

Nonequivalent-F-induced relaxations in LaF₃ single crystals over a broad temperature range

Jing Wang¹ · Chunchang Wang¹ · Xiaohong Sun¹ · Jian Zhang² · Jun Zheng³ · Chao Cheng³ · Hong Wang¹ · Yide Li¹ · Shouguo Huang¹

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Abstract The dielectric properties of LaF₃ single crystals were investigated in the temperature range from 110 to 773 K and the frequency range from 100 Hz to 10 MHz. Two thermally activated relaxations (R1 and R2) and a dielectric anomaly (A) were observed. The lower temperature relaxation (R1) was ascribed to a polaronic relaxations due to fluorine ions diffusion within the F₁ sublattice and fluorine ions hopping in F₁ sublattice. The higher temperature relaxation (R2) is Maxwell–Wagner relaxation due to the blocking of electrodes associated with the ionic exchange between F₁ and F_{2,3} sublattices and among the three nonequivalent sublattices. The anomaly appearing in the highest temperature range is related to the inductive effect arising from the coupled electron-ionic inductive response.

Introduction

Lanthanum trifluoride, LaF₃, the super-ionic (or fast-ion) conductor, has been received considerable attention due to its broad range of applications. Owing to the applicable

characteristic of ionic conductivity and super-ionic transitions, LaF₃ holds promise application as solid electrolyte used in battery industries. LaF₃ is a primary candidate material with high available refractive index for optical interference multi-layer [1]. It is also an important component of toothpaste to avoid tooth decay. Besides, LaF₃ can be applied as special ionic electrodes in detectors. For example, on account of the high chemical stability and high ionic conductivity, LaF₃-based chemical sensors can be applied to sense fluoride, oxygen, and carbon monoxide [2–5]. In addition, Nd³⁺- and Ce³⁺-doped LaF₃ crystals are potential hosts for UV or VUV lasers [6, 7].

LaF₃ has a trigonal (sp. gr. $P\bar{3}c1$), the so-called tysonite structure, but near hexagonal symmetry [8, 9]. The fluorine ions locate in three nonequivalent sublattice, F₁, F₂, and F₃, with populations in the ratio of 12:4:2 per unit cell [10, 11], while all cations (La³⁺) locate in planes which are perpendicular to the main symmetry axis *c*, remaining immobile up to the melting point of ~1770 K. F₁ anions, which form layers between La³⁺ planes, are very mobile [12, 13]. Consequently, the nonequivalent fluorine ions are responsible for the high ionic conductivity, which was supposed to be not only structurally but also dynamically nonequivalent. Fluorine ion is one of the smallest anions with high mobility, and thus, fluorides exhibit high ionic conductivity at solid state even at ambient temperature [14]. As a representative of super-ionic crystals, there is a diffuse transition of the ion system from the dielectric (DE) state to super-ionic (SI) state in LaF₃. This makes ac techniques be more suitable for characterizing the properties of the system. However, compared with the optical and structural properties of LaF₃, the dielectric properties of LaF₃ are still far from clear. Herein, we present investigations on the dielectric properties of LaF₃ single crystals

✉ Chunchang Wang
ccwang@ahu.cn

Jing Wang
Abbyzhengzhou@163.com

¹ Laboratory of Dielectric Functional Materials, School of Physics & Material Science, Anhui University, Hefei 230601, People's Republic of China

² School of Electronics Science and Applied Physics, Hefei University of Technology, Hefei 230009, People's Republic of China

³ Center of Modern Experimental Technology, Anhui University, Hefei 230039, People's Republic of China

in the frequency range from 100 Hz to 10 MHz over a broad temperature range from 110 to 773 K. Two sets of relaxations and a dielectric anomaly have been observed, and their mechanisms were discussed in details.

Experimental

The (001) oriented LaF_3 single-crystal samples with the size of $5 \times 3 \times 0.75 \text{ mm}^3$ were purchased from the MTI Corporation. Electrodes were made by coating both sides of the samples with silver paste and then fired at 773 K for 2 h in air followed by furnace cooling down to room temperature. The above thermal treatment was used to remove the polymeric component completely and to achieve good sample/electrode contacts. The temperature-dependent dielectric properties were measured using a Wayne Kerr 6500B precise impedance analyzer with the sample mounted in a holder placed inside a PST-2000HL dielectric measuring system (Wuhan Pusite Instrument Co., Wuhan, China). The ramp rate of temperature variations is 3 K/min automatically controlled by a PCT10 Stanford temperature controller (Stanford Research System Instrument, Sunnyvale, CA). The amplitude of ac measuring signal was 100 mV.

Results and discussion

General dielectric properties

Figure 1a and b show the real part $\epsilon'(T)$ of the complex permittivity and dielectric loss tangent $\tan \delta$ ($\tan \delta = \epsilon''/\epsilon'$, where ϵ'' is the imaginary part of the complex permittivity) for a LaF_3 crystal at various frequencies, respectively. It is clearly seen that the curves of both $\epsilon'(T)$ and $\tan \delta(T)$ exhibit as plateau in the temperature range below about 200 K. The dielectric plateau is independent of both frequency and temperature indicating the intrinsic dielectric response from the electronic and/or ionic polarizations. With the temperature increasing, $\epsilon'(T)$ exhibits two sets of frequency dispersion stepwise increases accompanied by two sets of peaks in the corresponding curves of $\tan \delta(T)$. The peaks are clearly seen in the enlarged view of the $\tan \delta(T)$ curve recorded at 300 Hz as shown in the inset of Fig. 1b. The peak positions of both peaks shift to higher temperatures with increasing measuring frequency, indicating that the crystal possesses two thermally activated relaxations. With further increasing temperature, a broad peak in $\tan \delta$ can be seen. The peak intensity monotonically increases with increasing frequency, but its position firstly moves to somewhat lower temperatures with increasing frequencies and then it shifts to higher temperature with further increasing frequency. This behavior is quite different from that of the well-known thermally activated behavior

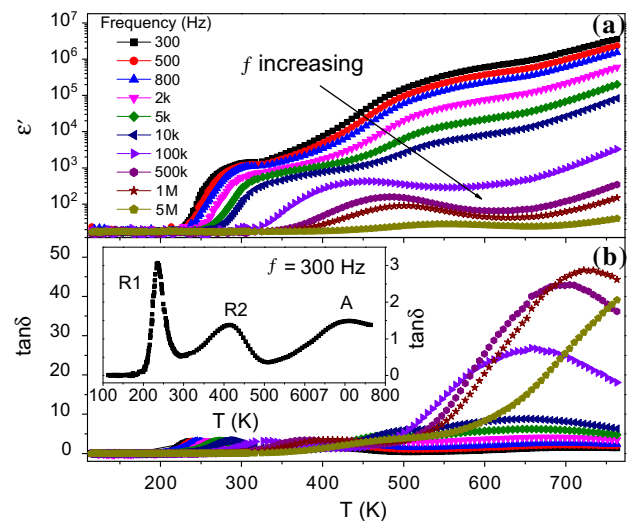


Fig. 1 Temperature dependence of ϵ' (a) and $\tan \delta$ (b) for LaF_3 single crystal measured with various frequencies. Inset (b) shows the enlarged view of $\tan \delta$ at 300 Hz

characterized by the feature that the relaxation peak moves to higher temperatures (frequencies) with increasing measuring frequency (temperature). We, thus, term it as the abnormal dielectric behavior. For brevity, the two relaxations and the anomaly dielectric behavior are hereafter labeled as R1, R2, and A in the order of ascending temperature as indicated in the inset of Fig. 1b.

First and foremost, we focus on the dielectric relaxations. Activation energy analysis is favorable for better understanding of the physical nature of the observed relaxation. To this end, detailed measurements of the frequency-dependent $\tan \delta$ were performed in the temperature ranging from 263 to 573 K (only the curves when dielectric peaks took place were shown). The inset plots the frequency dependence of $\tan \delta$ in the temperature range from 263 to 393 K, from which only one set of relaxation peaks can be seen. When the temperature reaches 343 K, another set of relaxation peaks comes into the measuring frequency window in the low-frequency range. For clarity, the low-frequency relaxation in the temperature range from 413 to 573 K was plotted in the main panel of Fig. 2. For a thermally activated relaxation, the high (low)-frequency relaxation in the frequency domain corresponds to the low (high)-temperature relaxation in the temperature domain. Therefore, the high-frequency relaxation shown in the inset is R1, while the low-frequency relaxation emerging afterward is R2. The relaxation parameters can be deduced from the plots of $\tan \delta$ with ease due to the well-defined peaks for the two relaxations. Figure 3 arrays the peak position f_p versus the reciprocal of the measuring temperatures T for R1 and R2. Referring to the Arrhenius law,

$$f_p = f_0 \exp(-E_{\text{relax}}/k_B T), \quad (1)$$

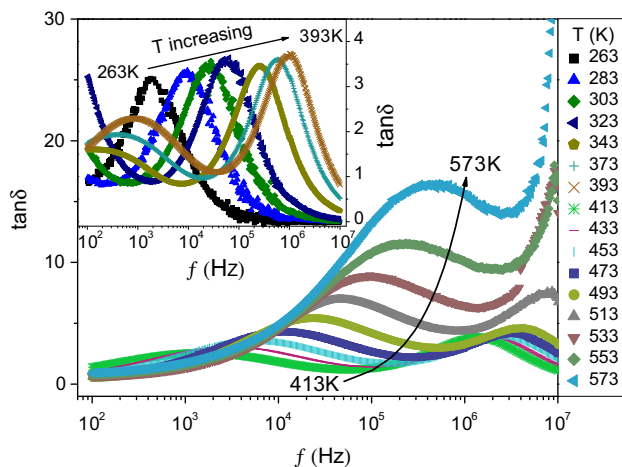


Fig. 2 Frequency dependence of $\tan \delta$ for LaF_3 single crystal obtained in the high-temperature range from 413 to 573 K in the main view. *Inset* displays the curves in the low-temperature range from 263 to 393 K. The selected temperatures are almost at temperature interval of 20 K

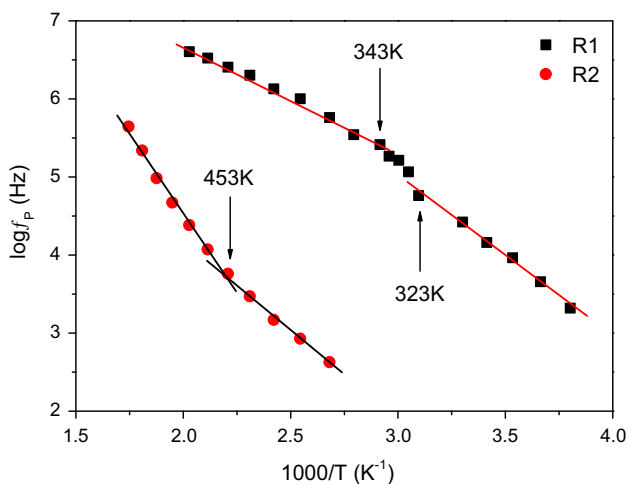


Fig. 3 The Arrhenius plots of $\log f_p$ versus $1/T$ for R1 and R2. The inflection temperatures were 323, 343, and 453 K (from right to left)

where f_0 is the pre-exponential factor, E_{relax} is the activation energy for relaxation, and k_B is the Boltzmann constant. The data of both R1 and R2 distinctly deviate from linear line leading to two Arrhenius segments. The calculated values of E_{relax} and f_0 of each segment for R1 and R2 are listed in Table 1. In the following, we will separately discuss the mechanism of R1 and R2 in details.

Origin of R1

LaF_3 , with the tysonite structure, exhibits a complicated process of ionic diffusion because of the nonequivalent fluorine sublattice (as described in the Introduction part). In

Table 1 Relaxation parameters (E_{relax} and f_0) for the low- and high- T segments of relaxations 1 and 2

Relaxation	Low- T segment		High- T segment	
	E_{relax} (eV)	f_0 (Hz)	E_{relax} (eV)	f_0 (Hz)
R1	0.404	1.29×10^{11}	0.267	2.39×10^9
R2	0.470	8.97×10^8	0.812	5.26×10^{12}

the temperature range of ~ 180 to 300 K, the motion is mainly contributed by the F_1 ions which form layers of fluorine ions (F_1 sublattice), while the motions of fluorine ions in F_2 and F_3 sublattices (in La plane) are comparatively slow [12, 15]. Therefore, the complicated process of ionic mobility can be satisfactorily described by a structural model with two fluorine sublattices, F_1 and $\text{F}_{2,3}$. The mechanism of fluorine ion transport in LaF_3 is of the Anion-Frenkel type, i.e., the ionic diffusion is accompanied by formation of point defects of the fluorine vacancy-interstitial type [16]. From Fig. 3, the two Arrhenius segments of R1 are separated by an intermediate temperature region of ~ 323 to 343 K. The activation energy (0.404 eV), for the low-temperature segment of R1, is quite close to the activation energy (0.36 eV) of fluorine diffusion for the fast ions (ions in F_1 sublattice) [12]. The reduction of the activation energy (0.267 eV) for high-temperature segment of R1 is in common with the study of transport properties of LaF_3 reported by Sher et al. [17]. Their results showed that the rate of conductivity increasing with temperature becomes slow down in the temperature above ~ 350 K. In other words, the activation energy for the ion diffusion is lower than before (the activation energy is deduced from the rate of conductivity increasing with temperature and is direct proportion to the rate). The decrease in activation energy for ionic conduction at high temperatures, as someone deems, is because of phase change (e.g., AgI). However, in the case of LaF_3 , which does not undergo a high-temperature phase change, it is most likely attributed to the super-ionic transitions (will be further explained thereafter). Besides, the low-temperature segment of R1 occurring in the temperature range of ~ 263 –323 K also corresponds to the region predominated by the ionic diffusion in F_1 sublattice. As fluorine ion is so small, its motion between F_1 sublattice and interstitial site can be assimilated to the motion of electron in polyvalent metal ions, which can lead a polaronic relaxation as well. To corroborate the inference, i.e., the polaronic nature of the low-temperature segment of R1, we resort to the different dielectric functions. Since the polaron relaxation can be described by Debye's theory [18], thus, from the spectroscopic plot of loss tangent, it can achieve the peak apex of $(\tan \delta)_{\text{max}} = (\epsilon_0 - \epsilon_\infty)/$

$2\sqrt{\varepsilon_0\varepsilon_\infty}$ at the frequency $f_{\tan\delta} = \sqrt{\varepsilon_0/\varepsilon_\infty}/2\pi\tau$. As to the spectroscopic plot of electric modulus ($M'' = 2\pi f C_0 Z'$, where Z' is the real part of complex impedance Z^* and C_0 is the vacuum capacitance of the measuring cell), the peak position and apex are $f_{M''} = (\varepsilon_0/\varepsilon_\infty)/2\pi\tau$ and $(M'')_{\max} = (\varepsilon_0 - \varepsilon_\infty)/2\varepsilon_0\varepsilon_\infty$, respectively, where ε_0 and ε_∞ are the static and high-frequency dielectric constants, and τ is the relaxation time, which obeys the Arrhenius law $\tau = \tau_0 \exp(E_a/k_B T)$. The peak positions and maxima for the two dielectric functions obey the following relations [19]:

$$(f_{\tan\delta})^2 / f_{M''} = (1/2\pi\tau_0) \exp(-W_H/k_B T) \quad (2)$$

$$T(\tan\delta)_{\max}^2 / M''_{\max} = \varepsilon_0 - \varepsilon_\infty \propto N_0 \exp(-E_g/2k_B T) \mu^2 / 3k_B T, \quad (3)$$

where W_H is the activation energy of dielectric relaxation, N_0 is the pre-exponential factor, E_g is the creating energy for a polaron, and μ is the dipole moment. Equations (2) and (3) predicate two linear relationship by the half-logarithmic plots of $(f_{\tan\delta})^2 / f_{M''}$ versus $1/T$ and $T(\tan\delta_{\max})^2 / M''_{\max}$ versus $1/T$. The upper (a) and lower (b) insets of Fig. 4 show the frequency dependence of $\tan\delta(f)$ and $M''(f)$ at the several temperatures, respectively. The peak position and intensity can be obtained effortlessly from the distinct peaks in the insets. The main panel displays the Arrhenius plots of $(f_{\tan\delta})^2 / f_{M''}$ and $T(\tan\delta_{\max})^2 / M''_{\max}$ against $1/T$. The two perfect linear lines confirm the polaronic nature of the low-temperature segment of R1 stemming from the ionic diffusion in F_1 sublattice.

As aforementioned, there is a diffuse transition of the ion system from the dielectric (DE) state to super-ionic (SI) state in LaF_3 . It is naturally to infer that the F_1 ions act as

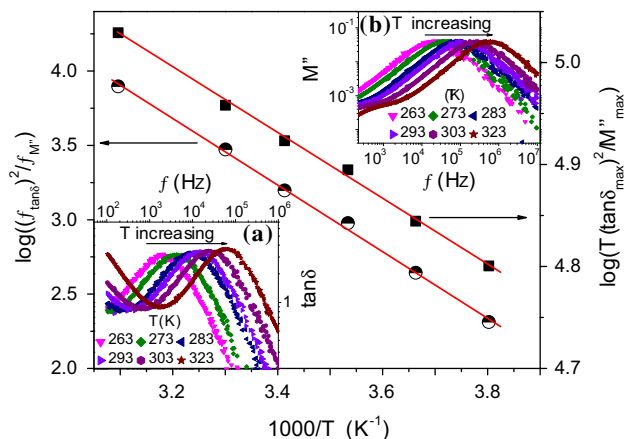


Fig. 4 The Arrhenius plots of $(f_{\tan\delta})^2 / f_{M''}$ (left) versus $1/T$ and $T(\tan\delta_{\max})^2 / M''_{\max}$ (right) versus $1/T$. The insets show the frequency dependence of $\tan\delta$ (a) and M'' (b) at several temperatures

localized carriers in the DE state, while it becomes delocalized carriers in the SI state, and the temperature range of ~ 323 to 343 K (shown in Fig. 3) is the transition region from DE state to SI state. To further verify the transition from the localized carriers to delocalized carriers, Fig. 5 compares the spectroscopic plots between the imaginary parts of the complex impedance (Z'') and complex electric modulus (M'' , which is defined as $M^* = j\omega C_0 Z^*$, where j is the imaginary unit of -1) for LaF_3 single crystal. A relatively significant mismatch between the peak position of Z'' and M'' can be seen at the temperature of 253 K (Fig. 5a). This confirms that the carriers are localized ones and have no contribution to long-range motion [20, 21]. Then the mismatch becomes smaller and smaller as the temperature increases until the two peaks forgather at ~ 323 K. The coincidence on the frequency scale for the Z'' and M'' peaks implies that the carriers are delocalized above the temperature of 323 K and can make contribution to long-range motion (i.e., conduction) [22, 23]. In this case, the imaginary parts of impedance and modulus can be expressed as

$$Z'' = R \left[\frac{\omega RC}{1 + (\omega RC)^2} \right]$$

and

$$M'' = \frac{C_0}{C} \left[\frac{\omega RC}{1 + (\omega RC)^2} \right] \quad (4)$$

Equation (4) indicates that when $\omega RC = 1$ is fulfilled, the spectroscopic plots of Z'' and M'' measured at fixed temperature should register peaks at the same frequency [24]. The result indicates that the low-temperature segment of R1 is related to the localized carriers, whereas the high-temperature segment of R1 is due to delocalized carriers. Consequently, the low-temperature segment of R1 is related to the ionic diffusion of the localized fluorine ions (short-range motion), while the high-temperature segment of R1 stems from the long-range motion of the delocalized fluorine ions. In concrete terms, the ions hopping of F_1 sublattice (long-range motion) is due to the effect of ionic exchange between F_1 and $F_{2,3}$ sublattices, i.e., the fluorine ions in $F_{2,3}$ sublattice jump into F_1 sublattice (the most mobile site) and then lead to the ions hopping within F_1 sublattice.

Origin of R2

We now turn our attention to the origin of the high-temperature relaxation (R2). To explore the mechanism of R2, we carried out impedance analysis, as it is a powerful technique to separate the interfacial effect from the bulk effect. Figure 6a–c display the Nyquist plot (Z'' vs.

Fig. 5 The spectroscopic plots of the impedance (Z'') and electric modulus (M'') at selected temperatures. The vertical lines indicate the peak positions in Z'' and M'' curves

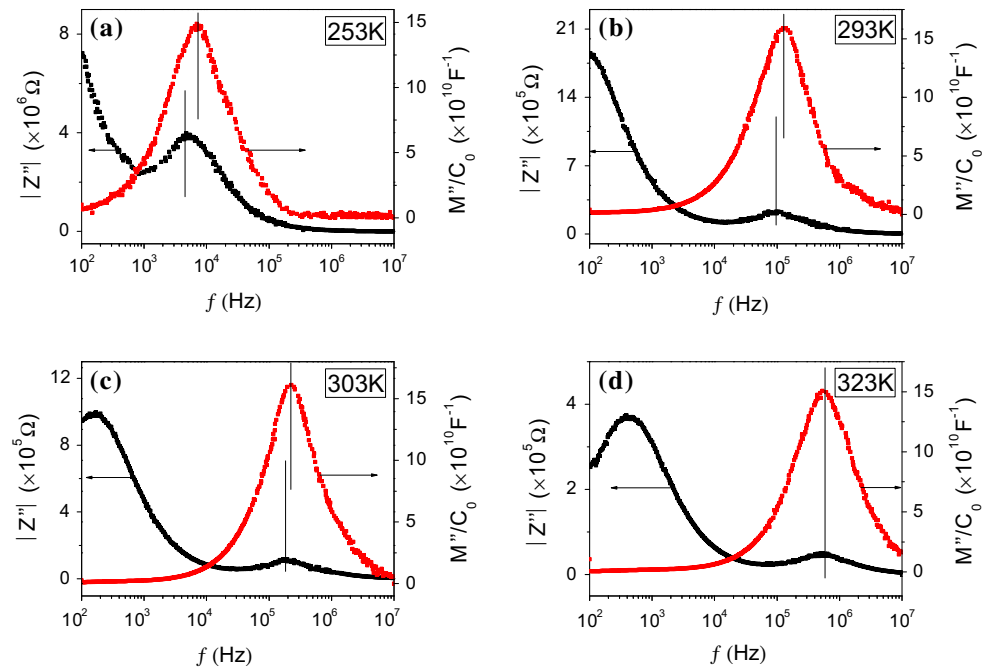
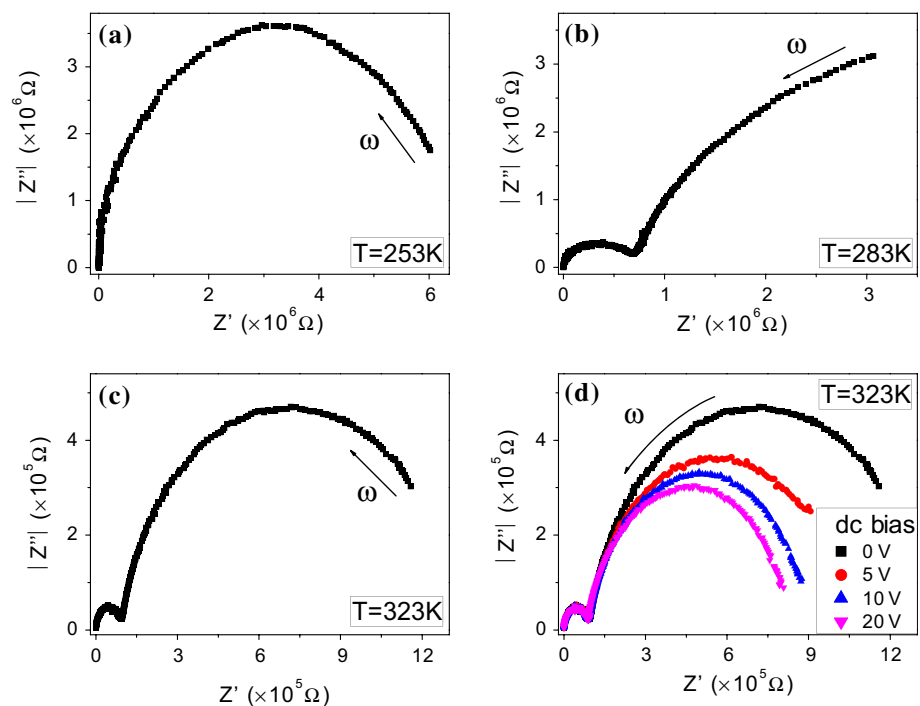


Fig. 6 **a–c** Complex impedance plots for LaF_3 single crystal at three selected temperatures. **d** Complex impedance for LaF_3 single crystal at 323 K under various dc biases



Z' , where Z' and Z'' are the real and imaginary parts of the complex impedance (Z^*) at selected temperatures. The plot obtained at 253 K shown in Fig. 6a shows one semicircle, which terminates at the origin point, indicating that only one relaxation appears at this temperature, which belongs to the bulk dielectric response [25]. When the temperature ascends to 283 K, apart from the semicircle, a second semicircular arc appears in the low-frequency range

(Fig. 6b). This indicates that an additional dielectric response from the sample/electrode contact comes into action. When the temperature is higher than 323 K, the low-frequency semicircular arc nearly develops to be a full semicircle (Fig. 6c). This finding confirms that there are two relaxation processes in the crystal with the first appeared relaxation being R1 and another one being the R2. This is to say that R2 can be inferred to be a Maxwell–

Wagner-type relaxation due to the sample/electrode contact. To demonstrate this inference, the Nyquist plot under various dc biases at 323 K is presented in Fig. 6d. One can clearly see that the semicircular arc in the high frequency range is independent of dc bias, whereas the low-frequency arc can be obviously depressed by the bias. This fact demonstrates that dielectric responses associated with the low- and high-frequency arcs are from interfacial and bulk contribution, respectively. Consequently, it is safely to conclude that R2 is a Maxwell–Wagner-type relaxation caused by sample/electrode contact.

The nuclear magnetic resonance investigation on the spin–lattice relaxation dispersion in LaF_3 revealed that, at the temperature of ~ 310 K, the exchange within the F_1 sublattice enters the fast motional limit [12]. With the temperature increasing, the ionic exchange between F_1 and $F_{2,3}$ sublattices starts [11] via the process of fluorine ions jumping into interstices and even onto the surface of the sample. The Arrhenius plot of R2 shows an inflection temperature of ~ 453 K. The low-temperature segment of R2 occurs in the temperature where the ionic exchange between F_1 and $F_{2,3}$ sublattices dominates the mobility. Since the sample-electrode contacts are usually associated with an energy barrier such as Schottky barrier, which leads to the active fluorine ions be blocked and induces a polarization there giving rise to the low-temperature segment of R2. However, at higher temperatures (above ~ 450 K), more and more ions in $F_{2,3}$ sublattice participate in the filling of interstices, and the internal mobility of $F_{2,3}$ sublattice also begins to take effect. To some extent, when the temperatures exceed ~ 450 K, sublattices of F_1 and $F_{2,3}$ are disordered [16], which leads to equivalence of the total fluorine ions. Therefore, the high-temperature segment of R2 can be attributed to the exchange of the fluorine ions among the three equivalent sublattices.

Generally, the Nyquist plot can be described by a double-layer model consisting of two RC (R = resistor and C = capacitor) units in series (inset of Fig. 7) with one for the bulk and another for the contact. Since the semicircle reaches its apex with the value of $Z'' = R_i/2$ at the frequency where $2\pi f R_i C_i = 1$ ($i = b, c$, representing the bulk and contact, respectively) is fulfilled (consult Eq. (4)) [26], we can easily deduce the resistance for the bulk and contact at different temperatures. It can be seen that the resistance for both bulk and contact follows the Arrhenius law which can be described as:

$$R = R_0 \exp(E_{\text{cond}}/k_B T), \quad (5)$$

where R_0 is the pre-exponential term and E_{cond} is the activation energy of conduction. The linear fits shown as straight lines in Fig. 7 reveal a transition temperature range of ~ 323 – 343 K for R1 and a crossover temperature of ~ 449 K for R2. These values (~ 323 to 343 K for R1 and

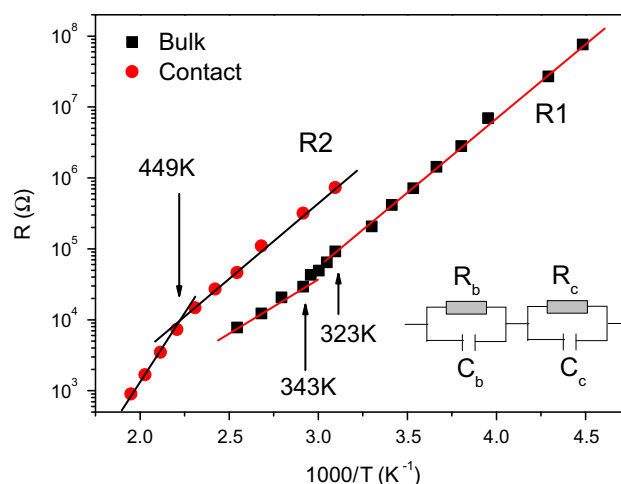


Fig. 7 The Arrhenius plots of R versus $1/T$ for the bulk and contact. The crossover temperatures were 323, 343, and 449 K (from right to left). The inset is the double-layer model for MW relaxation

~ 449 K for R2) are in good agreement with those obtained from the Arrhenius plots for the frequency-dependent loss tangent spectra (Fig. 3). The results indicate that the relaxation behavior actually reflects the conductivity behavior. The two linear segments of the resistance for the bulk yield the values of $E_{\text{cond}} = 0.421$, and 0.315 eV for the low- and high-temperature segments of R1, respectively. Since the localized charge carriers hopping between spatially fluctuating lattice potentials not only produce the conductivity effect but also give rise to dipolar effect, both effects have similar values of activation energy. The relaxation activation energy for the low- and high- T segments of R1, as expected, is close to E_{cond} of the grain, confirming the polaronic nature of R1. The activation energy of conduction E_{cond} is calculated to be 0.430 , and 0.676 eV for the low- and high-temperature segments of R2, notably deviate from the dielectric relaxation activation energy, owing to the fact that R2 is a Maxwell–Wagner relaxation instead of a polaron relaxation.

Origin of A

We now turn our attention to the anomaly in the curves of frequency-dependent $\tan \delta$, which appears in the temperature range above around 600 K. It is worth point out that another dielectric phenomenon—the high-frequency inductive effect—appears in this temperature range. The inductive effect can be clearly seen in Fig. 8, which illustrates the frequency dependence of the impedance at the selected temperatures. It is clearly seen that, when temperature is higher than ~ 600 K, a sharp impedance dips in the high frequency range indicative of the appearance of inductive effect. The inductive effect first moves to lower frequency and then moves toward higher frequency as the

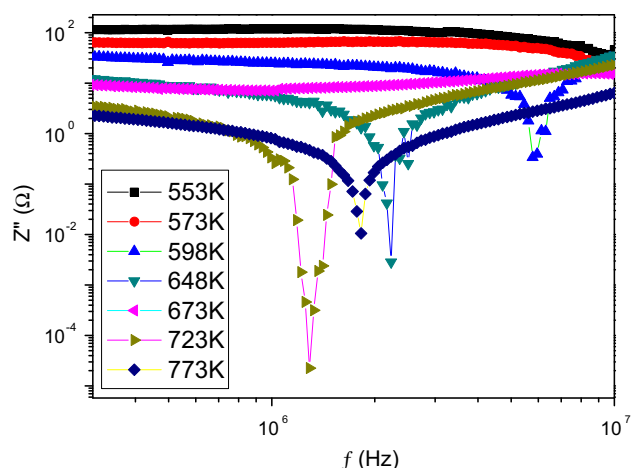


Fig. 8 Enlarged view of the frequency dependence of the impedance (Z'') obtained at various temperatures in the high frequency range

measuring temperature increases. This behavior is in good agreement with that of the anomaly found in the temperature domain, which strongly indicates that the high-frequency inductive effect underlies the dielectric anomaly. The origin of the inductive effect can be ascribed to the coupled electron-ionic inductive response as both drift and diffusion of electrons, holes, and ions are contributable to conductivity [27]. The exponential increase in $\varepsilon'(T)$ in the temperature above ~ 650 K (see Fig. 1a) leading to a remarkable background demonstrates the rapid increase in conductivity.

Conclusions

In summary, two dielectric relaxations and a dielectric anomaly labeled as R1, R2, and A in the order of ascending temperature were observed in LaF_3 single crystals. Both R1 and R2 show two linear segments in the Arrhenius plot. R1 was argued to be a polaronic relaxation with the low-temperature segment resulting from the ionic diffusion of localized fluorine ions in F_1 sublattice; and the high-temperature segment stemming from the fluorine ionic hopping in F_1 sublattice is due to the ionic exchange between F_1 and $F_{2,3}$ sublattices. R2 was confirmed to be a Maxwell–Wagner-type relaxation. The low- and high-temperature segments of are caused by the blocking of electrodes associated with the ionic exchange between F_1 and $F_{2,3}$ sublattices and the ionic exchange among the three nonequivalent sublattices, respectively. The anomaly is ascribed to the inductive effect arising from the coupled electron-ionic inductive response.

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