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## Dielectric properties of RbTiOAsO<sub>4</sub> single crystals

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Using the impedance analysis, we obtain the dielectric constants of RbTiOAsO<sub>4</sub> (RTA) single crystals for the three principle crystallographic axes in the frequency range of 1 kHz–6 MHz and in the temperature range of 303–1123 K. The conductivity of RTA along the polar *c* axis is five orders-of-magnitude smaller than that of KTiOPO<sub>4</sub> (KTP) in the temperature range of 500–970 K. The conductivities of RTA along the three principle axes have the same order of magnitude,  $10^{-5} \Omega^{-1} \text{m}^{-1}$  at 720 K, which is contrasted with the high anisotropy shown in KTP. © 1999 American Institute of Physics. [S0003-6951(99)01334-0]

New nonlinear optical materials capable of generating mid-infrared (IR) radiation have attracted much attention for scientific, commercial, and defense applications. Rubidium titanyl arsenate (RbTiOAsO<sub>4</sub>, RTA) has been developed recently<sup>1</sup> and possesses excellent nonlinear optical properties such as wide transparency in the IR region (0.35–5.3  $\mu\text{m}$ )<sup>2</sup> and the large second-order nonlinear optical coefficients ( $d_{33}=15.8$ ,  $d_{32}=3.8$ , and  $d_{31}=2.3 \text{ pm/V}$ ).<sup>3</sup> It is a member of isomorphous crystal family of MTiOXO<sub>4</sub>, where  $M = \{\text{K, Rb, or Cs}\}$  and  $X = \{\text{P or As}\}$ . In common with KTiOPO<sub>4</sub> (KTP), RTA is a positive-biaxial crystal belonging to the orthorhombic  $Pna2_1-mm2$  class with cell parameters  $a=13.264$ ,  $b=6.682$ ,  $c=10.769 \text{ \AA}$ , and  $Z=8$ .<sup>4</sup> RTA crystals exhibit ferroelectric phase below 1018 K and the polar axis is parallel to the *c* axis.

The optical properties,<sup>2,3</sup> frequency doubling,<sup>5</sup> and parametric oscillations<sup>6,7</sup> of RTA have been investigated. Other physical properties such as piezoelectric and acoustic properties<sup>8</sup> were also studied. Although dielectric constants are considered to be one of the fundamental quantities that represent the electrical properties of a material, no literature has yet reported the dielectric properties of RTA crystals. In this letter, we report the complete measurements of the dielectric constants in the frequency range of 1 kHz–6 MHz and in the temperature range of 303–1123 K, which includes the ferroelectric-paraelectric phase transition temperature.

The imaginary part of the dielectric constant  $\epsilon''$  is related to the ionic conductivity  $\sigma(\omega)$

$$\epsilon'' = [\sigma(\omega) - \sigma(0)] / \omega \epsilon_0, \quad (1)$$

where  $\sigma(0)$  is the direct current conductivity,  $\omega$  is the frequency of the applied field, and  $\epsilon_0$  is the dielectric permittivity of free space. For the bound carrier model, the conductivity is represented by the Arrhenius relation

$$\sigma = \sigma_0 \exp(-E/k_B T), \quad (2)$$

where  $E$  is the activation energy and  $\sigma_0$  is the constant, which is a function of the total number of the charge carriers, ionic jump frequency, and the hopping distance.

Single crystals of RTA were grown by the high temperature solution growth method with placing the [001] seed at

the surface of the solution. The starting materials for the synthesis of RTA and a flux, Rb<sub>5</sub>As<sub>3</sub>O<sub>10</sub> were; As<sub>2</sub>O<sub>5</sub> (99.9+% purity), TiO<sub>2</sub> (99.9+% purity), and Rb<sub>2</sub>CO<sub>3</sub> (99% purity). The weight ratio of RTA and the flux in the solution was 3:10. The temperature inside the three-zone furnace was controlled to within  $\pm 0.1$  K. The initial and final temperature were 1133 and 1073 K, respectively, and the temperature lowering rate varied from 0.5 K/day to 2.4 K/day depending on the stage of the growth. RTA crystals of  $18 \times 31 \times 24 \text{ mm}^3$  size and of excellent quality were grown for the period of 25 days. Thin plate samples were cut and polished perpendicular to the three principle axes. The thickness of the sample was less than 0.5 mm and the area was about  $7 \times 7 \text{ mm}^2$  for all samples. Both faces of the samples of  $6 \times 6 \text{ mm}^2$  in area were coated with Ag paste electrodes. However, in order to investigate the electrode effect on conductivity, we prepared a separate *c*-axis sample with a Pt electrode of 1  $\mu\text{m}$  thickness evaporated on both faces. An impedance analyzer (Hewlett Packard 4192A) was used to measure the real and imaginary parts of the dielectric constants, and the samples were placed in an electrically shielded oven in which the temperature was controlled to within  $\pm 0.1$  K by the Eurotherm 903P temperature controller. In order to examine the frequency dependence of the alternating current (ac) conductivity and to investigate a possible dielectric relaxation, we measured the dielectric constants in the frequency range of 1 kHz–6 MHz with 100 samplings, and at every 10 K in the temperature range of 303–1123 K. The heating rate of the sample was about 1 K/min.

The dispersions of the dielectric constants for the *a*, *b*, and *c* axes are shown in Figs. 1–3. As shown in Figs. 1 and 2, the dielectric behavior for the *b* axis is very similar to that for the *a* axis. There appears no relaxation peak for the three principle axes. Selective values of the RTA dielectric constants at the frequencies of 1 kHz and 1 MHz, and at the temperatures of 303 and 720 K are listed in Table I.

The temperature dependence of the ac conductivity was derived from the relation (2) and is depicted in Fig. 4 for the *a* and *c* axes. The conductivity plot for the *b* axis is not included since it is very similar to that for the *a* axis. The Arrhenius plot for the *c* axis looks very close to that for the

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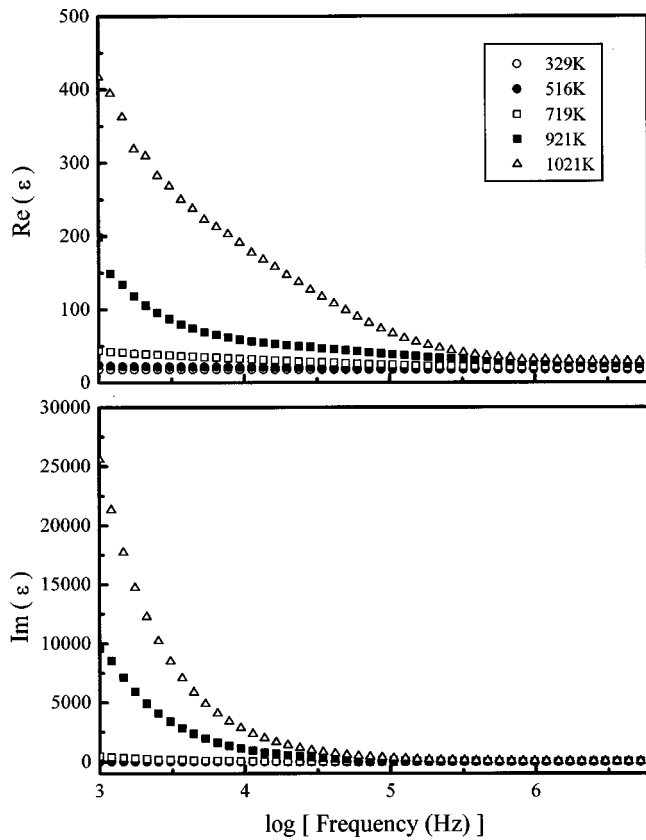


FIG. 1. The dispersion of the dielectric constant for the *a* axis.

*a* axis apart from the peak at 1018 K due to the phase transition. Since the dielectric polarization due to the ferroelectric phase transition is established only along the *c* axis, no dielectric peak is expected along the *a* and *b* axes. The acti-

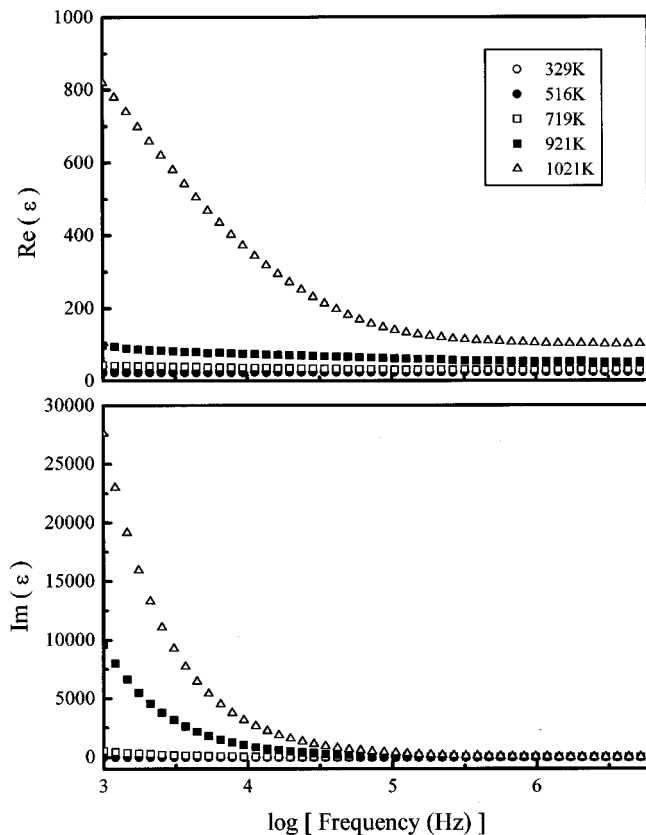


FIG. 2. The dispersion of the dielectric constant for the *b* axis.

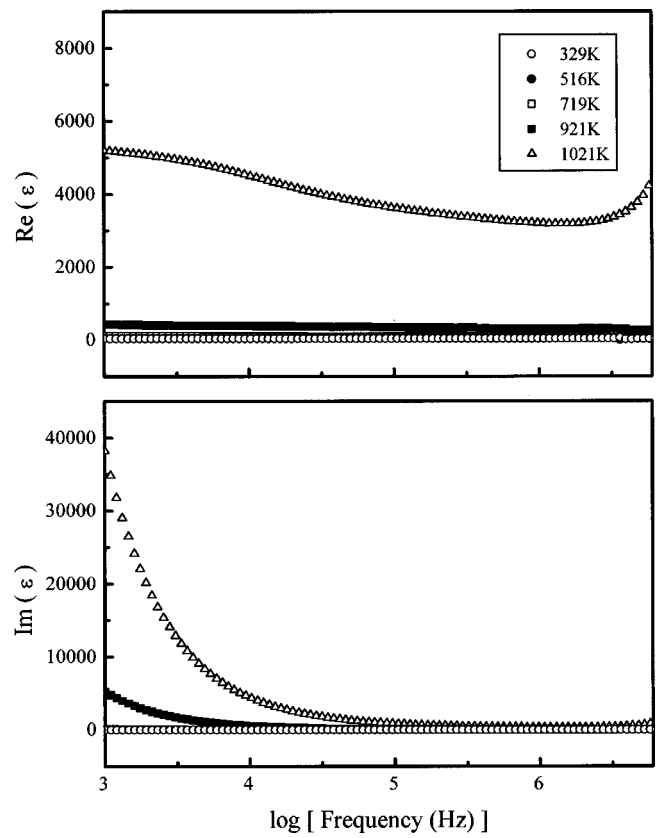


FIG. 3. The dispersion of the dielectric constant for the *c* axis.

vation energies at  $f=1$  kHz are 0.96, 0.8, and 1.1 eV for the *a*, *b*, and *c* axes, respectively. The ac conductivities of RTA at  $f=1$  kHz are  $2.2 \times 10^{-8}$ ,  $3.0 \times 10^{-8}$ , and  $3.7 \times 10^{-8} \Omega^{-1} \text{m}^{-1}$  at 303 K, and  $2.5 \times 10^{-5}$ ,  $3.5 \times 10^{-5}$ , and  $1.3 \times 10^{-5} \Omega^{-1} \text{m}^{-1}$  at 720 K for the *a*, *b*, and *c* axes, respectively. These are very contrasted with those of KTP, where the conductivity along the *c* axis is four orders-of-magnitude larger than that along the *a* and *b* axes.<sup>9</sup> Considering that RTA is isostructural with KTP, it is interesting to note the nearly isotropic behavior of the ac conductivity in RTA. The conductivity data along the *c* axis using both Ag and Pt electrodes showed almost the same values in the temperature range of room temperature to 900 K and the difference between the two data is not greater than 80% even above 900 K.

In Table II, the conductivity of KTP isomorphs at 1 kHz along the polar *c* axis is summarized. The replacement of  $\text{K}^+$  ions in KTP by  $\text{Rb}^+$  ions leads to reducing the conductivity by three orders-of-magnitude in RTP ( $\text{RbTiOPO}_4$ ).<sup>10</sup> And the replacement of phosphorus atoms in RTP by arsenic atoms reduces the ac conductivity by two orders-of-magnitude further in RTA. Consequently the conductivity of RTA becomes about five orders-of-magnitude smaller than that of KTP. In order to investigate the effect of impurities on con-

TABLE I. Dielectric constants of RTA at 303 and 720 K.

Dielectric constant	303 K		720 K	
	1 kHz	1 MHz	1 kHz	1 MHz
$\epsilon_a$	17.9	17.6	43.6	20.8
$\epsilon_b$	22.6	23.7	42.6	29.9
$\epsilon_c$	40.8	39.4	119.1	88.6

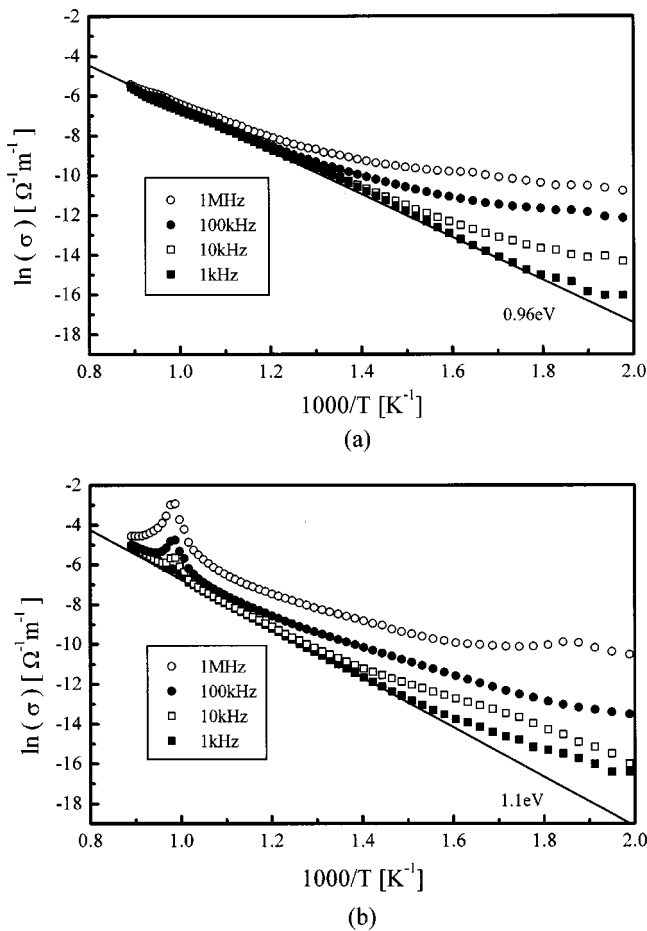


FIG. 4. Temperature dependence of the conductivity (a) along the  $a$  axis and (b) along the  $c$  axis.

ductivity, the impurity concentrations in the RTA dielectric samples were analyzed using an inductively coupled plasma emission spectrophotometer (ICPS-1000III, Shimadzu) and the result is summarized in Table III. Since ionic hoppings to the neighboring vacancy sites are responsible for the conductivity in KTP isomorphs,<sup>11</sup> the concentration of the  $\text{Rb}^+$  vacancy is of prime importance for the conductivity in RTA crystals. In order for the charge neutrality to be balanced, divalent impurities such as  $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$  may contribute to the increase in the concentration of  $\text{Rb}^+$  vacancy, and hence, to the increase in the conductivity. However, trivalent impurities such as  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Cr}^{3+}$  may replace the site of  $\text{Ti}^{4+}$ , which gives rise to the reduction in the concentration of ionic vacancies. Considering that the contents of the trivalent impurities are relatively small, it is highly unlikely for the conductivity to be decreased significantly by the presence

TABLE II. The conductivity of KTP isomorphs along the  $c$  axis measured at 1 kHz.

Material	Temperature (K)	Conductivity ( $\Omega^{-1}\text{m}^{-1}$ )
KTP <sup>a</sup>	597	$2 \times 10^{-2}$
RTP <sup>b</sup>	579	$4 \times 10^{-5}$
RTA	579	$6 \times 10^{-7}$
	597	$9 \times 10^{-7}$

<sup>a</sup>See Ref. 9.

<sup>b</sup>See Ref. 10.

TABLE III. Impurity concentration in the RTA dielectric samples.

Impurity	Mg	Al	Fe	Cu	Zr	Cr	Ni
(ppm)	38.8	13.6	5.6	28.0	48.0	1.7	<0.5

of these trivalent impurities. The tetravalent ion impurity,  $\text{Zr}^{4+}$  is more likely to replace  $\text{Ti}^{4+}$  rather than  $\text{As}^{5+}$ , when taking into account the electronic structure and ionic radius of  $\text{Zr}^{4+}$ ,  $\text{Ti}^{4+}$ , and  $\text{As}^{5+}$  ions. Thus, it is not probable that  $\text{Zr}^{4+}$  impurities contribute to the decrease in the concentration of the ionic vacancy. It therefore seems that the impurities of the RTA crystals might not give any significant effect on the reduction of the conductivity.

The observed low conductivity in RTA could be explained by analyzing the crystal structure of KTP isomorphs. The structure of KTP consists of a three-dimensional network of corner-shaped  $\text{TiO}_6$  octahedra and  $\text{PO}_4$  tetrahedra with open channels running parallel to the  $c$  axis.<sup>12,13</sup>  $\text{K}^+$  (or  $\text{Rb}^+$ ) ions then fit into the corners of the rectangular-shaped channels in a spiral fashion with the  $\text{PO}_4$  tetrahedra placed above and below them. The  $\text{K}^+$  (or  $\text{Rb}^+$ ) ions thus have to hop to the neighboring vacancy sites in a zig-zag manner along the channels, since the oxygen atoms of  $\text{PO}_4$  tetrahedra block the straight hopping motions of  $\text{K}^+$  (or  $\text{Rb}^+$ ) ions. Therefore, the heavier the mass of the ions ( $\text{Rb}^+$ ) and the larger the volume of the tetrahedra ( $\text{AsO}_4$ ), the more difficult for the ions to hop, which results in much smaller conductivity in RTA as compared with that of KTP and RTP.

In summary, complete dielectric constant measurements have been done on RTA crystals, and the ac conductivity of RTA was discussed in association with the crystal structure. Much smaller value of the electrical conductivity and wider transparency range in RTA crystals than KTP will help to facilitate device applications, such as periodically poled optical parametric oscillators.<sup>6,7</sup>

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