

Q. GUAN, J. WANG, W. CUI, J. WEI, Y. LIU, X. YIN

State Key Laboratory of Crystal Materials, Shandong University, China

The DC Conductive Property of KTiOPO_4 Crystal along its Z-Axis

The anomalous DC electrical conductive property of the KTP crystal along its z -axis is reported in this paper. The DC conductivity strongly depends on the measuring voltage. No Ohmic regime exists in the current-voltage relation. Ionic polarization occurs under high DC stresses. Electrode reactions were also observed. The phenomena are related to the easy movement of ions along the z -axis of the KTP crystal.

Introduction

Potassium titanyl phosphate KTiOPO_4 , (abbreviated as KTP), is an excellent material for frequency-doubling the Nd:YAG laser to the green (ZUMSTEG et al.). It has been studied extensively for the applications in second harmonic generation, optical parametric oscillation, as well as quasi-phase-matched optical waveguides (BIERLEIN, VANHERZEELE et al.). KTP is also known as a typical quasi-one-dimensional superionic conductor of potassium ions (YANG, BIERLEIN et al.). The electrical conductivity of flux grown KTP along the z -axis is higher than those perpendicular to the z -axis by several orders of magnitude (YANOVSKII et al.). This is thought to be related to the easy movement of potassium ions through potassium vacancies located along channels in the z -direction (VANHERZEELE, YANOVSKII, KALESINSKAS et al.). The ionic conduction property of this crystal has been employed in the fabrication of ion-exchanged waveguides (BIERLEIN et al.). However, the excessively high conductivity is also considered to be a disadvantage for the use in some other field, such as electro-optic applications (MCGEE et al.). The AC ionic conductivity of KTP has been broadly investigated by different authors under a wide range of temperatures and frequencies (FURUSAWA, YANOVSKII et al.). However, to our knowledge, no detailed study of ionic conduction of KTP single crystal under DC field has been reported. In a recent work, we investigated the DC electrical conduction of KTP crystal in detail; some anomalous behaviors of this crystal were observed under external DC field. The results together with our arguments are presented in this paper.

Experimental

The KTP crystals used in this experiment were grown using the flux method (LIU et al.). The samples were cut into rectangular shapes along their principal axes. The typical sample dimensions are $5 \times 5 \text{ mm}^2$ in surface area and 2 mm thickness. The silver electrodes were pasted onto the two large faces. The current of the samples under a DC field was measured by a Hewlett-Packard 4140B pA meter for the DC voltages lower

than 100 V; it was measured on a micro-galvanometer for voltages above 100 V. After each measurement with a voltage above 100 V, the sample was annealed at a temperature of 500 °C to eliminate its electrical history.

Results and discussion

The DC conductivity along the three principal axes were measured under various DC voltages in the range of 0.1–500 V. The conductivity measured along the x - and y -axes are 4.5×10^{-12} and $1.1 \times 10^{-12} (\Omega \cdot \text{cm})^{-1}$, respectively. They do not depend on the measuring voltages. But the conductivity along the z -axis strongly depends on the measuring voltages. They range from 7.0×10^{-10} to $5.6 \times 10^{-7} (\Omega \cdot \text{cm})^{-1}$, which are higher than those along the x - and y -directions by 2 to 5 orders of magnitude. The voltage dependence of current density of KTP crystal along the z -direction is shown in Fig. 1. From this figure we can see that the current density increases exponentially with the voltage at a small signal regime, then reaches saturation at a higher voltage.

The $J-U$ characteristic of KTP crystal along its z -axis deviates from linearity at very low voltage. This behaviour is anomalous comparing with that along the other two principal axes and of other crystals. For most other crystals, for example the widely investigated perovskite tantalates (WASER), they usually have a low field Ohmic regime in their $J-U$ relations. A non-Ohmic regime can only be seen when the applied voltage is above several thousand V/cm. This is proposed to be related to the one-way assistant effect of the high DC voltage on the ionic movement. This phenomenon shows that even a very low DC field has a significant one-way assistant effect on the movement of potassium ions along the z -direction of KTP crystal. In this case, the relation between conductivity σ and external field U is as follows:

$$\sigma \propto \exp(eUa/2kT), \quad (1)$$

where e is the charge of the carrier, a is the nearest trap distance.

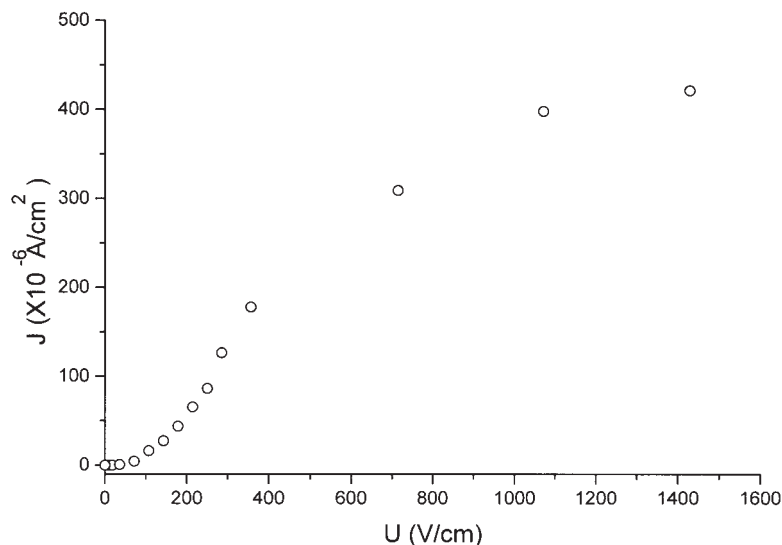


Fig. 1. A typical DC current density J and applied voltage U relationship of the KTP crystal along its z -axis. The sample dimensions are $7.0 \times 6.1 \text{ mm}^2$ in area and 2.8 mm thickness

The saturation of current density under high voltage is considered to be due to the ionic polarization of the crystal. To understand this phenomenon well, we recorded the time evolution of the current response under various DC voltages.

We found that the current density increased with time in a small range and reached its saturated value rapidly under low applied voltages; with increasing voltage, the current density increased at first, then decreased to a saturated value; if even higher, we could not see any increase of the current density, instead, it decreased to a saturated value. The results are shown in Fig. 2. After applying a high voltage of 1000 V/cm for 90 minutes, we measured the resistivity of the crystal by applying a voltage of 50 V/cm as soon as the high voltage was switched off. We found that the current along the previous high field direction was lower than that in the opposite direction by one order of magnitude.

Along with the current change, some reactions happened to the cathode metal material after applying a high DC voltage to the crystal for sufficient time. The cathode metal became sticky, and was very easy to remove from the crystal surface. We dissolved the removed electrode material into water, and measured its value using a pH indicator paper; we discovered that the mixture was alkalinous. We used the electron probe x-ray line scanning method to measure the Ag element distribution along the z -axis of the crystal. The result indicates that there is a silver enrichment region near the cathode side of the crystal (Fig. 3).

To explain the phenomena mentioned above, we regard the KTP crystal and the two attached metal electrodes as a solid-electrolyte cell. We assume the conduction property of KTP crystal along the z -axis under high voltage is related to the partial blockage of the movement of potassium ions by crystal-electrode interfaces. When a DC voltage is

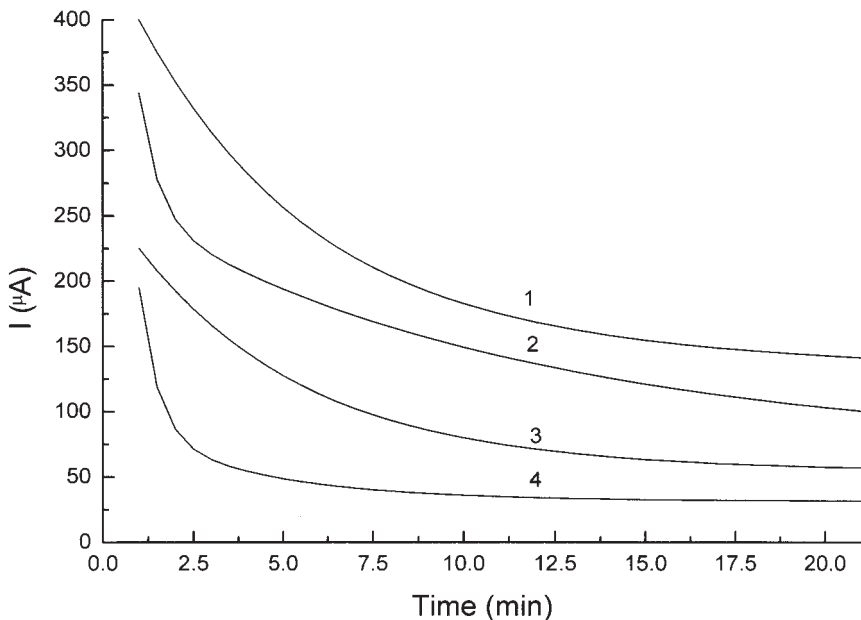


Fig. 2. The current changes with time of a KTP crystal along the z -axis under various high DC voltages. 1. 200 V; 2. 300 V; 3. 400 V; 4. 500 V. Sample thickness: 2.0 mm

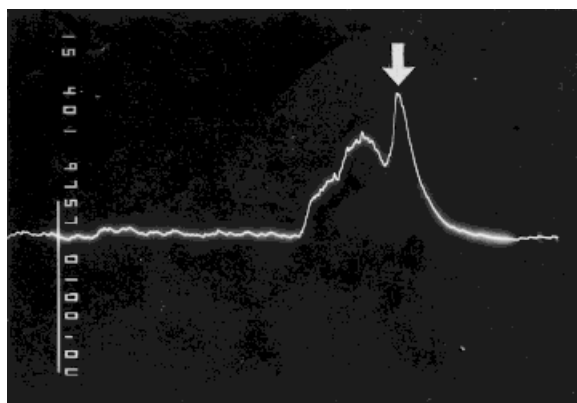


Fig. 3. The relative Ag element distribution along the z -axis of a KTP crystal after being applied a high DC voltage of 1400 V/cm for 120 minutes. The arrow mark indicates the surface of the crystal which once was pasted with silver as the cathode, the silver electrode was completely removed before the measurement. The lime mark represents 100 μm . The result was measured by the electron probe x-ray line scanning method

applied onto the crystal, the potassium ions move from the anode to the cathode through potassium vacancies driving by the field. If the voltage is not sufficiently high, the bulk conduction dominates the process, the current density reaches its saturated value in a short time. When the voltage is high enough, a large amount of potassium ions is driven to the cathode from the anode. Further movement of the potassium ions is partially blocked by the crystal-cathode interface. An accumulation region of potassium ions is formed close to the cathode and an internal field in an opposite direction to the external field is thus formed. This field decreases the current density.

The detected high Ag concentration near the cathode implies that an electrode reaction occurs when a high voltage is applied. At the anode, a silver atom loses an electron and changes to a Ag^+ ion. Because the diameter of Ag^+ ion is smaller than that of K^+ , it is reasonable to assume that Ag^+ ions could be driven to the cathode in a similar manner as K^+ ions. Therefore there is also an enrichment of Ag^+ ions near the cathode. Because of the accumulation of K^+ and Ag^+ at the cathode region, some of the K^+ ions may move out of the crystal and form K_2O which absorbs water from the air forming KOH. Therefore, the attachment between the crystal surface and metal electrode is destroyed by KOH and the mixture of the cathode material is alkalinous. The Ag^+ ion is also able to obtain an electron forming Ag atom at the cathode.

Crystal breakdown was also observed when applying a high voltage onto the KTP crystal for a long time. The cracks always appeared near the cathode region at first and then extended to the whole crystal. One explanation could be that the local current near the cathode is very high although the measured current decreased significantly from its initial value.

Conclusion

In conclusion, KTP crystal has an anomalous DC conduction property along its z -axis. No Ohmic regime exists in the $J-U$ relations. The exponential relation between J and U is considered to be related to the one way assistant effect of the applied field on the ionic conductivity. The decrease in current under high DC stress is related to the partial blockage of ionic movement by the crystal electrode interface. The electrode material is able to enter the crystal under high DC stresses. This may have potential use in waveguide fabrication. Further studies are necessary.

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Author's address:

c/o Q. GUAN, Ph.D.
Institute of Crystal Materials
Shandong University
Jinan, 250100, P.R. China

