Curie Temperature of BaTiO$_3$

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The Curie point (T_C) of BaTiO$_3$ was earlier reported to be 120 °C and has been recently believed to be 130 °C. Some experiments have been performed here to reconfirm the T_C. Firing conditions used for preparing BaTiO$_3$ were examined first with the use of pure BaCO$_3$ or Ba(NO$_3$)$_2$ and TiO$_2$. The x-dependence of T_C in (BaO)$_{1-x}$(TiO$_2$)$_{1+x}$ solid solution was measured. Data were scattered and suffered from individual variations. According to probability considerations, T_C of BaTiO$_3$ was evaluated from the intercept at $x=0$. On the other hand, composition dependence of T_C in some related solid solution systems, (Ba$_{1-y}$Pb$_y$)TiO$_3$. (Ba$_{1-y}$Sr$_y$)TiO$_3$ and (BaTiO$_3$)$_{1-y}$(KF)$_y$, was examined and the T_C of BaTiO$_3$ was estimated by extrapolation toward the limit $y\rightarrow0$. In conclusion, the Curie point of BaTiO$_3$ is determined as 123.0±0.6 °C.

KEYWORDS: BaTiO$_3$, Curie temperature, ferroelectricity

1. Introduction

The Curie point (T_C) of BaTiO$_3$ was described as 120 °C in early literature. In those days, in fact, most of the experiments indicated similar values for ceramics and KF-grown crystals. One of the authors (T.I.) attempted in 1958 to use pure TiO$_2$ chemicals refined by fractional distillation of TiCl$_4$. A sharp dielectric peak surprised him and suggested that T_C was at 130 °C. This value was certainly indicated by an experimental plot in a figure of his article, though his graphic data have been lost.[1]

When the author (T.I.) talked about his experiments with Professor Smakula at MIT in 1964, the latter gave an offhand suggestion that it must be due to the Ti-rich composition of the specimen.

Nowadays, no body is astonished at the value of 130 °C. This common sense, as it were, may be due to the success of Linz crystal in 1963 which was pulled from Ti-rich melt and showed the T_C at 130 °C.

Professor Smakula's comment has weighed on our minds for many years. What is the Curie temperature of BaTiO$_3$? In order to address the problem, we have performed a few experiments. We report a probable value for T_C of BaTiO$_3$, though our results may not be completely reliable.

2. Examination of Conditions for Firing BaTiO$_3$

Raw materials were 99.9% BaCO$_3$ or 99.99% Ba(NO$_3$)$_2$ (Wako Chem. Co.) and TiO$_2$ (anatase) (Pure Chem. Inst.). In the case of carbonate, specimens were prepared by the conventional ceramic firing technique for calcination (solid state reaction) and sintering. In the case of nitrate, reaction was carried out in a draft chamber at a temperature of 600 °C or higher, and sintering procedure was the same as above.

Dielectric measurements were made at 100 kHz with increasing and decreasing temperature, and a temperature corresponding to ε max in the rising run was regarded as T_C. Lattice parameters were determined by X-ray powder diffractometry with CuKα radiation at room temperature.

Care was taken regarding the degree of reaction, and firing conditions were examined. For instance, in the case of nitrate material, reaction was carried out at a temperature of 600, 620 or 640 °C and sintering of 1300, 1350 or 1400 °C. Results are shown in Fig. 1, where the ε-T curve and the corresponding T_C value are indicated for the respective data sets.

The reaction was not always completed in the first firing but sometimes proceeded during the second process of sintering. It is considered that the reaction began with Ba-rich composition and the Ti concentration gradually increased toward the nominal 50% composition. Roughly speaking, the higher the firing temperature, the higher the T_C. It seemed necessary to choose reaction and sintering temperatures higher than 620 °C and 1350 °C, respectively.

In the case of carbonate, a similar examination was made for combinations of temperatures at 50 °C intervals between 1050 and 1300 °C for reaction and between 1250 and 1400 °C for sintering. Contrary to our expectation, we did not observe a clear tendency for the relationship· between reaction degree and T_C. Nevertheless, sintering at temperatures higher than 1350 °C seemed necessary for our purpose.

Consequently we decided to adopt conditions of firing first at 1150 °C and second at 1350 °C. In the case of Ti-rich composition, the sintering temperature was chosen to be lower, say 1300 °C, taking account of the eutectic temperature at 1322 °C.

3. BaO-TiO$_2$ Solid Solution

The formula is described here as (BaO)$_{1-x}$(TiO$_2$)$_{1+x}$. For $x=0$, i.e., nominal BaTiO$_3$, about forty specimens were prepared by several of us under various conditions. Porosities were generally about 0.1–0.2, but sometimes reached 0.3 for samples sintered at lower temperatures. Obtained values for T_C were distributed between 120 and 126 °C, and did not always correspond to firing conditions. In addition, systematic errors were found owing to individual variations. A simple mean, therefore, could not be applied.

Specimens for $-0.06<x<+0.15$ were prepared and

T_C values are shown against x in Fig. 2, where different notations are used for corresponding workers. (Results indicated by rhombi will be explained later.) Scatter and personal variations are also observed.

Now suppose that more and more trials are repeated. Even if similar scatter and polarization exist, we expect that most of the additional data would fall in a limited range, for example, as indicated by broken lines in the figure. If there are sufficiently many specimens, we may assume a normal distribution. Then we consider that the broken lines delimit a range of $\pm 3\sigma$ with a probable error σ. Accordingly, we expect a value
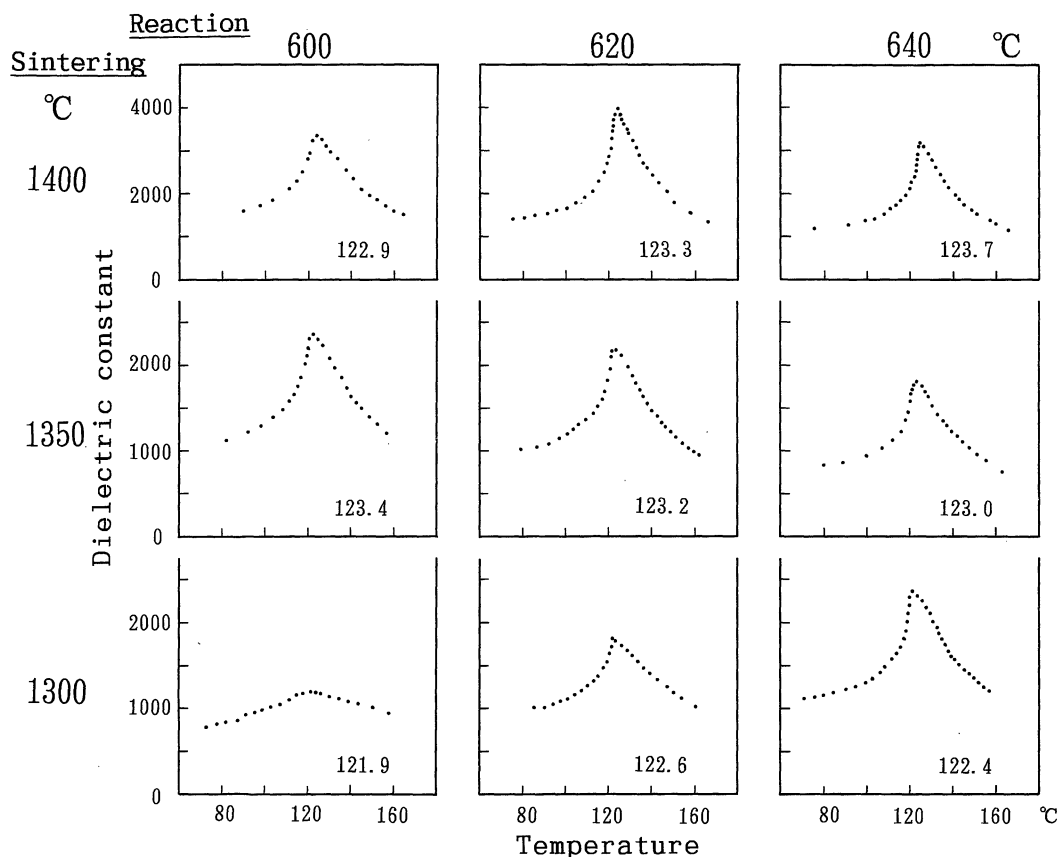

Fig. 1.   Dielectric constant vs temperature and the corresponding value of T_C for various reaction and sintering temperatures in the case of $Ba(NO_3)_2$.
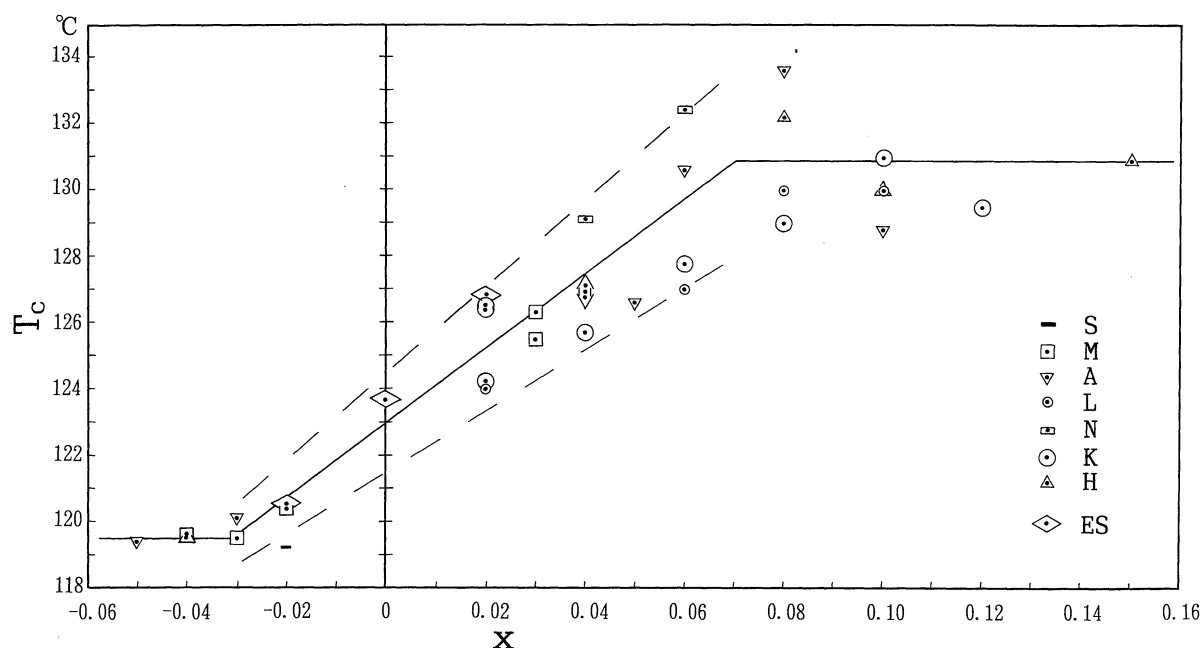

Fig. 2. T_C vs x in solid solution $(BaO)_{1-x}(TiO_2)_{1+x}$.

123.0 ± 0.6 °C as the Curie point of BaTiO$_3$.

The soluble range of the solid solution lies roughly within $-0.03 < x < +0.07$. Lattice constant c mainly depends upon x, as does a tetragonality $\delta = c/a - 1$. In the present experiment, δ was scattered between 1.02 and 0.82%. Roughly speaking, δ increased with x and was around 0.92% for $x \sim 0$. However, the scattering of data was now too large to conclude a correlation between $T_{\rm C}$ and δ.

In the preparation of Ti-rich specimens, we sometimes observed bronze-like color due to reduction. Such specimens showed a high electric conductivity and a dielectric constant of several thousand associated with high value of tan δ. These specimens were excluded from the present experiment.

4. Some Related Solid Solutions

It is well known that the substitution by Pb or Sr for Ba increases or decreases $T_{\rm C}$. Therefore the extrapolation of $T_{\rm C}$ vs y toward $y \to 0$ in the $({\rm Ba}_{1-y}{\rm A}_y){\rm TiO}_3$ system with A = Pb or Sr could be a means of estimating $T_{\rm C}$. On the other hand, it is assumed that a low $T_{\rm C}$, 120 °C, was due to substitution of Ba by K and O by F. Therefore the same extrapolation was attempted in $({\rm BaTiO}_3)_{1-y}({\rm KF})_y$ solid solution.

Raw materials were BaCO$_3$ and TiO$_2$, the same as used in the above experiment, and PbO, SrCO$_3$ and KF of reagent grade. The chemical grade of the substituting substance should not be a problem in this case.

Results are shown in Fig. 3. It is clear that the dispersion of data is unexpectedly smaller. All lines approximately intersect at a point on the ordinate. Thus we evaluate 123.0 ± 0.3 °C as the $T_{\rm C}$ of BaTiO$_3$. The probable error was estimated roughly by trial and error; it may actually be smaller than 0.3 °C.

5. Conclusions

It is considered that the reaction forming BaTiO$_3$ begins with Ba-rich composition and proceeds by Ti diffusion toward nominal composition. The Curie point in BaO-TiO$_2$ solid solution increases with increasing Ti concentration, though the data are markedly scattered and suffer from individual variations. Certain probability considerations lead us to the evaluation of $T_{\rm C}$ of BaTiO$_3$ as 123.0 ± 0.6 °C.

It did not seem easy to obtain homogeneous speci-

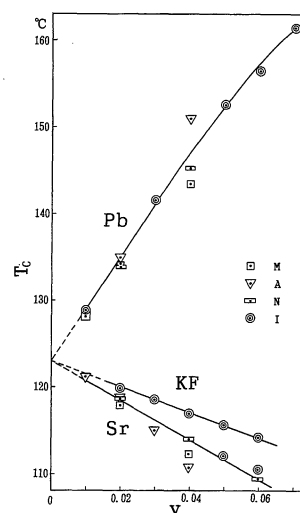Fig. 3. $T_{\rm C}$ vs y in $({\rm Ba}_{1-y}{\rm Pb}_y){\rm TiO}_3$, $({\rm Ba}_{1-y}{\rm Sr}_y){\rm TiO}_3$ and $({\rm BaTiO}_3)_{1-y}$-$({\rm KF})_y$ solid solution systems.

mens of BaTiO$_3$ and BaO-TiO$_2$ solid solution. Among them, BaTiO$_3$, 1:1 compound, appeared to be particularly difficult to prepare by our firing technique. During the present experiment, unfortunately we did not encounter the sharp dielectric peak which had been experienced long ago by the author (T.I.).

In contrast, substitution by other substances, *e.g.*, Pb, Sr or KF, enabled us to determine the $T_{\rm C}$ of BaTiO$_3$ within ± 0.3 °C.

The above conclusion was obtained using 99.9% BaCO$_3$ or 99.99% Ba(NO$_3$)$_2$ and 99.9% TiO$_2$. For confirmation, another trial was carried out with the use of 99.98% TiO$_2$ recently supplied. Three data points indicated by rhombi in Fig. 2 are thus added. These apparently lie within the above range. Even if similar experiments are repeated using such pure chemicals, the conclusion may not differ much from the present one.

In conclusion, the Curie temperature of BaTiO$_3$ is determined as 123.0 ± 0.6 °C.

1)   T. Ikeda: J. Phys. Soc. Jpn. **14** (1959) 168.