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Dielectric Relaxation in RS–ARS

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Dielectric relaxation in mixed crystals of Rochelle salt and ammonium Rochelle salt ($Na[K_{1-x}(NH_4)_x]C_4H_4O_6 \cdot 4H_2O$) with various compositions (x=0, 0.04, 0.09, 0.28, 0.40, 0.80) has been measured in the freqency region from 100Hz to 10GHz at temperatures from 4.2K to 290K. It is indicated that the dielectric relaxation observed in the frequency range between 100Hz and 1KHz for the quenched sample (x=0.80) at temperatures around 30K is connected with the well known relaxation observed at microwave frequencies. On the other hand, the sample of x=0 doesn't have such low frequency relaxation. A discussion is made to explain the fact. Finally, the distribution of relaxation time observed in the low frequency region is discussed together with on that observed for the relaxation in the microwave frequency region.

I. INTRODUCTION

Rochelle salt (RS) is a well-known ferroelectric substance in which the spontaneous polarization appears between two transition points along the ferroelectric a-axis. Frequency dependence of the complex dielectric constant along the a-axis in the microwave frequency region indicates a Debye-type dielectric relaxation [1–3]. This relaxation shows critical slowing-down behavior around the two transition points. Because of that, it has been sometimes considered that the ferroelectric phase transitions of RS are the order-disorder type. However, the mechanisum of the phase transition is still unclear.

The mixed crystal of RS and ammonium Rochelle salt (ARS), $RS_{1-x} - ARS_x$, changes its nature with the composition x, successively. The range of the composition can be devided into four regions [4]. In the region I, $0 \leq x \leq 0.025$, the ferroelectric phase appears between two transition points. With increasing x, these points come closer, and then the ferroelectric phase disappears. In region II, $0.025 < x < 0.18$, only the paraelectric phase exists. In the region III, $0.18 \leq x \leq 0.9$, another ferroelectric phase with the spontaneous polarization along a-axis shows up. In this case, there is only one transition point. In the region IV, there is a ferroelastic phase with the spontaneous polarization along the b-axis.

This system with such a complicated phase diagram is considered not only to be just an interesting target of study but also to be useful to understand RS.

We have studied the mixed crystal system by dielectric point of view. It has been shown, in our previous paper [5], that the mean field approximation is valid to explain the temperature dependence of the dielectric relaxation strength and time obtained for the relaxation observed at microwave frequency range. When we apply this approximation to the observed dielectric relaxation, elementary process of the dipolar relaxation is evaluated. We have reported that the process in the region I is somewhat different from that in the region III.

In this study, dielectric relaxation measurment on the sample x=0.40 at microwave frequencies has been made in addition to previous ones on x=0, 0.04, 0.09 and 0.28. It is shown that the x dependence of the elementary process is more clear. On the other hand, dielectric relaxation measurment at radio frequency region has been performed on a quenched sample (x=0.80) at temperature range around 40K. It is suggested that very broad relaxation observed in this measurment has the same origin of the relaxation in the microwave frequency range at higher temperatures. Finally, discussion is made on the distribution of relaxation times so as to be a nature of mixed crystals.

II. EXPERIMENTAL

The complex dielectric constants were measured in the frequency range between 50MHz to 10GHz at temperatures from 170K to 290K for x=0, 0.04, 0.09, 0.28, 0.40. In these measurments, a transmission line method was employed by use of a network analyzer (HP8510B). Details of the measuring system will be reported elsewhere. The measurments were done in a condition with a constant heating rate (0.402K/min). In order to obtain the starting temperature, the sample was cooled from a room temperature taking a time period of 6 hours. On the other hand, in the frequency range between 100Hz to 1MHz, complex dielectric constant was measured by use of a LCR meter (HP4284A) for x=0, 0.80. In this case, the heating-up process was also used. However, the sample was quenched from the room temperature down to the liquid herium temperature before the measurments.

III. RESULT AND DISCUSSION

In the microwave frequency regions, a Debye type dielectric relaxation is observed for all the compositions x as it has been reported in our previous paper [5] and by other workers [1–3]. Frequency dependence of the complex dielectric constants $\varepsilon^*(\omega)$ thus can be described by the Cole-Cole function [6],

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\triangle\varepsilon}{1+(i\omega\tau)^\beta}$$

$$\triangle\varepsilon = \varepsilon_s - \varepsilon_\infty$$

where ε_∞ is the high freqency limiting dielectric constant, ε_s is the static dielectric constant, $\triangle\varepsilon$ is the relaxation strength, τ is the relaxation time, β represents the distribution of τ with $0 < \beta \leq 1$, and ω is an angular freqency. The Cole-Cole function with β=1 gives the Debye function.

The temperature dependences of $\triangle\varepsilon$ and τ, for x=0, 0.09, 0.28, given by using the least square fit, are shown in Figs. 1(a) and 1(b). A sharp peak is observed for both $\triangle\varepsilon$ and τ. A critical slowing down behavior is observed in the temperature range around the transition point for x=0.28, 0.40. Similar behavior is found for x=0. For x=0.04 and 0.09, however, these parameters show a broad peak. It should be noted that, even in those cases, we still have critical-like behavior. As we have already reported, all the temperature dependences of $\triangle\varepsilon$ and τ in Figs. 1(a) and 1(b) are similar to each other, and it has been estimated that the mean field approximation is applicable to the process of these relaxation.

It has been found that for x=0, 0.04, 0.09, the dielectric dispersion is of monodispersive in the paraelectric and even in the ferroelectric phase of RS. For x=0.28, 0.40, the observed relaxation is almost of the Debye-type in the paraelectric phase. However, it turns to of the Cole-Cole type at temperature slightly above the transition point, and the value of β decreases with decreasing temperature in the ferroelectric phase as shown in Fig. 1(c).

On the other hand, as the results of the measurments in low frequency regions, one broad dielectric relaxation for x=0.80 is observed in the temperature range between 20K and 40K. Again we have fitted the frequency dependence of the complex dielectric constant for x=0.80 by use of the Cole-Cole function, and it is found that these relaxation is well explained by that function as we have just seen in the high frequency range. However, in contrast to the case of the high frequency range, the values of β are extremely low as shown in Fig. 2(c).

The temperature dependences of $\triangle\varepsilon$ and τ at low temperature for x=0.80 by using the least square fit are shown in Figs. 2(a) and 2(b). It has been found that the value of $\triangle\varepsilon$ is small and increases slowly with decreasing temperature. The value of τ rapidly increases with decreasing temperature.

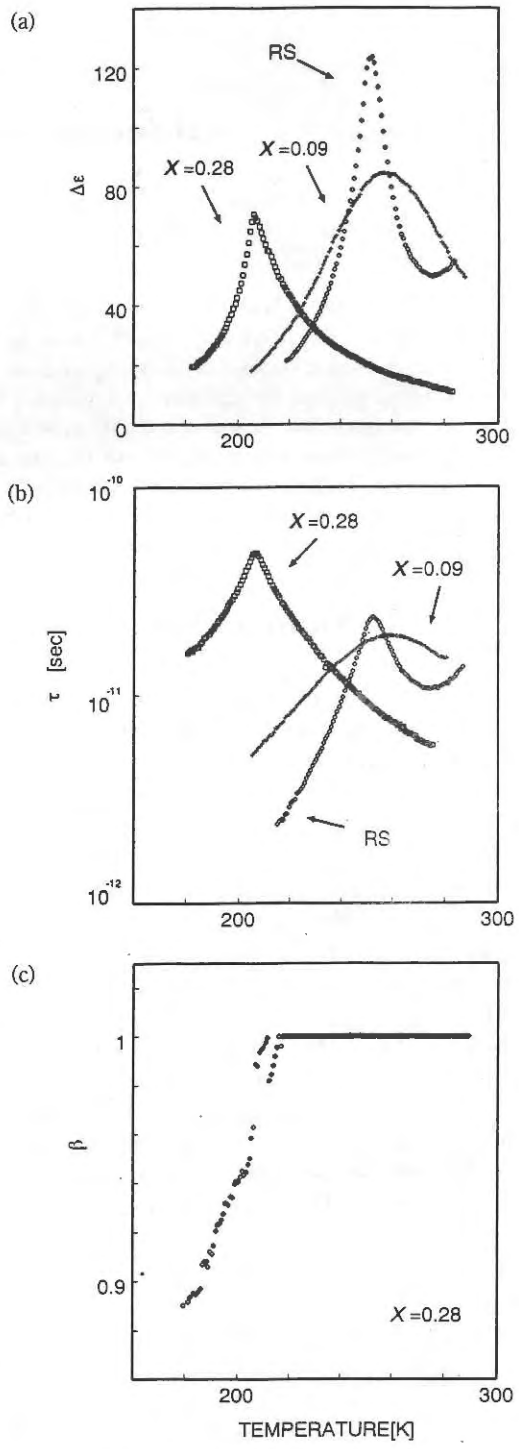

Fig. 1. Temperature dependence of $\triangle\varepsilon$ for x=0, 0.09, 0.28 (a), τ for x=0, 0.09, 0.28 (b) and β for x=0.28 (c).

Using the mean field approximation [7], the relaxation time is represented as

$$\tau = \tau_0 \triangle\varepsilon$$

where τ_0 is the microscopic relaxation time for the elementary process of dipolar relaxation. The temperature dependence of τ_0 is shown in Fig. 3(a) for the microwave frequency region. Each plot follows nearly straight line

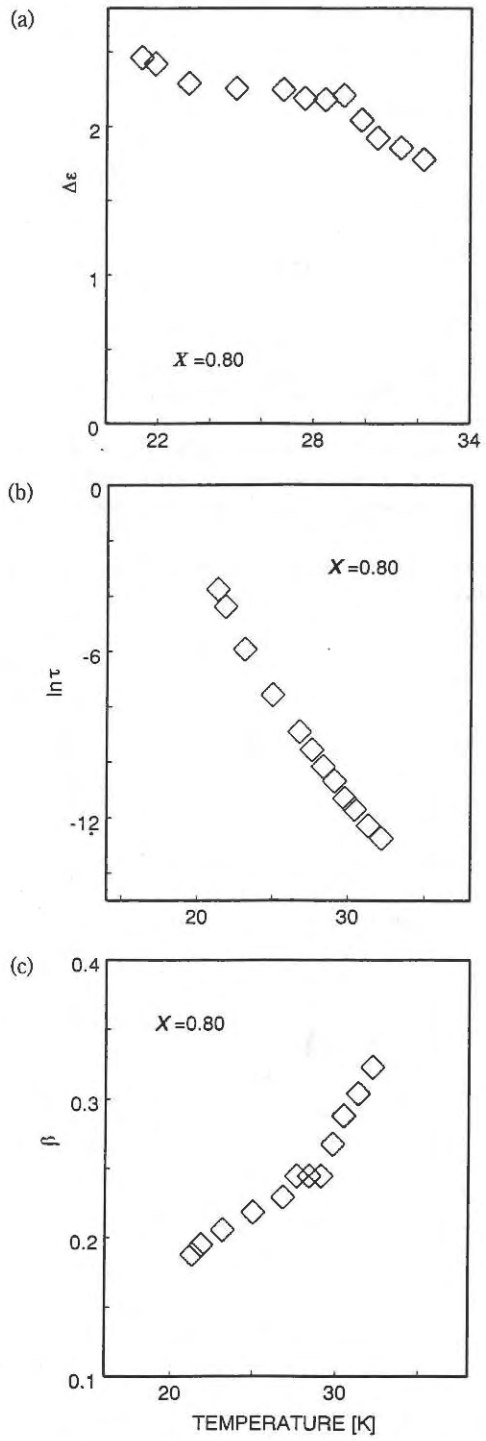

Fig. 2. Temperature dependence of $\Delta\varepsilon$ (a), τ (b) and β (c) for x=0.08.

and no critical behavior is seen. This indicates that the mean field approximation is usable in the regions I, II, and III.

Considering the double minimum potential model to explain the elementary process of dipolar relaxation, the microscopic relaxation time τ_0 is represented as

$$\tau_0 = C\exp(\frac{\Delta U}{kT}) \quad C : \text{constant}$$

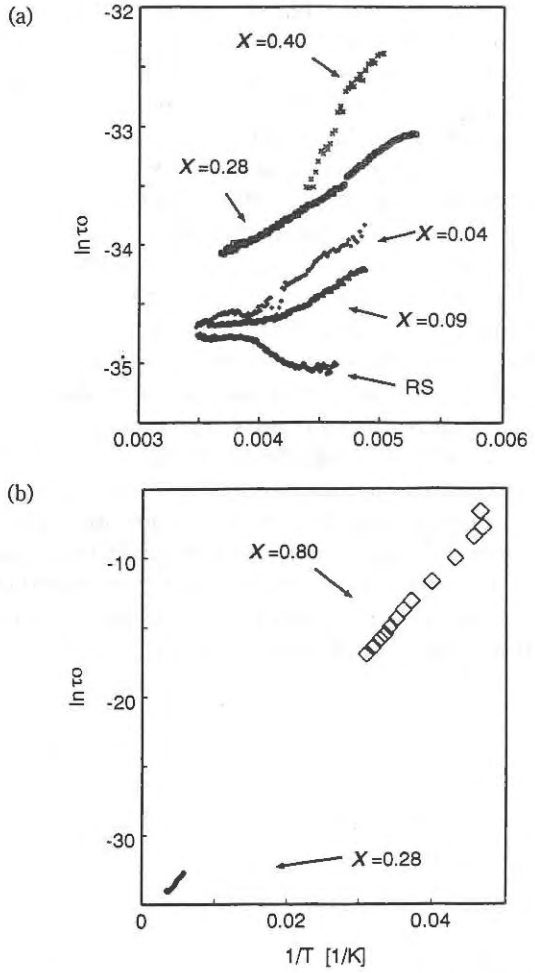

Fig. 3. Plots of τ_0 against $1/T$ for x=0, 0.04, 0.09, 0.28, 0.40 (a) and x=0.28, 0.80 (b).

where k is the Boltsmann constant, ΔU is the potential barrier height. As shown in Fig. 3(a) the values of ΔU for x=0.28, 0.40 are positive. The values for x=0.04 and 0.09 are also positive even the slope of the plots of $ln\tau_0$ against $1/T$ in the higher temperature range is very small. The slopes tend to increase as decreasing temperature. Finally, the positive values of ΔU can be considered to be characteristic feature of the regions II and III. It can be considered that this model is applicable to the process for x in the regions II and III. It should be pointed out that the value of ΔU increases with increasing x in the region III.

In contrast to the region II and III, the slope for RS is negative. This means that the double minimum potential model is not applicable in the region I. It can be considered that there is a qualitative difference between the relaxation proccesses in the regions I and III.

It should be pointed out that, in the region III, we also have dielectric relaxation processes in the cases of the quenched samples. Moreover, the Arrhenius plots in the low frequency region are in quite good agreement with those in the high frequency region as shown in Fig.

3(b). This fact suggests that all the relaxation observed in the region III has the same origin.

No dielectric relaxation has been observed at the low frequency region for RS. This fact would be corresponding to the negative value of $\triangle U$.

The distribution of the relaxation times in this mixed crystals was first reported by Horioka *et al* [8]. According to their results, the value of β depends on x but not much depends on temperature. In this work, the value of β for x=0.28 decreases with decreasing temperature in the temperature range from a point little above the transition point. However, the value of β doesn't differ very much in this case. This may be the reason of such difference. Figure. 2(c) suggests that the value of β approaches to unity at a significantly high temperature. It should be pointed out that the behavior of β in Fig. 1(c) is seen to be corresponding to this suggestion. The fact that the value of β decreases with decreasing temperature suggests the distribution of τ_0 is due to the distribution of $\triangle U$. It is possible to consider that this distribution comes from that the sample is mixed crystal as pointed out by Horioka *et al* [8].

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