Ferrielectricity*

CHARLES F. PULVARI

Department of Electrical Engineering, Solid State Research, The Catholic University of America, Washington, D. C.

A new group of materials has been found exhibiting ferroelectric behavior. It was found that this behavior appears in a mixture of antiferroelectric compounds (sodium vanadate and sodium niobate; also sodium niobate and silver niobate) neither of which exhibits this phenomenon at low field strength in their pure states. Coercivity as well as polarization is composition dependent. The onset of the ferroelectric state is a function of applied field, which in some compositions is considerably higher than the coercive field. Switching transients of a form not previously reported are exhibited by these materials.

DURING the course of a high-temperature ferro-electric research program a new group of materials has been found exhibiting ferroelectric behavior.

The materials here reported are essentially composed of two antiferroelectric materials and have been discovered in the heretofore not reported mixed crystal of sodium vanadate-niobate $Na(V_xNb_{1-x})O_3$. Although neither sodium niobate[1] nor sodium vanadate[2] exhibit ferroelectric properties at low field strength in their pure form, this new material shows an antiferroelectric Curie point at 375°C and a ferroelectric behavior below 225°C. These transition points vary slightly with composition. Using the above constituents mixed crystals up to a 50–50% composition were produced. However the chemical analysis of these crystals has not yet been done, because no suitable solvent was found so far. They were unsoluble even in hot hydrofluoric acid. The compositions however so prepared yielded good crystals. The crystals were cubic-like, light-transparent with clear cut shiny faces and had easy cleavage planes. Figure 1 shows a typical thin plate which has been cleaved from larger cubes and has been prepared for investigation. The photograph also shows the large homogeneous domain area which could be observed in cross-polarized light under a microscope. The large dark areas are homogeneous c domains and the white spikes are a domains. The a domains have been chosen purposely so as to bring out more pronounced the difference between the c and the a domains. From the mixed crystal compositions so far produced, large uniform domain structure was obtainable, and it is believed that this is due to the fact that vanadium fits very well into the niobate structure with its slightly smaller Goldschmidt radii. It is noted that this good domain structure was quite abundant and even in a small batch a large number of good samples could be produced.

Figure 2 shows dielectric anomaly of a 20% sodium vanadate and 80% sodium niobate mixed crystal.

It is noted that while the pure sodium niobate has an antiferroelectric Curie point of 375° and the pure vanadate has an antiferroelectric Curie point above 400°, the mixed crystal of the two antiferroelectrics shows a ferroelectric Curie point at about 225°C with a pronounced transition as shown in Fig. 2. This material exhibits well-saturated hysteresis loops from room temperature up to the ferroelectric Curie point. These hysteresis loops appear beyond a threshold field, below which minor loops are not observed.

Figure 3 shows the opening of hysteresis loops as the applied field increases. It is striking that in a large number of samples so far investigated the hysteresis loops opened only when a field much larger than the coercive field indicated by the hysteresis loop was applied.

In Fig. 3 the first line represents an applied field of 7.5 kv/cm. The second line represents an applied field of 12 kv/cm. The third picture shows a still larger applied field of 15 kv/cm at which field the hysteresis loop opens indicating a coercive field of 5 kv/cm which is three times smaller than the field required for opening the loop.

A less pronounced example of this type of loop is given in Fig. 4. In this case the straight line shows the necessary applied field of 8 kv/cm before the

FIG. 1. Cleaved thin plate of $Na(V_{0.2}Nb_{0.8})O_3$ crystal.

[1] G. Shirane *et al.*, Phys. Rev. **96**, 581 (1954).
[2] S. Sawada and S. Nomura, J. Phys. Soc. Japan **6**, 192 (1951).
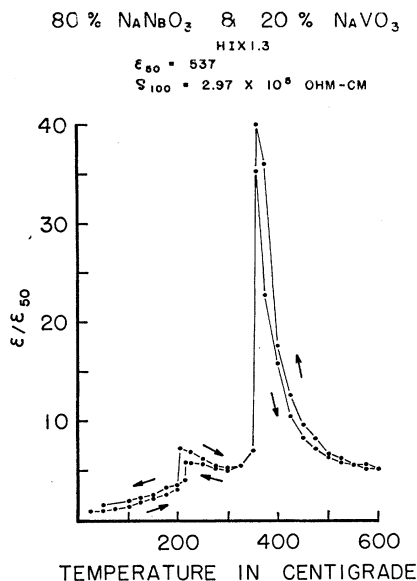
FIG. 2. Temperature dependence of the dielectric constant of sodium vanadate-niobate $Na(V_{0.2}Nb_{0.8})O_3$.

$E_c=6$ kv/cm loops open. It is noted that the coercive voltage measured from the loops are smaller than the opening field and decreases as the applied voltage increases.

Our preliminary work indicates that with the reported 50–50% composition limits the coercive field in these crystals varied between 6 to 18 kv/cm, and saturation polarization varied between 0.67–18.9 microcoulomb. It was found that as the vanadate substitution in-creases, coercivity decreases, and saturation polarization increased.

The transients obtained from this new material differ from those found in ordinary ferroelectrics. In some compositions simple transients were observed, in others transients with a number of peaks or even two time-separated transients appeared, indicating a here-tofore not reported peculiar switching mechanism.

Figure 5 shows a typical transient of this kind. Tran-sient measurements of the composition $Na(V_{0.2}Nb_{0.8})O_3$ are summarized in Fig. 6 in which the maximum value of the switching transient current (i_{max}) versus applied pulse field is displayed. It is noted that the transient current drops to such a low level below a certain applied field that it is very difficult to determine whether this plot can be described by the exponential expression used for ordinary ferroelectrics.

The first member of this new group of materials was produced by composing two antiferroelectric materials into a mixed crystal. A logical continuation of this work was to compose other antiferroelectric materials into a mixed crystal, and see whether the result would be similar to the first discovered material of this kind.

Since in the niobate group, silver niobate[3] is also known to be antiferroelectric, the composition

$$(Na_{1-x} Ag_x) NbO_3$$
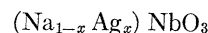
was investigated and showed also the previously discussed behavior with excellent hysteresis loops and transients. Sodium silver niobate mixed crystals containing up to 15% silver niobate were so far prepared and exhibited excellent hysteresis loops and transients.

FIG. 3. The opening of hysteresis loops in so-dium vanadate-niobate with increasing field. 6000 cps, $E_c=8$ kv/cm, $P_r=1.5$ μ coulomb.
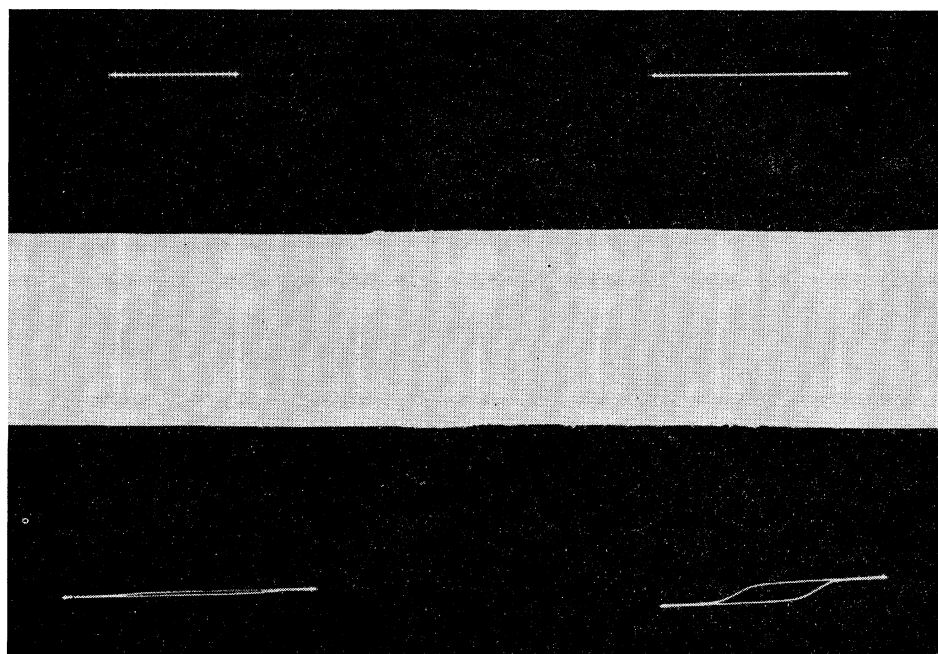
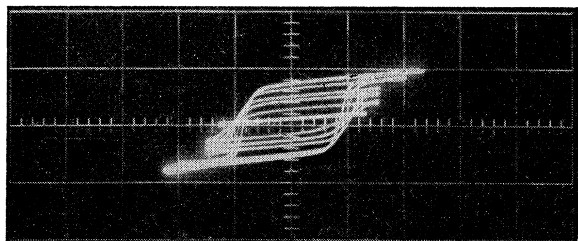[3] M. H. Francombe and B. Lewis, Acta Cryst 11, 175 (1958).

FIG. 4. Hysteresis loops at room temperature of sodium vanadate-niobate. 10 000 cps, $E_c = 6$ kv/cm, $P_r = 12.9$ μcoul.

As silver niobate substitution increases, coercivity tends to decrease more rapidly than with vanadate substitution. With the composition so far prepared the ferroelectric Curie point appears to be somewhat higher than in sodium niobate vanadate and it is in the region of 240°C, while the antiferroelectric Curie point remains at 375°C.

Figure 7 shows transients of a 10% silver and 90% niobate composition at room temperature. The transient shown was produced by a switching field of 18 kv/cm, while half of this field does not show switching. This composition had a coercive field of 6 kv/cm obtained by loop measurements.

Figure 8 shows the relation between switching time τ_s and applied field $1/E$ at room temperature and at 215° centigrade. It is noted that the measured points at the low-field end that fit an exponential low of the type $\tau = \tau_0{}^{\alpha/E}$, which is indicated by the straight lines, cover a rather short range for each temperature plot. It is also noted that below 8200 v/cm at room temperature and 6000 v/cm at 215°C, the transient currents decrease to an immeasurable low value. It is therefore difficult to determine exactly this relationship at this time.

Using the three antiferroelectrics of the niobate group, a few batches of the multicomponent system described by the following general formula

$$(Na_{1-y}Ag_y)_{1-z}(Nb_{1-x}V_x)_zO_3$$
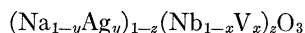
were also prepared. These compositions gave also good crystals as well as ferroelectric properties similar to those previously discussed.

On a macroscopic scale below the ferroelectric Curie

FIG. 5. Switching current transient of sodium vanadate-niobate Na(V$_{0.2}$Nb$_{0.8}$)O$_3$ at room temperature, with an applied potential of 125 volts and 250 volts; switching time $\tau_s = 6$ μsec and maximum switching current $i_{max} = 0.4$ ma.

point, the electrical behavior of these new materials appears to be similar to that which we associate with ferroelectrics. Between the ferroelectric and antiferroelectric Curie points the silver or vanadate sublattice seems to relax and the material appears to be antiferroelectric, because the antiferroelectric Curie point shown in Fig. 2 at 375°C remains in all compositions, so far investigated, unchanged and a degenerated double hysteresis loop also appears when high fields are applied. It was observed that domains have to be aligned at a temperature higher than the antiferroelectric Curie point. However, when the switching characteristics of ordinary ferroelectrics and these new
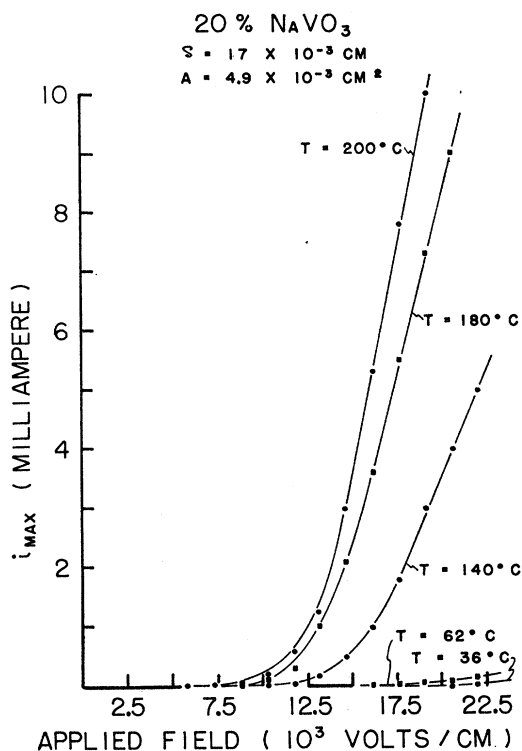

FIG. 6. Maximum switching current i_{max} versus applied field at various temperatures. Sample thickness $\delta = 17 \times 10^{-3}$ cm and area $A = 4.9 \times 10^{-3}$ cm^2.

materials are compared the following distinct differences become apparent:

(1) In general the tested samples indicate that the opening of a hysteresis loop requires a higher field than the coercive field measured on the hysteresis loop.

(2) The switching transients do not appear continuously with increasing field as is the case with ordinary ferroelectrics but appear rather abruptly beyond a certain threshold field. This apparent threshold field lies usually considerably higher than the coercive field determined from loop measurements.

(3) The transients appear in various forms depending on the sample preparation and composition.

FIG. 7. Switching current transient of sodium-silver niobate $(Na_{0.9}Ag_{0.1})NbO_3$ with an applied potential of 125 volts and 250 volts; switching time $\tau_s = 15$ μsec and maximum switching current $i_{max} = 4.8$ ma.

It is known that in ordinary ferroelectrics a threshold switching field cannot be expected because dipole-dipole interaction perpendicular to the direction of polarization is weak which is indicated by the very thin domain walls[4] separating oppositely polarized domains, while in antiferroelectrics the transverse coupling of the antidipole structure is so strong that a very high field is required to cause some of the dipoles to reverse and induce a ferroelectric state, which is observed by the well known double hysteresis loops.

As a result of this study it is assumed that the reported materials composed of two antiferroelectrics, the dipoles of which however are unequal, exhibit strong transverse dipole-dipole interaction and the resulting onset of the ferroelectric state at a maximum applied field.

This suggests that this new group of materials with ferroelectric properties be named "ferr*i*electrics" because of its analogy with ferr*i*magnetic materials. The term "ferrielectricity" was used earlier by Cross[5] as well as by Kanzig[6] and Goldsmith.[7]

Kanzig defines ferrielectrics as "crystals that exhibit at a given temperature antiferroelectric properties along one axis and ferroelectric properties along another

FIG. 8. Switching time τ_s vs applied field of sodium-silver niobate. $(Na_{0.9}Ag_{0.1})NbO_3$ at room temperature and 215° centigrade. Crystal thickness $\delta = 16 \times 10^{-3}$ cm and electrode area $A = 2.5 \times 10^{-3}$ cm^2.

axis," while Cross uses this term for a particular phase of ferroelectric and antiferroelectric mixed crystals. Goldsmith found an uncompensated antidipole structure in thiourea in a particular temperature range and suggested to specify this state by the term "ferrielectricity."

It is assumed that other materials composed of sublattices with interlaced unbalanced antidipole structure representing an incompletely compensated antiferroelectric material may also exhibit "ferr*i*electric" behavior. As a result of this finding a large number of possible ferr*i*electric materials are under investigation. The result of this work will be presented in a forthcoming paper.

[4] W. J. Merz, Phys. Rev. **95**, 690 (1954).

[5] L. E. Cross, Phil. Mag. **1**, 76 (1956).

[6] W. Kanzig, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 4.

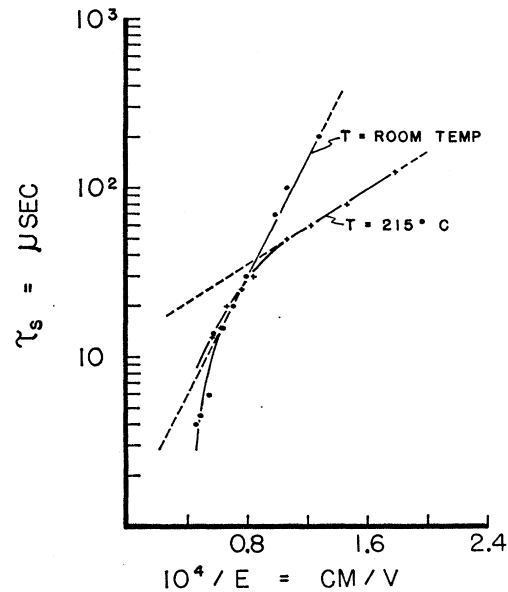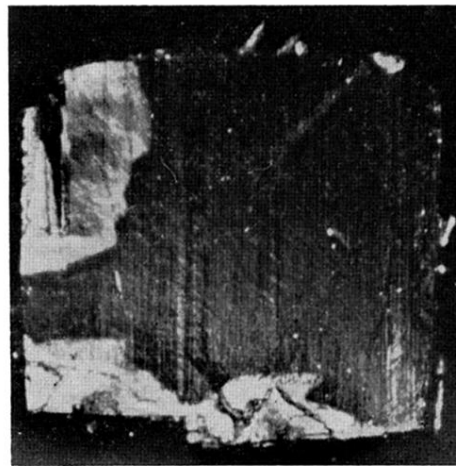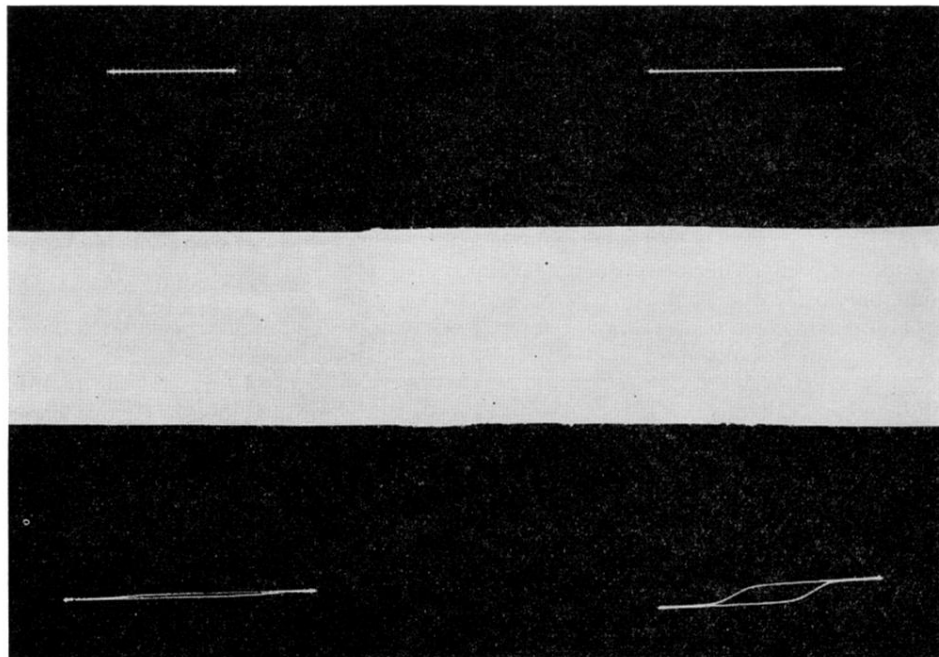[7] G. J. Goldsmith and J. G. White, J. Chem. Phys. **31**, 1175 (1959).

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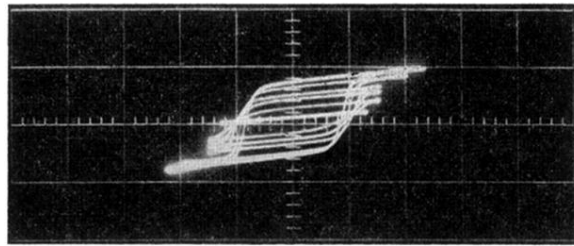
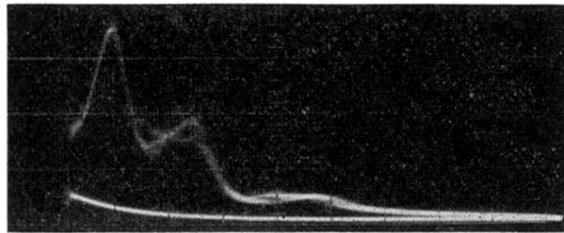FIG. 4. Hysteresis loops at room temperature of sodium vanadate-niobate. 10 000 cps, $E_c = 6$ kv/cm, $P_r = 12.9$ μcoul.

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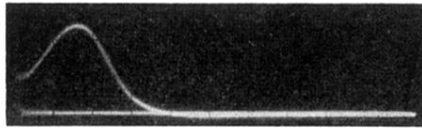
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