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Linking ionic conductivity and piezoelectric resonance in $KTiOPO_4$

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The interplay between the ionic conductivity and the ferroelectric polarization is a key point for understanding and tuning the properties of $KTiOPO_4$ (KTP) single crystals. We show here that the piezoelectric resonance undergoes a well-defined splitting at 200 K for several KTP samples exhibiting different geometries, crystalline orientations, and ferroelectric domain states. This method is a powerful way for probing the buildup of ionic space charges when the ionic conductivity stops to screen the ferroelectric polarization. We also show that it is useful to track the evolution of this space charge under several thermal and moderate electrical stresses.

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I. INTRODUCTION

Potassium titanyl phosphate $KTiOPO_4$ (KTP) is one of the major nonlinear crystals for visible and infrared generation.[1] KTP exhibits a unique combination of ferroelectric, conductivity, pyroelectric, and superionic properties. It undergoes a ferroelectric transition ranging between 1193 and 1233 K as a function of the flux growth conditions.[2] At room temperature, KTP has a noncentrosymmetric orthorhombic symmetry with space group $Pna2_1$ where TiO_6 octahedra and PO_4 tetrahedra share corners; potassium ions lay in the cavities formed by the TiO_6-PO_4 network.[3] The ionic conductivity of KTP results from a hopping of potassium among vacancies along the c axis.[4,5] Several reports have shown that this ionic conductivity decreases sharply at 200 K, giving rise to a superionic-to-insulator transition around this temperature.[6–10] This is usually ascribed to localization of potassium on lattice sites at this temperature. Potassium ions are also responsible for the ferroelectric polarization of KTP,[11] although the observation of spontaneous polarization at high temperature is difficult due to a screening effect induced by the high magnitude of the ionic conductivity. Hence at low temperature, when the conductivity is sufficiently diminished, several attempts had been made to observe hysteresis loop: Shaldin *et al.* obtained an unsaturated hysteresis loop at 130 K, whereas Rosenman *et al.* demonstrated a hysteresis loop for KTP with high and low concentrations of potassium at 300 and 190 K.[12,13] Since ionic conductivity and ferroelectric polarization of KTP are strongly connected, in this present paper we investigate an alternative way to establish this link while decreasing the conductivity contribution by means of low electric field. Here we demonstrate that the piezoelectric resonance is the appropriate method. As we used KTP single crystals, pyroelectricity and piezoelectricity can be observed without any need of poling the sample. We showed that the piezoelectric resonance of KTP cut in different shapes and crystalline orientations undergoes a well-defined splitting at about 200 K, which corresponds to superionic transition temperature. We ascribed this splitting to the building of an ionic space charge at the electrode interface, as confirmed by the evidence of dc electric field effect at this temperature. This shows that KTP is a unique material where large changes of conductivity and elastic properties can be simultaneously observed at a given temperature.

II. EXPERIMENTAL METHODS

Several bars and plates of KTP single crystals with electrodes coated on (100), (010), and (001) faces were used for the measurements described below. The dimensions were $4 \times 4 \times 1$ mm^3, $0.5 \times 2 \times 2$ mm^3, and $1 \times 4 \times 4$ mm^3 for the plates; $4 \times 1 \times 1$ mm^3, $7.89 \times 2.79 \times 1.02$ mm^3, and $5.09 \times 1.22 \times 1.78$ mm^3 for the bars. Gold was sputtered to make electrodes, and thin silver wires glued with silver paste to the center of the electrode were used for electrical contact.

The ac resistivity of KTP was measured from room temperature to 120 K using a HP 4194 A Impedance/Gain Phase Analyzer in the range 100 Hz–1 MHz. The samples were left for 10 min at each temperature in order to reach the thermal equilibrium.

Piezoresonances were obtained by measuring the conductance G and susceptance B as a function of frequency with an impedance/gain phase analyzer. The measurements of G and B were carried out with a 1 V sinusoidal voltage. Small frequency steps were applied in order to find the piezoresonance frequencies; then the selected length and thickness modes of each sample were measured between room temperature and 120 K. The methods for identification of the length and thickness modes can be found in Ref. 14. All measurements were done under helium atmosphere. Bias voltages up to 400 V cm^{-1} were applied in both positive and negative directions to study the influence of bias on KTP single crystals.

III. RESULTS

A. Resistance measurements

Figure 1(a) gives the plot of reactance X versus resistance R over the frequency range 100 Hz–1 MHz measured in a KTP crystal with electrodes perpendicular to [001] direction at 298 K. The ionic conductivity of KTP is strongly anisotropic so that it could be measured only along [001].[15] At 298 K the trace of the semicircle is seen at high frequency (left side) followed by a large linear increase at low frequency (right

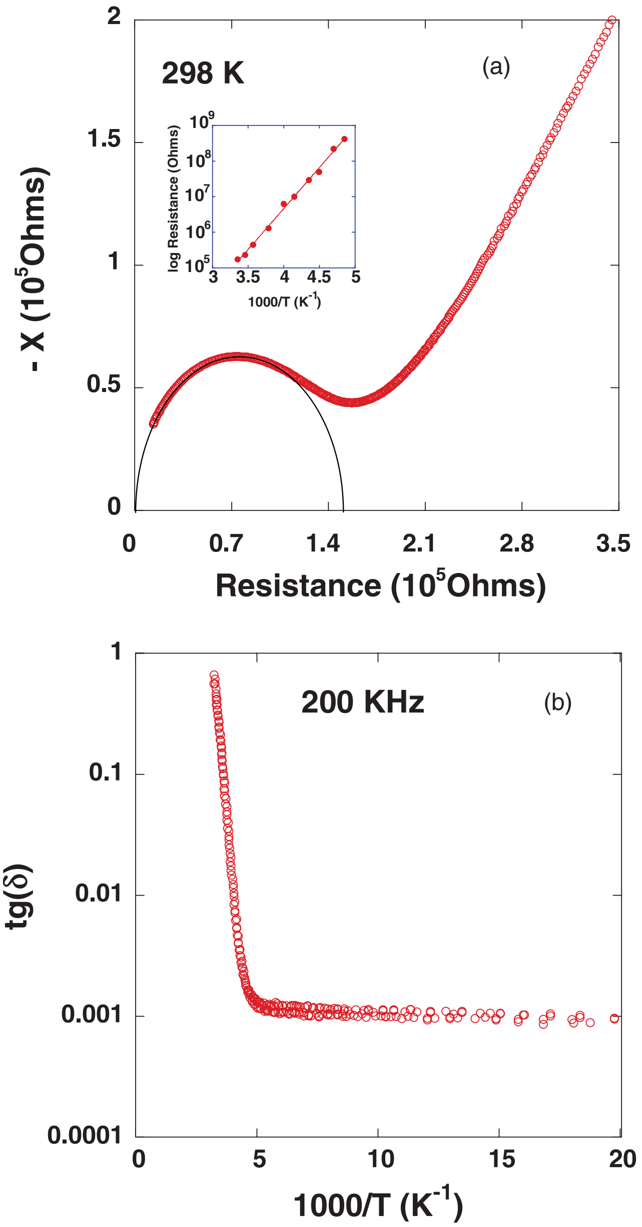


FIG. 1. (Color online) (a) Reactance ($-X$) as a function of resistance (R) at room temperature measured along the [001] direction of a KTP. The trace of a semicircle can be seen. Inset: log resistance as a function of inverse temperature. (b) Dielectric loss vs inverse temperature measured along the [001] direction at 200 kHz of KTP. The presence of a steep slope from room temperature to 200 K indicates the drastic decrease in ionic conductivity.

side). The intercept of the semicircle to the x axis then gives the resistance. Additionally, the temperature dependence of resistivity was plotted as conventional log R versus $10^3/T$ that can be fitted with Arrhenius law, which is shown as an inset in Fig. 1(a), and the activation energy was found out to be 0.48 eV. The difference between the previously reported activation energy of 0.2 eV[16] and the one we measured, 0.48 eV, lies in the different temperature ranges that were investigated. The literature data dealt with high-temperature ionic conductivity ($T > 300$ K) while we focused on low temperatures ($T < 300$ K). While a purely Arrhenius behavior with low activation energy was evidenced in the former case, the proximity to superionic transition temperature may artificially increase the activation energy in our experiments. Figure 1(b) shows the plot of log dielectric loss as a function of inverse temperature at 200 KHz. When the temperature decreases, the dielectric loss decreases drastically from room temperature, which can be evidenced from the steep slope until 200 K followed by a plateau at low temperature. A sudden change of slope indicates a superionic transition around 200 K since dielectric losses are proportional to conductivity.

B. Piezoelectric measurements

Figures 2(a)–2(e) give the plots of conductance G at room temperature and 200 K as a function of frequency for a KTP bar sample with the electrode coated on the (001) face. We interpret the observed peak of conductance as a transverse piezoelectric resonance for which the ultrasound vibrations occur along [100] while the generating electric field is applied along [001]. The corresponding resonance frequency f_r can be expressed as

$$f_r = \frac{1}{2l\sqrt{\rho s_{11}}}, \tag{1}$$

where l is the bar length, ρ is the crystal density, and s_{11} is the inverse elastic compliance along [100].[18] However, the lack of a reliable estimate of s_{11} precluded a quantitative computation of the f_r. However, we checked this mode assignment by decreasing the bar length, which led to an expected behavior of increase of the resonance frequency f_r. A single piezoresonance peak was observed at room temperature around 896 KHz. It is very clear from Fig. 2 that the peak shifts to higher frequency at low temperature, close to 210 K a second peak appeared, and a full splitting was observed at 200 K. But no splitting was observed in thickness mode, i.e., along [001] recorded at 2.9 MHz.

By plotting the resonance frequency before and after the splitting as a function of temperature allows the splitting to be seen more readily. AVANTAGE software developed by Thermo Fisher Scientific was used to fit the splitting and to deconvolute the peaks. The frequency of splitting was then taken from these deconvoluted peaks. The peak at room temperature is named Resonance Fr 1 and the new peak that appears is Resonance Fr 2. From Fig. 3 it can be seen that at higher temperature, there is only one resonance frequency, while the splitting happens around 210 K. The overall decrease of frequencies by increasing the temperature is expected since it results from the thermal expansion of the crystals. It can also be noted from Fig. 3 that Resonance Fr 1 disappears below 160 K.

Similarly, the conductance G of a KTP plate with electrode coated onto the (100) faces was measured as a function of frequency. Figures 4(a) and 4(b) give the corresponding plots at 298 and 170 K in transverse mode along "b" and "c," respectively. Here the peak at room temperature splits at 170 K exhibiting similar behavior as the KTP bar sample. It is difficult to assign this piezoresonance to one particular direction, i.e., "b" or "c," since the contribution for resonance comes from both [010] and [001] directions, the dimensions being the same in these directions. A splitting was also observed for this

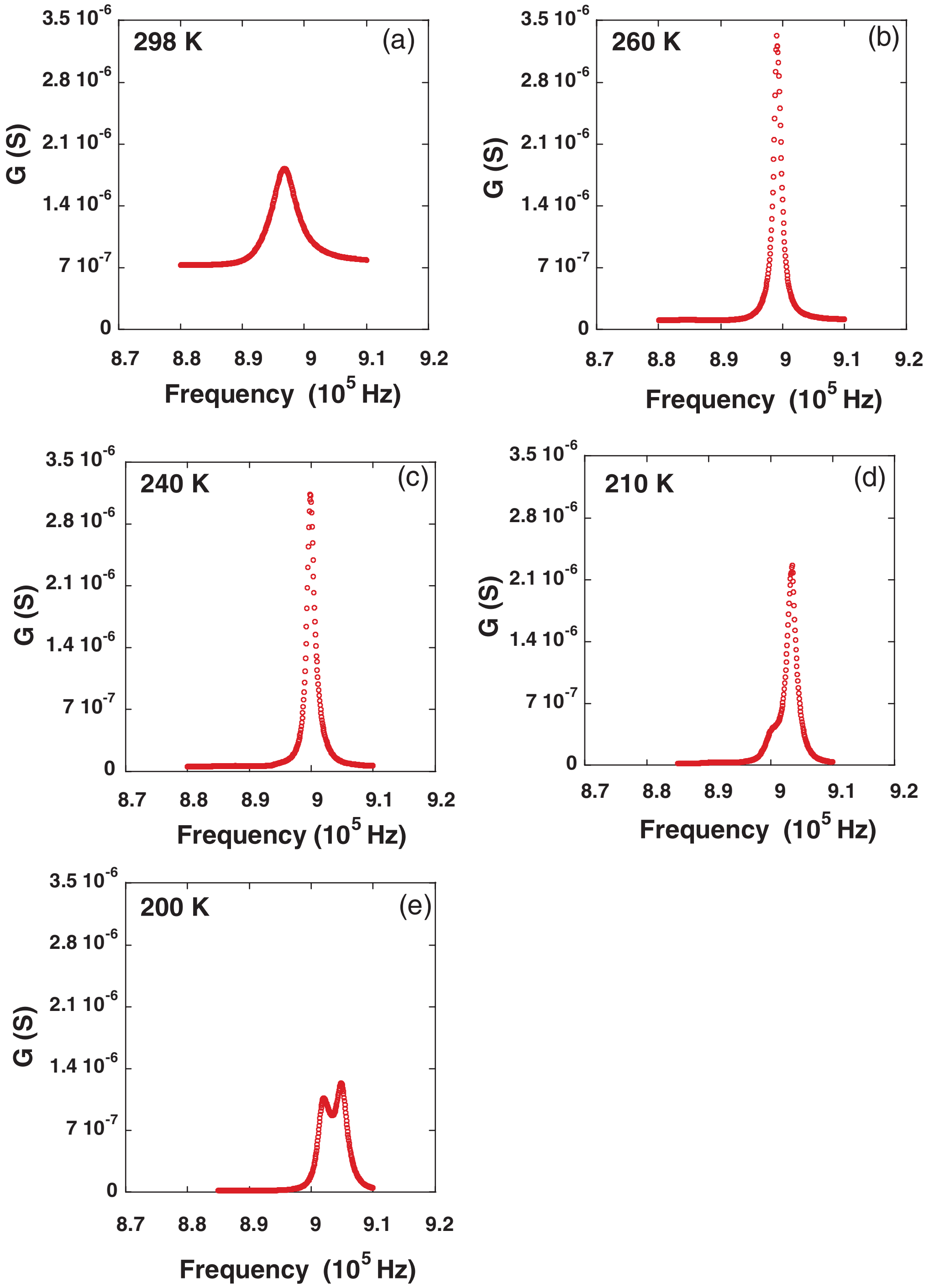


FIG. 2. (Color online) [(a)–(e)] Conductance G vs frequency in transverse mode along [100] from 298 to 200 K for KTP bar samples. When decreasing the temperature the base of conductance is shifted toward low value and at 210 K a small shoulder is visible, moving with temperature and developing into clear splitting of the piezoresonance at 200 K.

sample in thickness mode along [100], which is given in Figs. 5(a) and 5(b).

The results obtained for all the measured samples are summarized in Table I. The theoretical resonance frequency was calculated with the help of elastic compliance data taken from Ref. 17. It appears that the splitting occurs in all directions and there is no anisotropy in the splitting of piezoresonance peak. For samples 2 and 3 the length mode cannot be calculated since it involves two directions in length mode. Note that in KTP, the ionic conductivity decreases drastically due to the localization of the potassium ions and pyroelectric current starts to appear around 200 K.[11,15,16] As a consequence, we can assume that the potassium ions are at the origin of these splitting through their conductivity. This could be understood with the space-charge model as described by Coelho.[18] For this purpose, the effect of dc bias on the splitting of the

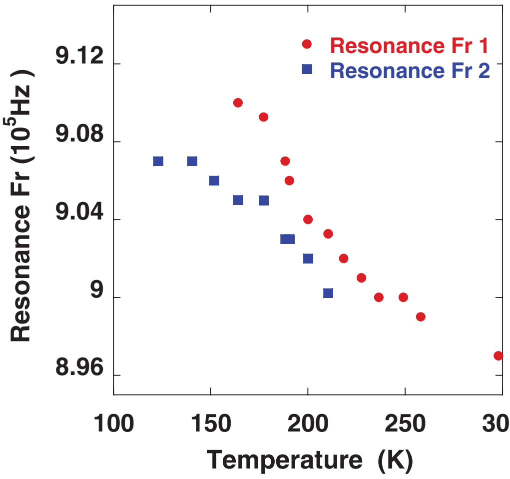
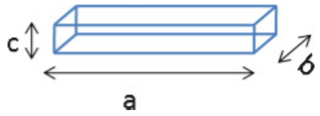
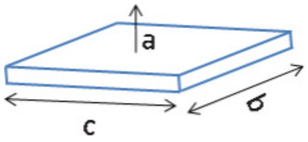
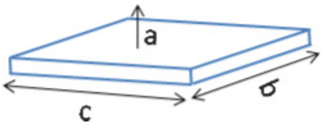
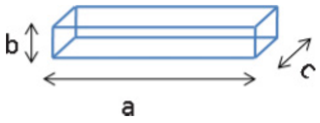
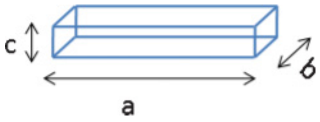
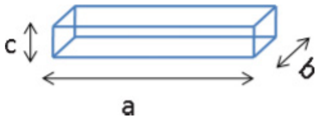


FIG. 3. (Color online) Resonance frequency before (Fr 1) and after splitting (Fr 2) as a function of temperature. With a decrease in temperature, the resonances move to high frequency and Fr 1 disappears below 160 K.

piezoelectric resonance was probed, which led to the results that are described hereafter.

Figures 6(a)–6(c) give the conductance as a function of frequency for the KTP bar sample with electrodes perpendicular to [001]. Both positive and negative bias up to 400 V cm^{-1} were applied by step. Figure 6(a) shows that there is no effect of the bias on the splitting at 180 K under isothermal conditions. Thus when the bias is applied after achieving splitting, we conclude that the potassium ions become rigid in their local position so that it cannot have any effect on splitting. Hence, the bias was applied before achieving splitting while cooling i.e. under field cooled condition. Figure 6(b) shows the splitting for two piezoresonances: one without bias (0 V cm^{-1} fields) at 180 K and the other after applying a bias of 400 V cm^{-1} during cooling at the same temperature. It is evident from the plot that there is an effect of the bias on the splitting which is irreversible. Figure 6(c) show the same kind of plot at 150 K indicating that the bias has considerable influence on the splitting, which is more pronounced than that at 180 K. As expected at higher temperature (240 K), the splitting disappears and there is no

TABLE I. Piezo measurements on several KTP samples with different orientations and dimensions.

Sample number	Orientation	Dimensions (mm)	Electroded face	Mode	Theoretical resonance frequency	Measured resonance frequency	Splitting
1		4 × 1 × 1		Length	454 KHz	890 KHz	Yes
			(001)	Thickness	3.51 MHz	2.9 MHz	No
				Length harmonics	1.36 MHz	2.7 MHz	Yes
2		1.08 × 4.18 × 4.18		Length		810 KHz	Yes
			(100)	Thickness	3.46 MHz	2.1 MHz	No
3		0.5 × 2 × 2		Length		1.5 MHz	Yes
			(100)	Thickness	7.49 MHz	5 MHz	Yes
4		5.09 × 1.22 × 1.78		Length	333 KHz	325 KHz	No
			(010)	Thickness	3.1 MHz	1.8 MHz	Yes
5		7.87 × 2.79 × 1.02		Length	230 KHz	450 KHz	No
			(001)	Thickness	3.4 MHz	3.5 MHz	Yes
6		7.87 × 2.79 × 1.02		Length	230 KHz	450 KHz	No
			(001)	Thickness	3.4 MHz	3.7 MHz	Yes

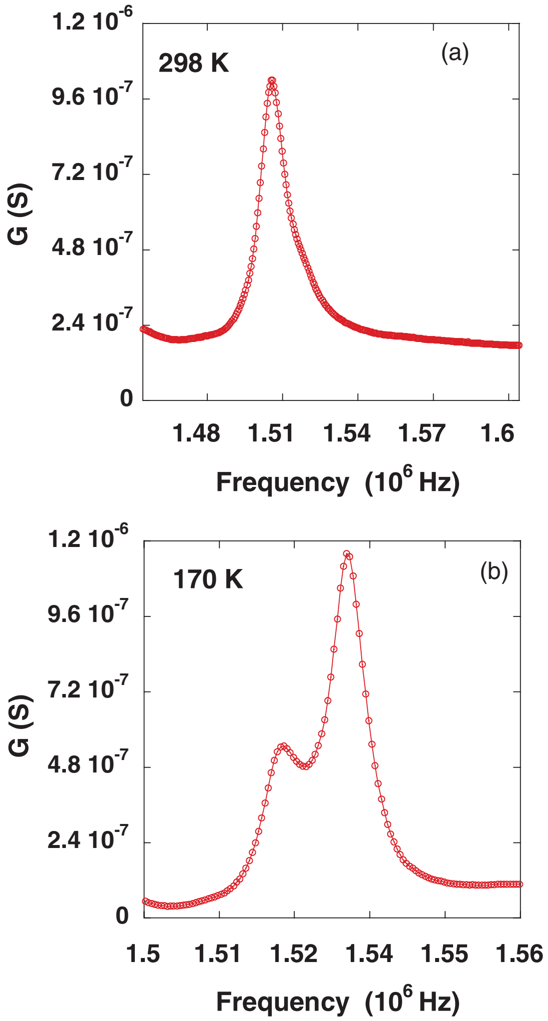


FIG. 4. (Color online) [(a),(b)] Conductance G vs frequency for the KTP plate sample in transverse mode along [010] and [001] at 298 and 170 K.

discernible difference before and after the application of the bias, as shown in Fig. 6(d). According to these measurements we can deduce the three following features: there is no effect of the bias on the splitting under isothermal condition; a field cooling has an effect on the splitting with an enhancement at lower temperature; and the bias has no influence on the piezoresonance at higher temperature when the splitting vanishes.

IV. DISCUSSION

Our observation of a large decrease of the dc conductivity and of a strong cusp in the ac dielectric losses, both at about 200 K, is consistent with previous reports on the superionic transition of KTP at 200 K. Actually the ionic conductivity of KTP decreases with temperature, and Jiang *et al.* reported that KTP undergoes a superionic transition at 180 K.[6] They also showed that thermal absorption takes place at the same temperature, which indicates a phase transition. Noda *et al.* and Park *et al.* observed dielectric dispersion at 223 and 193 K, respectively.[7,10] Shaldin *et al.* reported that pyroelectric current in KTP appears at 200 K and that a possible superionic phase transition can occur at the same temperature.[12] In addition, Rosenman *et al.* found that KTP becomes a superionic conductor at 170 K according to the Seebeck effect that gradually undergoes a transition from ionic conductivity to electronic conductivity below 200 K as reported by Antsigin *et al.*[8,9] Nonuniformity in these results for defining the superionic phase transition is not surprising since two different types of phase transitions generally occur in superionic conductors: In the first type, the transition happens sharply at a given temperature while transition occurs over a range of temperatures in the second type.[19] From these reports we can conclude that the transition in KTP is of second order; the mobile potassium gradually becomes immobile over a wide range of temperatures. Interestingly, Angert *et al.* have found that the Curie temperature seems to vary over a range of 100 K depending on the potassium concentration.[20] Potassium stoichiometry then affects the superionic phase transition, since the ionic conductivity of KTP is by vacancy mechanism involving potassium sites. As a first step for establishing a link between the ionic conductivity and lattice-related properties, we thus confirmed that all of the KTP single crystals we used have a standard ionic conductivity along the c axis. The first consequence of such ionic conductivity disappearance below

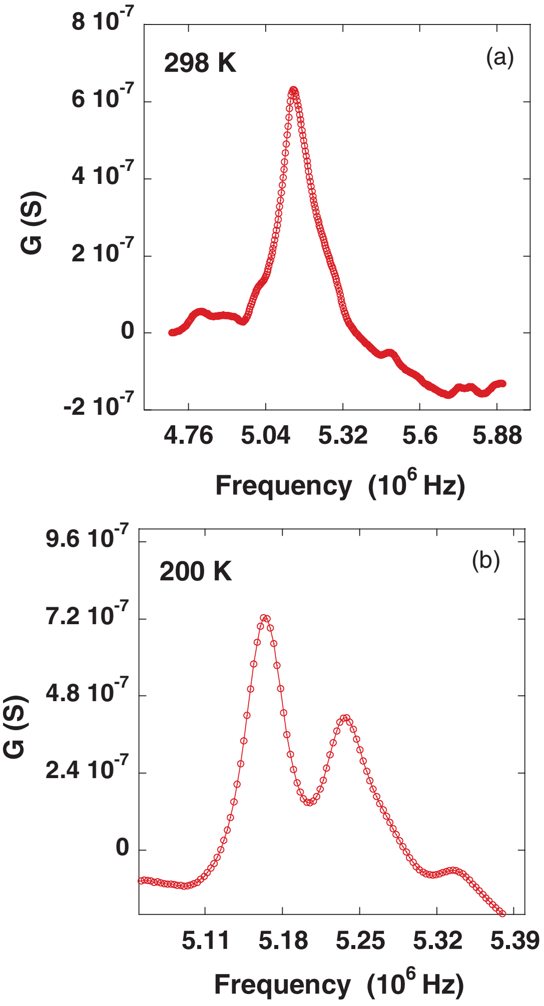


FIG. 5. (Color online) [(a),(b)] KTP plate sample conductance G vs frequency in thickness mode along [100] at 298 and 200 K.

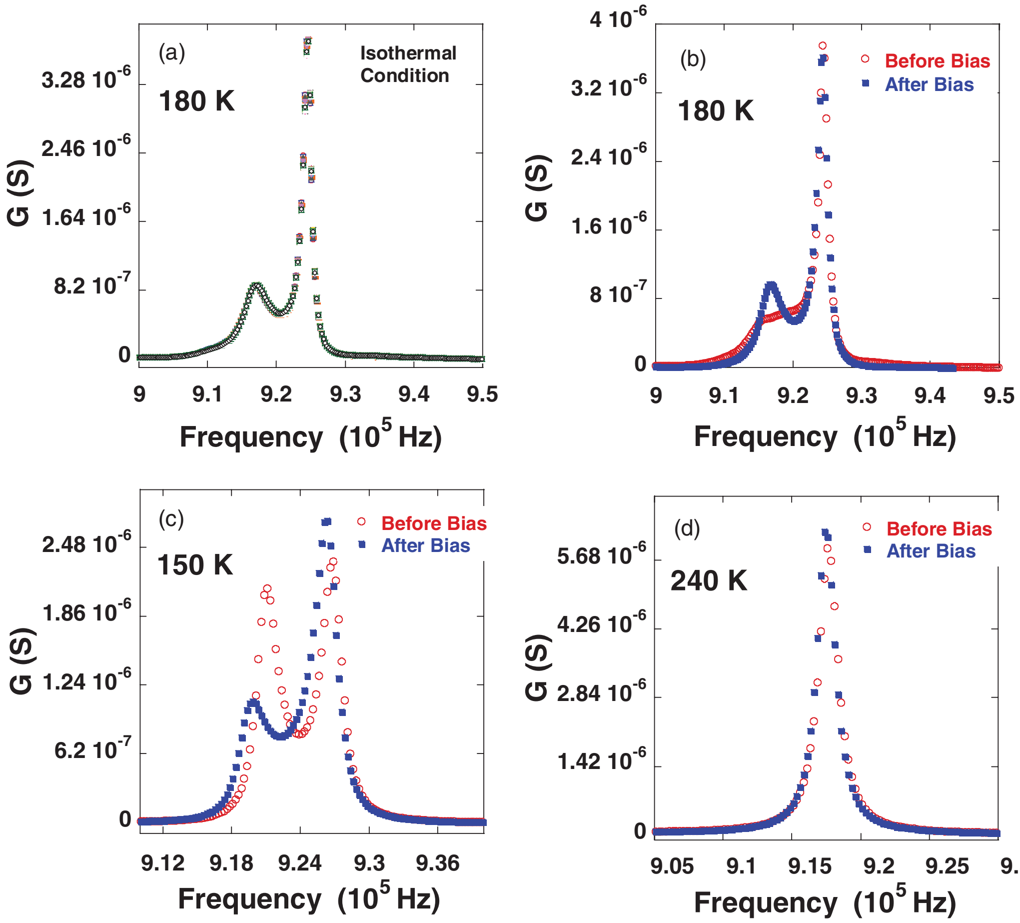


FIG. 6. (Color online) [(a)–(d)] Conductance G vs frequency in a KTP bar sample in transverse mode along [100] at 180, 150, and 240 K under 400 V cm^{-1} and without bias. (a) The bias was applied after splitting at 180 K under isothermal conditions and no effect was observed; (b) noticeable influence of the bias observed when it is applied during cooling before the actual splitting; (c) enhanced bias effect at 150 K under field cooling; and (d) at 240 K, far away from the temperature where the actual splitting starts to appear, the bias has no influence on the piezoresonance.

200 K is the increase of the pyroelectric current which can be integrated to lead to the polarization.[12] Note that it does not mean that the KTP ferroelectric transition takes place at 200 K, but only that the ferroelectric polarization is screened by the ionic conductivity at high temperatures. This confirms the previous observations of ferroelectric hysteresis loop on reducing the conductivity[12] and on the birefringence onset below 200 K.[21]

The original point we put in emphasis here is that the elastic parameters are affected by the conductivity suppression at 200 K. Indeed, the mechanical resonance frequency of any solid material involves the sample dimension that is resonating, as well as the density and the elastic compliance S_{ij} as indicated by Eq. (1). It is important to note that such a mechanical resonance can be excited through a small ac electric field, i.e., less than 10 V/cm in the case of KTP. Following Eq. (1), the splitting of the KTP piezoelectric resonance at 200 K can only result from a splitting of elastic parameters since the sample dimensions and density have no specific evolution at 200 K. Our investigation of several sample geometries and domain states (Table I) confirmed that there is no correlation between the crystal polarization state and the resonance splitting. As seen in Fig. 3, the splitting is just superimposed to the continuous increase of the resonance frequency on cooling, which stems from the thermal dilatation. We thus can conclude that the inverse elastic compliance which is single at high temperatures becomes split at $T < 200$ K. This feature seems to indicate that the crystal behaves like two slabs in the low-temperature state. It is important to note that the superposition of many ferroelectric domains will not result in a resonance splitting but rather leads to a broadening

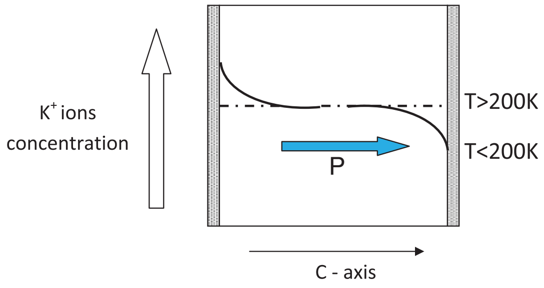


FIG. 7. (Color online) Schematic view of the space-charge distribution above and below the superionic transition temperature (200 K) in KTP within a single ferroelectric domain.

of the resonance peak. A space-charge bilayer is built in KTP upon decreasing the temperature below 200 K. Within a single ferroelectric domain and for temperatures higher than 200 K, K^+ ions are homogeneously distributed in all directions; in particular, along the thickness that is parallel to the *c* axis and below 200 K, K^+ ions localize in a way that is schematically shown in Fig. 7. This heterogeneous localization results from the electrical continuity at the electrode/crystal interfaces and from the built-in potential resulting from the polarization orientation. The extension of such space charge along the *c* direction is not known; however, since the polarization of KTP is directly resulting from the K^+ ions localization, the sample may be considered as a superposition of two slabs having the same elastic properties in the *ab* plane but not along *c*. This may explain the splitting of piezoelectric resonances below 200 K.

So this space-charge model thus provides a link between the ionic conductivity and the lattice elastic properties.[18] This is further confirmed by the poling experiments reported in Fig. 6, where using a slight electric field of 400 V/cm during the sample cooling through the 200 K temperature range, we were able to tune the amplitude of the split resonances. When the samples were cooled without this dc electric field (zero field cooled), a subsequent isothermal poling is not efficient for changing the resonance splitting. Translating this in terms of the space-charge model, we thus state that the dc electric field can alter the building of space charge only when its application starts before full localization and trapping of the mobile K ions. Conversely, once the splitting has been altered under field-cooled conditions, the only way to recover the original resonance shape is to rejuvenate the sample under heating in the temperature range where ionic conductivity is efficient. The way to cancel the dc field effect on the space charge is to remove the potassium gradients by thermally activating the hopping of individual ions. Additionally, splitting happens at different temperatures for the same sample depending on the sample thermal history which corroborates the presence of space charge. In Fig. 2 this splitting occurs at 200 K when the sample was cooled by steps of 20 K where the sample was left at each step for several minutes until it reached a thermal equilibrium, and for the same sample splitting appears at 180 K (Fig. 6) when it was cooled continuously without any steps. Furthermore, dependence of space charge with temperature also affects the dc field influence on the splitting. Figure 6(b) shows that the dc field enhances the amplitude of the split resonance at 180 K, whereas it suppresses the resonance amplitude at 150 K. These facts emphasize the space-charge effect which was created during the localization of K^+ ions at low temperature on the ferroelectric properties of KTP.

V. CONCLUSION

We have shown that the mechanical resonances of KTP single crystals undergo a well-defined splitting at about 200 K, which corresponds to the temperature where the ionic conductivity ends and pyroelectric currents as well as birefringence start to increase. This splitting of the piezoelectric resonance occurs for many crystal orientations and resonance modes whatever the ferroelectric domain state is. In most of the cases, it is observed when the probing ac voltage is applied parallel to the *c* axis, which is the main path for the ionic conductivity. We ascribed the splitting to the building up of ionic space charges in the single crystal. We thus suggest that the piezoelectric resonance is relevant parameter in order to track the space charge as a function of several external stresses using a very small applied voltage which is not perturbing the spontaneous balance between the ferroelectric polarization and the ionic conductivity in KTP, which is maybe true in other ferroelectric ionic conductors. While this space-charge model is strongly supported by the splitting of the piezoelectric resonance and its tuning under electrical poling, we have no direct evidence for it at the moment. To face this issue which is shared by all space-charged materials, further investigations are under way such as a systematic reduction of sample thickness and comparison of crystals exhibiting various potassium vacancies density.

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