Dielectric Properties of {N(CH3)4}2CoCl4-xBrx Crystals

Dielectric Properties of $\{N(CH_3)_4\}_2CoCl_{4-x}Br_x$ Crystal

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Abstract

Dielectric constant and differential scanning caloriemetry signal of $\{N(CH_3)_4\}_2CoCl_{4-x}Br_x$ type crystals where x is varied from 0 to 4.0 by 0.1 step were measured over the temperature range from −190°C to 50°C. The $x-T$ phase diagram of the mixed crystal system are determined. The phase I (P*mcn*) in $\{N(CH_3)_4\}_2CoCl_4$ shows a complete miscibility with phase I (P*mcn*) in $\{N(CH_3)_4\}_2CoBr_4$. A ferroelectric D−E hysteresis loop was observed in chlorine rich compound less than $x=0.4$ (phase III). An incommensurable phase II and II′ appears on the two sides of the ferroelectric area. Around $x\sim3$ a complicated triple point exists.

§ Introduction

Tetramethylammonium-tetrachlorocobaltate $\{N(CH_3)_4\}CoCl_4$ (hereafter $N(CH_3)_4$ is abbreviate as TMA) crystal undergoes successive phase transitions at about −151°C, −81°C, 3.0°C, 4.6°C, 7.1°C and 20°C and shows the ferroelectricity in temperature range between 4.6 °C and 7.1°C. These phases are denoted as I, II, III, II′, IV, V and VI in order of decreasing temperature.[1-3]

The structure of phase I is orthorhombic P*mcn*, phase II and phase II′ are incommenturate with $c\sim5c_0$ (where c_0 is c in phase I) and phase III is commensurate with $c=5c_0$, accompanied with the ferroelectricity along the a axis. The space group of phase III is $P2_1cn$. The phase IV and phase V are monoclinic structure. The phase IV ($P112/n$) shows commenturate with $c=3c_0$, while phase V ($P12_1/c1$) does not show lattice modulation. The lowest temperature phase VI is orthorhombic structure ($P2_12_12_12_1$) and shows commensurate with $c=3c_0$. While the tetramethylammonium-tetrabromocobaltate $(TMA)_2CoBr_4$ has one simple second-order phase transition at approximately 14.7°C. The two phases are denoted as phase I (P*ncm*) and phase II ($P12_1/c1$) in order of decreasing temperature.[4-6] The phase transition sequences of $(TMA)_2CoCl_4$ and $(TMA)_2CoBr_4$ crystals are shown in Table I. A study of $(TMA)_2CoCl_4$-$(TMA)_2CoBr_4$ system seemed therefore to be particular interest. In this paper, we report anomalous temperature dependence of the dielectric constants and (x-T)

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phase diagram of $(TMA)_2CoCl_{4-x}Br_x$ mixed crystal system.

§.1 Experimental

Single crystals of $(TMA)_2CoCl_{4-x}Br_x$ where x is varied from 0 to 4.0 by 0.1 step were prepared from aqueous solution containing (TMA)C1, (TMA)Br, $CoCl_2$ and $CoBr_2$ in desired proportions by slow evaporation method at 30°C. The composition was determined by means of elemental analysis for $x=0$, 1.0, 2.0, 3.0 and 4.0.[7] Other bromide compositions x were estimated by mixed ratio. Obtained crystals are prism-like pillar elongated along the c axis, and cleaving along the b plane as shown in Fig. 1. Their color is changed from cobalt blue to moss green with increasing x. The specimens for dielectric measurement were polished with wet filter paper which was soaked with methanol and water. (100), (010) and (001) plates were prepared and its typical size of specimens were about 0.05cm thick and 0.15~0.50 cm² in area. Ag paste was used as electrodes. The dielectric mesurement at constant freguency of 1.00 MHz and constant applied field 20V/cm were measured using LCR meter (HP 4285A) which was controlled using a computer (NEC PC9801DA). The samples were cooled and heated using a thermal programmable controller (ULVAC HPC-7000) over the temperature range from −190°C to 50°C. The rate of change of temperature was 19k/h. DSC signals were measured using DSC-10 (SEIKO) over a temperature range from −150°C to 200°C and typical temperature changing rate was 3K/min. The 60Hz D-E hysteresis loop was observed using Sawyer-Tower circuit.

$\{N(CH_3)_4\}_2CoCl_4$	Transition	$\{N(CH_3)_4\}_2CoBr_4$	Transition
I (Pmcn) $c=c_0$		I (Pmcn) $b=b_0$	
	20°C		
II (INC) $c \fallingdotseq 5c_0$			
	7.1°C		
III ($P2_1cn$) $c=5c_0$			
	4.6°C		
II′ (INC) $c \fallingdotseq 5c_0$			
	3.0°C		14.7°C
IV ($P112_1/n$) $c=3c_0$		II ($P12_1/c1$) $b=b_0$	
	−81°C		
V ($P12_1/c1$) $c=c_0$			
	−151°C		
VI ($P2_12_12_1$) $c=3c_0$			

Table I　Phase transition sequences of $(TMA)_2CoCl_4$ and $(TMA)_2CoBr_4$.

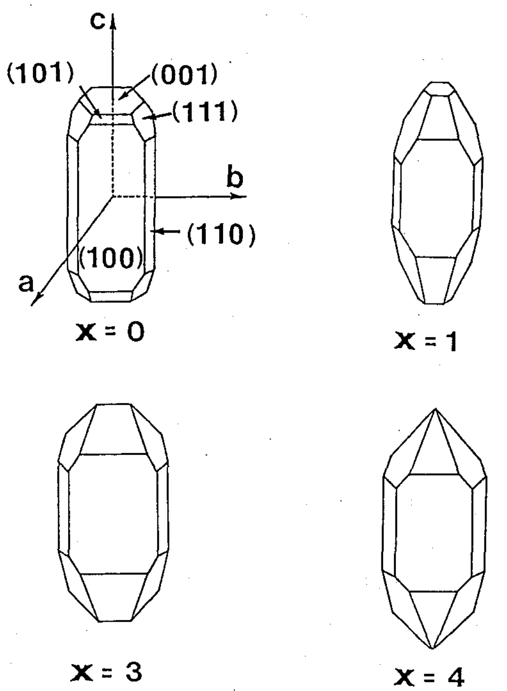

Fig. 1　Typical shapes of $(TMA)_2CoCl_{4-x}Br_x$ crystals.

§.2 Results and Discussion

The obtained results of dielectric constant in a composition range up to $x=1.4$ for (100) plate

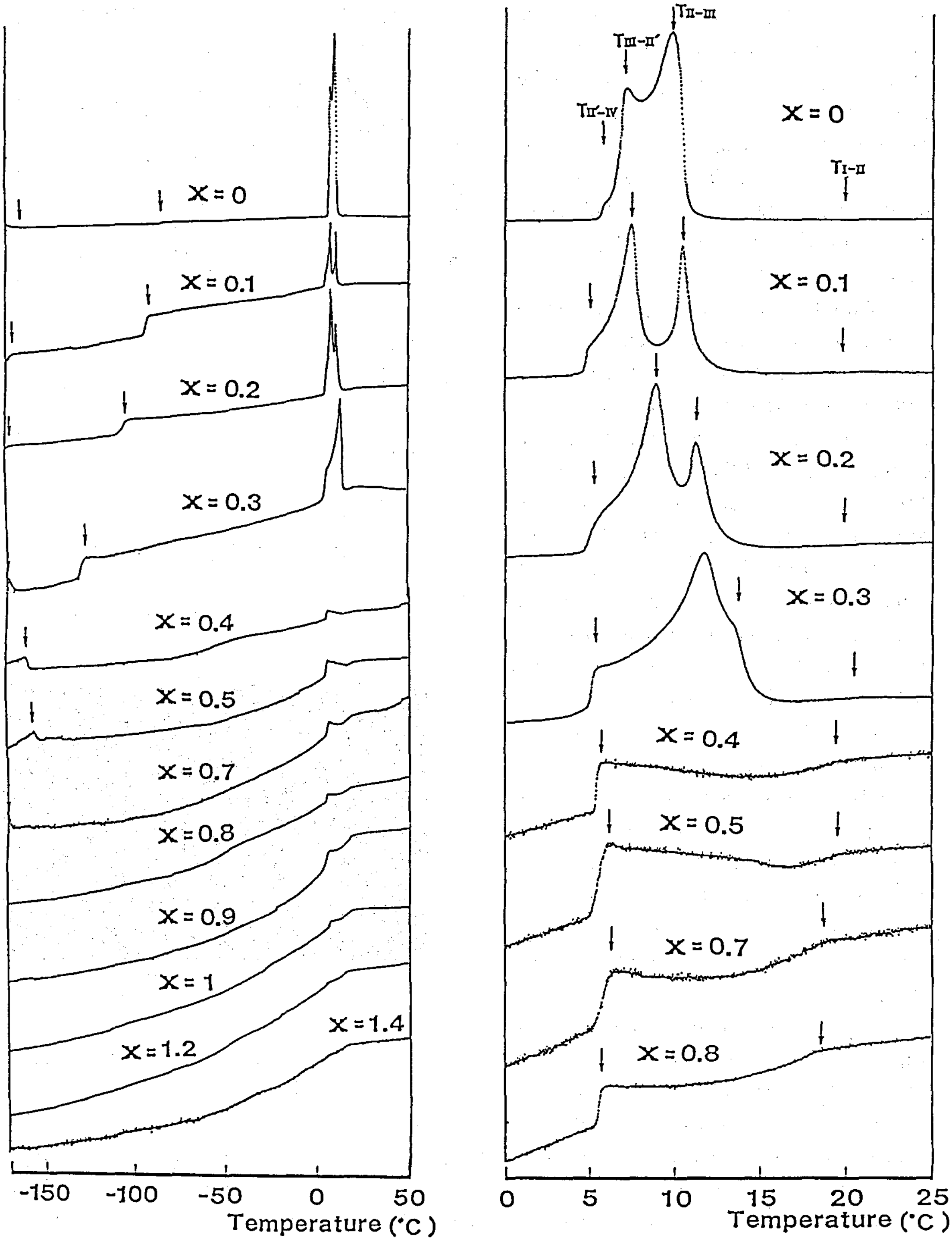

Fig. 2 Temperature dependence of dielectric constant of (100) plate of $(TMA)_2CoCl_{4-x}Br_x$ during cooling process.

are shown in Fig. 2(a) for measured temperature range and particular signal for higher temperature range are shown in Fig. 2(b). There are obvious differences between the signal up to 0.3 and that of over $x=0.4$. The x-T phase diagram was determined by means of DSC and dielectric measurements as shown in Fig. 3. In $(TMA)_2CoCl_4$-$(TMA)_2CoBr_4$ mixed system, phase I shows a complete solid solubility with common P*mcn*. This feature is similar to $(TMA)_2ZnCl_4$-$(TMA)_2ZnBr_4$ system which was pointed out by Colla *et al.*[8] The phase II and phase II′ are incommensurate and they exist between $x=0$ to $x\sim3$ and interrupted by a ferroelectric phase III. A ferroelectric D-E hysteresis loop was observed in chlorine rich compound less than $x=0.4$ as shown in Fig. 4. The phase II* bromine rich compound larger than $x=3$ has same symmetry group (P12₁/*c*1) as phase V chlorine rich compound less than $x=0.5$. The phase IV is commensurate phase (P112₁/*n*). A new phase IV′ is recognized and it corresponds to a part of coexistence region of two phases $(TMA)_2ZnCl_4$-$(TMA)_2ZnBr_4$ system. There is no phase boundary in $(TMA)_2CoCl_{4-x}Br_x$ system as exist for $x=2.7$ at low temperature region in $(TMA)_2ZnCl_{4-x}Br_x$ system.

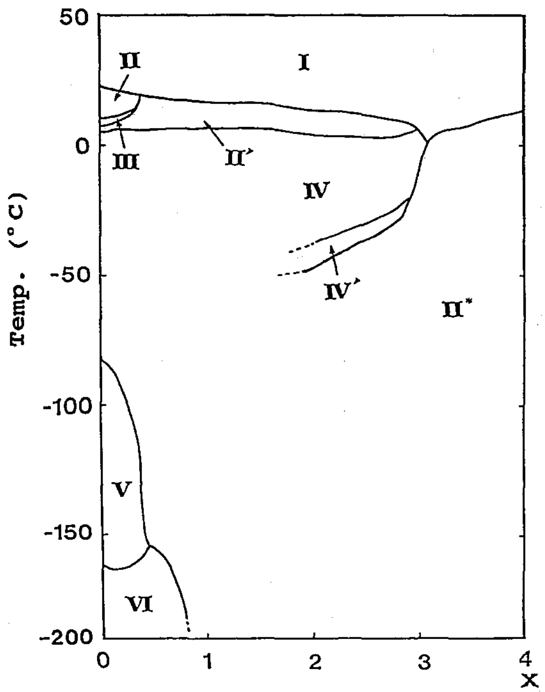

Fig. 3 Phase diagram in function of temperature and concentration of $(TMA)_2CoCl_{4-x}Br_x$.


Fig. 4 60Hz D-E hysteresis loop of (100) plate of $(TMA)_2CoCl_{3.8}Br_{0.2}$ at 12.2°C. Ps=2.1 x10^{-3} C/cm².

There are two kinds of tetrahedra, the organic $(CH_3)_4N$- and inorganic $M(Cl_{4-x}Br_x)$- ones. Although Colla *et al* pointed out that a large amount of enthalpy change around the P*mcn*-P12₁/*c*1 transition is due to internal thermal movements of organic groups, Perret *et al*[9] pointed out that the most inportant effect in phase transition of these systems is the rotation of the MX_4 inorganic tetrahedra around an axis passing through the M-atom and infer that the energies of the soft modes involved in the phase sequence are shifted in function of mass, of moment of inertia and of the size of tetrahedra. It may be cleared that inorganic tetrahedron play a major role in the phase sequences when Cl replaced by Br. An X-ray study of the mixed crystal is in progress.

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