⁷Li NMR study of milling effects on instability of lithium-sites in lithium substituted silver niobate

Koichi Nakamura* and Yoshitaka Michihiro

Department of Advanced Materials,

Institute of Technology and Science,

The University of Tokushima, Tokushima 770-8506, Japan

Chikako Moriyoshi and Yoshihiro Kuroiwa

Department of Physical Science, Faculty of Science,

Hiroshima University, Hiroshima 739-8526, Japan

Satoshi Wada

Department of Applied Chemistry, Faculty of Engineering,

University of Yamanashi, Yamanashi 400-8510, Japan

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Abstract

Site occupation and structural change in Li substituted AgNbO₃ were probed by ⁷Li NMR. Characteristic changes in the ⁷Li NMR spectra depending on Li content were observed. Analysis of integrated intensity of the spectra revealed that 16 % of substituted Li⁺ ions occupy quasi-stable sites induced in crystal structure at 300 K in the 5 mol.% Li substituted sample and would be in the state of motion, which are comparable to that of Li⁺ ion in LiNbO₃ at high temperature. On the other hand, it was found that the Li⁺/Ag⁺ sublattice in the 12.5 mol.% Li substituted sample is easily made unstable by structural disturbance introduced in structure and instability of the sublattice stimulates a local Li⁺ ion motion via quasi-stable sites at room temperature. An appearance of the quasi-stable sites in local structure due to the Li substitution is closely related to instability of the Li/Ag sublattice and Li⁺ ion dynamics in Li substituted AgNbO₃.

INTRODUCTION

Piezoelectric niobate and tantalate such as $\text{K}(\text{Nb}, \text{Ta})\text{O}_3$ and $\text{Ag}(\text{Nb}, \text{Ta})\text{O}_3$ have attracted considerable attention as new lead-free piezoelectric material because of requirement for cutting down environment pollutions. [1] Li-substituted KTaO_3 shows interesting dielectric properties have been reported. A quantum paraelectric state is affected by Li^+ ion substitution for the K sites. [2] They are closely related to the dipole moment induced by the off-centered Li^+ ion location with a displacement of $1.26\text{\AA}$. [3] AgNbO_3 is a typical ferroelectric niobate system with a perovskite structure, and a relationship between dielectric properties and the structure has been investigated. [4, 5] Recently, the crystal structure of a weak ferroelectric state of AgNbO_3 has been identified as orthorhombic $Pmc2_1$ space group with the lattice parameters of $a=15.64773(3)\text{\AA}$, $b=5.55199(1)\text{\AA}$, and $c=5.60908\text{\AA}$. [6]

Structural changes in Li-substituted $\text{Ag}_{1-x}\text{Li}_x\text{NbO}_3$ (ALN) have also received considerable interest in connection with the field such as Li^+ ion dynamics in dielectric materials. Li^+ ion motion is important in electrode/electrolyte materials for lithium ion secondary batteries. Indeed, amorphous LiNbO_3 draws attention as electrolytes for lithium thin film batteries and has been studied by electrochemical methods so far. [7, 8]

A single crystal LiNbO_3 is well known to show ionic conduction with high activation energy of 1.9 eV at high temperatures, while amorphous LiNbO_3 exhibits Li^+ ionic conduction with much smaller activation energy of 0.4 eV. [9] The motional narrowing in ^7Li NMR spectra was observed above room temperature in LiNbO_3 containing defects and lattice disturbance induced by milling. It indicates that some of Li^+ ions are mobile even at around room temperature. [10–12] Therefore, the study on a relationship between the structural change and ion dynamics in dielectric oxides would give important insight in developing advanced materials for ionic conductors, electrode/electrolyte, and piezoelectric materials.

The location of substituted Li^+ ions, Li-site occupation, Li^+ ion motion, and site instability are discussed by relatively analyzing integrated intensity of ^7Li NMR spectra of $\text{Ag}_{1-x}\text{Li}_x\text{NbO}_3$ ($x=0.05, 0.125$) system.

EXPERIMENTAL

The ALN single crystals were prepared by the slow cooling method without flux in air or under O_2 flow. Ag_2O , Nb_2O_5 , and Li_2CO_3 , weighted in proper molar ratios of Ag to Nb and Li to Ag, were used as starting materials for growth of the ALN single crystal. Finally, 5 mol.% and 12.5 mol.% Li substituted ALN crystals (abbreviated as ALN5 and ALN125, respectively) were obtained. The detailed preparation procedure and symmetry of ALN samples were described in a previous work, and ALN samples were confirmed as single phase without any impurity phases. [13] Crystal structures of ALN5 was also reported in other work.[14] Polycrystalline powdered $LiNbO_3$ (abbreviated as poly-LN) also was used for comparison.

The 7Li static and magic angle spinning (MAS) NMR were carried out on a Bruker Avance 300 wb spectrometer equipped with a 4 mm probe at a Larmor frequency of 116.64 MHz. The ALN crystal was crushed and ground in an agate mortar, and each powdered samples of ALN and LN was packed into a 4 ϕ zirconia rotor for NMR measurements. MAS-NMR was operated at a spinning speed of 7 kHz. A single pulse sequence (pulse width of 5 μs) was used. The number of scans from 8 k to 16 k was accumulated with a repetition time of 2 s for ALN samples because of restriction on experiment. All NMR spectra of ALN and LN samples were obtained under the same condition of repetition time, and relatively analyzed and discussed. 1.0M LiCl aqueous solution was used as the reference of 7Li nucleus (0 ppm).

Wet milling was carried out on a Fritsch planetary ball milling machine P-6 equipped with a zirconia vial of 30 cm^3 . Each of ALN125 and poly-LN was milled for various milling times with 2 ϕ zirconia balls in ethanol at a disc rotation speed of 550 rpm. Milled ALN125 sample after drying in a desiccator was used for NMR measurements.

RESULTS AND DISCUSSION

The 7Li static NMR spectra of ALN samples exhibit characteristic shapes with Li content as shown in Fig. 1. A sharp peak appears in a broad peak at around 0 ppm in the static spectrum (a) of ALN5, while no sharp peak is observed in the spectrum (b) of ALN125. The line shape of ALN125 is quite similar to that of poly-LN as shown in Fig. 1 (c). Each 7Li MAS spectrum shows a central peak at around 0 ppm with the spinning sidebands as

FIG. 1. ${}^7\text{Li}$ static NMR spectra of Li substituted AgNbO_3 and LiNbO_3 . (a) ALN5, (b) ALN125, and (c) poly-LN for comparison. Insets of (a) - (c) show ${}^7\text{Li}$ MAS NMR spectrum of ALN5, ALN125, and poly-LN, respectively. Peak heights of all spectra are normalized to unity.

shown in insets of (a) - (c) of Fig. 1. The MAS spectrum of ALN125 also is similar to that of poly-LN as shown in the inset (b) and (c). These results mean that the crystal structure of ALN125 is almost the same as that of LN with rhombohedral $R3c$ space group, although AN and ALN5 also belong to $Pmc2_1$.

In Li transition-metal oxides, a somewhat extended central peak is often observed without the satellite peaks in the static ${}^7\text{Li}$ NMR spectra at room temperature because of a relatively small quadrupole moment of ${}^7\text{Li}$ nucleus. The broad powder pattern of satellite peaks for $(\pm 3/2 \leftrightarrow \pm 1/2)$ transitions arising from the first order quadrupole interaction is observed

over both sides of the central peak of ^7Li nucleus ($I=3/2$) in powdered samples of ALN125 and poly-LN as shown in Fig. 1 (b) and (c). The quadrupole coupling constant C_Q ($= e^2qQ/h$) of ALN125 is estimated to be about 65.2 kHz, which is close to that of around 67 kHz for poly-LN. [10, 15] The asymmetric parameter η ($= (V_{xx} - V_{yy})/V_{zz}$; $V_{ii}(=xx,yy,zz)$ are components of the electric field gradient) for ALN125 also is consistent with that ($\eta \approx 0$) for poly-LN, indicating that the electric field gradient around Li^+ sites substituted for Ag^+ ions are axially symmetric in ALN125. [16] Thus, it was found that a local coordinated environment of all Li^+ ions substituted for the Ag^+ ions of ALN125 is very similar to that around the Li sites in poly-LN.

The Li sites in a single crystalline LN with a large activation energy of 1.9 eV are so stable that the Li^+ ions are settled in the rigid Li sublattice at around room temperature. [9] The motional narrowing of the central ^7Li line is observed above 700 K in powdered LN with the activation energy of around 1.25 eV, and sufficiently narrowed central line is accomplished with narrowed satellite lines at around 975 K. [12] Besides, the activation energy for hopping of the Ag^+ ions estimated from electrical conduction measurements is around 1.3 eV in AN. [17] The Ag^+ sublattice is considered to be essentially stable at around room temperature. Therefore, the Li^+ ions substituted in ALN125 also would be settled in the rigid lattice consisting of Ag^+ and Li^+ ions and do not diffusive at room temperature just as in the case of LN. [12]

The characteristic static NMR spectrum of ALN5 suggests that there are two kinds of the state of motion of Li^+ ions. In this case, the measured spectrum of Fig. 2 (a) is well reproduced by superposition (b), consisting of trial nearly Gaussian and Lorentzian line shapes (c) for broad and narrow lines, respectively. The decomposition of spectrum was done by using Dmfit program. [18] It seems that the narrow and broad line shapes are due to mobile Li^+ ions and immobile Li^+ ions settled in the rigid lattice in ALN5, respectively. Such a difference in the state of motion of Li^+ ions would be connected with the location around Li^+ ions in the crystal structure of ALN5. Amount of mobile Li^+ ions in ALN5 was determined to be about 16 % by estimating an integrated intensity ratio R ($\equiv I_{\text{narrow}}/I_{\text{total}}$) of the narrow line area I_{narrow} in (c) to the total one I_{total} in (b) of Fig. 2. It is noted that a peak split due to the Li location at crystallographically different sites is not observed in the MAS spectrum of ALN5 as shown in the inset (a) of Fig. 1. It is likely that Li^+ ions substituted for Ag^+ ions with larger ionic radius would be easily drawn toward oxygen ions

FIG. 2. ^7Li static NMR spectra of ALN5. (a) measured spectrum, (b) superposed total spectrum, and (c) decomposed spectra. The broad and narrow line-shape components are identified as immobile and mobile Li^+ ions, and their line widths are around 8.3 and 1.2 kHz, respectively.

and the sites occupied by Li^+ ions would be unstable compared to regular Ag/Li sites. Such a quasi-stable site, which would be slightly apart from the regular Ag^+/Li^+ sites, seems to be created without a large distortion in the locally coordinated environment around the Ag^+/Li^+ ions. This situation might be similar to that for off-centered Li^+ ions observed in KTaO_3 . [3] Besides, local Li^+ ion motion is inferred by analogy from Li^+ ion dynamics in milled LN. Thus, only 16 % of 5 mol.% Li^+ ions substituted in ALN5 are considered to occupy the quasi-stable sites and to be possible to hop locally.

The line width of ^7Li nucleus in ALN is described by the second moment $^7\langle\delta\omega^2\rangle$ based on the dipole interaction with neighboring ^7Li , $^{107/109}\text{Ag}$ and ^{93}Nb as following

$$^7\langle\delta\omega^2\rangle = ^7\langle\delta\omega^2\rangle_{II} + ^{107/109}\langle\delta\omega^2\rangle_{IS} + ^{93}\langle\delta\omega^2\rangle_{IS}, \quad (1)$$

where ${}^7\langle\delta\omega^2\rangle_{II}$ denotes a contribution to ${}^7\text{Li}$ spin from like spin (I) of ${}^7\text{Li}$, and ${}^{107/109,93}\langle\delta\omega^2\rangle_{IS}$ denote that to ${}^7\text{Li}$ spin from unlike-spins (S) of ${}^{107/109}\text{Ag}$ and ${}^{93}\text{Nb}$, respectively. Here, ${}^6\text{Li}$ nucleus was neglected in this calculation because of less abundance. The second moment of ALN5 was calculated on the assumption that ALN5 belongs to $Pmc2_1$ space group, while it was estimated as $R3c$ for ALN125. Supposing simply the normalized gaussian curve of

$$f(\omega) = \frac{1}{\Delta\sqrt{2\pi}} \exp\left\{-\frac{(\omega - \omega_0)^2}{2\Delta^2}\right\} \quad (2)$$

as a shape function for rigid lattice, the half width at half intensity δ is given by $\delta = 1.18\Delta$ with $\Delta^2 = {}^7\langle\delta\omega^2\rangle$. The line width of ALN5 was determined to be around 5.0 kHz by using ${}^7\langle\delta\omega^2\rangle$ of $1.8 \times 10^{-8} \text{ (rad/s)}^2$ and that of ALN125 was similarly around 5.1 kHz for ${}^7\langle\delta\omega^2\rangle$ of $1.9 \times 10^{-8} \text{ (rad/s)}^2$. In the motional narrowing region, an aspect of ion motion is characterized by a hopping time τ of ion, which is connected with the line width. The line width of ALN5 at 300 K is close to that of LN at high temperature [19], and it suggests that some of Li^+ ions are mobile at 300 K. Unfortunately, the diffusion coefficient for hopping Li^+ ions at room temperature has yet to be known in ALN5 so that a jump distance of the Li^+ ions could not be estimated.

Fig. 3 shows the XRD patterns of ALN125 before and after milling for 3 h. The diffraction angle was adjusted by the wave length because the XRD profiles were measured by using various wave lengths; 0.06731 nm for 0 h and 0.15406 nm for 3 h. Each reflection line became weaker and broader with increasing milling time. This means that milling promotes dislocation of atoms in this lattice plane and a decrease of grain size. The reflection between the average grain size d and the width β of the XRD line caused by physical broadening is given by a Scherrer equation

$$d = \frac{k\lambda}{\beta \cos \theta} \quad (3)$$

with the wave length λ , the Scherrer constant k (assumed to be one in this estimation), and the diffraction angle θ . The grain sizes of the milled ALN125 were approximately estimated to be 151 and 28 nm for 0 and 3 h, respectively.

The local structure in the ALN system is dependent on the Li content, and it was found that the Li/Ag rigid site also is sensitive to a disturbance of crystal structure. We observed an instability in the local structure around the Li sites even in ALN125. It is considered that the Li-O bond is easily thrown out of balance by inducing defects and/or lattice disturbance

FIG. 3. XRD patterns of ALN125 before and after milling for 3 h. The diffraction angle is adjusted by the wave length for comparison.

in the ALN system, and it would result in unstable Li location. The instability of Li sites was readily accomplished by a mechanical milling process.

Fig. 4 shows the static ^7Li NMR spectra of ALN125 and poly-LN before and after milling. The spectrum (a) of ALN125 before milling drastically became narrower after milling as seen in Fig. 4 (b), in which the broad satellite line can be hardly observed. The milling process causes a large distribution of the electrical field gradient due to structural disturbance induced in structure, and it results in smearing out satellite peaks in ALN125 after 10 h of milling. As a result, a part of Li^+ ions is considered to become diffusive. The narrowed line width is only 600 Hz at 300 K. It is narrower than the width of the narrowed line of ALN5 at room temperature, indicating that a fast Li^+ ion hopping occurs in ALN125 after milling.

The spectrum (d) of the powdered LN after milling also shows the narrowed ^7Li NMR line and smearing out of broad shoulders which are seen in the spectrum (c). The spectrum (d) reminds us that of ALN5 as shown in Fig. 1 (a), indicating the motion of a small amount of Li^+ ions. Thus, an extrinsic disturbance of lattice induced by milling also contributes to

FIG. 4. Changes in the ^7Li static NMR spectra of ALN125 and poly-LN at two conditions: before milling and after 10 h of milling. (a) ALN125 before milling, (b) ALN125 after 10 h of milling, (c) poly-LN before milling, and (d) poly-LN after 10 h of milling. Peak heights of all spectra are normalized to unity.

the local motion of Li^+ ions as with the intrinsic quasi-stable Li sites in ALN5.

Fig. 5 shows the ratio R of mobile Li^+ ions against milling time in ALN125. The narrowed peak intensity in ALN125 after 10 h of milling is much larger than that in poly-LN after 10 h of milling. The intensity ratio R of the narrow line in the spectrum (b) of Fig. 4 reached 52 % at room temperature, while it is only 4 % for LN after 16 h of milling reported previously

FIG. 5. Integrated intensity ratio R of ALN125 and poly-LN against milling time.

by Heitjans *et al.* [20] and 10 % for poly-LN after 10 h of milling. It is interesting that such a large number of Li^+ ions are in the state of motion in ALN exposed to milling compared to the case of LN. It suggests that the ALN system would intrinsically possess instability of the Ag/Li sublattice and the structural disturbance induced slightly in structure easily permit release of the Li^+ ions from the sublattice. This might be related to the result that there are essentially the atomic displacements along c -axis in AN. [6] Thus, it seems that the Li/Ag sublattice in ALN is more fragile than that in LN.

CONCLUSION

We have shown the characteristic changes in the Li static NMR spectra depending on local structure with Li content and the appearance of quasi-stable Li sites in the ALN system. In ALN5, amount of substituted Li^+ ions occupying the quasi-stable sites at room temperature is merely 16 % in ALN5, while all Li^+ ions substituted in ALN125 occupy the stable sites that are almost the same as the Li sites in LN. The ALN system possesses the instability in local structure so that structural disturbance such as defect and lattice disturbance introduced by milling in the Ag/Li sublattice easily causes the Li^+ ion motion

and 52 % of 12.5 mol.% Li^+ ions become mobile in ALN125 with the Li rigid site at room temperature. Thus, the Ag/Li sublattice of the ALN system is sensitive to the change in local structure and a slight disturbance of the sublattice can cause the Li^+ ion motion. A relationship of the local structure and the Li^+ ion dynamics in the ALN system would provide interesting subjects in an application to ionic conductors.

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* nakamura.o.koichi@tokushima-u.ac.jp

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