Dielectric Dispersion of Barium Titanate Ceramics at Low Frequencies

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1. Introduction

Studies on the dielectric dispersion of barium titanate ceramics at low frequencies seem never to have been fully done hitherto. Grant(1) gave the Cole-Cole diagram of the complex dielectric constant of the substance at 80°C. The diagram is a circular arc between 100kc/s and 800c/s, but at lower frequencies down to 80c/s it deviates from the circular arc and approches a straight line. He could not conclude whether the deviation was due to the dc conductivity of the specimen or to another dispersion. We, the present authors, examined experimentally the dielectric dispersion at lower frequencies and at higher temperatures. The result shows that the phenomenon mentioned above must be attributed to the second dispersion rather than to dc conductivity.

2. Experimental Procedure

(Material)

A large number of barium titanate ceramics were prepared by the usual method, and specimens of comparatively high dispersion chosen from among them were mainly used. For comparison measurements were made about a single crystal kindly offered by Murata Manufacturing Co.

(Dielectric measurements)

The measurement was carried out as shown in Fig. 1 on a bridge of a special feature provided with a conductance shifter devised by Nakajima and Kondo(2) for use with very low frequencies. The balancing of the bridge at frequencies higher than 30c/s was detected by the special circuit similar to the type devised by Brown and Ramsay (3) which was described in a previous paper.(4) At 1 c/s a null detecter of the type devised by Nakajima and Kondo(2) was used.

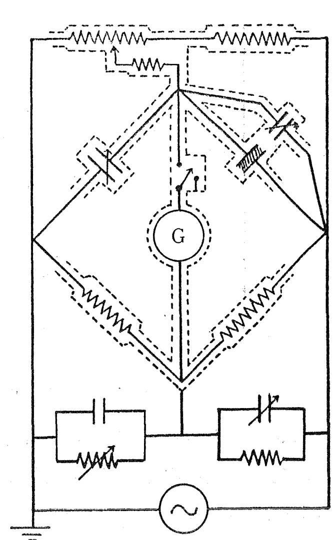

Fig. 1. Very low frequency bridge

An RC type oscillator was used for frequencies higher than 30 c/s, and a motor-driven sine potentiometer was used at 1 c/s. Somewhat high voltages, of the order of 10 v per mm, were applied to the specimen for the sake of the accuracy of the measurement.

3. Experimental Result and Discussion

The temperature dependency of the dielectric constant and tan δ of one specimen at 20 kc/s, 30 c/s and 1 c/s is shown in Fig. 2.

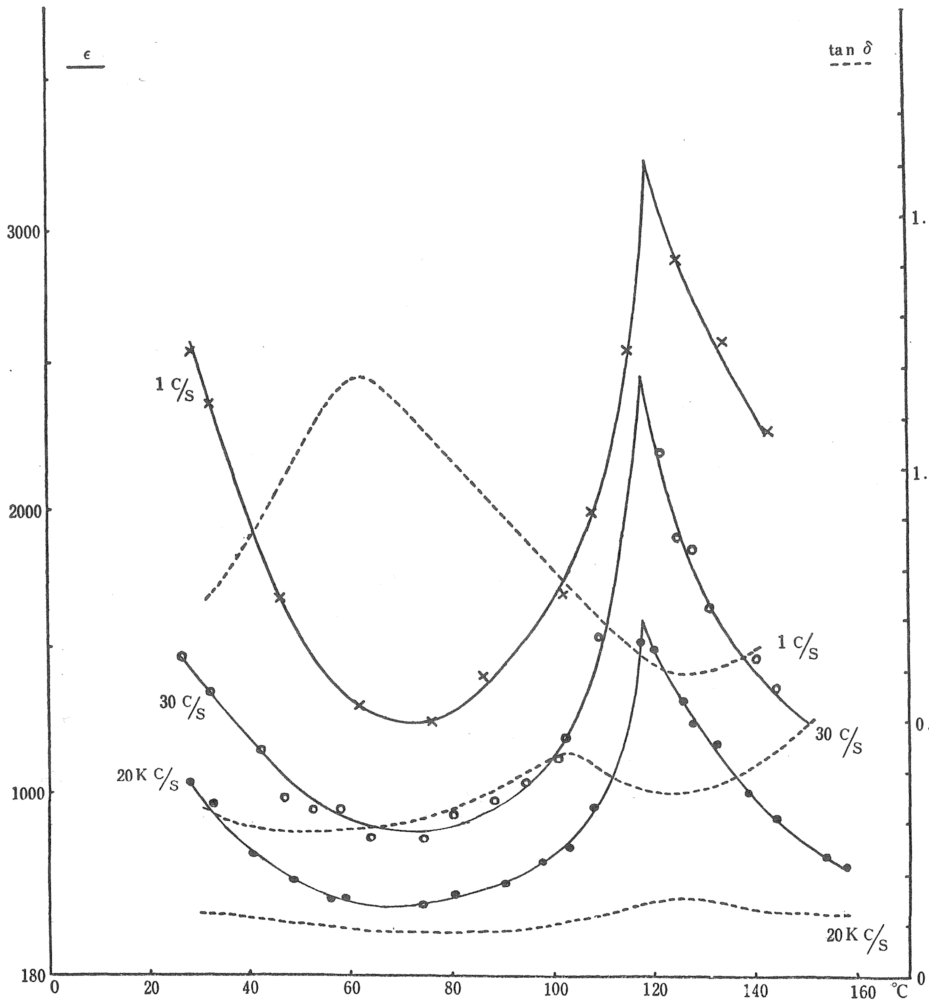

Fig. 2. Temperature dependency of dielectric constant and tan δ

The specimen is 1.05 mm in thickness and its Curie point is about 119°C. It is seen that the dielectric dispersion of the specimen is conspicuous. The relations of the real part ε' and the imaginary part ε'' of the complex dielectric constant at several temperatures below the Curie point are shown in Fig. 3. In the figure the points corresponding to 1 c/s are not shown. They are nearly situated on the parts of the lines deviating from the circular

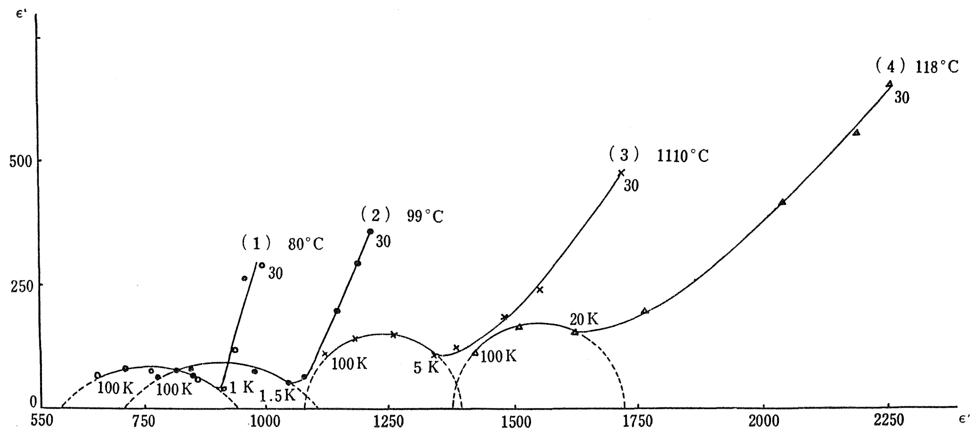

Fig. 3. Complex dielectric constant at several temperatures below Curie point

arcs and approaching straight lines. In the calculation of the values of ε'' the dc conductance errors were not corrected because they were negligibly small compared to the total conductance as will be described below. Curve (1) in Fig. 3 at 80°C is generally similar to that given by Grant[1] and shows a broader distribution in relaxation time. But as the temperature rises the arc gradually changes to a semicircle and curve (4) at 118°C is just a semicircle showing a single relaxation time. Every part deviating from the circular arc is nearly a straight line, and its inclination become smaller as the temperature rises. The

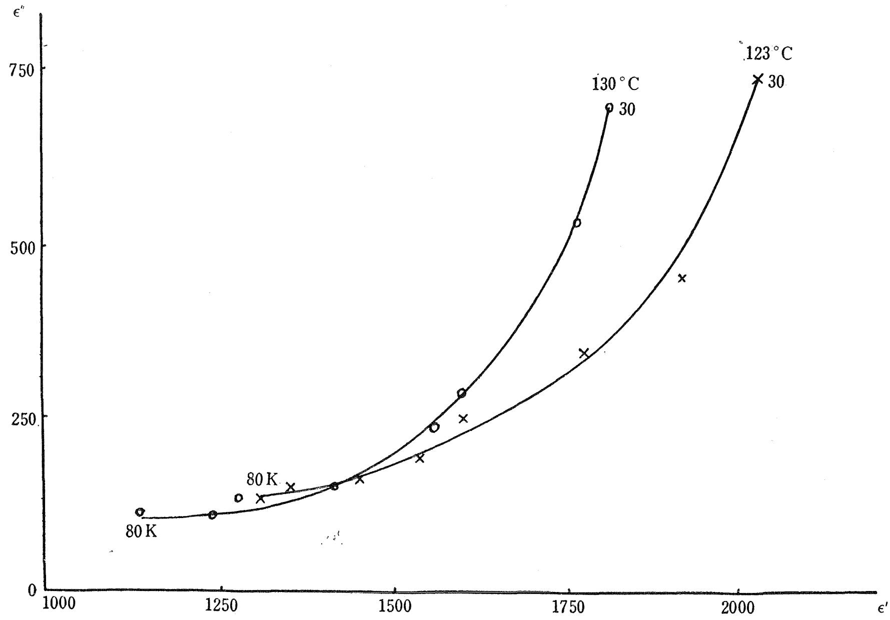

Fig. 4. Complex dielectric constant at higher temperatures than Curie point

result obtained with the same specimen as the above at temperatures higher than Curie point is shown in Fig. 4 as an example.

The curves in the figure lack the usual small circular arc at the lower end. Assuming the loci at low frequencies to be straight lines their inclinations appear to become larger as the temperature rises contrary to the phenomenon seen at temperatures lower than Curie point. For comparison the result obtained with a single crystal of butterfly type is shown in Fig. 5. It is seen that the dielectric dispersion and its anomalous character at low frequencies still exist in the single crystal.

Now we shall discuss on the mechanism responsible for the anomalous character, that is, the deviation from a circular arc at low frequencies. In the first place, the anomalous character can not be attributed to the dc conductivity, because as seen in curve (4) in Fig. 2 the part deviating from the circular

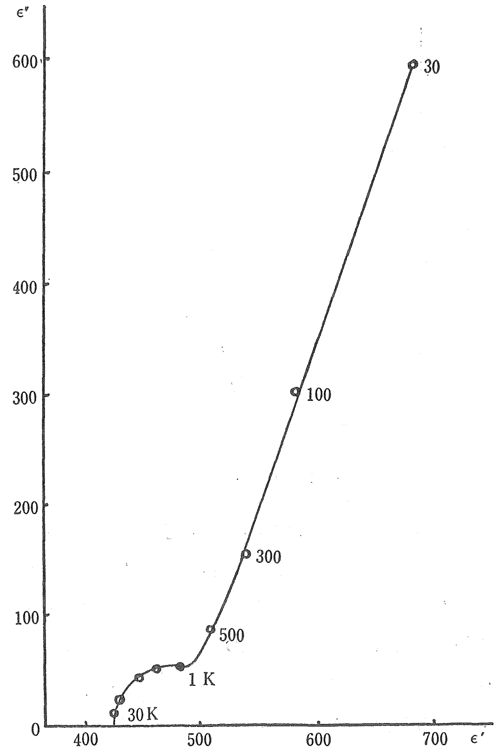

Fig. 5. Complex dielectric constant of a single crystal at 95°C.

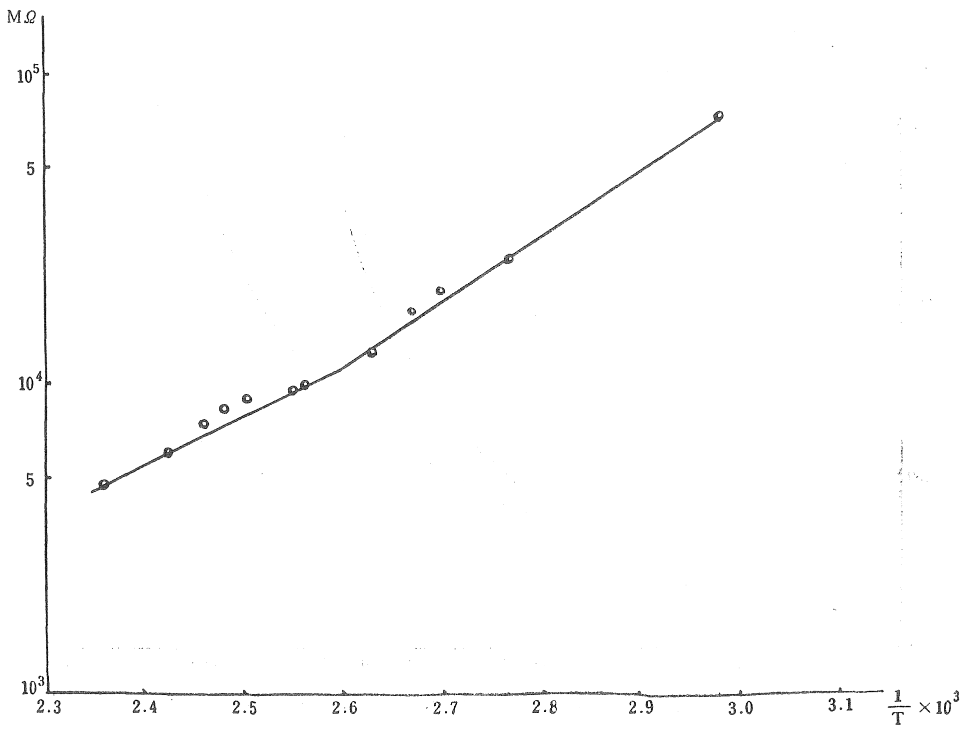

Fig. 6. Temperature dependency of the resistance

arc extends far to the right from it. If the dc conductivity is the principal cause the deviating part must extend towards the region above the intersection of ε' axis and the circular arc as discussed by Grant.(1) Furthermore we measured directly the dc conductivity of the specimen by a vacuum tube electrometer and examined the extent of its contribution to the total conductance. The temperature dependency of the resistance of the specimen as used in Fig. 3 is shown in Fig. 6. The relation ρ (T) may be represented generally by the formula $\rho = Ke^{\frac{\varphi}{kT}}$ as usual. But it is seen that the activation energy above the Curie point is a little smaller than that below it. This abnormality may perhaps be attributed to the semiconductive character of the specimen due to the impurity as was discussed by Saburi.(5) At any rate the dc conductance for the case of Fig. 6 at 118°C amounts only to 0.3 % of the total conductance for the case of curve (4) in Fig. 3 at 30 c/s, and to 3 % at 1 c/s. And so we must attribute the anomalous character at low frequencies to some other mechanism.

Subsequently we examined whether the mechanism is the electrode polarization of Cole's theory(6) or not. According to the theory, electrode polarization is a surface effect and negligible when the electrode seperation is large. Therefore we studied with a thick specimen of 5.28 mm, and found also the same anomalous character mentioned above for a thin specimen. Thus the electrode polarization theory must be abondoned here.

Now we notice that the diagrams shown in Fig. 3 are analogous to that of ice reported by Humbel, Jona and Scheerer.(7) The anomalous character of ice at low frequencies was clearly explained by Steinmann and Gränicher(8) by the space charge polarization theory of Macdonald.(9) And it seems reasonable to suppose that the anomalous character of barium titanate ceramics at low frequencie is due to the space charge polarization originating from the semiconductive property. But there is no reason at present to suppose it should not be attributed to the usual interfacial polarization due to the inhomogeneity of the specimen.

The authors express their gratitude to Murata Manufacturing Co. for the gifts of single crystals of barium titanate.

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