Nature of Aging in Ferroelectric Ceramics

G. H. JONKER

In the ferroelectric and piezoelectric applications of $BaTiO_3$ and $Pb(Zr,Ti)O_3$, dependence on time of many of their physical properties is encountered; this phenomenon is usually detrimental but is sometimes useful. Since aging is commonly considered to be related to the mobility of the ferroelectric domain structure, information on the nature of the aging process can be obtained by studying the changes in the hysteresis loops which occur with aging, as shown in Fig. 1. A "fresh" ceramic sample of $BaTiO_3$ (just cooled to a temperature below the Curie point) exhibits a normal loop which on aging constricts gradually, resulting in decreasing remanent polarization.

The rate and amount of constriction during aging are very sensitive to impurities and to slight variations in the Ba-Ti ratio. In the extreme case, the remanent polarization vanishes. This behavior can easily be confused with the double hysteresis loops exhibited by $BaTiO_3$ and $PbZrO_3$ as a result of field-enforced paraelectric-ferroelectric and antiferroelectric-ferroelectric transitions, respectively. The constriction disappears if the sample is subjected to strong ac fields for prolonged times; this process is called deaging.

The extremely constricted loop can be viewed as the result of reestablishment of the aged domain pattern after each half cycle. Strong fields are needed to disturb this pattern; however, after this disturbance a memory of the original state is retained, demonstrating that aging involves stabilization of the domain pattern. There is a general agreement[1] that such stabilization occurs, but several mechanisms are possible:

(1) Gradual equilibration of the domain pattern with respect to sizes and types of domains, with minimization of elastic and dielectric free energy.[1,2]

(2) Segregation of impurities and vacancies on domain walls and crystal boundaries.

(3) Ordering of impurities and vacancies inside the ferroelectric domains with respect to the polar axis.

Microscopy of single crystals and ceramics has demonstrated that process (1) occurs; however, its role in stabilization of the domain pattern is unclear.

In the present work, an experiment was conducted that demonstrated aging simply and indicated clearly that process (2) or (3) is its principal cause. The ceramic samples were solid solutions of 95% $BaTiO_3$ and 5% $BaZrO_3$. This composition has the advantage that aging can be followed over a reasonable time interval in the orthorhombic modification as well as in the tetragonal. In pure $BaTiO_3$ the transition from tetragonal to orthorhombic structure occurs at 5° to 10°C. As shown in Fig. 2, this transition temperature is raised to 30°C by the addition of 5% $BaZrO_3$. The ceramic samples were subjected to a temperature-time cycle, as shown in Fig. 3. At 50°C (in the tetragonal form), the samples age rather rapidly; some showed extreme constriction within a few hours. When such a specimen was cooled to a temperature below 30°C, the normal loop reappeared immediately. Subsequently, the sample again aged, but much more slowly than at 50°C. After 1 day, reasonable constriction was obtained. When the ceramic was heated above the transition temperature, the hysteresis loop immediately returned to the nomal shape. The results of this experiment can be understood easily in terms of two ferroelectric structures which have different orientations of the polar axes and thus completely different domain patterns. Therefore, stabilization of the domain pattern in one structure has no influence on that in the other.

When a sample aged at 50°C is alternately heated and cooled, the normal loop is exhibited on cooling, but the constricted loop reappears if the sample is reheated immediately. This experiment can be performed using a continuous ac field. If the time between cooling and heating is increased, the con-

Presented at the 73rd Annual Meeting, The American Ceramic Society, Chicago, Ill., April 28, 1971 (Electronics Division, No. 35-E-71). Received July 6, 1971; revised copy received September 27, 1971.

The writer is with the Department of Electronics, Twente University of Technology, Enschede, The Netherlands. At the time this note was written, he was on leave of absence at the State University of New York College of Ceramics at Alfred University, Alfred, N. Y. 14802.

[1] R. C. Bradt and G. S. Ansell, "Aging in Tetragonal Ferroelectric Barium Titanate," *J. Amer. Ceram. Soc.*, **52** [4] 192–99 (1969).

[2] A. Cohen, R. C. Bradt, and G. S. Ansell, "Dielectric Aging in Tetragonal Solid Solutions of Calcium Titanate in Barium Titanate," *ibid.*, **53** [7] 396–98 (1970).

[3] K. Okazaki and K. Sakata; *Electrotech. J. Jap.*, **7**, 13 (1962).

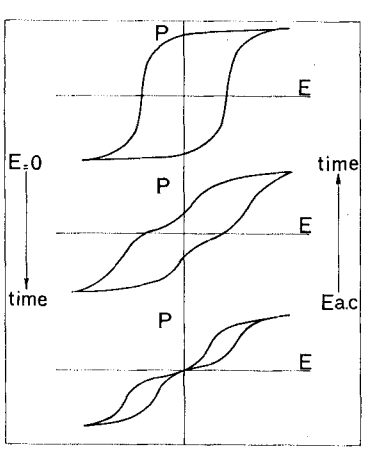

Fig. 1. Ferroelectric hysteresis loops showing increasing constriction on aging.

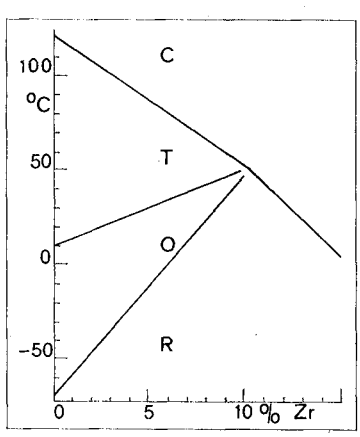

Fig. 2. Part of phase diagram for system $BaTiO_3$-$BaZrO_3$. *C*=cubic, *T*=tetragonal, *O*=orthorhombic, and *R*=rhombohedral.

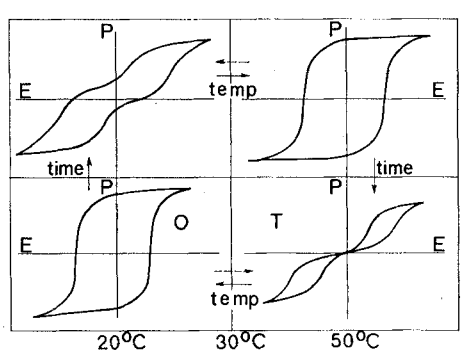

Fig. 3. Temperature-time cycle for $Ba(Ti_{0.95}Zr_{0.05})O_3$.

striction gradually disappears, demonstrating that the "memory" of the aged state fades gradually. The same reversibility occurs for a sample aged in the orthorhombic state and heated and cooled past the transition temperature. The conditions are less favorable in this case because the orthorhombic memory disappears much faster at the higher temperature.

The concept[1,2] that the aged state is determined by the equilibrium domain pattern would hold if only one pattern existed. This condition may be met in small crystallites, which contain only a few domains, but in ceramics with coarser crystallites (>10 μm) the number of domains inside each crystallite is so large that many low-energy patterns are possible. This statement is supported by the fact that comparable constrictions of hysteresis loops (asymmetric) can be obtained for any degree of prepolarization of the sample.[3] Therefore, it is thought that the present experiments indicate clearly that the domain pattern is stabilized by a diffusion process, e.g. mechanism (2) or (3), and that the resulting "diffusion pattern" forms the memory. In mechanism (2), this pattern would consist of an inhomogeneous distribution of the defects, which would accumulate on either domain walls or grain boundaries. In mechanism (3), a one-step diffusion process, local inhomogeneity with respect to the polar axis would exist. When the transition to a different structure occurred, this pattern would diffuse away slowly. At the same time, a new pattern is built up to accommodate the new domain pattern.

The diffusion pattern differs from the space-charge polarization proposed in Ref. 3. Since the domain pattern typically results from depolarization, there is no depolarizing field inside the domains.

Carbide Synthesis by Freeze-Drying

F. K. ROEHRIG and T. R. WRIGHT

VERY fine ceramic powders can be produced by freeze-drying.[1-3] The present note describes the use of this process for the generation of fine tungsten carbide powders. The chief advantages of the process over more conventional powder synthesis techniques are the generation of ultrafine particles and control of composition and purity.

Ultrafine WC and W_2C were prepared by freeze-drying a suspension of colloidal graphite in an ammoniacal tungstic acid solution. The solution-suspension was frozen rapidly to retain in the solid state the almost ideal mixing that existed in the liquid state and freeze-dried to remove the solvent. The resultant WO_3 was reduced using high-purity H_2; the resulting intimate mixture of W and C was reacted in vacuum at 1500°C for 30 min to form the carbide.

Figure 1 shows tungsten carbide particles synthesized by this process. The overall particle "chain" is ≈0.7 μm in diameter; however, individual particles are from 200 to 500 Å in size. The bonding together of the individual particles indicates that the vacuum conversion treatment may have been conducted at too high a temperature. These "chains" may be broken up by subsequent comminution. A BET surface analysis indicated that the mean particle size was ≈350 Å, in fair agreement with the values determined by electron microscopy. A high-precision X-ray powder pattern of the freeze-dried powder revealed the lines of WC and W_2C. The experimental lattice parameters agree quite well with literature values (Table I). Analysis of the powder revealed some free carbon, ≈85 wt% WC, and 15 wt% W_2C.

Fig. 1. Transmission electron micrograph of tungsten carbide (×66,000).

Table I. X-Ray Lattice Parameters for WC and W_2C

Material	Lattice parameters (Å) Exptl.	Ref. 4
WC	$a=2.905$	$a=2.9063$
	$c=2.835$	$c=2.8386$
W_2C	$a=2.98$	$a=2.992$
	$c=4.73$	$c=4.722$

Other carbide systems, e.g. Mo_2C, TiC, TaC, HfC, and VC, might be synthesized by freeze-drying if the thermodynamics of the particular system were favorable. The present work clearly demonstrates the feasibility of synthesizing ultrafine carbide powders.

Received July 29, 1971; revised copy received November 16, 1971.

The writers are with the Materials Application Division of Battelle Columbus Laboratories, Columbus, Ohio 43201.

[1] F. J. Schnettler, F. R. Monforte, and W. W. Rhodes; pp. 79–90 in Science of Ceramics, Vol. 4. Edited by G. H. Stewart. The British Ceramic Society, Henry Blacklock & Co., Ltd., Manchester, 1968.

[2] D. W. Johnson and F. J. Schnettler, "Characterization of Some Oxide Powders Formed by Freeze-Drying," *J. Amer. Ceram. Soc.*, **53** [8] 440–44 (1970).

[3] Y. S. Kim and F. R. Monforte, "Theoretically Dense (99.9%) Polycrystalline Alumina Prepared from Cryochemically Processed Powders," *Amer. Ceram. Soc. Bull.*, **50** [6] 532–34 (1971).

[4] E. K. Storms, The Refractory Carbides. Academic Press, New York, 1967.