Journal of Magnetics 5(3), 73-75 (2000)

Phase Transitions in $KTiOPO_4$ Studied by ^{31}P Nuclear Magnetic Relaxation

K. S. Kim, C. H. Lee, Cheol Eui Lee*, N. S. Dalal[1], R. Fu[1], S. Y. Jeong[2], J. N. Kim[2] and S. C. Kim[2]

Department of Physics, Korea University, Seoul 136-701, Korea
[1]Department of Chemistry, Florida State University, Tallahassee, FL 32306-4390, U. S. A.
[2]Research Center for Dielectric and Advanced Matter Physics, Pusan National University, Pusan 609-735, Korea

(Received 2 August 2000)

Undoped and Cr-doped samples of electrooptic material $KTiOPO_4$ were studied by ^{31}P nuclear magnetic resonance (NMR). Spin-lattice relaxation time (T_1) measurements manifested phase transition behaviors that are attributed to changes in the dominant charge carriers in different temperature ranges.

1. Introduction

$KTiOPO_4$ (KTP), whose orthorhombic crystal structure is illustrated in Fig. 1 [1-4], is an important new electrooptic material, with a rare combination of pyroelectricity and superionic conductivity [5-13]. It exhibits high nonlinear optical coefficients and shows a strong low frequency dielectric dispersion associated with the thermally activated hopping process presumably involving K^+ ions. KTP is a particularly efficient doubler of the Nd:YAG fundamental frequency (λ = 1.06 μm) into the green part of the spectrum and is advantageous in use because of its high laser-damage threshold, large temperature range for phase matching, and mechanical robustness. The relationship of the crystal structure and nonlinear optical properties has been studied by various workers [1, 14, 15].

Besides the high temperature ferroelectric phase transition [6, 12, 16], a low temperature superionic transition around 200 K accompanied by an off-pyroelectric current generation has been reported [5, 6]. In addition, a room temperature transition involving the creation of polarons has been suggested from the temperature dependence of the ac conductivity [13]. The phase transitions at around 200 and 300 K involve changes in charge-carriers, but no structural changes.

While properties of KTP have been investigated by various experimental techniques, studies of microscopic environments and lattice dynamics using NMR 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 employing ^{31}P NMR. Recently, paramagnetic impurity-doped KTP has attracted much attention for use in optical waveguides and refractivity variation [17]. Thus, Cr-doped KTP was also studied in this work in comparison to undoped KTP. Ion exchange method is used for the substitution of Rb^+, Ba^+, Cs^+ ions for K^+ ions for refractive index change, and ion implantation method for the substitution of Fe^{3+}, Cr^{3+}, V^{4+}, Mo^{5+} ions for K^+ ions for reduced ion conductivity [17]. EPR (electron paramagnetic resonance) studies have revealed that the Cr^{3+} paramagnetic impurity in KTP substitutes for the Ti(1) and Ti(2) positions [18].

Undoped and Cr-doped (0.05%) KTP crystals made by the flux method were used in this work. ^{31}P NMR spin-lattice relaxation time (T_1) measurements were made in the temperature range 77 to 390 K using the inversion recovery method at the Larmor frequency of 17.9 MHz.

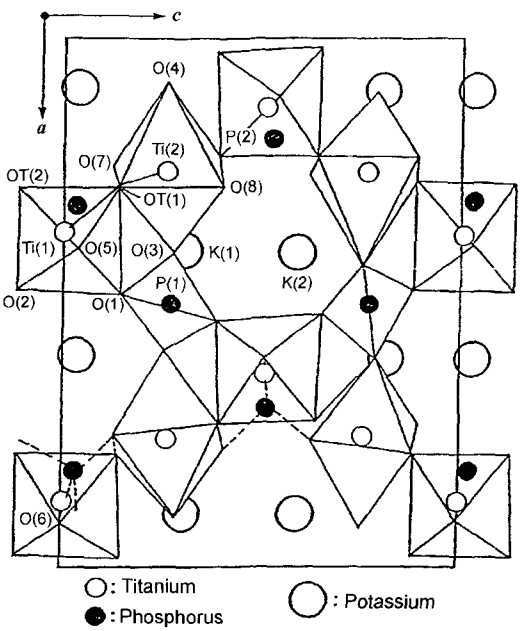

Fig. 1. The crystal structure of $KTiOPO_4$ along the *ac* plane.

*Corresponding author: E-mail address: rscel@korea.ac.kr

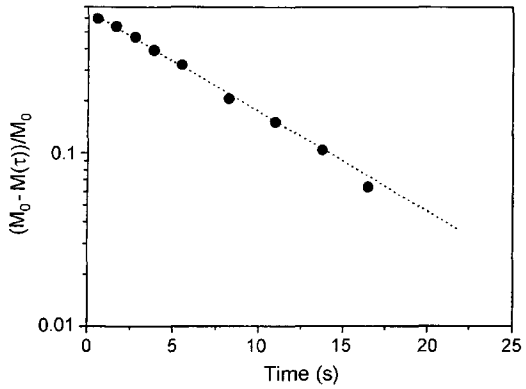

Fig. 2. The variation of magnetization (17.9 MHz ^{31}P NMR spin-lattice relaxation pattern) in undoped KTP at room temperature.

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

Figure 3 shows the spin-lattice relaxation rates ($1/T_1$) vs the inverse temperature ($1/T$). In the case of the undoped KTP, it is shown that different limits are satisfied for $\omega\tau$ in each of the three temperature ranges separated by T_{c1} = 200 K and T_{c2} = 300 K, respectively. 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. These observations can be used to establish T_{c1} and T_{c2} as phase transition temperatures in a way or another.

The activation energies for the undoped KTP obtained from the distinct slopes in Fig. 3 are 0.025 eV in the low temperature phase (phase I) below T_{c1}, 0.070 eV in the intermediate phase (phase II) between T_{c1} and T_{c2}, and 0.12 eV in the high temperature phase (phase III) above T_{c2} [13, 19]. 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, respectively [5, 6, 13].

From the slope changes in the spin-lattice relaxation rates for the Cr-doped KTP in Fig. 3, the phase transition temperatures T_{c1}' and T_{c2}', corresponding to T_{c1} and T_{c2} in undoped KTP, appear to be around 170 K and 340 K, respectively. In other words, the phase transitions associated with the superionic conduction and large polaron formation

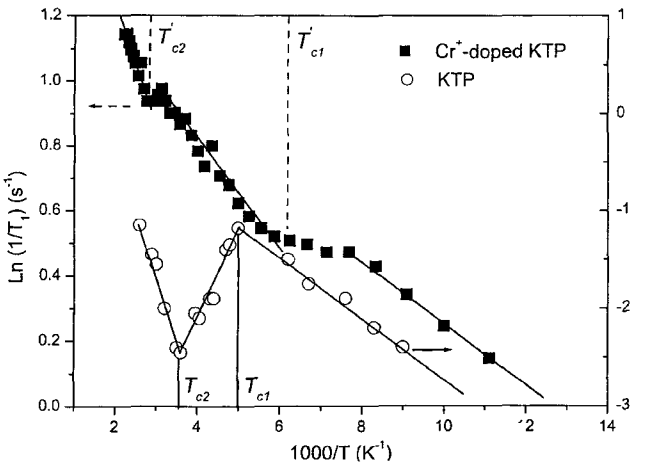

Fig. 3. The spin-lattice relaxation rates ($1/T_1$) vs the inverse temperature ($1/T$) for undoped and Cr-doped KTP. Note the different vertical scales for the undoped and Cr-doped KTP measurements.

take place at temperatures considerably shifted in comparison to the case of undoped KTP system. This indicates that the substitution of Cr^{3+} for Ti^{4+} in Cr-doped KTP [18], which gives rise to an additional electron in the TiO_6 octahedron interacting with the K^+ ion, gives rise to significant modification in the charge conduction and lattice deformation in the KTP lattice. In fact, in the undoped KTP the limit $\omega\tau \ll 1$ was applied 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. Much enhanced spin-lattice relaxation rates in Fig. 3 are also observed, attributed to the paramagnetic impurities. The activation energies for the Cr-doped KTP obtained from the slopes in Fig. 3 are 0.08 eV, 0.14 eV, and 0.28 eV in the phase I, II, and III, respectively.

In summary, ^{31}P NMR spin-lattice relaxation measurements were made in this work on flux grown samples of undoped and Cr-doped $KTiOPO_4$ (KTP). As a result, two phase transitions, corresponding to the change of the dominant charge carriers, were identified and characterized.

Acknowledgments

This work was supported by the Korea Science and Engineering Foundation (996-0200-003-2). Help from Dr. D. Y. Han at the Korea Basic Science Institute (KBSI) is gratefully acknowledged.

References

[1] R. Masse and J. C. Grenier, Bull. Soc. Mineral Crystallogr., **94**, 437 (1971).
[2] I. Tordjman, R. Masse, and J. C. Guitel, Z. Kritallogr. **139**, 103 (1974).
[3] P. A. Thomas, A. M. Glazer, and B. E. Watts, Acta. Cryst., B**46**, 333 (1990).
[4] D. R. Allan, J. S. Loveday, R. J. Nelmes, and P. A. Tho-

mas, Ferroelectrics **124**, 367 (1991).
[5] Yu. Shaldin and R. Poprawski, J. Phys. Chem. Solids **51**, 101 (1990).
[6] V. D. Antsigin, V. A. Gusev, V. N. Semenenko, and A. M. Yurkin, Ferroelectrics **143**, 223 (1993).
[7] F. C. Zumstag, J. D. Bierlein, and T. E. Gier, J. Appl. Phys., **47**, 4980 (1976).
[8] J. D. Bierlein and C. B. Arweiler, Appl. Phys. Lett., **49**, 917 (1986).
[9] J. D. Bierlein, H. Vanherjeele, J. Opt. Soc. Am., B **6**, 622 (1989); D. K. T. Chu, J. D. Bierlein, and R. G. Hunsperger, IEEE Trans. on Ultrason., Ferroelect., and Freq. Cont., **39**, 683 (1992).
[10] B. Mohamadou, G. E. Kugel, F. Brehat, B. Wynke, G. Marnier, and P. Simon, J. Phys.: Condens. Matter **3**, 9489 (1991).
[11] D. K. T. Chu and H. Hsiung, Appl. Phys. Lett., **61**, 1766 (1992).
[12] L. K. Cheng and J. D. Bierlein, Ferroelectrics **142**, 209 (1993).
[13] B. C. Choi, J. B. Kim, and J. N. Kim, Solid State Commun. **84**, 1077 (1992); B. C. Choi, J. B. Kim, and J, N, Kim, Ferroelectrics **155**, 183 (1994).
[14] M. M. Eddy, T. E. Gier, N. L. Keder, N. L. Stucky, D. E. Cox, J. D. Bierlein, and G. Jones, Inorg. Chem., **27**, 1856 (1988).
[15] G. D. Stucky, M. L. F. Phillips, and T. E. Gier, Chem. Mater., **1**, 492 (1989).
[16] R. F. Bordui, R. G. Norwood, and M. M. Fejer, Ferroelectrics **115**, 7 (1991).
[17] M.G. Roelofs, P. A. Morris, and J. D. Bierlein, J. Appl. Phys., **70**, 720 (1991).
[18] D. Bravo, M. J. Martin, J. Garald, F. Diaz, C. Zaldo, and F. J. Lopez, Phys. Rev., B **50**, 16224 (1994).
[19] S. Sigaryov, J. Phys. D. Appl. Phys., **26**, 1326 (1993).