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High-energy proton-irradiation effects on the charge transport and electric dipole moment of KH_2PO_4

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ABSTRACT

We have studied the charge transport and dielectric properties of KH_2PO_4 (KDP) single crystals, irradiated by proton beams with high energies up to 20 MeV, by means of the temperature-dependent electrical conductivity and dielectric constant measurements. It is shown that the electrical conductivity and the electric dipole moment may be sensitively controlled by the proton irradiation energy and dose. The activation energy and the dipole moment were shown to be strongly correlated.

1. Introduction

KH_2PO_4 (KDP)-type materials have been investigated to a great extent for application as proton conductors [1,2]. As a typical proton conductor, KDP shows relatively high electrical conductivity at room temperature possessing the potential to be used as electrolytes in fuel cells [2,3]. The KDP crystal is an interesting hydrogen-bonded system undergoing a ferroelectric phase transition at $T_C = 122$ K, above which temperature it has a tetragonal structure whose space group belongs to *I*42*d*. The KDP structure consists of PO_4 tetrahedra joined by hydrogen bonds to the neighboring tetrahedra. In KDP, the hydrogen bonds mostly lie in the *ab* plane normal to the *c* axis [4,5]. The hydrogen atoms are placed in the double well potential of the hydrogen bonds in KDP, the hydrogen bonds playing an essential role in the proton conduction. In the paraelectric phase, proton transport in KDP can be understood by the interbond proton motion and rotational motion of the oxyanion PO_4. There have been considerable efforts to explain the mechanism of the proton dynamics [6–9], and to modify the electrical properties by gamma-ray and X-ray irradiation as well as by ion irradiation [10–15].

We have recently shown that proton irradiation may be used to modify the hydrogen bond geometry of the KDP system thus systematically controlling the charge transport and the electrical dipole moment. In this work, we have studied the high-energy proton irradiation effects on the KDP system by means of the electrical conductivity and impedance measurements in the transverse (*a*-axis) direction [13,14]. While a proton irradiation energy of 1 MeV was used in our previous work, we have employed much higher irradiation energies of up to 20 MeV in this work.

2. Experimental

The *a*-cut KDP single crystals with dimensions of 10 mm × 10 mm × 1 mm supplied by the Crystal Bank at Pusan National University were irradiated by proton beams to various doses at the irradiation energies of 6.5 MeV, 10 MeV, and 20 MeV by using a tandem accelerator at the Korea Institute of Radiological & Medical Sciences (KIRAMS). X-ray diffraction (XRD) measurements were made on the KDP samples before and after proton irradiation. The electrical conductivity measurements were carried out along the *a* axis by using the conventional two-probe method at temperatures ranging from 303 K to 423 K. A Keithley 4200 was used for the dc electrical conductivity measurements, and the impedance and ac electrical conductivity measurements were carried out by using a QuadTech 7600 impedance analyzer. High-resolution ^{1}H nuclear magnetic resonance (NMR) chemical shift measurements

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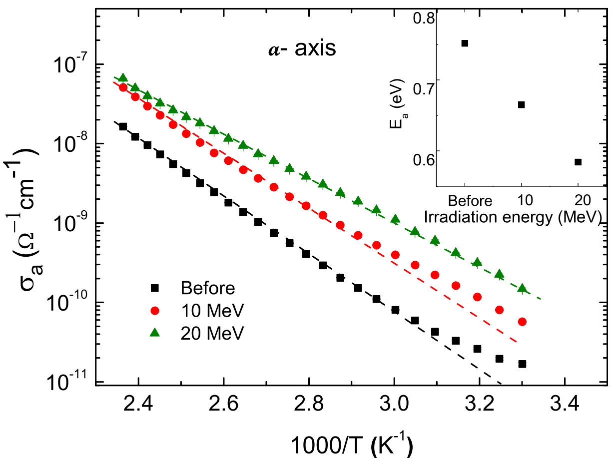

Fig. 1. Temperature-dependent dc electrical conductivity along the *a* axis of the proton-irradiated KDP samples for different irradiation energies with a dose of 1×10^{13} H^+/cm^2. The electrical conductivity data were well fitted by the Arrhenius equation, the dotted lines representing the linear fits. Inset: activation energy of proton hopping for different proton-irradiation energies.

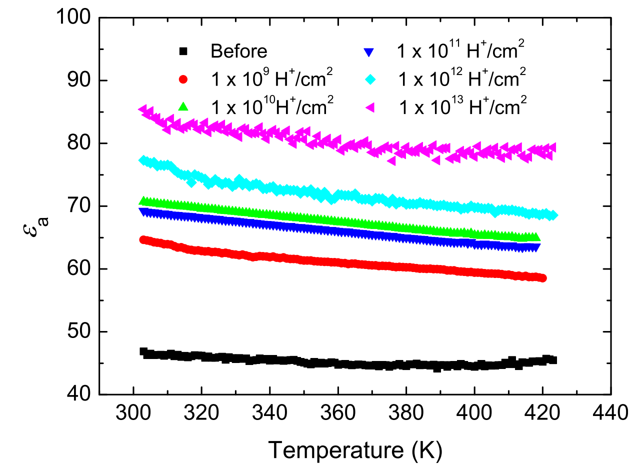

Fig. 3. Temperature-dependent transverse dielectric constant (ε_a) measured at 10 kHz of the KDP samples proton-irradiated with 6.5 MeV to various doses.

on the samples were carried out by using a Varian Unity-Inova 500 MHz NMR spectrometer operating at 500 MHz with magic-angle spinning (MAS) at 40 kHz, with reference to tetramethylsilane.

3. Results and discussion

High energy irradiation leads to atomic displacements arising from collisions, thus producing hydrogen defects such as vacancies and interstitials. The hydrogen bond lengths may change due to the defects, particularly the hydrogen vacancies, closely having to do with proton transport within the hydrogen bond network [6,16]. Fig. 1 shows the temperature-dependent dc electrical conductivity of KDP irradiated at the high irradiation energies of 10 MeV and 20 MeV to a dose of 1×10^{13} H^+/cm^2. At the irradiation energy of 10 MeV, most of the protons would stop at 0.65 mm from the surface of the 1-mm thick samples while they would penetrate the samples at the energy of 20 MeV with a stopping range of 2.2 mm according to simulation using SRIM program [17]. The electrical conductivity data were well fitted by the Arrhenius equation, $\sigma T = \sigma_0 \exp(-E_a/k_B T)$, from which the activation energy was obtained. Increase of the electrical conductivity and decrease of the activation energy with increasing irradiation energy are noticed in Fig. 1. Thus, the dc electrical conductivity in Fig. 1 indicates that charge transport in KDP is enhanced in proportion to the proton-irradiation energy at sufficient high irradiation energies, which may be explained by the creation of more *L* defects arising from the hydrogen vacancies [6,16].

Figs. 2 and 3 respectively show the temperature-dependent ac electrical conductivity and dielectric constant measurements of the KDP samples irradiated with 6.5 MeV to various proton irradiation doses. The ac electrical conductivity was also well fitted by the Arrhenius equation, the relatively large error of data that increases as the temperature decreases being attributed to the instrumental measurement limit due to the smaller conductivity at low temperatures (Fig. 2). From the dielectric constant measurements (Fig. 3), the electric susceptibility χ_a can be obtained through the relation $\varepsilon_a = 4\pi\chi_a + 1$ [18]. Fig. 4 shows the temperature-dependent inverse susceptibility thus obtained for various proton irradiation doses. Above the Curie temperature ($T > T_C$), the electric susceptibility follows the relation derived by using the mean field approximation, $\chi_a^{-1} = kT/N\mu_2^2$, where μ_2 is the transverse dipole moment and N is approximately $1 \times 10^{22}/cm^3$ for the PO_4 groups

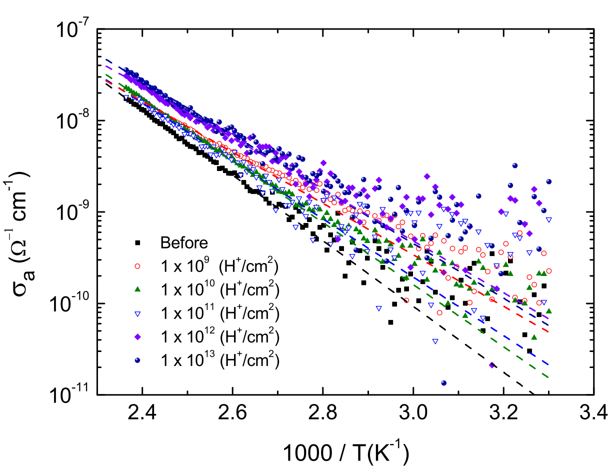

Fig. 2. Temperature-dependent ac electrical conductivity along the *a* axis measured at 1 kHz of the KDP samples proton-irradiated with an energy of 6.5 MeV to various doses. The dotted lines represent linear fits.

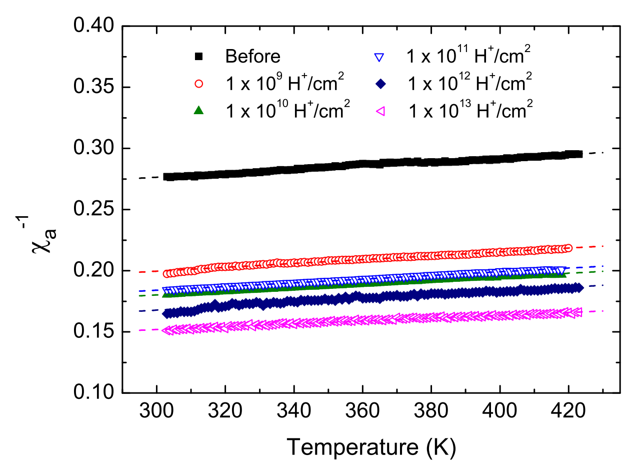

Fig. 4. Temperature-dependent inverse susceptibility (χ^{-1}) measured at 10 kHz of the KDP samples proton-irradiated with 6.5 MeV to various doses. The dotted lines represent linear fits.