

## Ferroelectricity and Antiferroelectricity in Ceramic $\text{PbZrO}_3$ Containing Ba or Sr\*

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Phase transitions in solid solutions  $(\text{Pb}-\text{Ba})\text{ZrO}_3$  and  $(\text{Pb}-\text{Sr})\text{ZrO}_3$  have been studied by dielectric, dilatometric, and calorimetric measurements. It is shown that when the Ba concentration in  $(\text{Pb}-\text{Ba})\text{ZrO}_3$  compositions exceeds a threshold value of about 5 percent, a ferroelectric intermediate phase begins to appear between the paraelectric and antiferroelectric phases of pure  $\text{PbZrO}_3$ . The temperature range of this intermediate phase increases with the Ba concentration. Though no intermediate phase can be observed in compositions which contain Ba ions with less than this threshold concentration, a forced transition from the antiferroelectric phase to a ferroelectric phase can be caused by the application of a strong electric field at temperatures just below the Curie point. In the  $(\text{Pb}-\text{Sr})\text{ZrO}_3$  system we can also observe an intermediate phase, but this phase proves to be another antiferroelectric phase and not a ferroelectric one. It is concluded, from these situations, that the antiferroelectric phase in pure  $\text{PbZrO}_3$  must be very peculiar, the free energy of this phase being closely adjacent to those of a ferroelectric phase as well as another antiferroelectric phase.

### I. INTRODUCTION

IT has been known that  $\text{PbZrO}_3$  has several points of resemblance to  $\text{BaTiO}_3$  in dielectric and structural properties; namely,  $\text{PbZrO}_3$  has a crystal structure of a tetragonal modification of perovskite type,<sup>1</sup> and its dielectric constant shows a sharp maximum at the Curie point near  $230^\circ\text{C}$ .<sup>2</sup> However, our detailed investigations<sup>3,4</sup> on the dielectric properties of this crystal have revealed that the dielectric response of this substance can be explained well if we assume that it is antiferroelectric. Moreover, the x-ray analysis of a single crystal by Sawaguchi *et al.*<sup>5</sup> has shown that the superstructure of this crystal is due to the antiparallel displacement of Pb ions in the plane perpendicular to the  $c$  axis.

Very recently, Roberts<sup>6</sup> observed a very weak piezoelectric effect in polarized  $\text{PbZrO}_3$  ceramic. So, in reference of the foregoing structure analysis, it must be concluded that this crystal is strongly antiferroelectric in the plane perpendicular to the  $c$  axis though, possibly, very weakly ferroelectric in the  $c$  direction. Nevertheless, we shall continue to use as before the word "antiferroelectric," because the predominant properties of this crystal seem to be properly represented by this word.

A recent study<sup>7</sup> of the  $\text{Pb}(\text{Zr}-\text{Ti})\text{O}_3$  system has shown that when Ti ions replace some of the Zr ions in  $\text{PbZrO}_3$ , another transition besides the ordinary Curie point can be observed at lower temperature. The intermediate phase between these two transitions is

undoubtedly ferroelectric, because typical hysteresis loops can be observed there.

As stated before, the x-ray analysis has shown that the ions which are responsible for the anomalous dielectric properties of  $\text{PbZrO}_3$  are Pb ions, and that Zr ions may be considered as a sort of spacer. If the appearance of the ferroelectric intermediate phase in  $\text{Pb}(\text{Zr}-\text{Ti})\text{O}_3$  is mainly caused by the replacement of spacer ions, Zr, with smaller Ti ions, a similar phenomenon may be expected upon the replacement of Pb ions with larger ones such as Ba, and at the same time, an inverse situation may be expected upon the replacement of Pb ions with smaller ones such as Sr. Though such a simple interpretation may, of course, be insufficient because the role of the substituted ion depends not only on its ionic radius but also on its polarizability as well as electronic configuration, nevertheless, the study of these  $(\text{Pb}-\text{Ba})\text{ZrO}_3$  and  $(\text{Pb}-\text{Sr})\text{ZrO}_3$  systems will be of some value for elucidating the physical role of the substituted ions in  $\text{PbZrO}_3$ .

The  $(\text{Pb}-\text{Ba})\text{ZrO}_3$  system has already been studied by Roberts<sup>2</sup> and the decrease of the Curie temperature with increasing Ba concentration was reported. However, no special attention was paid to the existence of another transition, because at that time  $\text{PbZrO}_3$  had been considered as an ordinary ferroelectric. Roberts reported that polarized  $(\text{Pb}70-\text{Ba}30)\text{ZrO}_3$  shows a piezoelectric effect at room temperature, and our preliminary dielectric test<sup>3</sup> of  $(\text{Pb}80-\text{Ba}20)\text{ZrO}_3$  also revealed that this solid solution shows, in fact, hysteresis loops below its Curie point. If this phase is really of the same nature as the ferroelectric intermediate phase in  $\text{Pb}(\text{Zr}95-\text{Ti}5)\text{O}_3$ ,<sup>7</sup> and if it is essentially different from the antiferroelectric phase in pure  $\text{PbZrO}_3$ , there must be a phase boundary somewhere between these two phases.

A re-examination of this  $(\text{Pb}-\text{Ba})\text{ZrO}_3$  system has now been carried out with the special purpose of finding another transition. Moreover, an investigation has been made on the  $(\text{Pb}-\text{Sr})\text{ZrO}_3$  and  $(\text{Pb}-\text{Ca})\text{ZrO}_3$  systems,

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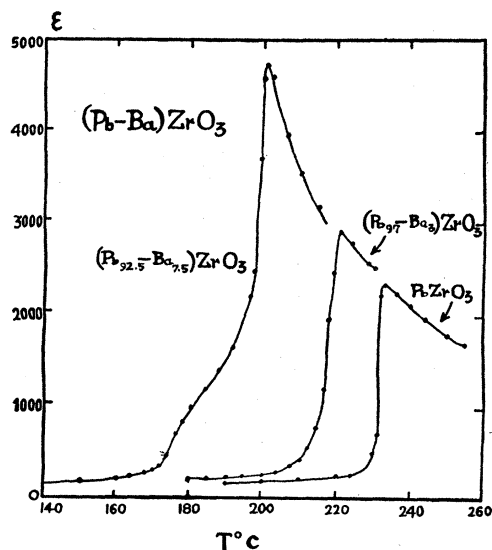


FIG. 1. Permittivity vs rising temperature curves of  $(\text{Pb}-\text{Ba})\text{ZrO}_3$  compositions.

comparing the results with those of the  $(\text{Pb}-\text{Ba})\text{ZrO}_3$  system.

## II. DIELECTRIC STUDY OF $(\text{Pb}-\text{Ba})\text{ZrO}_3$

The specimens of  $(\text{Pb}-\text{Ba})\text{ZrO}_3$  and  $(\text{Pb}-\text{Sr})\text{ZrO}_3$  composition were made from  $\text{PbO}$ ,  $\text{ZrO}_2$ , and the respective alkali earth carbonates. Use was made of the same high purity  $\text{ZrO}_2$  chemicals as used for the previous study<sup>4</sup> of  $\text{PbZrO}_3$ ; this  $\text{ZrO}_2$  contains small amount of Ti(0.2 percent), Fe(0.05 percent), and Si(0.03 percent) as impurities. These ingredients were mixed in the desired proportions and sintered at temperatures from 1200° to 1350°C after the preliminary calcination. The

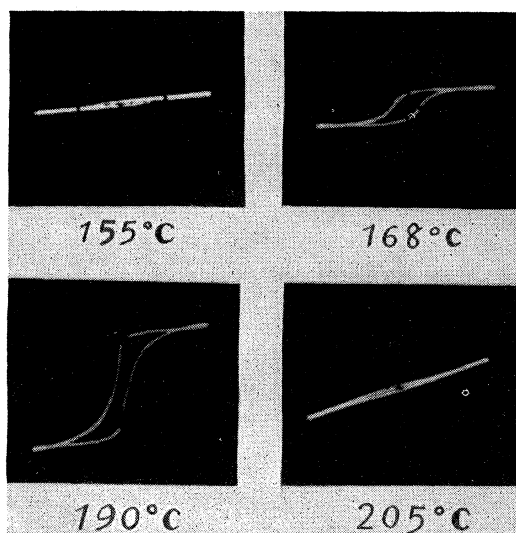


FIG. 2. Hysteresis loops of  $(\text{Pb}92.5-\text{Ba}7.5)\text{ZrO}_3$  at  $E_{\text{max}}=20$  kv/cm.

higher the Pb concentration, the lower was the sintering temperature.

The dielectric test samples were ceramic disks of 1 mm in thickness and were covered with silver electrodes fired on both faces. The permittivity of these specimens was measured with a beat frequency equipment under an ac field of 1 Mc/sec and 10 v/cm. All of the dielectric measurements were made with the sample immersed in a bath of liquid paraffin, which improved the insulation as well as the constancy of the temperature.

Figure 1 shows the permittivity vs rising temperature curves of  $(\text{Pb}-\text{Ba})\text{ZrO}_3$  compositions together with that of pure  $\text{PbZrO}_3$ . In accordance with the previous data,<sup>2</sup> the Curie temperature decreases with increasing Ba concentration. Whereas the curve for  $(\text{Pb}97-\text{Ba}3)\text{ZrO}_3$  shows only one sharp maximum at 222°C, the one for  $(\text{Pb}92.5-\text{Ba}7.5)\text{ZrO}_3$  clearly shows another small anomaly at about 175°C besides a sharp maximum at

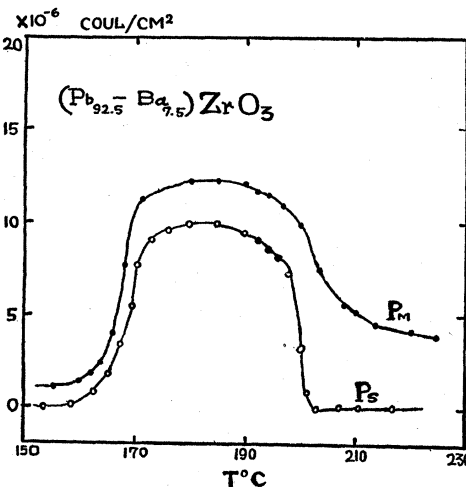


FIG. 3. Maximum polarization  $P_m$  and spontaneous polarization  $P_s$  of  $(\text{Pb}92.5-\text{Ba}7.5)\text{ZrO}_3$  with rising temperature, estimated from hysteresis loops at  $E_{\text{max}}=20$  kv/cm.

200°C. This small anomaly suggests the existence of another transition in this specimen.

The properties of these two transitions in  $(\text{Pb}92.5-\text{Ba}7.5)\text{ZrO}_3$  were studied more precisely by using a cathode-ray oscillograph. Figure 2 shows a series of  $D-E$  curves of this specimen under an ac field of 20 kv/cm and 50 cycles/sec. As expected, the  $D-E$  characteristic is almost linear in the lowest phase, and it shows typical hysteresis loops in the intermediate phase between 175° and 200°C, indicating that this phase is certainly ferroelectric. The spontaneous polarization can be roughly estimated from these figures and is plotted in Fig. 3, together with the maximum polarization at this field strength. It is interesting to note that these hysteresis loops can be easily saturated, and they show relatively large spontaneous polarizations.

The effect of a dc biasing field of 10 kv/cm upon the permittivity of this specimen was studied, with the result shown in Fig. 4. In the antiferroelectric phase

below 175°C, the permittivity is almost independent of the biasing field, except that a slight increase is observed just below the lower transition point. In the ferroelectric region, on the other hand, it decreases considerably with increasing dc bias. The upper transition temperature is raised by dc field, while the lower one is decreased. Namely, the temperature range of the ferroelectric phase is enlarged by the application of a biasing field. This is just the expected result, because the free energy of the ferroelectric phase should be lowered considerably by an electric field as compared with those of the antiferroelectric and paraelectric ones. All of the dielectric properties of this specimen in the three phases are respectively of the same nature as those of the corresponding three phases in  $\text{Pb}(\text{Zr}95-\text{Ti}5)\text{O}_3$ .<sup>7</sup>

The phase diagram of the  $(\text{Pb}-\text{Ba})\text{ZrO}_3$  system obtained from the permittivity measurements at rising temperature is shown in Fig. 5. This figure shows that these solid solutions are ferroelectric at room temperature in the concentration range between about  $(\text{Pb}85-\text{Ba}15)\text{ZrO}_3$  and  $(\text{Pb}65-\text{Ba}35)\text{ZrO}_3$ . This result is consistent with the previous observations of ferroelectricity in the specimens of  $(\text{Pb}80-\text{Ba}20)\text{ZrO}_3$ <sup>3</sup> and  $(\text{Pb}70-\text{Ba}30)\text{ZrO}_3$ .<sup>2</sup> The upper phase line in this figure is in good agreement with the previous data obtained by Roberts.<sup>2</sup>

It must be noticed here that the ferroelectric intermediate phase does not appear until the Ba concentration reaches a threshold value which seems to be slightly above 5 percent. In solid solutions derived from  $\text{PbZrO}_3$ , such as  $\text{Pb}(\text{Zr}-\text{Ti})\text{O}_3$  and  $(\text{Pb}-\text{Ba})\text{ZrO}_3$ , this threshold concentration and consequently the lower phase line seem to depend very sensitively on the impurities already contained even in pure  $\text{PbZrO}_3$ , particularly in  $\text{ZrO}_2$  chemicals. For the precise determination of the phase diagram near the  $\text{PbZrO}_3$  end, we must use the highest purity  $\text{ZrO}_2$  chemical, which contains no impurities such as Ti, Ba, Sr, and the like. So the values obtained here for the  $(\text{Pb}-\text{Ba})\text{ZrO}_3$  system are approximate ones, because even our purest  $\text{ZrO}_2$  cannot help containing a small amount of Ti.

### III. FORCED TRANSITION BY ELECTRIC FIELD

In the course of the previous study<sup>4</sup> of the dielectric properties of pure  $\text{PbZrO}_3$ , anomalous hysteresis loops of very impressive form were obtained at a high field strength and at temperatures just below the Curie point (see Figs. 8 and 9 of reference 4). In these figures we guessed that the central portion of the loop would correspond to the antiferroelectric phase while the outer portion to a ferroelectric phase. Namely, we considered that the forced transition from the antiferroelectric phase to the ferroelectric phase is caused by the application of a strong electric field. These anomalous hysteresis loops can also be observed in the present  $(\text{Pb}-\text{Ba})\text{ZrO}_3$  compositions which contain Ba ions in a concentration less than the threshold value of about

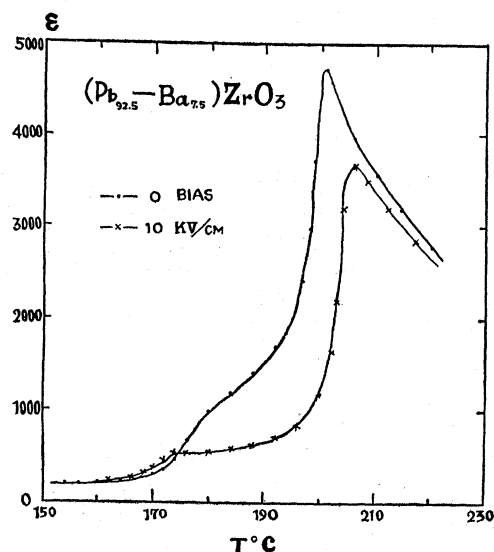


FIG. 4. Effect of a dc biasing field of 10 kv/cm on the permittivity of  $(\text{Pb}92.5-\text{Ba}7.5)\text{ZrO}_3$ .

5 percent (Fig. 6). We shall define a critical field strength  $E_c$  at which the forced transition does occur.

Using a specimen of  $(\text{Pb}97-\text{Ba}3)\text{ZrO}_3$  we have estimated  $E_c$  as a function of temperature. It is shown in Fig. 7 by open circles. It decreases with increasing temperature and reaches a lowest value  $E_l$  near the Curie temperature. This value  $E_l$  of varied  $(\text{Pb}-\text{Ba})\text{ZrO}_3$  compositions decreases monotonically with increasing Ba concentration, and seems to reach zero at the concentration at which the ferroelectric intermediate phase begins to appear under zero external field (Fig. 8).

If our foregoing interpretation is right, this forced transition should be caused also by a strong dc biasing field. Figure 9 shows a series of the permittivity vs

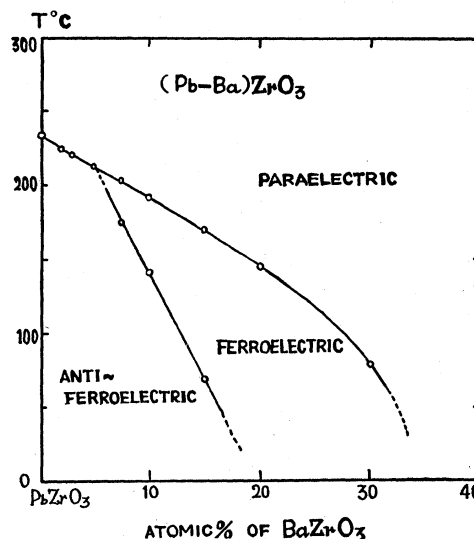


FIG. 5. Phase diagram of the  $(\text{Pb}-\text{Ba})\text{ZrO}_3$  system.

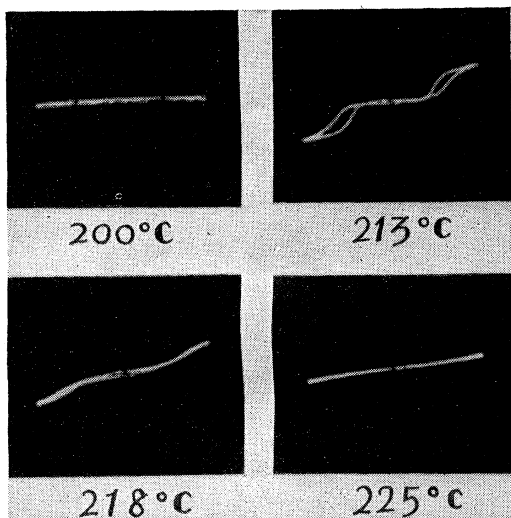


FIG. 6. Hysteresis loops of  $(\text{Pb}_{97}-\text{Ba}_3)\text{ZrO}_3$  at  $E_{\text{max}}=20$  kv/cm.

rising temperature curves of a  $(\text{Pb}_{97}-\text{Ba}_3)\text{ZrO}_3$  specimen under various biasing field strengths. When the applied field is less than a critical value of about 11 kv/cm, which is approximately equal to  $E_t$  of this specimen, the Curie temperature decreases slightly with increasing biasing field, accompanied by a slight increase of the permittivity just below the Curie point. On the contrary, when the dc field strength exceeds this critical value, the Curie temperature increases with biasing field strength, and at the same time we can detect another small anomaly in the permittivity curve on the lower temperature side which suggests the existence of another transition. This lower transition temperature decreases with increasing biasing field (Fig. 10). In the new phase between these two transitions, the permittivity decreases considerably with increasing dc field,

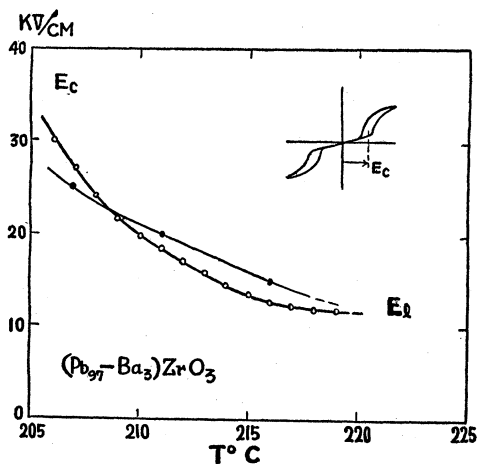


FIG. 7. Threshold field  $E_c$  of  $(\text{Pb}_{97}-\text{Ba}_3)\text{ZrO}_3$  as a function of temperature. Open circles are estimated from the hysteresis loops; solid circles are estimated by the permittivity measurements under the application of a dc biasing field.

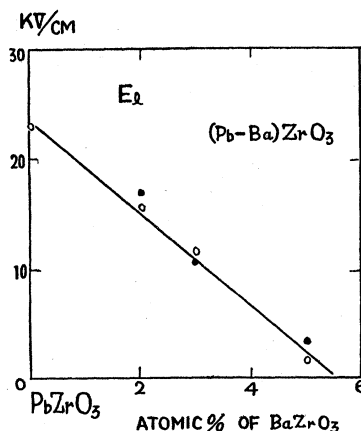


FIG. 8. Threshold field  $E_t$  as a function of composition of  $(\text{Pb}-\text{Ba})\text{ZrO}_3$ . Open circles are estimated from hysteresis loops; solid circles are estimated by the permittivity measurements under the application of dc biasing field.

just as expected by analogy with the case of the ferroelectric phase in  $(\text{Pb}_{92.5}-\text{Ba}_{7.5})\text{ZrO}_3$ . Therefore, it is certain that this new intermediate phase is also ferroelectric.

The critical value of the dc biasing field at which the intermediate phase begins to appear is estimated also for  $(\text{Pb}_{98}-\text{Ba}_2)\text{ZrO}_3$  and  $(\text{Pb}_{95}-\text{Ba}_5)\text{ZrO}_3$  by similar measurements, and is shown in Fig. 8 by solid circles. These values are in good agreement with the estimates from the anomalous hysteresis loops. Moreover, it must be noticed here that the lower phase line in Fig. 10 should coincide with the  $E_c$  vs temperature curve in Fig. 7, because it gives the field strength at which the forced transition occurs at a given temperature, and so

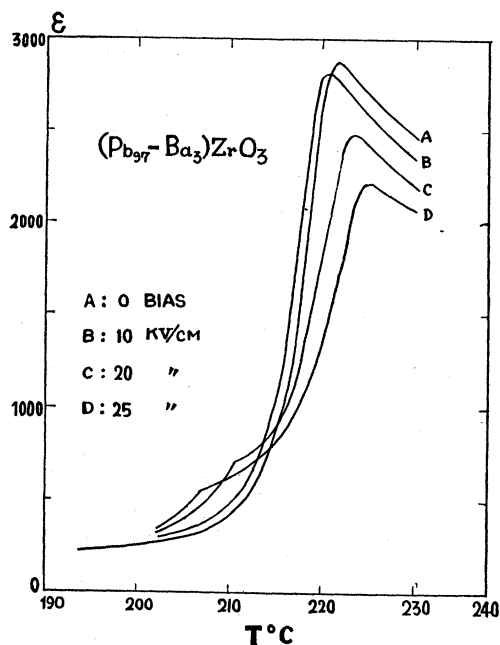


FIG. 9. Effect of a dc biasing field on the permittivity of  $(\text{Pb}_{97}-\text{Ba}_3)\text{ZrO}_3$ .

both curves have the same physical meaning. In Fig. 7 we plotted the lower transition points obtained from Fig. 10 by solid circles, and the qualitative agreement is in fact fairly satisfactory.

We assume that the forced ferroelectric phase may be an extension of the intermediate phase in  $(\text{Pb}92.5\text{—Ba}7.5)\text{ZrO}_3$ . The decisive evidence, however, should be given by an x-ray study under the application of a strong dc field, which is now in progress.

#### IV. DIELECTRIC STUDY OF $(\text{Pb—Sr})\text{ZrO}_3$

Figure 11 shows the permittivity  $\epsilon$  vs rising temperature curves for several  $(\text{Pb—Sr})\text{ZrO}_3$  compositions. These curves show two anomalies just as in the case of  $(\text{Pb}92.5\text{—Ba}7.5)\text{ZrO}_3$ , but a careful comparison reveals the following differences. First, the peak value of the permittivity at the Curie point decreases rapidly with increasing Sr concentration. Secondly, the permittivity change at the lower transition is rather sharp and

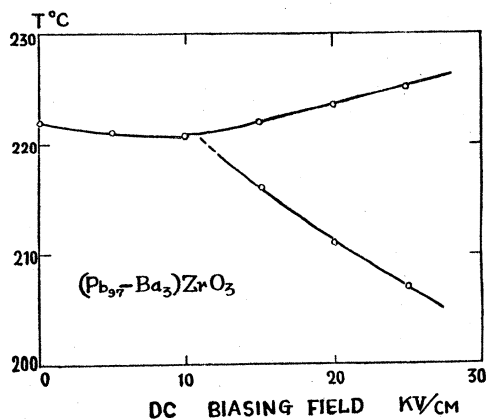


FIG. 10. Transition temperature vs dc biasing field curve of  $(\text{Pb}97\text{—Ba}3)\text{ZrO}_3$ .

pronounced compared with the small anomaly in the  $(\text{Pb—Ba})\text{ZrO}_3$  compositions.

There is no doubt that the lowest phase here is also antiferroelectric, being of the same nature as that of pure  $\text{PbZrO}_3$ . So the foregoing differences should be attributed solely to the essential differences of the respective intermediate phases in both systems. To confirm this point we have carried out a detailed study of the dielectric properties of this intermediate phase with the specimen of  $(\text{Pb}95\text{—Sr}5)\text{ZrO}_3$ .

In the first place, we have observed the  $D$ - $E$  characteristics of this specimen. If the intermediate phase between  $222^\circ\text{C}$  and  $245^\circ\text{C}$  is of the same ferroelectric phase as that of  $(\text{Pb}92.5\text{—Ba}7.5)\text{ZrO}_3$ , typical hysteresis loops should be observed in this temperature range. However, observation under an ac field of  $30\text{ kV/cm}$  has shown that the  $D$ - $E$  characteristic of this specimen is almost linear except just below the upper transition temperature where it shows a slight upward curvature (Fig. 12), suggesting that this intermediate phase may not be ferroelectric. It should be noted here that the

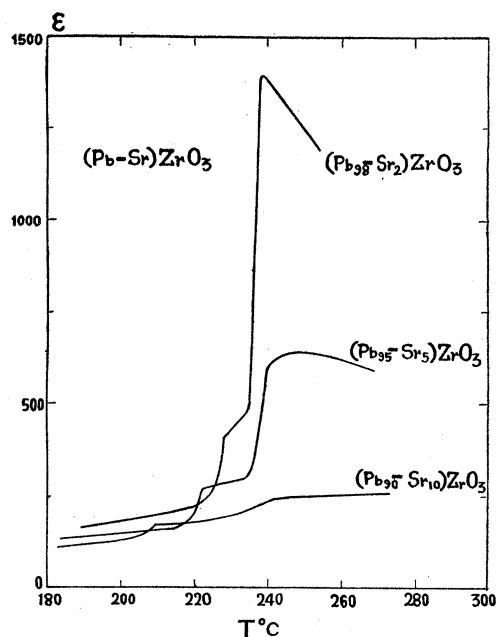


FIG. 11. Permittivity vs rising temperature curves of  $(\text{Pb—Sr})\text{ZrO}_3$  compositions.

anomalous hysteresis loops, such as observed in  $(\text{Pb}97\text{—Ba}3)\text{ZrO}_3$ , cannot be observed for this specimen and for  $(\text{Pb}98\text{—Sr}2)\text{ZrO}_3$  up to an ac field strength of  $30\text{ kV/cm}$ . Even in the specimen which contains only 1 percent of Sr ions, we cannot observe the anomalous hysteresis loops up to a field strength of about  $40\text{ kV/cm}$ .

Figure 13 shows the maximum polarization  $P_{\text{max}}$  estimated on cathode-ray oscillograph under maximum ac amplitudes of  $20\text{ kV/cm}$  and  $30\text{ kV/cm}$ . These curves very much resemble the permittivity vs temperature curve of this specimen (Fig. 11). If we reduce these

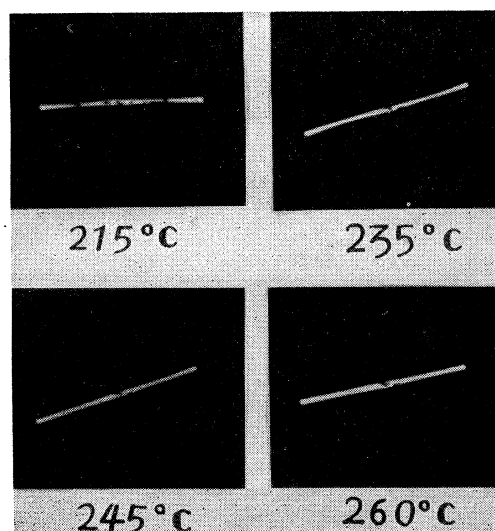


FIG. 12. Hysteresis loops of  $(\text{Pb}95\text{—Sr}5)\text{ZrO}_3$  at  $E_{\text{max}} = 30\text{ kV/cm}$ .

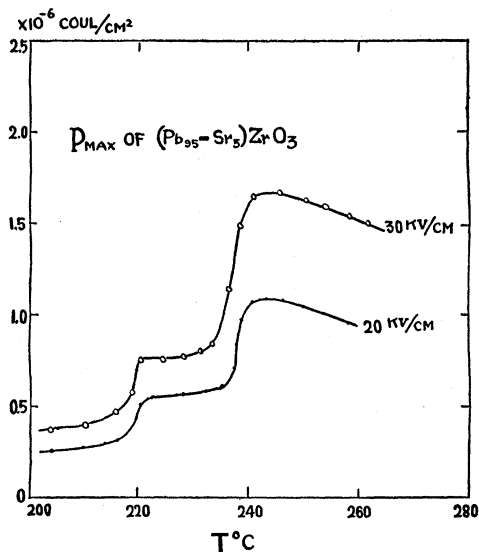


FIG. 13. Maximum polarization of  $(\text{Pb}_{95}\text{-Sr}_5)\text{ZrO}_3$  at ac amplitudes of 20 kv/cm and 30 kv/cm.

curves to  $4\pi \cdot P_m/E$ , they both coincide with each other, and, moreover, they are approximately equal to the permittivity curve. So the two anomalies in these  $P_{\text{max}}$  curves can be considered as a mere consequence of the corresponding changes in the permittivity at the two transitions, owing to the good linearity of the  $D$ - $E$  relation for this specimen. A comparison of these results with those of pure  $\text{PbZrO}_3$  suggests that the intermediate phase in  $(\text{Pb}_{95}\text{-Sr}_5)\text{ZrO}_3$  is also antiferroelectric but not ferroelectric.

To confirm the previous assumption from another point of view, a study was made of the effect of a dc biasing field of 10 kv/cm upon the permittivity of this specimen (Fig. 14). As expected, the results are essentially different from those with  $(\text{Pb}_{92.5}\text{-Ba}_{7.5})\text{ZrO}_3$ .

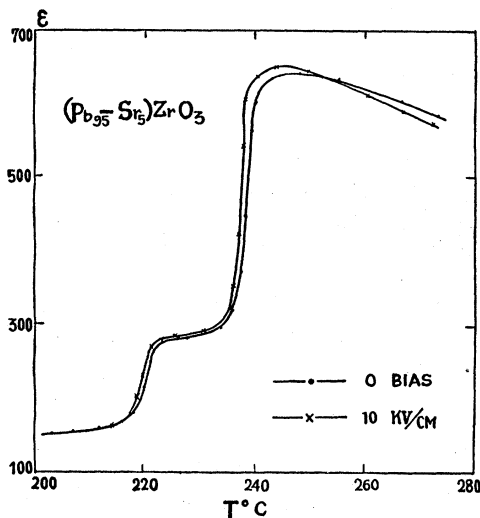


FIG. 14. Effect of a dc biasing field of 10 kv/cm on the permittivity of  $(\text{Pb}_{95}\text{-Sr}_5)\text{ZrO}_3$ .

The effect near the upper transition point is completely of the same nature as observed in pure  $\text{PbZrO}_3$ . Also, no marked effect was observed around the lower transition point, except a very slight decrease of the transition temperature.

The absence of spontaneous polarization in the intermediate phase was proved directly by a pyroelectric test. A dc field of 10 kv/cm was applied to the specimen while it was being cooled from  $270^\circ$  to  $230^\circ\text{C}$ , and both electrodes were connected to a galvanometer circuit while the temperature was maintained at  $230^\circ\text{C}$ . After the initial discharging current had disappeared we raised the temperature through the upper transition point near  $245^\circ\text{C}$  but no further discharging current could be observed at this point. A similar pyroelectric test on  $(\text{Pb}_{92.5}\text{-Ba}_{7.5})\text{ZrO}_3$  shows plenty of discharge current at the Curie point. Thus, we conclude that

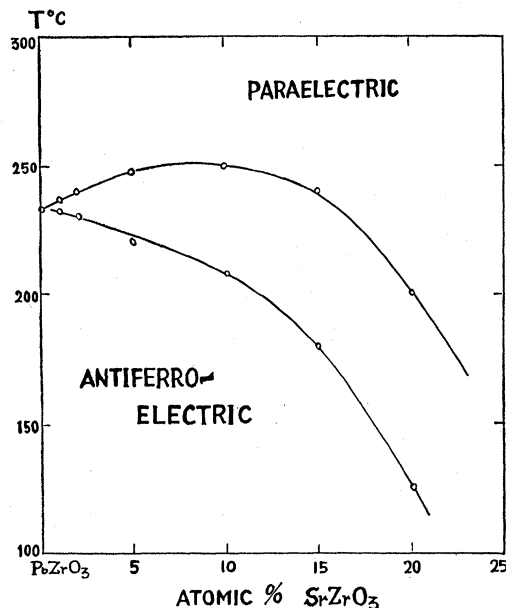


FIG. 15. Phase diagram of the  $(\text{Pb-Sr})\text{ZrO}_3$  system.

spontaneous polarization is either absent in  $(\text{Pb}_{95}\text{-Sr}_5)\text{ZrO}_3$ , or, if it were to exist it must be very small, far less than one-hundredth that of  $(\text{Pb}_{92.5}\text{-Ba}_{7.5})\text{ZrO}_3$ .

The phase diagram of this  $(\text{Pb-Sr})\text{ZrO}_3$  system is shown in Fig. 15. It should be noted here that the Curie temperature of this system increases with the Sr concentration up to Sr 10 percent and then decreases, in contrast with the monotonic decrease in the  $(\text{Pb-Ba})\text{ZrO}_3$  system. This figure shows that the threshold concentration at which the intermediate phase begins to appear is less than Sr 1 percent. In the course of the former study of the dielectric properties of pure  $\text{PbZrO}_3$ , we observed a small anomaly at  $225^\circ\text{C}$  in the cooling curves of the permittivity and of the maximum polarization (Figs. 2 and 6 of reference 4). Now this anomaly can be interpreted reasonably, if we consider that it is

of the same nature as that of the lower transition in the present (Pb-Sr)ZrO<sub>3</sub> system.

## V. DILATOMETRIC AND CALORIMETRIC STUDIES

### A. Thermal Expansion

The previous study<sup>3</sup> of the thermal expansion of PbZrO<sub>3</sub> has shown a large volume expansion at the antiferroelectric *vs* paraelectric transition near 230°C. The linear thermal expansion of (Pb-Ba)ZrO<sub>3</sub> and (Pb-Sr)ZrO<sub>3</sub> compositions has now been measured by the same simple dilatometer that was used for the previous study. Curves for (Pb92.5-Ba7.5)ZrO<sub>3</sub> and (Pb95-Sr5)ZrO<sub>3</sub> are shown in Fig. 16, together with the one for pure PbZrO<sub>3</sub>. The heating and cooling rates are both about 1°C/min.

The curve for (Pb92.5-Ba7.5)ZrO<sub>3</sub> is completely of the same nature as that for Pb(Zr95-Ti5)O<sub>3</sub>.<sup>7</sup> Namely, with rising temperature it transforms from the antiferroelectric phase to the ferroelectric one through the transitional region near 175°C accompanied by a large volume expansion, and further transforms to the paraelectric phase at the Curie point near 200°C accompanied by a relatively small volume contraction. These situations can be made more clear when we extrapolate the linear part in the paraelectric phase to lower

TABLE I. Volume expansion coefficient ( $\times 10^{-6}/^{\circ}\text{C}$ ).

Composition	Lowest phase	Cubic phase
PbZrO <sub>3</sub>	28	23
(Pb92.5-Ba7.5)ZrO <sub>3</sub>	27	18
(Pb95-Sr5)ZrO <sub>3</sub>	28	34

temperatures. That is to say, the ferroelectric phase shows an anomalous volume expansion compared with this extrapolation and the antiferroelectric phase shows an anomalous contraction.

The situation is very different for (Pb95-Sr5)ZrO<sub>3</sub>. In this specimen the volume of the antiferroelectric intermediate phase is between the lowest antiferroelectric phase and the paraelectric phase. Namely, both antiferroelectric phases in this specimen show a volume contraction compared with the extrapolation from the paraelectric phase. Some of the numerical data are shown in Table I and II. Table II gives the aforementioned volume contraction, or expansion, compared with the extrapolation from the cubic phase. It is to be noticed that the value of this anomalous volume contraction at the lowest phase is nearly the same for these three specimens.

The cooling curves are also shown in Fig. 16. The curve for (Pb92.5-Ba7.5)ZrO<sub>3</sub> shows a large temperature hysteresis at the lower transition, just as in the case of Pb(Zr95-Ti5)O<sub>3</sub>. On the other hand, we can perceive only a small temperature hysteresis at the lower as well as at the upper transition in (Pb95-Sr5)-ZrO<sub>3</sub>. This difference may be the result of a relatively

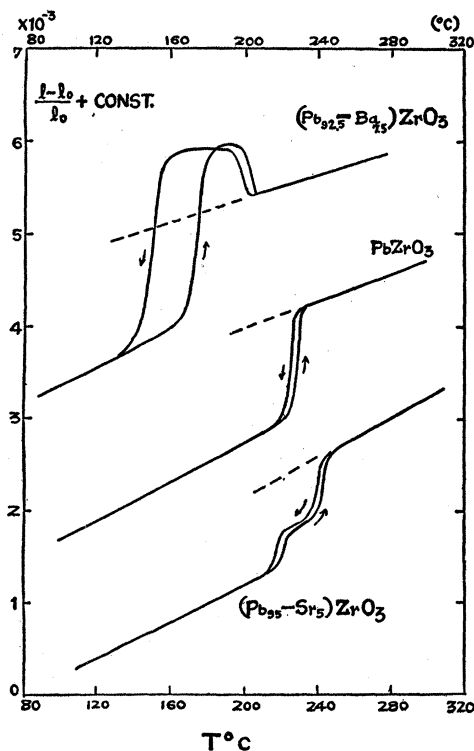


FIG. 16. Linear thermal expansion of PbZrO<sub>3</sub>, (Pb92.5-Ba7.5)ZrO<sub>3</sub>, and (Pb95-Sr5)ZrO<sub>3</sub>.

large volume change at the antiferroelectric *vs* ferroelectric transition in the former specimen.

### B. Specific Heat

The specific heat *vs* temperature curves of (Pb92.5-Ba7.5)ZrO<sub>3</sub> and (Pb95-Sr5)ZrO<sub>3</sub> were measured by using an adiabatic calorimeter of the Nagasaki-Takagi type,<sup>8</sup> which is an improvement of Sykes' calorimeter.<sup>9</sup> A powdered specimen of about 25 g, contained in a thin glass vessel, was heated by a rate of about 1°-2°C/min. For comparison with the results of these two solid solutions, re-examination of the specific heat curve of pure PbZrO<sub>3</sub> was carried out with the high purity specimen. The results obtained are shown in Fig. 17.

The curve for PbZrO<sub>3</sub> shows a very sharp maximum at the Curie point at 233°C, in accordance with the very steep changes in the permittivity and dilatometry

TABLE II. Anomalous volume contraction or expansion ( $\Delta v/v$ ), estimated from the extrapolation of the linear part in the cubic phase ( $\times 10^{-4}$ ).

Composition	Lowest phase	Intermediate phase
PbZrO <sub>3</sub>	-34 at 220°C	...
(Pb92.5-Ba7.5)ZrO <sub>3</sub>	-36 at 150°C	+19 at 190°C
(Pb95-Sr5)ZrO <sub>3</sub>	-31 at 210°C	-20 at 230°C

<sup>8</sup> S. Nagasaki and Y. Takagi, J. Appl. Phys. Japan 17, 104 (1948).

<sup>9</sup> C. Sykes, Proc. Roy. Soc. (London) A143, 422 (1935).

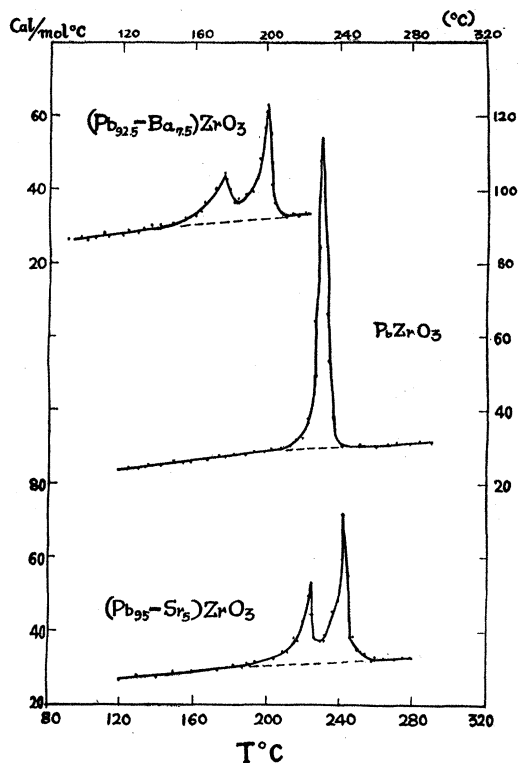


FIG. 17. Specific heat curves of  $\text{PbZrO}_3$ ,  $(\text{Pb}_{92.5}\text{-Ba}_{7.5})\text{ZrO}_3$ , and  $(\text{Pb}_{95}\text{-Sr}_5)\text{ZrO}_3$ .

curves of this specimen. Though the peak value is finite, it may be certain that the main part of the transition energy consists of the latent heat. By assuming that the normal specific heat corresponds to a broken line shown in the figure, the transition energy is estimated to be about 440 cal/mole, in good agreement with the previous data.<sup>3</sup>

The curves for the two solid solutions clearly show two sharp maxima at their respective two transitions. It is interesting that the same type of specific heat anomaly is observed in these different types of transitions. The transition energies estimated from these curves are given in Table III.

#### VI. FURTHER STUDY OF $(\text{Pb-Ca})\text{ZrO}_3$

Investigations of the  $(\text{Pb-Ba})\text{ZrO}_3$  and  $(\text{Pb-Sr})\text{ZrO}_3$  systems have revealed that the phase diagram of solid solutions derived from  $\text{PbZrO}_3$  can show two different types; namely, the properties of the intermediate phase are either ferroelectric or antiferroelectric according to the nature of the substituted ions. So it seems interesting to study whether the  $(\text{Pb-Ca})\text{ZrO}_3$  system really belongs to one (more probably to the latter) of these two types of phase diagrams.

The permittivity vs temperature curves for  $(\text{Pb}_{95}\text{-Ca}_5)\text{ZrO}_3$  shows, in fact, two anomalies at 235° and 250°C. The characteristic form of the curve is very similar to that of  $(\text{Pb}_{95}\text{-Sr}_5)\text{ZrO}_3$ , suggesting that the

intermediate phase in this system may also be antiferroelectric. The study of the  $D$ - $E$  relation has proved that this is the case. Moreover, the dilatometry curve for this specimen has a very similar form to that of  $(\text{Pb}_{95}\text{-Sr}_5)\text{ZrO}_3$ .

#### VII. DISCUSSIONS

In the previous study of pure  $\text{PbZrO}_3$ , we assumed the existence of the free energy curve of the ferroelectric phase which lies slightly above that of the antiferroelectric phase (Fig. 18). A further support of this assumption is given by the present study of the  $(\text{Pb-Ba})\text{ZrO}_3$  system. Namely, the appearance of the ferroelectric intermediate phase and the realization of the forced transition can be well explained if we assume that the free energy of the ferroelectric phase is very close to that of the antiferroelectric phase, so that the former easily becomes lower than the latter either by the replacement of Pb ions with Ba ions or by the application of a strong electric field. Such a situation must be a very special one; namely,  $\text{PbZrO}_3$  must be a very special example of the antiferroelectricity.

Moreover, the study of the  $(\text{Pb-Sr})\text{ZrO}_3$  system has shown that there must be another antiferroelectric phase, the free energy of which is also very adjacent to that of the original antiferroelectric phase of pure  $\text{PbZrO}_3$  (Fig. 18). The effect of the substituted Sr ions seems to lower the free energy of this other antiferroelectric phase, though the inevitability of this effect is not yet fully understood.

The crystal structure of this antiferroelectric intermediate phase must, of course, be different from those of the corresponding phase in  $(\text{Pb-Ba})\text{ZrO}_3$  and of the antiferroelectric phase of pure  $\text{PbZrO}_3$ , as is actually shown by preliminary comparison of the Debye photographs of these three phases. Detailed results of the x-ray study will be reported in a subsequent paper.

Recently, Kittel<sup>10</sup> has discussed the possibility of realization of an antiferroelectric crystal and has shown that this should be expected to occur in nature. His theory gives some criteria for identifying antiferroelectric crystals. Takagi<sup>11</sup> has also presented a theory of antiferroelectric crystal containing rotatable polar molecules and has added to Kittel's criteria some more criteria helpful for identifying the antiferroelectric crystals. Very recently, Takagi<sup>12</sup> has extended Kittel's theory and has proved that the main conclusions

TABLE III. Transition energy.

Composition	Lower transition	Upper transition
$\text{PbZrO}_3$	...	440 cal/mole
$(\text{Pb}_{92.5}\text{-Ba}_{7.5})\text{ZrO}_3$	190 cal/mole	230 cal/mole
$(\text{Pb}_{95}\text{-Sr}_5)\text{ZrO}_3$	180 cal/mole	230 cal/mole

<sup>10</sup> C. Kittel, Phys. Rev. **82**, 729 (1951).

<sup>11</sup> Y. Takagi, Phys. Rev. **85**, 315 (1952).

<sup>12</sup> Y. Takagi, presented at the meeting of the Phys. Soc. Japan on October 5, 1951, held at Tokyo University, Tokyo, Japan.



obtained in his first paper are still valid for more general cases not based upon a specific model of rotatable dipoles. Some of the criteria given by these theories are really satisfied in the two antiferroelectric phases in the present case.

Kittel has also shown that the peak value of the permittivity at the antiferroelectric *vs* paraelectric transition is generally not pronounced for both first and second kinds of transition. In addition to this general case, however, Takagi's theory has emphasized the possibility that the permittivity can in some special cases show a very sharp maximum at the Curie point. In such special cases, a ferroelectric state instead of an antiferroelectric one can be realized by a very small change of the polarizabilities of the constituent ions. This theoretical prediction is in good accordance with the observation of the sharp change of permittivity in pure  $\text{PbZrO}_3$  and of the appearance of the ferroelectric phase in  $(\text{Pb}-\text{Ba})\text{ZrO}_3$  compositions. It should be added here that Takagi's theory has predicted the possibility of a forced transition by a strong electric field in such special cases.

Attention must now be paid again to the low peak value of the permittivity at the antiferroelectric *vs* paraelectric transition in the  $(\text{Pb}-\text{Sr})\text{ZrO}_3$  system. It has been known that all of the solid solutions, such as  $(\text{Pb}-\text{Ba})\text{TiO}_3$ <sup>13,14</sup> and  $(\text{Pb}-\text{Sr})\text{TiO}_3$ ,<sup>13,15</sup> show the same ferroelectric transition of  $\text{BaTiO}_3$  type with a large peak value of the permittivity at this point. Moreover, the ferroelectric transition in the  $(\text{Pb}-\text{Ba})\text{ZrO}_3$  system also shows the same type of large permittivity anomaly, though this ferroelectric phase seems to be different from that of  $\text{BaTiO}_3$ . So the observations on the

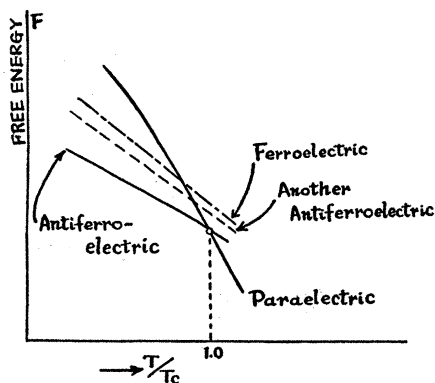


FIG. 18. Free energy curves for  $\text{PbZrO}_3$ .

$(\text{Pb}-\text{Sr})\text{ZrO}_3$  system must be attributed to the fact that the upper transition in this system is an antiferroelectric *vs* paraelectric transition in contrast with the ferroelectric *vs* paraelectric transition in all other systems. Also, we can consider that  $(\text{Pb}-\text{Sr})\text{ZrO}_3$  compositions show the general characteristic of a small permittivity change at the antiferroelectric Curie point, in accordance with the theoretical prediction. Of course, there exists a suspicion that this low peak value is the result of the sluggishness of the transition, but this possibility has been removed by observation of the sharp changes in the thermal expansion and specific heat curves at this point (Figs. 16 and 17). With decreasing Sr concentration, the situation seems to approach a special case in which a sharp change of permittivity does occur.

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<sup>13</sup> G. H. Jonker and J. H. van Santen, *Chem. Weekblad* 43, 672 (1947).

<sup>14</sup> G. Shirane and K. Suzuki, *J. Phys. Soc. Japan* 6, 274 (1951).

<sup>15</sup> S. Nomura and S. Sawada, *J. Phys. Soc. Japan* 5, 279 (1950).

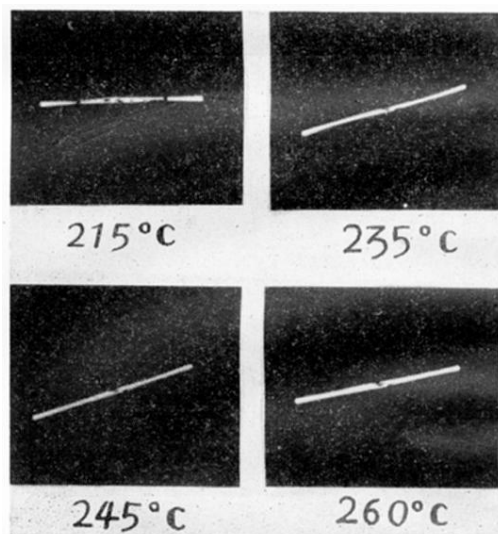


FIG. 12. Hysteresis loops of (Pb95-Sr5)ZrO<sub>3</sub> at  $E_{\max}=30$  kv/cm.

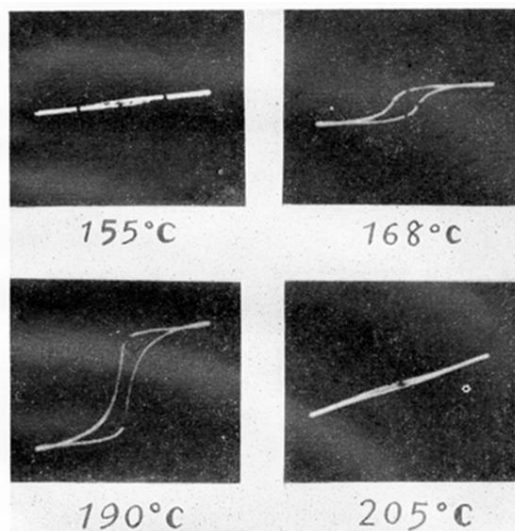


FIG. 2. Hysteresis loops of (Pb92.5-Ba7.5)ZrO<sub>3</sub> at  $E_{\max}=20$  kv/cm.

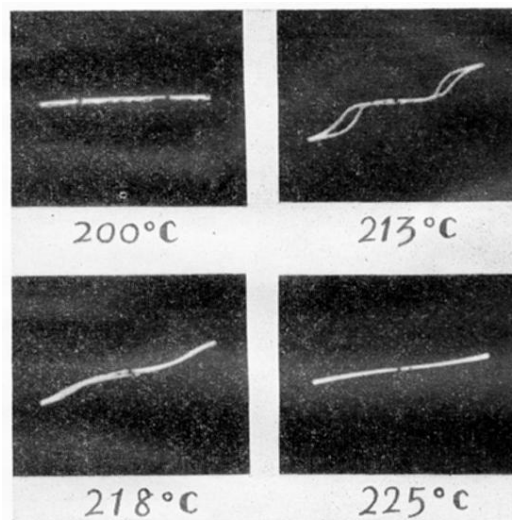


FIG. 6. Hysteresis loops of (Pb97-Ba3)ZrO<sub>3</sub> at  $E_{\max} = 20$  kv/cm.