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Mechanism of the ferroelectric phase transitions in LiNbO_3 and LiTaO_3

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The temperature dependences of the nuclear-electric-quadrupole frequency ω_Q of ^{117}In doped in LiTaO_3 ($T_C = 938$ K) and $\text{Li}_{1-x}\text{In}_{x/3}\text{TaO}_3$ with $x = 0.2$ ($T_C = 818$ K) show that the order-disorder of the Li ions is not the driving mechanism for the ferroelectric instability in LiNbO_3 and LiTaO_3 systems, and imply that the oxygen order-disorder is the driving mechanism. The significantly different temperature dependences of ω_Q of ^{111}Cd in these materials compared, to those of ^{117}In , demonstrate that this order-disorder is of dynamic character.

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I. INTRODUCTION

Ferroelectric LiNbO_3 (LN) and isostructural LiTaO_3 (LT) are known as important optical, electro-optical, and piezoelectric materials. Although their diffraction-derived structural data¹ were obtained three decades ago, the mechanism of ferroelectric-to-paraelectric phase transitions is not yet fully understood. The ferroelectric Curie temperatures of LN and LT are $T_C = 1483(10)^2$ and $938(5)$ K,³ respectively, which are quite high compared to those of other ferroelectrics. It can be helpful in designing useful high- T_C ferroelectrics if we understand the ferroelectric transition mechanism in LN and LT systems.

These oxides undergo only one structural phase transition, which corresponds to a ferroelectric transition. The ferroelectric structure [Fig. 1(a)] belongs to the $R3c$ space group. The atomic arrangement consists of oxygen octahedra sharing faces along the polar trigonal axis. When the spontaneous polarization direction is upward, the Nb (Ta) ion on this axis is displaced upward from the center of its octahedron. The next octahedron above is empty and the one more above contains a Li ion displaced upward from the bottom-triangle oxygen base of that octahedron. The paraelectric structure [Fig. 1(b)] belongs to the $R\bar{3}c$ space group. The Nb (Ta) ion is located at the center of its octahedron. The average Li position is on the triangle oxygen base: the Li ion is disordered and occupies the previously empty octahedron half the time (dynamic disorder) or unit cells in the other half (static disorder).

There are two opposite interpretations of the role of the order-disorder of Li in the transition mechanism. In one interpretation it is the driving mechanism (active role), and in the other it is not (passive role). A recent theory by Safaryan⁴ is considered the former example. Another theoretical calculation by Inbar and Cohen⁵ explored the latter example, which shows that order-disorder of the oxygen ions, rather than Li, is the driving mechanism: The Li displacement alone results in a single minimum in the local potential energy, and the oxygen displacements result in double wells; moreover, strongly coupled oxygen and Li displacements result in much deeper double wells.

Safaryan⁴ presumed that, at low temperature, the free space among the oxygen ions of the triangle base is too small for Li to easily pass through to the other side. With increasing temperature, however, the size of the opening becomes wider, so that Li comes closer to the triangle oxygen base and is more easily disordered. Simultaneously, the Coulomb interactions among Li and Nb (Ta) make the Nb (Ta) ion come closer to the center of its oxygen octahedron. At T_C , the Li ion occupies both sites, above and below the oxygen triangle, with equal probability (dynamic disorder), and Nb (Ta) occupies the center of its octahedron. According to this proposition, if we replace a Li ion by an ion of a smaller size or about the same size but with a higher charge, we expect that the substitute ion can easily go through the oxygen triangle at a lower temperature than the Li ion does; in the latter case, because of its stronger Coulomb interaction with the oxygen ions, the substitute ion must come closer to the oxygen triangle than the Li^+ ion does, forcing the space of the triangle to be more open. Therefore, by replacing some of the Li ions by ions having either a smaller size or about the

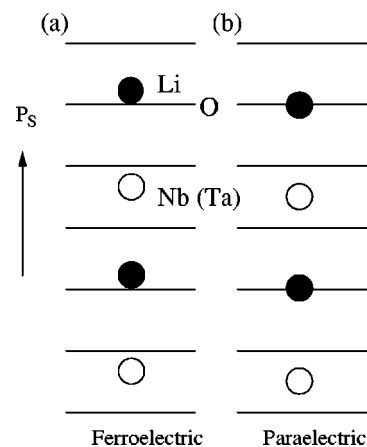


FIG. 1. The (a) ferroelectric and (b) paraelectric structures of LN and LT. The arrow indicates the direction of the spontaneous polarization (P_S) in the ferroelectric phase. Nb (Ta) is represented by the open, Li by the solid circles. The horizontal lines stand for the oxygen planes.

same size but a higher charge, we may be able to obtain a ferroelectric material with a lower T_C .

It was really observed⁶ that the T_C of In-doped LT, $\text{Li}_{1-x}\text{In}_{x/3}\text{TaO}_3$, depends linearly on the In concentration, and at $x=0.2$ (hereafter named 8-mol % In-doped LT) T_C goes down to 818(5) K. Here the charge on In, which occupies the Li site, is considered to be close to $3+$,⁷ although its ionic size⁸ is 80 pm, a little larger than that of Li^+ (76 pm). If we trace the behavior of the In ion under increasing temperature, we can test the proposition of Safaryan. One of the In isotopes, ^{117}In , is a nuclide to which the perturbed-angular-correlation (PAC) technique is applicable, giving information about the local structure around an In ion. The PAC of ^{117}In in LT and 8-mol % In-doped LT will therefore be decisive for this purpose. We performed PAC measurements on ^{117}In (arising from ^{117}Cd via nuclear decay) in polycrystalline samples of 8-mol % In-doped LT in a temperature range covering T_C of 818 K. In addition, we performed PAC measurements on ^{111}Cd ($\leftarrow^{111m}\text{Cd}$). Although Cd also occupies the Li site, as was confirmed in our previous PAC measurements for LN and LT,⁷ the order-disorder transition of Cd can be different from that of In. Owing to the much larger ionic size⁸ of Cd^{2+} (95 pm) than that of Li^+ and In^{3+} , Cd may not even be dynamically disordered. Combined with the results for LT in Ref. 7, in this paper, we discuss the mechanism of the ferroelectric phase transition in LN and LT systems. We assume that because LN is isostructural to LT, the discussions based on the PAC data for LT and 8-mol % In-doped LT also apply to the case of LN.

II. EXPERIMENTS

8-mol % In-doped LT polycrystalline samples containing either ^{117}Cd or ^{111m}Cd were prepared with an identical method⁷ for LN and LT containing those Cd isotopes. The parent nuclei ^{117}Cd and ^{111m}Cd were separately produced by irradiating enriched ^{116}CdO and ^{110}CdO , respectively, with thermal neutrons available at the research reactor of Kyoto University. The irradiated oxides, mixed with high-purity powders of Li_2CO_3 , In_2O_3 , and Ta_2O_5 , and then pressed into pellets, were sintered in air at 1100 °C for about 1 h, and thus were obtained $\text{Li}_{0.8}\text{In}_{0.063}\text{Cd}_{0.005}\text{TaO}_3$ containing ^{117}Cd and $\text{Li}_{0.8}\text{In}_{0.06}\text{Cd}_{0.01}\text{TaO}_3$ containing ^{111m}Cd . Owing to the short half-lives of ^{117}Cd (2.5 h) and ^{111m}Cd (49 min), in most cases samples were prepared for each PAC measurement temperature. For $\text{Li}_{0.8}\text{In}_{0.06}\text{Cd}_{0.01}\text{TaO}_3$ containing ^{111m}Cd , PAC measurements were performed on the same samples at two or three different temperatures between 410 and 710 K, where there is a small, broad peak in the temperature dependence of ω_Q of ^{111}Cd [see Fig. 3(b)]. This procedure was intended to diminish the sample dependence of the measured quadrupole frequency, if any, and was repeated once in order to obtain better statistics. The room-temperature x-ray-diffraction pattern of a $\text{Li}_{0.8}\text{In}_{0.06}\text{Cd}_{0.01}\text{TaO}_3$ sample after PAC measurement, being similar to that of LT, showed a single phase of it.

The PAC method⁹ is mostly applied to an ensemble of nuclei emitting two consecutive γ rays. The intermediate level is split by the interaction of the electric quadrupole

moment of the nuclei with an extranuclear electric-field gradient (EFG). Detection of the first γ rays with a detector sorts out a set of nuclei in intermediate states with spin alignments against the direction of the detector from the source. Then time-differential measurements of the second γ rays from the same nuclei with another detector permits a determination of the spin precession frequency of the nuclei in intermediate states, and then a determination of the magnitude of the splitting of the level. The time dependence of the coincidence counts $N(\theta, t)$ of the 90–344-keV cascade γ rays for samples containing ^{117}Cd , and that of 151–245-keV γ rays for samples containing ^{111m}Cd , were taken in a temperature range between 4.2 and 1223 K using a measurement system consisting of four BaF_2 scintillation detectors and standard fast-slow electronic modules. Here θ and t denote the angle and the time interval, respectively, between the cascade γ rays. The directional anisotropy $A_{22}G_{22}(t)$ was obtained as $2[N(\pi, t) - N(\pi/2, t)]/[N(\pi, t) + 2N(\pi/2, t)]$. The value of A_{22} depends only on the nuclear properties. The perturbation factor $G_{22}(t)$ for a unique static quadrupole interaction in randomly oriented microcrystals has the form, in the case of ^{117}In , with an intermediate level having a nuclear spin of $I=3/2$,

$$G_{22}(t) = [1 + 4 \cos(\omega t)]/5, \quad (1)$$

where $\omega = 6\omega_Q(1 + \eta^2/3)^{1/2}$, and η is an asymmetry parameter of the EFG, taking a value between 0 and 1. In the case of ^{111}Cd with its intermediate level having $I=5/2$,

$$G_{22}(t) = \sum_{n=0}^3 S_n(\eta) \cos(\omega_n t), \quad (2)$$

where $\omega_0=0$ and $\omega_n = 6\omega_Q C_n(\eta)$ ($n=1,2,3$). S_n and C_n in Eq. (2) are numerically calculated for a given asymmetry parameter. It should be noted that in the case of ^{117}In , $G_{22}(t)$ contains only one frequency component, and the values of ω_Q and η cannot be determined independently from the spectrum, whereas in the case of ^{111}Cd they can be determined because the amplitudes S_n and frequencies ω_n in Eq. (2) are modified in a characteristic way as a function of η .

III. RESULTS AND DISCUSSION

The PAC spectra measured at 4.2 and 1223 K of ^{117}In and ^{111}Cd in 8-mol % In-doped LT are shown in Fig. 2. Each anisotropy is modulated in a manner characteristic of the single electric quadrupole interaction in polycrystalline samples, depending on the spin value of the intermediate nuclear level. The PAC spectra of ^{117}In and ^{111}Cd were analyzed with a single quadrupole frequency having a Lorentzian distribution around the central value ω_Q . Equations (1) and (2), modified for the Lorentzian distribution, were fitted using the least-squares method to the observed time spectra of ^{117}In and ^{111}Cd , respectively. The η values thereby determined were scattered around 0.13. Considering that the quality of the present PAC spectra is not good enough to determine the η value accurately, we set $\eta=0.13$ for all ^{111}Cd spectra. In evaluating the error in the ω_Q value we took into account the η value determined in the fit. As discussed be-

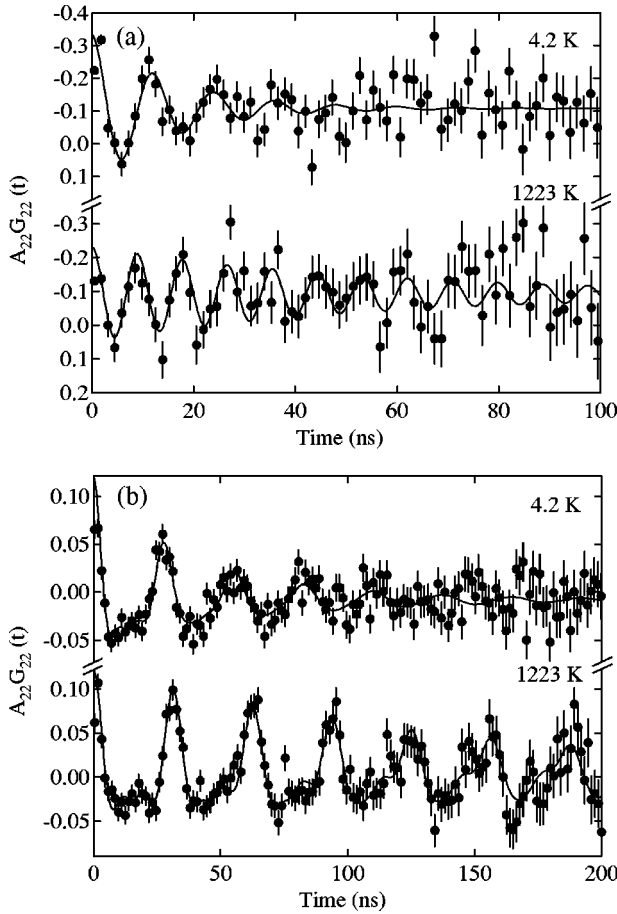


FIG. 2. PAC spectra of (a) ^{117}In ($\leftarrow^{117}\text{Cd}$) in $\text{Li}_{0.8}\text{In}_{0.063}\text{Cd}_{0.005}\text{TaO}_3$ and of (b) ^{111}Cd ($\leftarrow^{111m}\text{Cd}$) in $\text{Li}_{0.8}\text{In}_{0.06}\text{Cd}_{0.01}\text{TaO}_3$ at 4.2 and 1223 K. The solid curves represent the fits of Eqs. (1) and (2) in the text.

low, since ^{117}In is not considered to be in the same physico-chemical state as ^{111}Cd , or to be subject to the same asymmetry of the EFG as ^{111}Cd , we safely set $\eta=0$ for all the ^{117}In spectra. This is because the Li site has a threefold-symmetric axis and the EFG at this site is thus axially symmetric. Furthermore, even when $\eta=0.13$ is used for ^{117}In , the ω_Q value thus obtained differs by only 0.3%, which is well within the statistical error attached to ω_Q . The temperature dependence of the ratio δ of the distribution width $\Delta\omega_Q$ to ω_Q determined in the fit, has a general trend. In the case of ^{117}In , δ decreases from about 25% to 5% with increasing temperature, and for ^{111}Cd it changes from about 15% to 4%. The solid curves in Fig. 2 are results of the fits using $\eta=0$ for ^{117}In and $\eta=0.13$ for ^{111}Cd .

Figure 3(a) shows the temperature dependences of ω_Q of ^{117}In in LT (Ref. 7) (solid squares) and 8-mol % In-doped LT (open squares). The ω_Q of ^{117}In in each oxide increases with increasing temperature up to about T_C , and levels off at temperatures above (the ω_Q for LT seems to decrease gradually above about 1100 K). This temperature dependence is similar to the ^7Li -nuclear magnetic resonance quadrupole coupling constant¹⁰ for LT (see Fig. 5 of Ref. 7), indicating that In behaves like Li. However, according to the proposi-

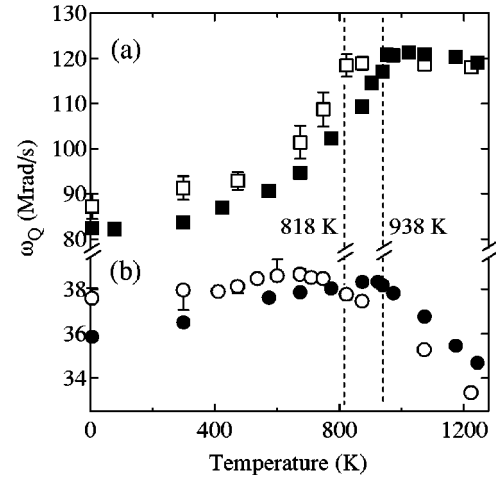


FIG. 3. Temperature dependences of ω_Q of (a) ^{117}In ($\leftarrow^{117}\text{Cd}$) in LT (solid squares) (Ref. 7) and in 8-mol % In-doped LT (open squares), and those of (b) ^{111}Cd ($\leftarrow^{111m}\text{Cd}$) in LT (solid circles) (Ref. 7) and 8-mol % In-doped LT (open circles). The two broken lines show the Curie temperatures of LT and 8-mol % In-doped LT.

tion of Safaryan,⁴ as described in Sec. I, the In ion should become disordered at a lower temperature than the Li ion would require. From the observation that the temperature dependence of ω_Q of ^{117}In faithfully reflects the respective phase transition at T_C , we conclude that the order-disorder of the Li ions is not the driving mechanism of the ferroelectric phase transition in LN and LT systems.

The fact that the value of ω_Q of ^{117}In in 8-mol % In-doped LT below its T_C is always larger than that in LT indicates that the In ion is closer to the oxygen triangle in 8-mol % In-doped LT than in LT. To rephrase, the oxygen triangle is displaced toward the In ion by a great amount of In ions located at Li sites having higher charges. However, the oxygen triangle does not allow the In ion to be disordered until the temperature reaches T_C . We speculate that in the paraelectric phase the oxygen triangle, rather than the In or Li ion, is disordered: the order-disorder of the oxygen triangle plays a key role in the phase transition in the LN and LT system. This speculation is consistent with the calculation results of Inbar and Cohen.⁵ Locally, the order-disorder of the oxygen triangle appears to be identical to that of the In or Li ion, but, globally, they are not identical with each other.

We then discuss the type of order-disorder of the oxygen triangle, dynamic or static. Although ω_Q of ^{117}In and the ^7Li quadrupole coupling constant¹⁰ for LT change significantly with temperature below T_C , they remain constant at temperatures above T_C . The constant part of the temperature dependence for ^{117}In or ^7Li means that the geometry among the In or Li ions and the oxygen ions in the triangle hardly changes, despite the high temperatures; this indicates that a local system consisting of In or Li ions and oxygen ions is unusually stable. This large stability is also indicated by the observation that despite the large difference between the two T_C 's, the value of ω_Q of ^{117}In for In-doped LT above its T_C is about the same as that for LT. We consider that the constant temperature dependence could represent the dynamic

disorder of the oxygen triangle: The oxygen triangle moves to and fro through the In or Li ions, and the local system is more stabilized. This consideration is further supported by the following discussion of the temperature dependences of ω_Q of ^{111}Cd .

The temperature dependences of ω_Q of ^{111}Cd in LT (Ref. 7) (solid circles) and 8-mol % In-doped LT (open circles) do not show a leveled-off part at temperatures above their respective T_C [Fig. 3(b)]. In particular, the latter temperature dependence does not even reflect the phase transition at $T_C = 818$ K. These significantly different temperature dependences of ω_Q of ^{111}Cd can be qualitatively understood if we assume the order-disorder of the oxygen triangle to be of dynamic character. From the diffraction data of Ref. 1, the shortest distance between the center of the triangle and the edge of the oxygen sphere (radius of 140 pm) (Ref. 8) is only 60 pm at 820 K, say, although it will be longer because the oxygen triangle must come closer to the substitute Cd^{2+} ion and the space of the triangle must be made more open. Accordingly, the oxygen triangle cannot easily go through Cd, owing to its narrow space compared with the large ionic radius (95 pm) (Ref. 8) of Cd. The crystal being softened with increasing temperature, the triangle oxygen ions are likely to be pushed away by Cd, rather than drawn closer, making the value of ω_Q of ^{111}Cd smaller.

IV. CONCLUSIONS

In order to study the mechanism of ferroelectric phase transitions in LN ($T_C = 1483$ K) and LT ($T_C = 938$ K), the

electric quadrupole frequencies ω_Q of ^{117}In and ^{111}Cd in 8-mol % In-doped LT ($T_C = 818$ K) were measured in a temperature range from 4.2 to 1223 K by means of the PAC technique. A well-defined, essentially single, static electric quadrupole frequency was observed for each probe nuclide in this oxide, as in LT.⁷ The temperature dependences of ω_Q of ^{117}In in LT and 8-mol % In-doped LT show that the order-disorder of the Li ions is not the driving mechanism for the ferroelectric instability, and imply that the order-disorder of the oxygen triangles is the driving mechanism. Moreover, the significantly different temperature dependences of ω_Q of ^{111}Cd in these materials demonstrate that the order-disorder of the oxygen triangle is of dynamic character. It was shown that, different from $^{117}\text{In}^{3+}$, $^{111}\text{Cd}^{2+}$ was inadequate to probe the phase-transition mechanism in the LN and LT systems, owing to its relatively large ionic size. However, this very difference was effective in elucidating the dynamic nature of the order-disorder of the oxygen triangle. Combined PAC studies using ^{117}In and ^{111}Cd (occupying the same site because the chemical elements of those parent nuclei are the same, Cd) will find use in other physical systems.

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