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Composition dependence of phase transition observed by ^{23}Na NMR spin-lattice relaxation in $Na_{1-x}Ag_xNO_2$ mixed crystals

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The effect of Ag impurity on the phase transition in a mixed system $Na_{1-x}Ag_xNO_2$ was first investigated by employing ^{23}Na NMR spin-lattice relaxation. The critical temperature (T_c) of the ferroelectric to paraelectric phase and the activation energy (E_a) for NO_2^- reorientational motion increased and decreased, respectively, with increasing Ag content. The decrease of E_a is explained in terms of the larger size of impurity ion than that of host ion, which may be applicable to other isomorphic mixed systems. The change of E_a is found to be linearly correlated with the shift of T_c for various Ag concentrations. [S0163-1829(99)09641-1]

A systematic change in the static and dynamic features of the local structure may be achieved by introducing impurities in the crystal, the influence of which is directly reflected in quadrupolar nuclear magnetic resonance (NMR) and in nuclear quadrupole resonance (NQR). Thus the study of the impurity effects on the lattice dynamics including phase transition using nuclear resonance has been active to present.[1–4] In the mixed crystals, such as $K_2(Sn_{1-x}Re_x)Cl_6$, $(K_{1-x}A_x)_2SnCl_6$ ($A=$Rb, NH_4),[5] and $(Rb_{1-x}M_x)_2ZnCl_4$,[6] it was shown by ^{35}Cl NQR that the substituting impurities cause remarkable shifts of the transition temperatures. These shifts are related with the changes of structural stability and of the anion dynamics.

In this study, the influence of substitutional Ag impurity ion on the phase transition of ferroelectric $NaNO_2$ was investigated with an isomorphic mixed system $Na_{1-x}Ag_xNO_2$. The Ag impurity effect in $Na_{1-x}Ag_xNO_2$ is expected to be mainly from the difference in the ionic sizes between Na^+ and Ag^+ since both ions are monovalent. Temperature dependence of the spin-lattice relaxation time for ^{23}Na NMR in the mixed crystals was investigated in a systematic manner. From these results, the phase-transition temperature and the activation energy of the reorientational motion for NO_2^- ion have been obtained as a function of Ag impurity concentration. Above all, the variation of the activation energy in the mixed system is interpreted in terms of the ionic size difference between host and impurity ion. The results of this study is expected to be applied to other isomorphic mixed systems.

The mixed-crystalline powder $Na_{1-x}Ag_xNO_2$ ($0 \leqslant x \leqslant 0.16$) were prepared by slow evaporation of an aqueous mixture solution of $NaNO_2$ and $AgNO_2$, which are isomorphic to each other. The samples with molar ratio up to $x=0.16$ were only obtained, because of low solubility of $AgNO_2$. The sample preparation and characterization were already described in detail elsewhere.[7,8] The spin-lattice relaxation time (T_1) was obtained at 105.805 MHz Larmor frequency ($B_0=9.4$ T) by employing a Bruker DSX 400 spectrometer with increasing temperature from 297 K up to 458 K. The sample temperature was constantly maintained by controlling nitrogen gas flow and heater current, giving an accuracy of ± 0.2 K. T_1 was measured with an inversion recovery ($\pi - t - \pi/2$), where π and $\pi/2$ pulse lengths were 6.4 and 3.2 μs, respectively. The signal measured here is dominantly the central transition, and broadened by the second-order quadrupole interaction. The recovery traces of magnetization of all mixed crystals in the temperature range investigated were well fitted with a single exponential function. Thus the spin-lattice relaxation rate $W(1/T_1)$ is determined from a fit of the recovery pattern given by the following equation:[9]

$$\frac{S(\infty)-S(t)}{S(My)} = A \exp(-2Wt), \tag{1}$$

where $S(t)$ is the nuclear magnetization at t.

The incommensurate phase between ferroelectric and paraelectric phases in a narrow temperature range (1.2 K) of $NaNO_2$ single crystals had been usually found as a splitting and anomalous line shape of ^{14}N NQR line[10] and ^{23}Na NMR line.[11] However, any evidence on incommensurate phase in the line-shape measurement was not observed in our powder samples studied here. The temperature dependence of the spin-lattice relaxation rate ($1/T_1$) of ^{23}Na NMR for $NaNO_2$ matrix in the mixed crystals are displayed in Fig. 1(a). The enlarged part of Fig. 1(a) near T_c is shown in Fig. 1(b), where the values of $1/T_1$ is shifted upward progressively for a better view. The $1/T_1$ for the pure $NaNO_2$ shows a phase transition from the ferroelectric to the paraelectric at $T_c = 436.7 \pm 0.3$ K, as expected from previous studies.[9] The T_c in mixed crystals $Na_{1-x}Ag_xNO_2$ with $x=0.0084$, 0.026, 0.079, and 0.16 are found to be 437.6 ± 0.3 K, 438.2 ± 0.4 K, 439.2 ± 0.6 K, and 440.4 ± 0.9 K, respectively, as indicated by arrows in Fig. 1(b). In Fig. 2, the T_c values are plotted versus Ag concentration, together with T_c determined with differential scanning calorimetry (DSC) measurements. Both results are consistent with each other, except for the small differences of absolute T_c values, possibly due to the differences of temperature calibration and of inherent measuring temperature states (constant versus scanning tempera-

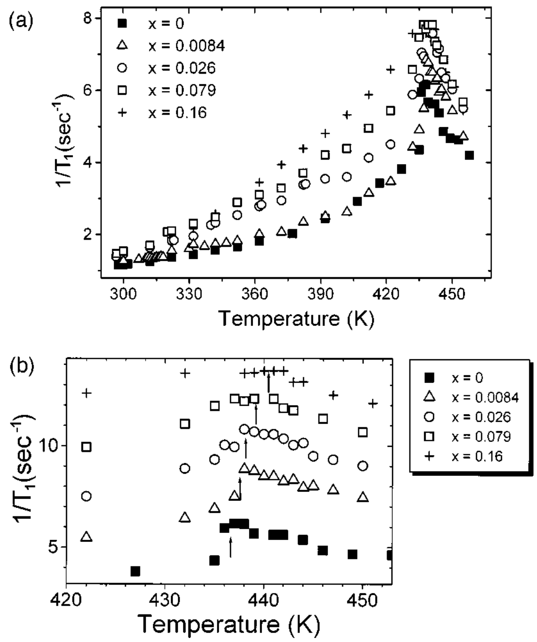

FIG. 1. (a) Spin-lattice relaxation rate $(1/T_1)$ as a function of temperature in the mixed crystals $Na_{1-x}Ag_xNO_2$. (b) An enlarged part of Fig. 1(a) near T_c. The values of $1/T_1$ is shifted upward 2, 3, 4.5, and 6 for $x=0.0084$, 0.026, 0.079, and 0.16, respectively, for a better view and each T_c position is guided with an arrow.

ture). The increase of T_c due to impurity is rather anomalous, which is in contrast to that observed in gamma-ray irradiated $NaNO_2$ crystal.[12]

The spontaneous polarization (P_s) in the ferroelectric $NaNO_2$ is given as[13]

$$P_s=\tanh[(T_c/T)(P_s+P_s^3\Delta)], \tag{2}$$

where Δ is an anomalous volume expansion parameter of 0.39 which was taken from Ref. 13. In Ref. 13, the P_s, obtained experimentally from the x-ray-diffraction intensity measurement, was best fitted with Eq. (2) for $\Delta=0.39$. In Eq. (2), the P_s decreases with increasing temperature then goes to zero discontinuously at T_c and the P_s is larger for the sample with a higher T_c at a given temperature. Consequently, the increase of P_s will results in a shift of T_c into the higher temperature. The increase of P_s in $Na_{1-x}Ag_xNO_2$ may be caused by substitution of the Ag^+ ion, which is larger in ionic size and electronegativity than those of the Na^+ ion, into the Na site. On the other hand, the decrease of T_c observed in gamma-ray irradiated $NaNO_2$ crystal may be due to reduction of the P_s by point-charge defects created by the irradiation. However, for more convincing explanation about the increase of T_c in $Na_{1-x}Ag_xNO_2$ due to the impurity, a rigorous study on the mechanism of P_s variation in the mixed crystals may be required.

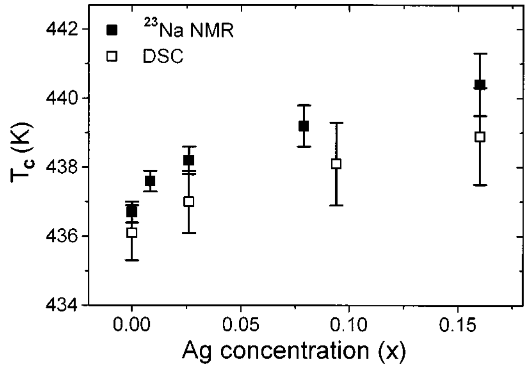

FIG. 2. T_c as a function of x in the mixed crystals $Na_{1-x}Ag_xNO_2$.

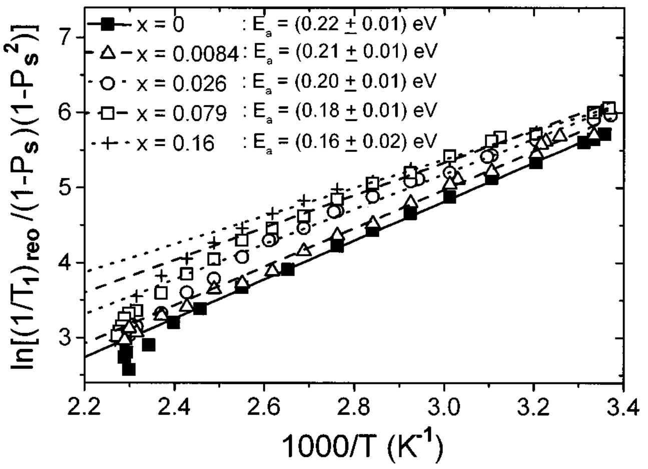

FIG. 3. $\ln[(1/T_1)_{reo}/(1-P_s)(1-P_s^2)]$ is plotted against the reciprocal temperature for the mixed crystals $Na_{1-x}Ag_xNO_2$.

The relaxation rate for ^{23}Na NMR in the pure $NaNO_2$ above 300 K is the sum of contributions from the lattice vibration $(1/T_1)_{ph}$ and the reorientation of NO_2^- ion $(1/T_1)_{reo}$. Each motion is assumed to be independent and its contribution to relaxation is given by

$$(1/T_1)=(1/T_1)_{ph}+(1/T_1)_{reo}, \tag{3}$$

$$(1/T_1)_{ph}\sim T^2, \tag{4}$$

$$(1/T_1)_{reo}\sim(1-P_s)(1-P_s^2)\exp(E_a/kT), \tag{5}$$

where E_a is the activation energy for the reorientational motion of NO_2^- ion.[9]

In the pure $NaNO_2$ and mixed crystals $Na_{1-x}Ag_xNO_2$, the quadrupole relaxation $(1/T_1)_{ph}$ caused by phonons of the crystal lattice is assumed to be proportional to T^2, and taken as $(4\times10^{-7}\,T^2)s^{-1}$.[9] Under this assumption, the relaxation rate due to the reorientational motion of NO_2^- group, $(1/T_1)_{reo}$, is obtained by subtracting the values of estimated $(1/T_1)_{ph}$ from measured $1/T_1$. Using Eq. (2), the P_s is obtained by taking T_c observed from $1/T_1$ measurement of the pure $NaNO_2$ and $Na_{1-x}Ag_xNO_2$ mixed crystals. Thus by applying Eq. (5), the slope of $\ln[(1/T_1)_{reo}/(1-P_s^2)(1-P_s)]$ versus $1/T$ gives the activation energy E_a, as shown in Fig. 3. The E_a in the mixed system decreases monotonically with the increasing Ag impurity.

The ionic radii of Na^+ and Ag^+ are $r_{Na}=0.95$ Å and $r_{Ag}=1.26$ Å, respectively. Substitution of the Ag^+ ion, which is larger in ionic size than that of the Na^+ ion, into the Na^+ site in $Na_{1-x}Ag_xNO_2$ causes the gradual increase of the lattice constant, demonstrated already by the x-ray-diffraction study.[7] The increase of the lattice constant may cause the barriers hindering the motion of the NO_2^- anion coupled to the cation to be somewhat reduced. Thus Ag impurity in the mixed crystals causes a decrease of the potential barrier of the NO_2^- motion. In this sense, the monotonic reduction in activation energy with the increasing Ag impurity in $Na_{1-x}Ag_xNO_2$ is understandable in terms of the size of cations. Likewise, ^{35}Cl NQR study of $(Rb_{1-x}Cs_x)_2ZnCl_4$ doped with greater cation impurity (Cs) revealed an appreciable reduction in the activation energy of the anion $(ZnCl_4)$ motion.[6] From ^1H NMR study of $[M(H_2O)_6][SnCl_6]$ with different M^{2+} ion, it is shown that the larger M^{2+} ion leads to lowering of the activation energy for the flipping motion of H_2O molecule.[14] In the case of $(Rb_{1-x}Cs_x)_2ZnCl_4$ and $[M(H_2O)_6][SnCl_6]$, the decrease of E_a may also be attributed to the release of hindrance for the motion, caused by the volume expansion due to substitution of the bigger impurity ion. Therefore it may be generalized that the variation of E_a for the motion of the species in the different isomorphic crystal systems is correlated with the size difference between impurity and host ion.

In Figs. 1(a) and 1(b), the relaxation rate of the pure $NaNO_2$ changes sharply near T_c, whereas those of the mixed crystals vary smoothly near T_c. This gradual rising of $1/T_1$ value near T_c for the sample with increasing x results from the reduced E_a of NO_2^- reorientation and the slower variation of P_s versus temperature due to the *random* substitution of Ag impurity at the ^{23}Na site. The variation of $E_a(\Delta E_a)$ is found to be linearly proportional to ΔT_c obtained with ^{23}Na NMR, as shown in Fig. 4, which indicates a direct correlation between the changes of activation energy and of critical temperature in mixed crystals $Na_{1-x}Ag_xNO_2$, where ΔE_a is defined as $\Delta E_a = E_a(x) - E_a(x=0)$. Thus a *linear* relationship is observed.

In summary, the Ag impurity effect on the temperature behavior of the ^{23}Na spin-lattice relaxation time in the isomorphic mixed system $Na_{1-x}Ag_xNO_2$ was systematically investigated. Our experimental results show that the substitution of larger Ag impurity in both ionic size and electronegativity compared to the host Na ion causes an increase of the critical temperature and a decrease of the activation energy for NO_2^- reorientation. Easier NO_2^- motion in $Na_{1-x}Ag_xNO_2$ with bigger x values is well explained with the larger impurity ion than the host ion. It is shown that the variation of the activation energy is linearly correlated with the shift of the critical temperature for various x in $Na_{1-x}Ag_xNO_2$. $1/T_1$ values near T_c vary more gradually for the sample with higher Ag content, which results from the random substitution of Ag impurity at the Na site.

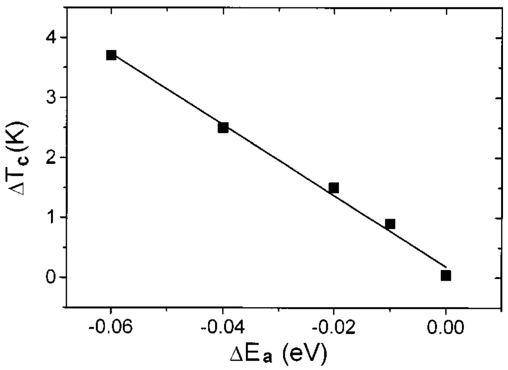

FIG. 4. Correlation between the change of activation energy (ΔE_a) and the shift of phase transition temperature (ΔT_c) for various Ag impurity concentration x in mixed crystals $Na_{1-x}Ag_xNO_2$.

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