Tsukuba, Japan, and fabricates new lead-free piezoelectric ceramics.