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High resolution ^{31}P nuclear magnetic resonance study of Cr^{3+} -doping effects on KTiOPO_4

Cheol Eui Lee ^{a,*}, N.S. Dalal ^b, R. Fu ^b^a Department of Physics, Institute for Nano Science, Korea University, Seoul 136-701, South Korea^b Department of Chemistry, Florida State University and National High Magnetic Field Laboratory, Tallahassee, FL 32306-4390, USA

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Abstract

^{31}P nuclear magnetic resonance was employed to investigate Cr^{3+} -doping effects on KTiOPO_4 . The high resolution ^{31}P isotropic chemical shift and linewidth measurements sensitively revealed changes in the microscopic environments caused by the doping. © 2002 Elsevier Science B.V. All rights reserved.

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KTiOPO_4 (KTP) is a superior electro-optic material being employed for several nonlinear optical applications [1–4]. It shows high nonlinear optical coefficients, 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. The structure is characterized by chains of TiO_4 octahedra, which are linked at two corners, and the chains are separated by PO_4 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 [10,11].

Recently, paramagnetic impurity-doped KTP has attracted much attention for use in optical waveguides

and refractivity variation [12]. Ion exchange method is used for the substitution of Rb^+ , Ba^{2+} , and Rb^{2+} ions for K^+ ions for refractive index change, and ion implantation method for the substitution of Fe^{3+} , Cr^{3+} , V^{4+} , and Mo^{5+} ions for K^+ ions for reduced ion conductivity [12]. Electron paramagnetic resonance (EPR) studies have revealed that the Cr^{3+} paramagnetic impurity in KTP substitutes for the Ti(1) and Ti(2) positions [13]. Thus, it is expected that paramagnetic impurity doping will give rise to modifications to the local lattice environments and possibly to the charge dynamics in KTP. It is the purpose of this work to study the Cr^{3+} -doping effects in KTP in comparison to undoped KTP employing ^{31}P NMR.

Undoped and Cr^{3+} -doped (0.05%) KTP crystals made by the flux method were used in this work. High resolution chemical shift and linewidth measurements were made with magic angle spinning (MAS) at 3 kHz employing a 600-MHz NMR spectrometer [14] at the National High Magnetic Field Laboratory in Tallahassee, FL.

Our previous spin–lattice relaxation measurements in the laboratory frame and in the rotating frame have revealed phase transitional behaviors in undoped and doped KTP systems [11,15,16]. While the phase transitions were observed at 200 and 300 K for the undoped KTP, they were shifted to 155 and 335 K for the doped KTP. In other words, the transitions associated with the

* Corresponding author.

E-mail address: rscel@korea.ac.kr (C.E. Lee).

superionic conduction and large polaron formation 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^{3+} -doped KTP [13], 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 [15].

In order to investigate the lattice deformation associated with the room temperature polaron formation, high resolution ^{31}P NMR techniques were employed for the chemical shift measurements, since the lattice deformation would cause a distortion in the electron clouds in the PO_4 tetrahedra and give rise to chemical shift changes. At the ^{31}P NMR frequency of 243 MHz, the MAS spectra gave rise to two well separated peaks corresponding to the two distinct P sites in the KTP structure. Figs. 1 and 2 show the temperature dependences of the two isotropic chemical shifts, CS1 and CS2, for undoped and Cr^{3+} -doped KTP, respectively, where a ^{31}P standard, a solution of H_3PO_4 , was used for the reference frequency. Indeed, it is interesting to note that the temperature slopes of the chemical shifts for the two sites in undoped as well as Cr^{3+} -doped KTP are very similar around room temperature where the polaron formation takes place in both systems, whereas opposite trends in the slopes are observed above and below the room temperature regime. It is also noticed that the temperature regime of similar slopes is slightly higher in doped KTP as would be expected. Besides, the chemical shifts are much better separated in the doped KTP, which appears to be in good agreement with the observation that the paramagnetic impurities in the KTP system give rise to strong distortions in the oxygen environments [13].

The high resolution ^{31}P NMR measurements were also taken for the intrinsic linewidth excluding such ef-

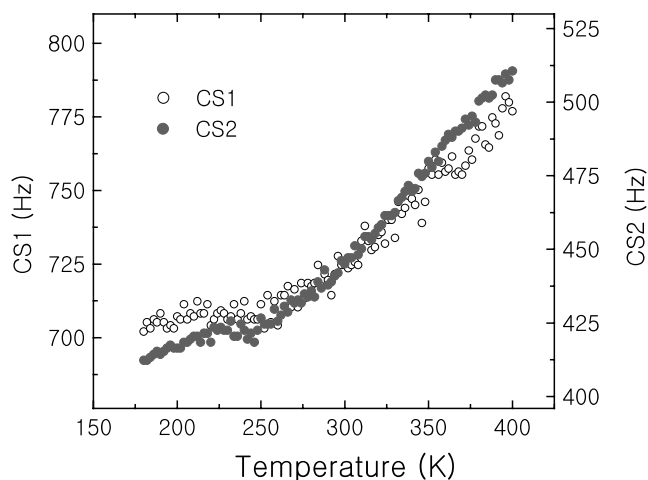


Fig. 1. Temperature dependence of the chemical shifts of the two inequivalent P sites in undoped KTP.

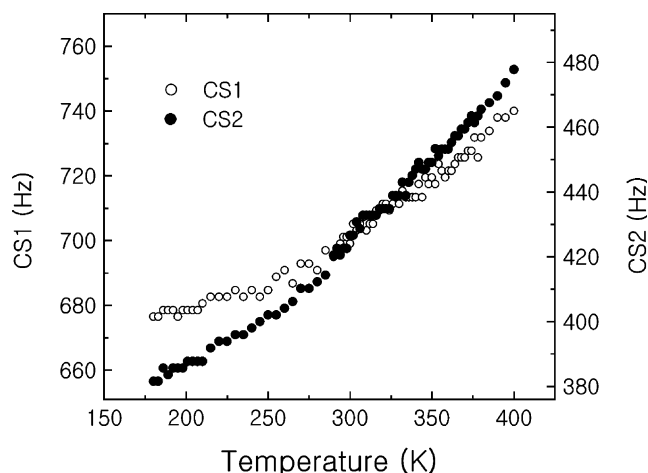


Fig. 2. Temperature dependence of the chemical shifts of the two inequivalent P sites in Cr^{3+} -doped KTP.

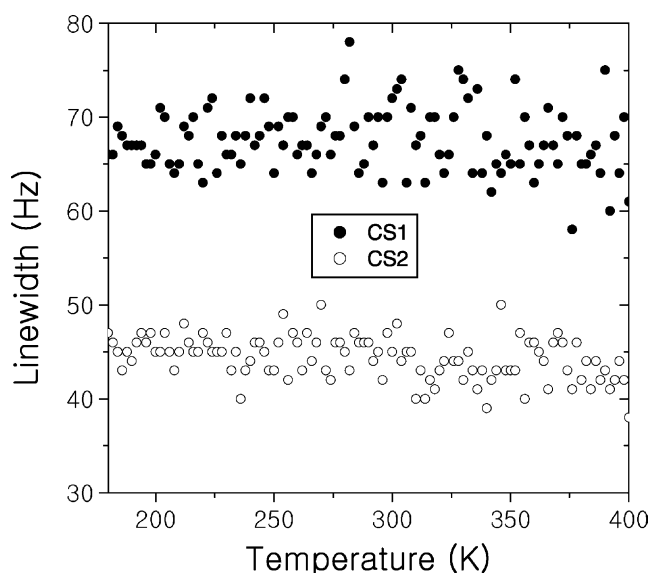


Fig. 3. Temperature dependence of the high resolution ^{31}P NMR linewidths for undoped KTP.

fects as the dipolar broadening. Figs. 3 and 4 show the temperature dependences of the linewidths for the two inequivalent P sites for the undoped and the doped KTP systems, respectively. For the undoped KTP, the two P sites have quite distinct linewidths, about 70 and 45 Hz, respectively, indicative of quite different local environments. On the other hand, in the case of the doped KTP system, it is shown that the two P sites have almost identical linewidths, about 60 Hz, in between those of the undoped KTP. In fact, the two linewidths are indistinguishable in Fig. 4. This indicates that the Cr^{3+} doping renders the local distribution around the two P sites quite similar, which can be ascribed to the lattice deformation caused by the incorporation of the Cr^{3+} impurities. Thus, significant changes in the local environment due to the impurity ion doping, giving rise to

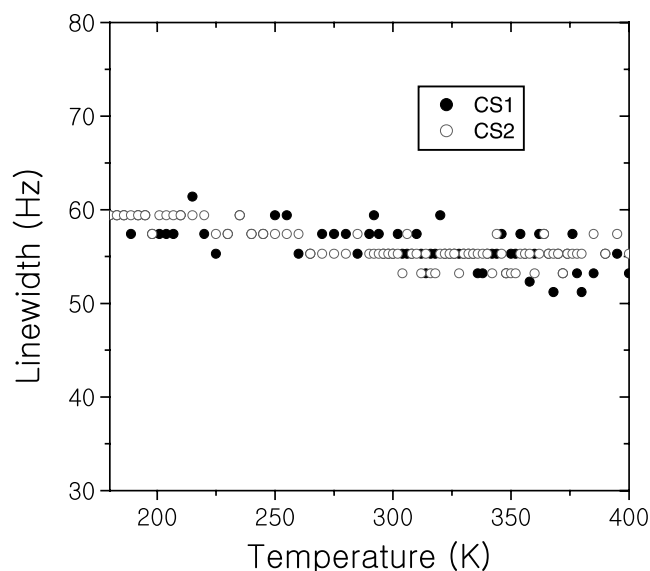


Fig. 4. Temperature dependence of the high resolution ^{31}P NMR linewidths for doped KTP.

shifts in the phase transition temperatures, is sensitively reflected in the intrinsic linewidths as well.

In summary, ^{31}P NMR high resolution chemical shift measurements were made in this work on flux grown samples of undoped and Cr^{3+} -doped KTP. As a result, changes in the phase transition temperatures and in the local environments due to the doping were sensitively reflected and attributed to the changes in the lattice environments due to the impurity incorporation in the KTP system.

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