Nuclear Magnetic Relaxation Study of Phase Transitions in KTiOPO₄ Systems

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Undoped and Cr-doped KTiOPO₄ (KTP) systems were studied by means of laboratory- and rotating-frame $^{31}$P nuclear magnetic relaxation time measurements. As a result, two phase transitions associated with the changes of the dominant charge carriers were well characterized. It was also found that the Cr-doping of the KTP system results in significant shifts in the phase-transition temperatures.

Potassium titanyl phosphate (KTiOPO₄, KTP) is a superior electro-optic material being employed for several nonlinear optical applications including, in particular, frequency doubling of the Nd:YAG laser fundamental frequency [1-4]. It shows high nonlinear optical coefficients, a high optical damage threshold, and thermally stable phase-matching properties, as well as low dielectric constants, which are attractive for various electro-optic applications. KTP also exhibits a strong low-frequency dielectric dispersion associated with the thermally activated hopping process presumably involving K⁺ ions.

KTP has an orthorhombic crystal structure, shown in Fig. 1, with lattice constants $a = 12.814$ Å, $b = 6.404$ Å, and $c = 10.616$ Å. The structure is characterized by chains of TiO₄ octahedra, which are linked at two corners, and the chains are separated by PO₄ tetrahedra. Alternating long and short Ti-O bonds in the two chains per unit cell give rise to large nonlinear optic and electro-optic coefficients [1,5].

Besides the high temperature ferroelectric phase transition [6-8], a low temperature superionic transition around 200 K accompanied by an off-pyroelectric current generation has been reported in KTP [6,9]. In addition, a room temperature transition involving the creation of polarons has been suggested from the temperature dependence of the ac conductivity [10]. While the properties of KTP have been investigated by various experimental techniques, studies of microscopic environments and lattice dynamics using NMR (nuclear magnetic resonance) would provide additional valuable information. Thus it is the purpose of this work to reveal the nature of the phase transition behaviors associated with the charge-carrier dynamics in this system by employing $^{31}$P NMR.

Recently, paramagnetic impurity-doped KTP has attracted much attention for use in optical waveguides and for refractivity variation [11]. Thus, Cr-doped KTP was also studied in this work and compared with undoped KTP. The ion exchange method was used for the substitution of Rb⁺, Ba²⁺, and Cs⁺ ions for K⁺ ions for refractive index changes, and the ion-implantation method was used for the substitution of Fe³⁺, Cr³⁺, V⁴⁺, Mo⁵⁺, and Ti⁴⁺ ions for K⁺ ions for reduced ion conductivity [11]. EPR (electron paramagnetic resonance) studies have revealed that the Cr³⁺ paramagnetic impurity in KTP substitutes at the Ti(1) and Ti(2) positions [12].

Undoped and Cr-doped (0.05 %) KTP crystals made with the flux method were used in this work. $^{31}$P NMR laboratory-frame spin-lattice relaxation time ($T_1$) measurements were made in the temperature range from 77 to 390 K at the Larmor frequencies of 17.9 MHz and 81 MHz, and the rotating-frame spin-lattice relaxation time ($T_{1\rho}$) measurements for the Cr-doped KTP were made at the rotating-frame frequency of 12.5 kHz [13].

The spin-lattice relaxation patterns for the KTP sys-
tems were quite well described with a single-exponential form at all temperatures, indicative of a strong spin diffusion. In the simple NMR theory, the general behavior of the spin-lattice relaxation rate \( \frac{1}{T_1} \) for random motions of the Arrhenius type with a correlation time \( \tau \) is described in terms of three regions: the fast, the intermediate, and the slow motion regions. For the fast motion region, i.e., for \( \omega \tau \ll 1 \), \( \frac{1}{T_1} \sim \exp[-E_a/kT] \), and for the slow motion region, i.e., for \( \omega \tau \gg 1 \), \( \frac{1}{T_1} \sim \omega^{-2} \exp[-E_a/kT] \), where \( \omega \) is the Larmor frequency and \( E_a \) is the activation energy.

![Crystal structure of KTiOPO$_4$ along the ac plane.](image)

**Fig. 1.** Crystal structure of KTiOPO$_4$ along the ac plane.

Figure 2 shows the spin-lattice relaxation rate \( \frac{1}{T_1} \) of the undoped KTP measured at 17.9 MHz and 81 MHz vs the inverse temperature \( \frac{1}{T} \). At 81 MHz, \( \ln(1/T_1) \) is well fitted by a single negative slope, which indicates that the limit \( \omega \tau \gg 1 \) is satisfied in the whole temperature range. An activation energy of 25 meV was obtained from the slope. In contrast, at 17.9 MHz different limits are satisfied for \( \omega \tau \) in each of the three temperature ranges separated by \( T_{c1} = 200 \text{ K} \) and \( T_{c2} = 300 \text{ K} \). Specifically, the limit \( \omega \tau \gg 1 \) would apply for \( T < T_{c1} \) and \( T > T_{c2} \), and the limit \( \omega \tau \ll 1 \) for \( T_{c1} < T < T_{c2} \). This indicates that at 17.9 MHz, the spectral density is dominated by distinct motions in each temperature range with a characteristic activation energy. It may also be mentioned that the ratio of the spin-lattice relaxation rates measured at 17.9 MHz and 81 MHz for \( T < T_{c1} \) is consistent with the \( \omega^{-2} \) dependence described above. These observations establish \( T_{c1} \) and \( T_{c2} \) as phase-transition temperatures.

The activation energies for the undoped KTP obtained from the distinct slopes in Fig. 2 are 25 meV in the low-temperature phase (phase I) below \( T_{c1} \), 70 meV in the intermediate phase (phase II) between \( T_{c1} \) and \( T_{c2} \), and 120 meV in the high-temperature phase (phase III) above \( T_{c2} \) [10, 14]. In other words, greater thermal activation energies are necessary in higher temperature phases, indicative of greater effective masses. In fact, the dominant charge carriers are known to be electrons in phase I, K$^+$ ions in phase II, and polarons in phase III, which are effectively K$^+$ ions accompanied by lattice deformation [6,9,10]. It is also illuminating to note that the activation energy of 25 meV obtained at 17.9 MHz in the low-temperature phase where electrons are the dominant charge carriers is the same as that obtained at 81 MHz in the whole temperature range. This indicates that at 81 MHz, only the electron motions can be detected, which...
would be the case if the K$^+$ ions and the polarons, which have greater effective masses than the electrons, possess spectral density components mostly at frequencies lower than 81 MHz.

Figure 3 shows the laboratory-frame spin-lattice relaxation rate ($1/T_1$) at 17.9 MHz and the rotating-frame spin-lattice relaxation rate ($1/T_{1\rho}$) measurements for the Cr-doped KTP. From ultralow-frequency anomalies reflected in the $1/T_{1\rho}$ in Fig. 3, the phase-transition temperatures $T_{c1}$ and $T_{c2}$, corresponding to $T_{c1}$ and $T_{c2}$ in undoped KTP, can be identified to be around 155 K and 335 K, respectively. In other words, the phase transitions associated with the superionic conduction and large polaron formation take place at temperatures considerably shifted in comparison to the case of the undoped KTP system. This indicates that the substitution of Cr$^{3+}$ for Ti$^{4+}$ in Cr-doped KTP [12], which gives rise to an additional electron in the TiO$_6$ octahedron interacting with the K$^+$ ion, causes significant modification in the charge conduction and lattice deformation in the KTP lattice. In fact, in undoped KTP, the limit $\omega \tau \ll 1$ holds in the temperature range between $T_{c1}$ and $T_{c2}$ whereas the limit $\omega \tau \gg 1$ appears to hold in the Cr-doped KTP at the Larmor frequency of 17.9 MHz. Much enhanced spin-lattice relaxation rates are also observed in Fig. 3, and are attributed to paramagnetic impurities. The activation energies for the Cr-doped KTP obtained from the slopes in Fig. 3 are 8 meV, 14 meV, and 28 meV in the phases I, II, and III, respectively. Thus, the Cr-doping is also shown to give rise to modified activation energies in each phase.

In summary, $^{31}$P NMR laboratory- and rotating-frame spin-lattice relaxation measurements were made in this work on flux-grown samples of undoped and Cr-doped KTP. As a result, two phase transitions, corresponding to the change of the dominant charge carriers, were identified and characterized in each KTP system. In particular, the Cr-doping was shown to give rise to significant shifts in the phase-transition temperatures, presumably due to modified charge conduction and lattice deformation.

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REFERENCES