Dielectric Properties of (TMA)x(TEA)(2-x)CoBr4 Crystals

Dielectric Properties of $(TMA)_x(TEA)_{(2-x)}CoBr_4$ Crystals

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Abstract

Dielectric constants of $\{N(CH_3)_4\}_x\{N(C_2H_5)_4\}_{(2-x)}$ $CoBr_4$ crystals where x varied from 0.5 to 1.5 by 0.1 step were measured over the temperature range from－190℃ to 50℃. The phase Ⅱ which is ferroelectric at x=1.0 was vanished over the x=1.5 and the phase Ⅲ which was antiferroelectric at x=1.0 was recognized at only the region between x=0.5 and x=1.5.

Introduction

A large number of substances with the chemical formula A_2MX_4, representative in K_2SeO_4[1]and $\{N(CH_3)_4\}_2$ MX_4 where M=Zn,Co and Mn and X=Cl and Br, have been studied to show similar successive phase transitions.[2)－5)] Our attention was payed to $ABMX_4$ type where A=tetramethylammonium $N(CH_3)_4$ (hereafter N $(CH_3)_4$ is abbreviated as TMA) and B=tetraethylammonium $N(C_2H_5)_4$ (hereafter $N(C_2H_5)_4$ is abbreviated as TEA). Our aim to investigate the influence of a mixed system $(TMA)_x(TEA)_{(2-x)}$ $CoBr_4$ where x is varied from 0.5 to 1.5 by 0.1 step. The crystal of $(TMA)_2$ $CoBr_4$ (that is x=2.0) undergoes a second-order phase transition at approximately 14.7℃. The phase Ⅰ is *Pncm* and phase Ⅱ is $P\,12_1/c_1$ in order of decreasing temperature. $(TEA)_2CoBr_4$ (that is x=0) crystal undergoes a phase transition at about 9℃. This phase transition is first order and phase Ⅰ is $P4_2/nmc$. We found that $(TMA)(TEA)CoBr_4$ [6] (that is x=1.0) has four phases, phase Ⅰ (T> －164℃), phase Ⅱ(－164℃>T>－172℃), phase Ⅲ (－172℃>T>－179℃) and phase Ⅳ (－179℃>T), and found that the phase Ⅱ is ferroelectric phase and the phase Ⅲ is antiferroelectric phase, respectively. We will report the results for anomalous temperature dependence of dielectric constant and the diagram of these phases varies dependent on the mole fraction of TMA(x).

$1 Experimental

Single crystal of$(TMA)_x(TEA)_{(2-x)}$ $CoBr_4$ where x varied from 0 to 2.0 by 0.1 step were prepared from aqueous solution by slow evaporation method at 30℃. The TMA content x was determined by chemical analysis for x=0, 1.0 and 2.0, but x values of other crystals were determined by mixed ratio. The obtained crystals were prism-like pillar and their color were cobalt blue. The specimens for dielectric measurements were polished with wet filter paper which was soarked with methanol and water. The (001) plate specimens were prepared and typical size of specimens were about 0.08 cm thick and 0.15～0.50 cm^2 in area. Ag paste was used as electrodes. The dielectric measurement at constant frequency of 1.00 MHz. and constant applied field of 20 V/cm were performed by using LCR-meter (HP－4285 A),which was controlled by computer. The sample was

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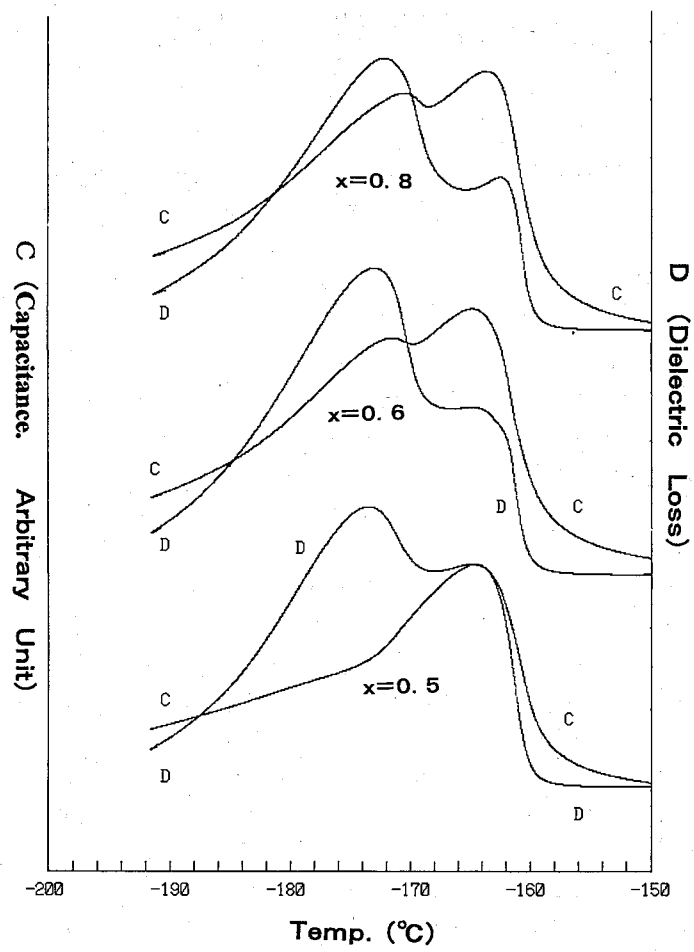

Fig. 1 Capacitance C and dielectric loss D for x=0.5,x=0.6 and x=0.8 in $(TMA)_x(TEA)_{(2-x)}$ type crystal system.

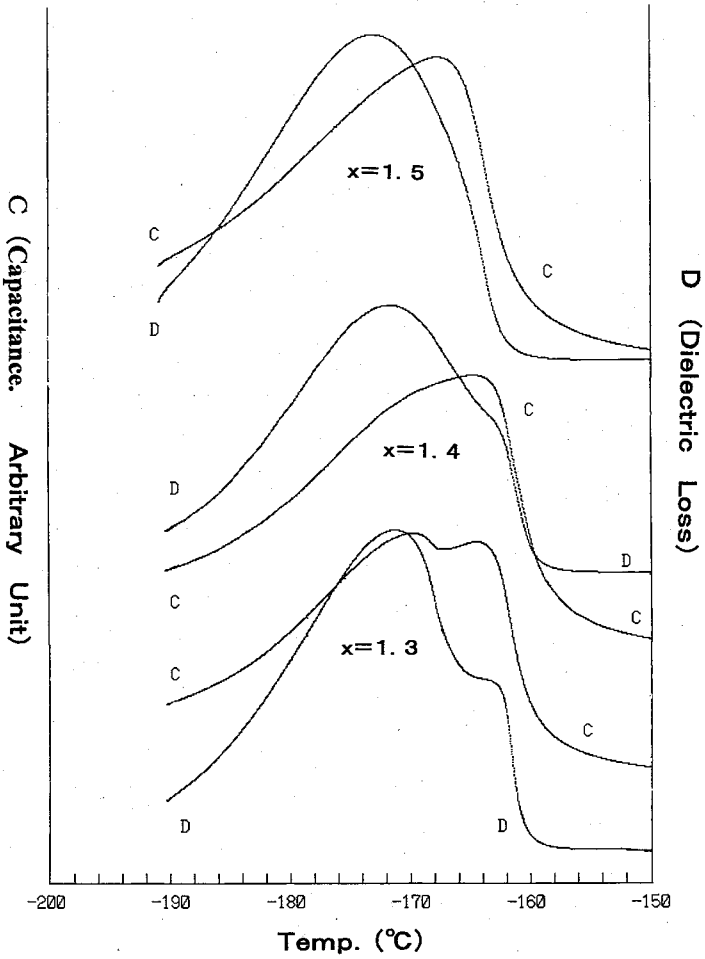

Fig. 2 Capacitance C and dielectric loss D for x=1.3,x=1.4 and x=1.5 in $(TMA)_x(TEA)_{(2-x)}$ type crystal system.

cooled and heated using a thermal programmable controller (ULVAC HPC－7000) over a temperature range from －190℃ to 50℃. The typical temperature changing rate during a measurement was 16 K/h. The 60 Hz. D-E hysteresis loop was observed by using Sawyer-Tower circuit.

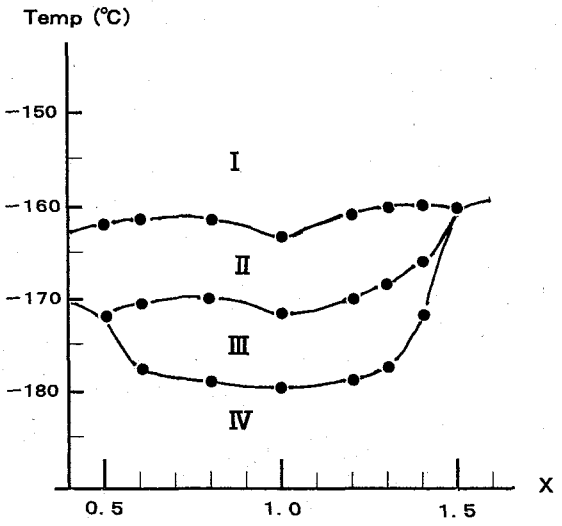

Fig. 3 Phase diagram of$(TMA)_x(TEA)_{(2-x)}$type crystal system in a region of x=1.0±0.5

$2. Results and Discussion

Capacitance C and dielectric loss D of (001) plate for x=0.5, 0.6 and 0.8 are showed in Fig.1. and for x=1.3,1.4 and 1.5 are showed in Fig.2, respectively. In Fig.1,the capacitance C of the sample for x=0.5,the peak between phase Ⅱ and phase Ⅲ are disappeared. In Fig.2,the C for x= 1.4 have a sholder and for x=1.5,the sholder was vanished, that is, phase Ⅱ and phase Ⅲ are vanished at x=1.5. These phase diagram was shown in Fig.3. It is widely noted that free rotation of methyle group is maintained fairly low temperature. The carbons of methylene group in TEA are disordered[4] and two TMA molecules (for x=2.0) rotate around C-N axis at different angles and change rotation direction in each phase.[7] For x lower than 0.5 and higher than 1.5,we concider that one of TMA (or TEA) which was substituted by-TEA (or TMA) plays the role of to stop the rotation around C-N axis. Dielectric studies and X-ray analysis for other x in this mixed crystal system are now progress.

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