Dielectric Properties of (NMt4)(NEt4)CoX4(X:Co,Br) Type Crystals

Dielectric Properties of $(NMt_4)(NEt_4)CoX_4$(X : Cl, Br) Type Crystals

Nagahide IZUMI

Institute of Physics, Faculty of Education
Kanazawa University, Kakuma, Kanazawa, 920

Abstract

Single crystal $(NMt_4)(NEt_4)CoCl_4$ and $(NMt_4)(NEt_4)CoBr_4$ were grown by slow evaporation method and dielectric constant have been measured over a temperature range from −190°C to 50°C. Two phase transition points, −165°C and −171°C, have been observed for $(NMt_4)(NEt_4)CoCl_4$ crystal. For $(NMt_4)(NEt_4)CoBr_4$ crystal, two phase transition points, −163°C and -178°C, were also observed and moreover found that this temperature region were ferroelectric phase.

$ Introdution

The crystal of tetramethylammonium (hereafter the fomula $N(CH_3)_4$ is abbreviated as NMt_4) tetrachlorocobaltate $(NMt_4)_2CoCl_4$ undergoes successive phase transition at about −151, −81, 3.0, 4.6, 7.1 and 20°C on heating and shows the ferroelectricity in temperature range between 4.6°C and 7.1°C.[1)~3)] These phase are denoted as I, II, III, II′, IV, V, VI in the order of decreasing temperature. The structure of these phase are as follow, phase I is *Pnmc*, phase II and II′ are incommensurate, phase III shows commensurate accompanied with ferroelectricity along *a* axis and space group is $P2_1cn$, phase IV shows commensurate (space group P112/n), phase V is $P12_1/c1$ and phase VI is orthorhombic with space group $P2_12_12_1$.

On the other hand, the crystal of tetraethylammonium (hereafter the fomura $N(C_2H_5)_4$ is abbreviated as NEt_4) tetrachlorocobaltate $(NEt_4)CoCl_4$ undergoes phase transition at about −53°C.[4)] The phases are denoted as I, II in order of decreasing temperature. Space group of phase I is $P4_2/nmc$.

The crystal of $(NMt_4)_2CoBr_4$ undorgoes phase transition at about 14.7°C and two phases are denoted as I (space group *Pncm*) and II (space group $P12_1/c1$).[5)~7)] The crystal of $(NEt_4)_2CoBr_4$ undergoes phase transition at about 9°C and two phases are denoted as phase I (space group $P4_2/nmc$) and II. $(NMt_4)CoCl_4$ crystal have successive phase transition but $(NMt_4)CoBr_4$

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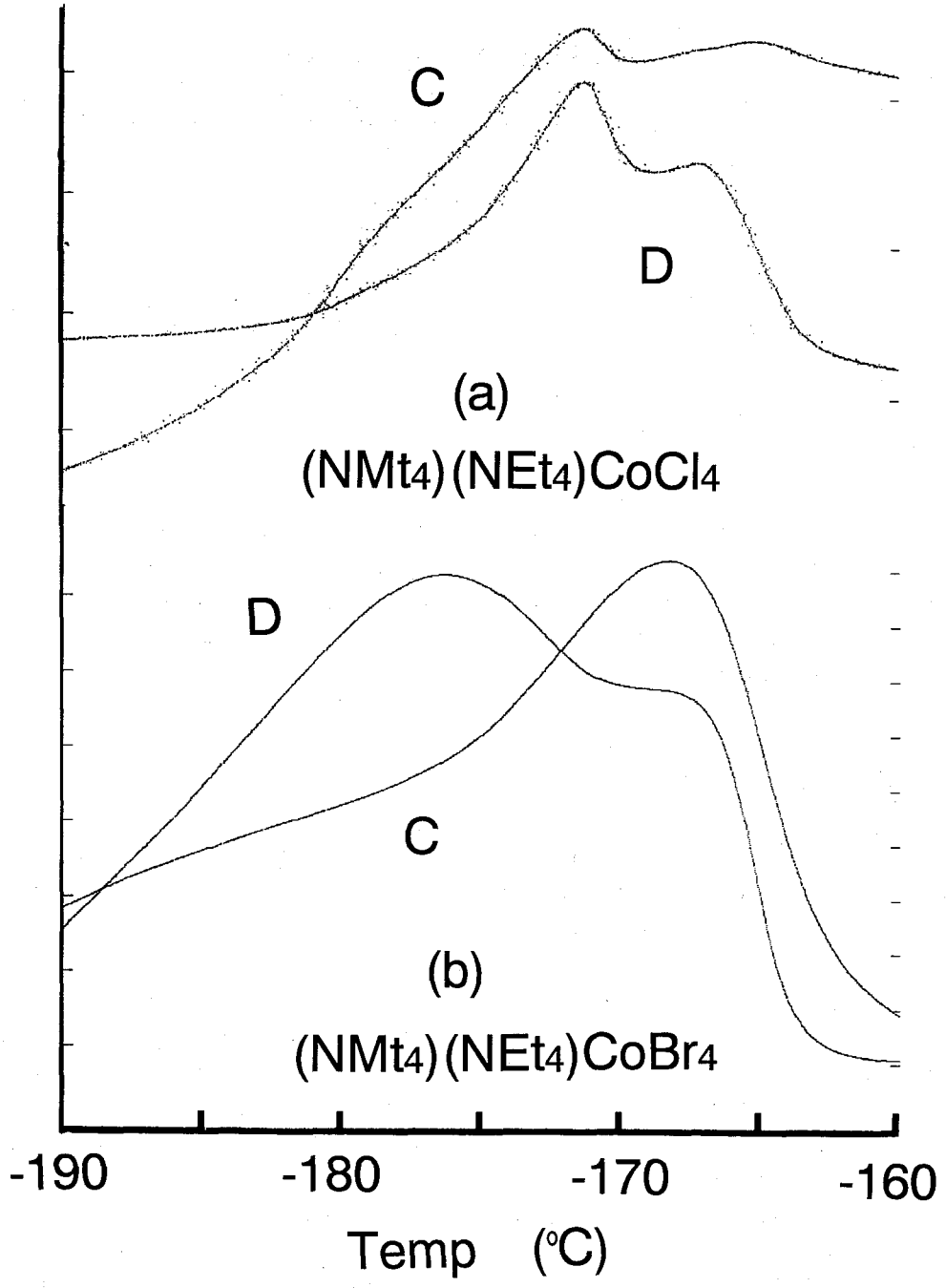

Fig. 1 Capacitance C and dielectric loss D (a) for $(NMt_4)(NEt_4)CoCl_4$ crystal, and (b) for $(NMt_4)(NEt_4)CoBr_4$ crystal, respectively.

has one simple second order phase transition, $(NEt_4)_2CoCl_4$ and $(NEt_4)_2CoBr_4$ have one simple first order phase transition.[8)]

A study of $(NMt_4)(NEt_4)CoX_4$ mixed crystal system seems, therefore, to be particular

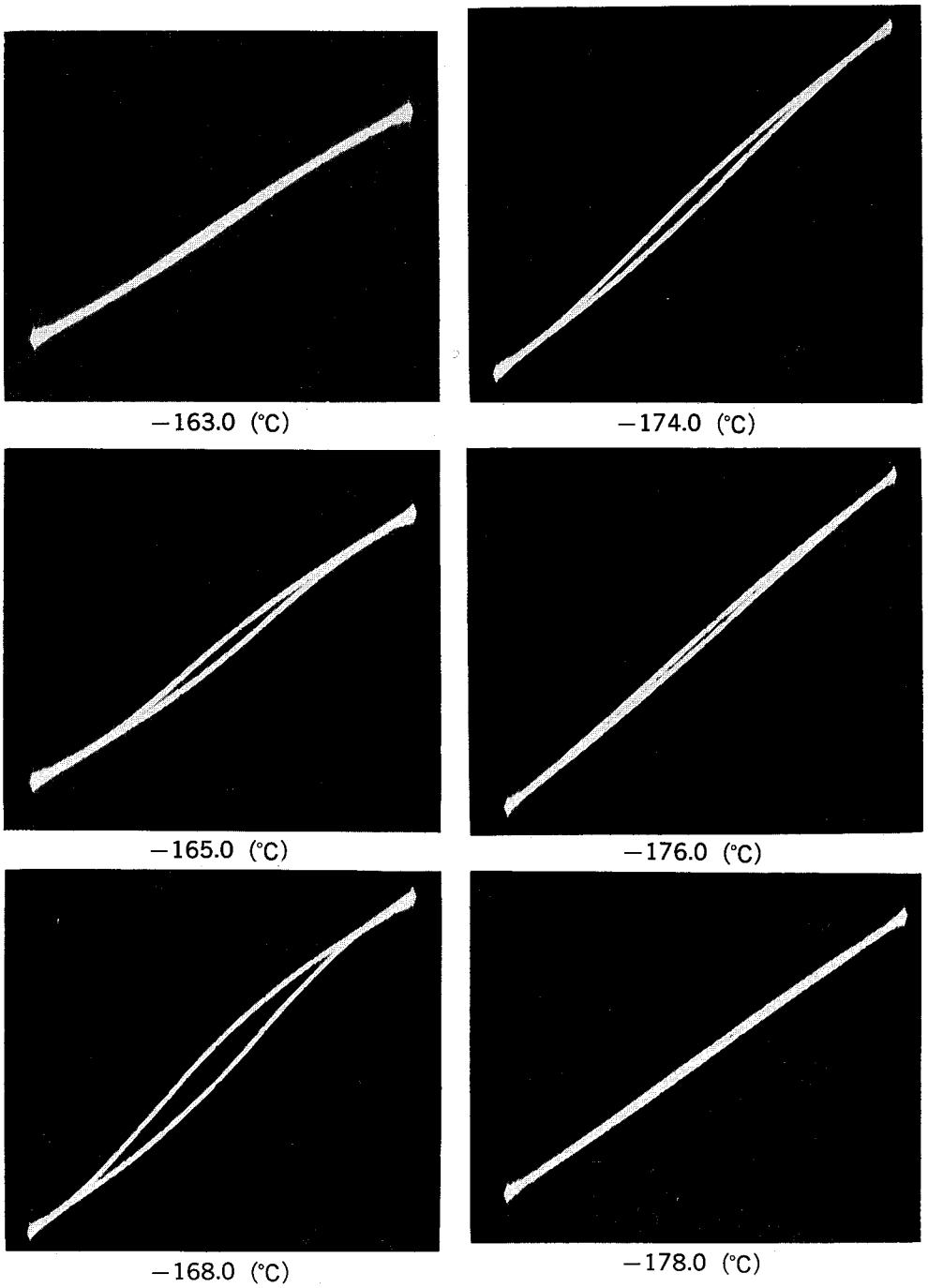

Fig. 2 D-E hysteresis for $(NMt_4)(NEt_4)CoBr_4$ crystal in the temperature region from −163°C to −178°C.

Table 1　Phase diagram of $(NMt_4)(NEt_4)CoCl_4$ and $(NMt_4)(NEt_4)CoBr_4$.

$(NMt_4)_2CoCl_4$	$(NEt_4)_2CoCl_4$	$(NMt_4)(NEt_4)CoCl_4$	$(NMt_4)_2CoBr_4$	$(NEt_4)_2CoBr_4$	$(NMt_4)(NEt_4)CoBr_4$
I Pncm			I Pncm	I	
— 20℃ —			— 14.7℃ —	$P4_2/nmc$	
II (I.C)				— 9 ℃ —	
— 7.1℃ —					
III $P2_1cn$ (F)					
— 4.6℃ —	I $P4_2/nmc$		II		
II′ (I.C)			$P12_1/c1$	II	
— 3.0℃ —					
IV $P112/n$ (C)	— −53℃ —				
— −81℃ —		— −165℃ —			— −163℃ —
V $P12_1/c1$	II				(F)
— −151℃ —		— −171℃ —			— −178℃ —
VI $P2_12_12_1$ (C)					

interest. In this paper, we report the dielectric properties of $(NMt_4)(NEt_4)CoCl_4$ and $(NMt_4)(NEt_4)CoBr_4$.

$. 1 Experimental

Single crystal $(NMt_4)(NEt_4)CoCl_4$ was prepared from aqueous solution by slow evaporation method at 30°C. At first, the crystal of $(NMt_4)_2CoCl_4$ was obtained from stoichiometric proportion of $N(CH_3)_4Cl$ and $CoCl_2$, and $(NEt_4)CoCl_4$ was also obtained from $N(C_2H_5)_4Cl$ and $CoCl_2$. These crystals were reduced to powder, and mixed in stoichiometric proportion.

Single crystal of $(NMt_4)(NEt_4)CoBr_4$ was grown as similar way to $(NMt_4)(NEt_4)CoCl_4$.

The crystals for dielectric measurement were polished with wet filter paper which was soaked with methanol and water. Typical size of specimens were about 0.05cm in thickness and 1 cm^2 in area. Ag paste was used as electrodes. Dielectric constant and loss were measured with LCR meter, YHP-4285A, at a constant frequency 1.00 MHz. which was controled by computer (NEC PC-9801DA) over a temperature range from −190°C to 50°C. Typical changing rate of temperature during the measurement was about 19k/hour. The 60 Hz D-E hysteresis loop was observed by Sawyer-Tower circuit.

$. 2 Results and Discussion

Typical results of capacitance C and dielectric loss D for (100) plate of $(NMt_4)(NEt_4)CoCl_4$ and $(NMt_4)(NEt_4)CoBr_4$ crystals were shown in Fig. 1. In $(NMt_4)(NEt_4)CoBr_4$ crystal, two transition points were found, one was about −163°C and another was −178°C. In this temperature region, D-E hysteresis loop was observed as shown in Fig. 2. This result shows that the temperature region between −163°C to −178°C in $(NMt_4)(NEt_4)CoBr_4$ crystal is ferroelectric phase. For $(NMt_4)(NEt_4)CoCl_4$ crystal, howeve, D-E hysteresis loop was not observed in the temperature region from −165°C to −171°C. The phase diagram of $(NMt_4)(NEt_4)CoCl_4$ and $(NMt_4)(NEt_4)CoBr_4$ were shown in Table 1.

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