Dynamic dielectricity of multiferroic spinel CdCr$_2$S$_4$

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Abstract. Dynamic dielectric properties were studied on the newly discovered multiferroic spinel, CdCr$_2$S$_4$. Two single crystals, grown under the same condition but from different batches were used, which showed identical behavior. Frequency-dependent dielectric constant as a function of temperature ($\epsilon'(\omega)$) exhibits relaxation behavior only below ferromagnetic transition temperature, $T_C \sim 84$ K, which indicated that the charge dipoles were associated with ordered magnetic spins. By fitting with extended Debye model (Cole-Cole equation), the relaxation characteristic time ($\tau$) at different temperatures was obtained. When $55 < T < 84$ K, the $\tau$ value decreases with decreasing temperature. It is somehow unusual as it doesn’t obey the thermal activation model (Arrhenius law). These results suggest that the relaxation behavior is strongly affected by spin not by thermal fluctuation. Different ac voltages were also selected to study the field effect on the relaxation behavior. For $V_{ac} = 20$ V, $\epsilon'(\omega)$ dramatically changes and $\tau$ value becomes difficult to obtain as $T < 55$ K, suggesting that some unknown phases could exist below 55 K. Complex relaxation behavior below $T_C$ could be originated from the coupling among spin, lattice and dipole via exchange restriction.

1. Introduction
Chromium based spinel CdCr$_2$S$_4$ was discovered as an insulating ferromagnet from 1965.[1] Magnetic, electrical transport, thermal and optical properties indicated strong coupling between spin, dipoles and lattice degrees of freedom in this spinel.[2, 3, 4] Recently, CdCr$_2$S$_4$ had regained great attention because of its relaxor-type ferroelectricity and colossal magnetocapacitance.[5, 6, 7] However, Catalan and Scott suggested that relaxor multiferroic behavior were extrinsic, which resulted from the residual chlorine impurities reacted as an agent of chemical transport reaction for synthesizing the single crystals.[8] Furthermore, it was also claimed that these phenomena have not been observed on polycrystal sample made by solid state reaction. Nevertheless, grain boundary of polycrystal sample might cause high resistivity and affect the result of dielectric measurements. Therefore, the existence of relaxor ferroelectricity as well as magnetocapacitance is still an open issue. Studying the dynamical dielectric properties at different temperatures can provide more information to understand the interesting behavior of CdCr$_2$S$_4$.

In this work, the single crystal samples were grown by chemical vapor transport method with chlorine gas as transport gas. Two single crystals, grown under the same condition but from different batches, were used to perform the frequency- and temperature-dependent dielectric measurements. Two different ac voltages were selected for studying the relaxation behavior. Magnetic properties were confirmed by SQUID magnetometer(Quantum Design MPMS XL-7) and Curie temperature, $T_C$, was found to be at 84 K in the magnetic field of 50 Oe, similar
to the earlier reports.[5, 6, 7] A commercial LCR meter (Agilent 4980) equipped with closed-cycle refrigerator and temperature controller were used to measure the capacitance within the temperature region of 30 ~ 300 K. Dielectric constant was derived by using the equation of parallel capacitor: 

$$C = \varepsilon_0 \varepsilon_r \frac{A}{d},$$

where $\varepsilon_0$ is the dielectric permittivity of free space, $A$ is the electrode area, and $d$ is the separation length of electrode. Two single crystal samples showed nearly identical behavior in all measurements.

![Graphs showing dielectric curves at different temperatures](image)

**Figure 1.** Real part of frequency dependent dielectric curves at different temperatures. The upper and lower panels are measured with ac voltage level 2 V and 20 V, respectively. (a) and (e) show curves at 200 K ≤ $T$; (b) and (f) show curves at 85 ≤ $T$ ≤ 140 K; (c) and (g) show curves at 55 ≤ $T$ ≤ 80 K; (d) and (h) show curves at $T$ ≤ 50 K. The arrows in (a) and (e) show the evolution of $\tau_E$; those in (b),(c),(f) and (g) show the evolution of $\tau_1$; and that in (d) shows the evolution of $\tau_2$.

**2. Results and discussions**

Real part of frequency-dependent dielectric constant, $\varepsilon'(\omega)$, measured at various temperatures with ac voltage level 2 ($\varepsilon'_{2V}(\omega)$) and 20 V ($\varepsilon'_{20V}(\omega)$) is shown in Fig. 1. As the $\varepsilon'(\omega)$ curves are quite different and showed unique behavior in different temperature ranges, we separated the curves into four groups. With decreasing temperature, several interesting phenomena are observed. In Fig. 1(a) and (e), the $\varepsilon'$ value is large at low frequency and suddenly dropped down to very small value above certain frequency. This step-like feature could be attributed to the relaxation behavior (with characteristic relaxation time, $\tau_E$) of contact resistance between electrode and the sample at high temperatures. When temperature is decreased, this step is shifted towards the lower frequency, indicating the slowing down of the relaxation dynamics as expected for thermally activated processes. In the temperature range of 90 ≤ $T$ ≤ 200 K, the value of $\varepsilon'$ is very small and nearly frequency-independent. In Fig. 1(b) and (f), we can clearly
see that the value of $\epsilon'$ at low frequency again increased at $T_C \sim 85$ K, indicating another relaxation component with characteristic relaxation time, $\tau_1$. It is suggested that a dielectric relaxation showed up by the assistance of magnetic ordering. In the temperature range of 300-85K, the $\epsilon'(\omega)$ curves for different ac voltage levels show similar behavior, but they become distinguishable as $T \leq 80$ K. First, we focus on $\epsilon'_2(V)$. In Fig. 1(c), we can see the blue-shift behavior of the relaxation ($\tau_1$) with decrease of temperature, which is finally shifted out of our measuring frequency range. In addition, a diverge character of $\epsilon'$ at low frequency is seen, which could be related with the contribution of dc conductivity. Finally, in Fig. 1(d), another small relaxation component ($\tau_2$) can be hardly seen, where the dc conductivity still dominates the dielectric constant value at low frequency region.

![Figure 2](image2.png)

**Figure 2.** A typical fitting result with Cole-Cole relation of complex impedance spectrum.

![Figure 3](image3.png)

**Figure 3.** Temperature dependence (inverse $T$ scale) of $\tau_1$.

As shown in Fig. 2, the arrow indicates the frequency of the relaxation where $\epsilon'$ and $\epsilon''$ show an inflection and a peak, respectively. We use Cole-Cole relation to fit the complex impedance spectrum at temperatures between 55 and 85 K. The general form of Cole-Cole relation which includes a residual dc-conductivity part is shown in the inset of Fig. 2.[9] An additional relaxation component is used to fulfill the low frequency part, which has a very long relaxation time. The obtained $\tau_1$ values are plotted in Fig. 3 as a function of $1/T$ with a logarithmic y-axis. Therefore, if this relaxation is Arrhenius-type, the variation of $\tau_1$ with a logarithmic y-axis.

The low temperature character of $\epsilon'_2(V)$ curves exhibit different behavior compared to $\epsilon'_2(V)$. In Fig. 1(g), the $\tau_1$ relaxation is also shifted toward higher frequency with decreasing temperature. However, $\tau_1$ value for $V_{ac} = 20$ V decreases slowly compared to that of $V_{ac} = 2$ V as shown in Fig. 3. Another significant change is that the dielectric constant is strongly
suppressed when temperature is lower than 50 K (see in Fig. 1(h)), which is nearly ~ 100 times smaller than that of 55 K. In addition, the $\tau_1$ relaxation disappears at $T < 50$ K, therefore, the $\epsilon'_{20}(\omega)$ curves become similar to those at $90 \leq T \leq 200$ K. The sudden change between Fig. 1(g) and (h) indicates that the mechanisms of dielectric property are different, suggesting a possible transition temperature at $T \sim 55$ K. In our previous temperature dependent ($\epsilon'_f(T)$) study, a field-induced dielectric peak, $T_p$, was observed around 54 K which is consistent with the present result.[10]

Compared to Hemberger and Lunkenheimer’s reports, we observe the complex relaxation behaviors below $T_C$ but there are some significant differences.[5, 6, 7] They found two kinds of relaxation phases below $T_C$, but the boundary temperature is 28 K which is much lower than ours. In addition, below 28 K, they still observed the $\tau_1$ relaxation which in our case is absent. With the application of higher ac voltage, there is a transition around 55 K below which $\tau_1$ relaxation is hardly observed. It is worth to mention that Lunkenheimer’s observation did not show such electric-field-dependent properties. Although these differences between Lunkenheimer et al. and ours could be arose from the different samples, which seems to support that these dielectric properties are extrinsic in nature. However, the complex behavior related to the interplay of spin, dipole and lattice in CdCr$_2$S$_4$ is worth to further investigate. As Catalan and Scott suggested that these properties could be related to chlorine-based impurities or sulfur deficiency, further studies are needed.

3. Summary
We performed frequency-dependent dielectric measurements as a function of temperature on single crystal CdCr$_2$S$_4$. When $T < T_C$, a dielectric relaxation component is observed, suggesting the magnetic ordering assists the release of charge dipoles. At $T < 54$ K, this relaxation component is suppressed by higher ac voltage, indicating the dipoles are freezed by higher voltage and a field-induced phase is proposed. Our result has significant difference with previous studies,[5, 6, 7] indicating the dielectric property could be sample dependent. Since the complex dielectric properties are suggested to be arose from chlorine-based impurities or sulfur deficiency, our studies on different impurity content and the doping effect are in progress.

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