Behavior of Impurities In and Cd in the LiNbO₃–LiTaO₃ System

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The temperature dependences of the nuclear-electric-quadrupole frequency \( \omega_Q \) of \(^{117}\)In and \(^{111}\)Cd doped in ferroelectrics LiTaO₃, \( \text{Li}_{1-x}\text{In}_x\text{Ta}_3\text{O}_9 \) with \( x = 0.2 \), and \( \text{Li}_{1-x}\text{Cd}_x\text{Ta}_2\text{O}_7 \) with \( x = 0.167 \), measured by the perturbed-angular-correlation technique, indicate that In behaves like Li; further, in a certain temperature range above the phase-transition temperature, a local system consisting of In (Li) and oxygen ions is very stable, by taking resonance structures, whereas Cd does not behave like Li, and a system consisting of Cd and oxygen ions does not take resonance structures, because the ionic size of Cd is large. It is considered that the resonance structures are due to a disordering of the oxygen ions, and that the order-disorder of oxygen ions is the driving mechanism for ferroelectric instability in the LiNbO₃–LiTaO₃ system.

(Received January 21, 2002; Accepted March 8, 2002)

**Keywords**: lithium niobate, lithium tantalate, impurities, indium, cadmium, ferroelectric phase transition, perturbed-angular-correlation technique

1. Introduction

Lithium niobate, LiNbO₃, and isostructural lithium tantalate, LiTaO₃, are ferroelectric and are known as, for example, important non-linear optic materials. Numerous studies on these materials have been conducted so far. Although their diffraction-derived structural data were obtained three decades ago, even a fundamental question concerning the mechanism of these ferroelectric-to-paraelectric phase transitions has not yet been answered.

LiNbO₃ and LiTaO₃ adopt an ilmenite (FeTiO₃)-related structure (not the perovskite structure) because of the similar ionic sizes of \( \text{Li}^+ \) (76 pm), \( \text{Nb}^{5+} \) (64 pm), and \( \text{Ta}^{5+} \) (64 pm). These oxides undergo only one structural phase transition (corresponding to a ferroelectric-to-paraelectric phase transition) at temperatures \( T_c \) of 1483(10) K and 938(5) K, respectively. The ferroelectric structure 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 downward, the Nb (Ta) ion on this axis is displaced downward from the center of its octahedron [Fig. 1(a)]. The next octahedron above contains a Li ion displaced upward from its center and the one more above has no metal ion inside it. The paraelectric structure belongs to the \( R3c \) space group. The Nb (Ta) ion is located at the center of its octahedron [Fig. 1(b)]. The average Li position is on the upper-triangle oxygen base of the octahedron; the Li ion is disordered and occupies the previously empty octahedron half of its time (dynamic disorder) or in half of the unit cells (static disorder).³,²

In a recent theory of the ferroelectric transition in LiNbO₃, it is assumed that the dynamic order-disorder of Li ions (Fig. 2) is the driving mechanism.⁵ Another theoretical calculation, however, shows that the order-disorder of oxygen ions, the displacements of which are strongly coupled with those of Li ions, is the driving mechanism.⁶ According to the former theory, a large decrease of \( T_c \) (≈ 818(5) K) observed in In-doped LiTaO₃, \( \text{Li}_{0.1}\text{In}_{0.067}\text{Ta}_3\text{O}_7 \), can be explained as the order-disorder of In ions taking place at a much lower temperature than that of Li ions in LiTaO₃. Let us note that In ions doped in LiTaO₃ are considered to occupy the Li sites from a PIXE (proton-induced X-ray emission)/channeling experiment on 0.59-mol% In in 6-mol% Mg-doped LiNbO₃.¹⁰

Previously, we examined the above explanation by measuring with the perturbed-angular-correlation (PAC) technique the temperature dependence of the magnitude of the local field, i.e., electric field gradient (EFG), at \(^{117}\)In in LiTaO₃ and \( \text{Li}_{0.1}\text{In}_{0.067}\text{Ta}_3\text{O}_7 \). We observed that the temperature dep-
pendences of the electric quadrupole frequency $\omega_Q$ of $^{117}$In in these oxides were similar to that of the $^7$Li-nuclear magnetic resonance coupling constant$^{13}$ for LiTaO$_3$ and faithfully reflected the phase transition at the respective $T_C$. These observations suggested that although an In ion was disordered in the paraelectric phase, its order-disorder did not take place at a much lower temperature than that of the Li ion would require. We therefore considered that the order-disorder of Li is not the driving mechanism of ferroelectric instability.$^{12}$ A comparison of the magnitude of $\omega_Q$ of $^{117}$In in Li$_2$O$_3$–In$_2$O$_3$TaO$_3$ with that for LiTaO$_3$ further implied that displacements of oxygen ions were the cause of the ferroelectric instability.

Additional measurements of $\omega_Q$ of $^{111}$Cd in the oxides$^{11,12}$ which also occupy those Li sites$^{11}$ showed their temperature dependences to be quite different from those of $^{117}$In. In the case of Li$_0.5$In$_0.05$TaO$_3$, the temperature dependence does not even reflect the phase transition at $T_C = 818$ K. This observation indicates that, different from In, Cd is not disordered in the paraelectric phase. If the order-disorder of Li ions should be the driving mechanism, the existence of Cd ions in LiTaO$_3$ could make $T_C$ even increase. It is therefore worth conducting PAC measurements of the temperature dependence of $\omega_Q$ of $^{117}$In and $^{111}$Cd in Cd-doped LiTaO$_3$. In this paper, we report on the results for Li$_1-x$Cd$_x$TaO$_3$ ($x = 0.167$), i.e., Li$_{0.833}$Cd$_{0.083}$TaO$_3$ in a temperature range between 77 and 1223 K. Using these results, together with our previous PAC results on $^{117}$In and $^{111}$Cd in LiTaO$_3$$^{11}$ and Li$_{0.8}$In$_{0.067}$TaO$_3$$^{12}$, we discuss the behavior of In and Cd and the driving mechanism for ferroelectric instability in the LiNbO$_3$–LiTaO$_3$ system.

2. Experimental Procedures

2.1 Sample preparation

The parent $^{117}$Cd and $^{111}$mCd nuclei were separately obtained by irradiating enriched $^{116}$CdO and $^{110}$CdO, respectively, with thermal neutrons at the Kyoto University Research Reactor. The irradiated oxide was mixed with appropriate amounts of high-purity powders of Li$_2$CO$_3$, Ta$_2$O$_5$, and CdO for a chemical composition of Li$_{0.833}$Cd$_{0.083}$TaO$_3$. By pressing the mixture into a pellet and heating in air at 1100°C for about 1 hour, the sample was obtained. Owing to the short half-lives of $^{117}$Cd and $^{111}$mCd, samples were prepared for each PAC-measurement temperature. The room-temperature X-ray-diffraction pattern of a sample after a PAC measure-

Fig. 2 Local structures around a Li ion in the (a) ferroelectric and (b) paraelectric phases of the LiNbO$_3$–LiTaO$_3$ system. Li is represented by the hatched circles and O by the open circles. The two Li ions in (b) represent a single Li ion as being dynamically disordered, occupying the previously empty octahedron space during half of its time.

2.2 PAC measurements

The PAC method is mostly applied to an ensemble of nuclei emitting two consecutive $\gamma$ rays. Figure 3 shows relevant parts of the decay schemes of (a) $^{117}$Cd $\rightarrow$ $^{117}$In and (b) $^{111}$mCd $\rightarrow$ $^{111}$Cd. The 749-keV excited level of $^{117}$In is populated by the $\beta^-$ decay of the parent $^{117}$Cd with a half-life $t_{1/2} = 2.49$ h, which decays to the 315-keV excited level through the 660-keV intermediate level having a spin $I = 3/2$, $t_{1/2} = 53.6$ ns, and an electric quadrupole moment $Q = (-)0.59$ b.$^{13}$ The 396-keV excited level of $^{111}$Cd, i.e., $^{111}$mCd with $t_{1/2} = 48.54$ min, decays to the ground level through the 245-keV intermediate level having $I = 5/2$, $t_{1/2} = 85.0$ ns, and $Q = +0.77$ (12) b.$^{13}$ 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 90-keV (151-keV) $\gamma$ rays with a detector sorts out a set of $^{117}$In ($^{111}$Cd) nuclei in intermediate states with spin alignments against the direction of the detector from the source. Time-differential measurements of the 344-keV (245-keV) $\gamma$ rays from the same nuclei with another detector permits a determination of the spin precession frequency of $^{117}$In ($^{111}$Cd) nuclei in intermediate states, and then a determination of the magnitude of the splitting of the level. Thus the PAC of the 90- and 344-keV (151- and 245-keV) $\gamma$ rays emitted in successive $\gamma$ transitions reveals an electric

Fig. 3 Partial decay schemes of (a) $^{117}$Cd $\rightarrow$ $^{117}$In and (b) $^{111}$mCd $\rightarrow$ $^{111}$Cd.
quadrupole interaction during the stay of $^{117}\text{In}$ ($^{111}\text{Cd}$) nuclei in intermediate states.

The time dependences of the coincidence counts $N(\theta, t)$ of the 90–344-keV cascade $\gamma$ rays for samples containing $^{117}\text{Cd}$ and of the 151–245-keV $\gamma$ rays for $^{111m}\text{Cd}$ were taken in a temperature region between 77 and 1223 K using a measurement system consisting of standard fast-slow electronic modules and four BaF$_2$ scintillation detectors. Here $\theta$ and $t$ denote the angle and time interval, respectively, between the cascade $\gamma$ rays. The directional anisotropy $A_{22}G_{22}(t)$ was obtained according to eq. (1):

$$A_{22}G_{22}(t) = 2[N(\pi, t) - N(\pi/2, t)]/[N(\pi, t) + 2N(\pi/2, t)],$$

(1)

The coefficient $A_{22}$ depends only on the nuclear properties, and the values for $^{117}\text{In}$ ($^{111}\text{Cd}$) and $^{111m}\text{Cd}$ ($^{111m}\text{Cd}$) are $-0.36$ and $+0.18$, respectively.\(^{14}\)

We give the relevant expressions of $G_{22}(t)$ for a unique static quadrupole interaction. The perturbation factor $G_{22}(t)$ for an ensemble of randomly oriented microcrystals is a function of the electric quadrupole frequency $\omega_Q$ and the asymmetry parameter $\eta$ of EFG through the interaction Hamiltonian. The quantities $\omega_Q$ and $\eta$ are defined as follows: $h\omega_Q = -eQV_{zz}/[4(2I - 1)]$ and $\eta = (V_{xx} - V_{yy})/V_{zz}$. The three components of EFG in the principal-axis system are chosen such that $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$, and thus the asymmetry parameter $\eta$ takes a value between 0 and 1. In the case of $^{117}\text{In}$, $G_{22}(t)$ has the form

$$G_{22}(t) = [1 + 4\cos(6\omega_Q(1 + \eta^2/3)^{1/2}t)]/5,$$

(2)

and in the case of $^{111}\text{Cd}$,

$$G_{22}(t) = S_0 + S_1\cos(6\omega_QC_1t) + S_2\cos(6\omega_QC_2t) + S_3\cos(6\omega_QC_3t).$$

(3)

The $S_n$ and $C_n$ in eq. (3) are numerically calculated for a given value of $\eta$. For an axially symmetric case of $\eta = 0$, $S_n$ and $C_n$ can be calculated analytically: $G_{22}(t) = [7 + 13\cos(6\omega_Qt) + 10\cos(12\omega_Qt) + 5\cos(18\omega_Qt)]/35$. It should be noted that the sign of $\omega_Q$ cannot be determined from the spectrum, because $\omega_Q$ is an argument of the cosine function, and that in the case of $^{117}\text{In}$, $G_{22}(t)$ contains only one frequency component and the values of $\omega_Q$ and $\eta$ cannot be determined independently from the spectrum, whereas in the case of $^{111}\text{Cd}$, they can be determined because $S_n$ and $C_n$ in eq. (3) are each modified in a characteristic way as a function of $\eta$.

### 3. Results

The PAC spectra $A_{22}G_{22}(t)$ measured at 77, 673, and 1223 K of $^{117}\text{In}$ in Li$_{1.083}$Cd$_{0.083}$TaO$_3$ are shown in Fig. 4, and those for $^{111}\text{Cd}$ in Fig. 5. The anisotropy in each spectrum is modulated in a manner characteristic of a single electric quadrupole interaction in polycrystalline samples, depending on the spin value of the intermediate nuclear level. We analyzed the PAC spectra with a single quadrupole frequency having a Lorentzian distribution around the central value $\omega_Q$. Equations (2) and (3), modified for the Lorentzian distribution, were fitted using the least-squares method to the observed time spectra of $^{117}\text{In}$ in a time range between 5–100 ns and those of $^{111}\text{Cd}$ between 1–200 ns, respectively. [The experimental points near $t = 0$ ns were not used in the fit so as to avoid any influence of the prompt peak of $N(\theta, t)$ at $t = 0$]. The value of $\eta$ was most reliably determined to be 0.11 for the $^{111}\text{Cd}$ spectrum at 1223 K, because at this temperature the ratio $\delta$ of the distribution width $\Delta\omega_Q$ to the central value $\omega_Q$ was 4% and small. To facilitate the analysis, we used $\eta = 0.11$ for all $^{111}\text{Cd}$ spectra. As discussed later, since $^{111}\text{In}$ is not considered to be in the same physicochemical state as $^{111}\text{Cd}$, i.e., to be subject to the same asymmetry of the EGF as $^{111}\text{Cd}$, we safely set $\eta = 0$ for all $^{117}\text{In}$ spectra. This is because the EFG at Li is axially symmetric (the Li site...
has a threefold symmetric axis) and the value of \( \eta \) for \(^{117}\text{In} \) is thus not considered to be far from zero. A small deviation of the value of \( \eta \) from 0 hardly affects the value of \( \omega_Q \). Even when \( \eta = 0.11 \) is used for \(^{117}\text{In} \), the thus-obtained \( \omega_Q \) value differs by only 0.2%, which is well within the statistical error attached to \( \omega_Q \). The temperature dependence of \( \delta \), determined in the fit, has a general trend. In the case of \(^{117}\text{In} \), \( \delta \) changes from about 20 to 2% with increasing temperature, and in the case of \(^{111}\text{Cd} \) it decreases from about 10 to 4%. The solid curves in Figs. 4 and 5 are results of fits using \( \eta = 0 \) for \(^{117}\text{In} \) and \( \eta = 0.11 \) for \(^{111}\text{Cd} \).

In Fig. 6 are plotted the \( \omega_Q(T)/\omega_Q(77 \text{K}) \) values of \(^{117}\text{In} \) (open squares) and \(^{111}\text{Cd} \) (closed circles) in \( \text{Li}_{0.833}\text{Cd}_{0.083}\text{TaO}_3 \) vs temperature \( T \). The absolute values of \( \omega_Q(77 \text{K}) \) of \(^{117}\text{In} \) and \(^{111}\text{Cd} \) are 88.5(2.4) and 37.9(2) Mrad/s, respectively. The \( \omega_Q \) of \(^{117}\text{In} \) increases by about 35% with increasing temperature from 77 to about 800 K, seems to level off in a certain temperatures range, and then decreases gradually. Different from the case of \(^{117}\text{In} \), the \( \omega_Q \) of \(^{111}\text{Cd} \) changes little with increasing temperature up to about 700 K, and then decreases rapidly.

4. Discussion

In a previous work,\(^{11}\) we confirmed that an order of 1 mol% of Cd occupy the Li sites of \( \text{LiNbO}_3 \) and \( \text{LiTaO}_3 \). We now examine whether an order of 10 mol% of Cd occupy the Li sites and thus a compound with the chemical formula \( \text{Li}_{0.833}\text{Cd}_{0.083}\text{TaO}_3 \) was actually prepared. The observation of a well-defined single \( \omega_Q \) for \(^{111}\text{Cd} \) (also for \(^{117}\text{In} \)) in the present sample means that for Cd there is one site with a relatively large EFG and are possibly additional sites with zero or small EFG. (Note that since the chemical element of the parent nuclei of \(^{117}\text{In} \) and \(^{111}\text{Cd} \) is the same, cadmium, \(^{117}\text{In} \) is considered to be located at the same site as Cd.) The second possibility should be considered since the Cd site of, say, CdO, which is a starting material for the sample and may partly remain as it is, is of zero EFG, because CdO has a cubic structure. This possibility is, however, very small, if any, from the facts that the X-ray-diffraction pattern of the sample shows a single phase and that the value of \( A_{22} \) obtained in the fit for \(^{111}\text{Cd} \) (also for \(^{117}\text{In} \)) is close to that in Ref. 14. Considering furthermore that the positive temperature dependence of \( \omega_Q \) of \(^{117}\text{In} \) at low temperature is similar to that for \( \text{LiNbO}_3 \) and \( \text{LiTaO}_3 \) (Ref. 11), we conclude that an order of 10 mol% of Cd occupy the Li sites; thus a compound with the chemical formula \( \text{Li}_{0.833}\text{Cd}_{0.083}\text{TaO}_3 \) was prepared.

In order to examine the present results with respect to the phase-transition mechanism, we describe in some detail the two opposing interpretations of the role of the order-disorder of Li in the phase transitions and the relevant PAC results on \( \text{LiTaO}_3 \)\(^{11}\) and \( \text{Li}_{0.8}\text{In}_{0.067}\text{TaO}_3 \)\(^{12}\), which were mentioned in the Introduction. The two opposite interpretations mean that in one interpretation the order-disorder of Li is the driving mechanism of the phase transitions, and in the other it is not. Theoretical calculations by Inbar and Cohen\(^8\) show that the Li displacement alone results in a single minimum in the local potential energy, i.e., the order-disorder of Li is not the driving mechanism, and that displacements of the oxygen ions (the upper oxygen triangle in Fig. 2) result in double minima; moreover, strongly coupled oxygen and Li displacements bring about much deeper double minima. On the other hand, a recent theory by Safaryan\(^7\) explored the former example.

Safaryan presumed that at low temperature the free space in the upper triangle of oxygen ions (Fig. 2) 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 the Li ion approaches closer to the upper triangle and is more easily disordered; at the same time, Nb (Ta) approaches closer to the center of the oxygen octahedron surrounding it. At \( T_C \), the Li ion occupies both sites, above and below the oxygen triangle, with equal probability (dynamic disorder), the Nb (Ta) ion occupying the center of its octahedron.

According to this proposition, a decrease of \( T_C \) with increasing \( x \) in \( \text{Li}_{1-x}\text{In}_x\text{TaO}_3 \) (at \( x = 0.2 \), i.e., for \( \text{Li}_{0.8}\text{In}_{0.067}\text{TaO}_3 \), \( T_C \) goes down to 818 K (Ref. 9)) can be explained as follows. Since the charge on an In ion at the Li site of \( \text{LiTaO}_3 \) is considered to be close to \( 3^+ \), and its ionic size (80 pm) is about the same as that of \( \text{Li}^+ \) (76 pm),\(^4\) the In ion must come closer to the upper oxygen triangle than does a Li ion, because of its stronger Coulomb interaction with oxygen ions. This makes the inner space of the triangle more open, and thus a single In ion doped in \( \text{LiTaO}_3 \) as an impurity becomes disordered at a much lower temperature than Li would require. With increasing amount of doped In beyond a certain amount, interactions among ions could also shorten the distance between Li and its upper oxygen triangle, making \( T_C \) decrease. In a heavily In-doped \( \text{LiTaO}_3 \), such as \( \text{Li}_{0.8}\text{In}_{0.067}\text{TaO}_3 \), the temperature where In ions start to be disordered could coincide with that for Li ions, and also with \( T_C \). On the other hand, if we replace Li by ions with a larger ionic radius, those ions may become disordered at a higher temperature, or may not become disordered at all. Cd is considered to be such an ion (95-pm ionic radius).\(^5\)

Figure 7 shows the temperature dependences of the absolute value of \( V_T \) (lattice) at \(^{117}\text{In} \) in \( \text{LiTaO}_3 \) (open circles),
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Li sites are of highly-ionic character, V_{zz}(lattice) is expressed as $V_{zz} = (1-R)V_{zz}(valence)+(1-\gamma_\infty)V_{zz}(lattice)$, where $V_{zz}(valence)$ is due to the noncubic electron distribution in partially filled valence orbitals of the probe ion and $V_{zz}(lattice)$ to the charges on the lattice ions surrounding the probe ion noncubically symmetrically. $R$ and $\gamma_\infty$ are the Sternheimer shielding and anti-shielding factors, respectively, both representing the effect of the distortion of the closed-shell electron distributions in the probe ion. In the present case, where In and Cd ions at the Li sites are of highly-ionic character, $V_{zz}(valence)$ may be neglected, and thus $V_{zz}(lattice) = V_{zz}/(1-\gamma_\infty)$. We plotted $V_{zz}(lattice)$, instead of $\omega_Q$ or $V_{zz}$, in order to compare below the relative distance to the upper oxygen triangle among Li, Cd, and In. The solid line in Fig. 7 represents the temperature dependence of $V_{zz}(lattice)$ at $^{117}\text{In}$, derived in the same way from the $^7\text{Li}$-nuclear magnetic resonance quadrupole coupling constant $\omega_Q (=e\gamma_Q Q/h)$ for LiTaO₃ (Ref. 16). Note that the $V_{zz}(lattice)$ values for $^7\text{Li}$ are multiplied by a factor of 4. Here relevant values are given. The calculated values $^{17}$ of $\gamma_\infty$ for In$^{3+}$, Cd$^{2+}$, and Li$^+$ are $-25.8$ (also refer to Ref. 11), $-29.27$, and $0.2575$, respectively, and the value of $Q$ for $^7\text{Li}$ is $-0.040$ b.$^{13}$

As can be seen in Fig. 7, $V_{zz}(lattice)$ at $^{117}\text{In}$ in LiTaO₃ (open circles) increases with increasing temperature up to about 940 K, and levels off at temperatures above about 1100 K, and then decreases gradually. This temperature dependence is very similar to that for $^7\text{Li}$ (solid line), indicating that In behaves like Li and is disordered at high temperature. Since the lowest temperature where $V_{zz}(lattice)$ at $^7\text{Li}$ is constant corresponds to $T_C = 938(5)$ K for LiTaO₃, such a temperature for $^{117}\text{In}$ must be that where In starts to be disordered. Dynamic disorder, as Safaryan proposed, is implied by the constant part of the temperature dependence of $V_{zz}(lattice)$ at $^7\text{Li}$ or $^{117}\text{In}$. The constant means that the geometry among Li or In and the oxygen ions in the upper triangle hardly changes, despite the high temperatures. The local system consisting of Li or In and oxygen ions is extremely stable, so that the values of $V_{zz}(lattice)$ at $^{117}\text{In}$ in the constant part for the three oxides are essentially the same (about $6 \times 10^{-22}$ V m$^{-2}$). This stability could be due to a large resonance energy of the dynamically disordered local system. Moreover, a part of our speculation, i.e., an In ion comes closer to the upper oxygen triangle than a Li ion does, is supported by the fact that $V_{zz}(lattice)$ at $^{117}\text{In}$ is larger than at $^7\text{Li}$ (by a factor of about 4). Although it might be plausible that In in LiO$_3$ becomes disordered at $T_C = 818$ K, the fact that an In ion, doped very thinly in LiTaO₃, becomes disordered at $T_C = 938$ K contradicts our speculation derived above from the proposition of Safaryan. We therefore, for the moment, consider that Li ions become dynamically disordered at $T_C$, but that their order-disorder is not the driving mechanism of the ferroelectric phase transition in the LiNbO₃–LiTaO₃ system.

As for $V_{zz}(lattice)$ at $^{111}\text{Cd}$ in LiTaO₃ (open circles), as shown in Fig. 8, it does not show a constant part, although it increases with increasing temperature up to about 940 K and then decreases rapidly, reflecting the phase transition in LiTaO₃. From the observation that the value of $V_{zz}(lattice)$ at $^{111}\text{Cd}$ in LiTaO₃ at low temperature agrees with that for $^{117}\text{In}$, the position of Cd in the oxygen octahedron is considered to be identical to that of In. However, as expected from its large ionic radius, the absence of a constant part of $V_{zz}(lattice)$ at $^{111}\text{Cd}$ indicates that the Cd ions are not disordered. The temperature dependence of $V_{zz}(lattice)$ at $^{111}\text{Cd}$ in LiTaO₃ (open circles in Fig. 8) does not even show the phase transition at $T_C = 818$ K. If the order-disorder of Li ions should be the driving mechanism, the existence of Cd ions, contrary to In ions, could make $T_C$ even increase through interactions among ions. To our knowledge, $T_C$ of Cd-doped LiTaO₃ has not yet been measured. The temperature dependence of $V_{zz}(lattice)$ at $^{117}\text{In}$ in LiO$_3$ is shown in Fig. 7, however, suggests...
that $T_c$ of Li$_{0.833}$Cd$_{0.167}$TaO$_3$ is about 800 K, which is even lower than $T_c = 938$ K for LiTaO$_3$. Our consideration about the phase-transition mechanism is thus borne out: the order-disorder of Li ions is not the driving mechanism of the ferroelectric phase transitions in the LiNbO$_3$–LiTaO$_3$ system. The observation that $T_c$ of Li$_{0.833}$Cd$_{0.167}$TaO$_3$ can be lower than that of LiTaO$_3$, furthermore, implies that oxygen displacements play a key role in the phase transitions: Ions which move through Coulomb interactions with increasing temperature are oxygen ions rather than Li, and ions which become disordered must be oxygen ions rather than Li, as shown in Fig. 9. Our PAC results therefore support the calculation results of Inbar and Cohen. 8)

From the viewpoint of oxygen displacements playing a key role in the phase transitions, our PAC results are understandable, e.g., the temperature dependences of $V_{zz}$ (lattice) at $^{117}$In in LiTaO$_3$ and Li$_{0.833}$In$_{0.167}$TaO$_3$ faithfully reflect the corresponding $T_c$, the value of $V_{zz}$ (lattice) at $^{117}$In in Li$_{0.8}$In$_{0.2}$TaO$_3$ below its $T_c$ is always larger than in LiTaO$_3$, and $T_c$ of Li$_{0.833}$Cd$_{0.167}$TaO$_3$ can be lower than that of LiTaO$_3$.

The overall temperature dependence of $V_{zz}$ (lattice) at $^{111}$Cd is interpreted as follows. At low temperature, with increasing temperature the upper oxygen triangle moves little toward Cd, because of its large ionic radius. Although with further increasing temperature the crystal becomes softened, since the upper oxygen triangle cannot go through a large Cd, it is pushed away from Cd by their thermal motions, rather than drawn closer, making $V_{zz}$ (lattice) at $^{111}$Cd smaller. However, a further consideration is needed on, for example, why the temperature dependence of $V_{zz}$ (lattice) at $^{111}$Cd in Li$_{0.8}$In$_{0.2}$TaO$_3$ (open squares in Fig. 8) does not show the phase transition at $T_c = 818$ K.

5. Conclusions

In order to study the mechanism of the ferroelectric phase transitions in LiNbO$_3$ ($T_c = 1483$ K) and LiTaO$_3$ ($T_c = 938$ K), the nuclear-electric-quadrupole frequencies $\omega_Q$ of $^{117}$In arising from $^{117}$Cd and $^{111}$Cd arising from $^{111m}$Cd, chemically introduced in Li$_{0.833}$Cd$_{0.167}$TaO$_3$, were measured in a temperature range from 77 to 1223 K by means of time-differential perturbed-angular-correlation technique. A well-defined, essentially single, static electric quadrupole frequency was observed for each probe. The behavior of In is very different from that of Cd. The $\omega_Q$ of $^{117}$Cd changes little with increasing temperature up to about 700 K, and then decreases rapidly. On the other hand, the $\omega_Q$ of $^{117}$In increases rapidly with increasing temperature up to about 800 K, seems to hold constant in a certain temperature range, and then decreases gradually. This large difference is due to their very different ionic sizes. The temperature dependence for $^{117}$In indicates that the ferroelectric phase-transition temperature of Li$_{0.833}$Cd$_{0.167}$TaO$_3$ is about 800 K, which is much smaller than that of LiTaO$_3$, 938 K. This result and our previous results on LiTaO$_3$ and In-doped LiTaO$_3$ can be understood if we consider that the order-disorder of oxygen ions, not of lithium ions, is the driving mechanism for the ferroelectric instability in the LiNbO$_3$–LiTaO$_3$ system. It is considered that in a certain temperature range above the phase-transition temperature, a local system consisting of In (Li) and oxygen ions is very stable, by taking resonance structures due to the disorder of oxygen ions, whereas a system consisting of Cd and oxygen ions does not take such resonance structures, because the ionic size of Cd is large.

Acknowledgements

This work was supported by the Ministry of Education, Culture, Sports, Science, and Technology of Japan [Grant-in-Aid for Scientific Research on Priority Areas (B) No. 751].

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