

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
20 September 2001 (20.09.2001)

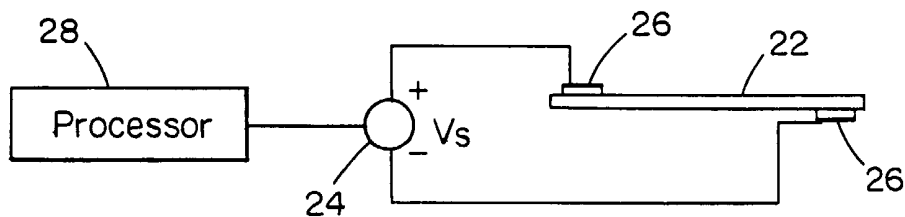
PCT

(10) International Publication Number
WO 01/69696 A2

- (51) International Patent Classification⁷: **H01L 41/00** (74) Agents: SMITH, James, M. et al.; Hamilton, Brook, Smith & Reynolds, P.C., Two Militia Drive, Lexington, MA 02421 (US).
- (21) International Application Number: PCT/US01/06744
- (22) International Filing Date: 2 March 2001 (02.03.2001) (81) Designated States (*national*): CA, JP, KR.
- (25) Filing Language: English (84) Designated States (*regional*): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).
- (26) Publication Language: English
- (30) Priority Data: 09/524,045 13 March 2000 (13.03.2000) US
Published:
— without international search report and to be republished upon receipt of that report
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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.
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(54) Title: RHOMBOHEDRAL-PHASE BARIUM TITANATE AS A PIEZOELECTRIC TRANSDUCER



(57) Abstract: A piezoelectric transducer includes a barium-titanate-based piezoelectric material having a poled, rhombohedral structure. The rhombohedral barium titanate structure can include a dopant, such as KNbO₃, BaHfO₃, BaSnO₃, BaZrO₃ or KTaO₃. The piezoelectric transducer can be used either as an actuator or as a sensor.

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RHOMBOHEDRAL-PHASE BARIUM TITANATE
AS A PIEZOELECTRIC TRANSDUCER

BACKGROUND OF THE INVENTION

Piezoelectric transducers are characterized in that they have the ability to (1)
5 generate a voltage when stress is applied and/or (2) produce a mechanical force
when a voltage is applied. These properties are generally referred to as the
"piezoelectric effect" and are found only in a limited number of materials.
Specifically, when stress is applied to these materials, displacement of the crystalline
structure produces a charge (or voltage) proportional to the strain. Conversely, when
10 an electric field (or voltage) is applied to the material, the shape of the crystalline
structure changes, thereby changing the dimensions of the material.

The ability of a piezoelectric transducer to generate a voltage when strained
enables its use as a sensor to detect displacement by monitoring the voltage that it
generates. Conversely, the characteristic expansion or contraction of the
15 piezoelectric transducer when a voltage is applied enables its use as an actuator to
produce a controlled force or movement. Both of these effects are useful for a
variety of electronic applications.

Tetragonal-phase barium titanate (BaTiO_3) was once the material of choice
for fabricating piezoelectric transducers. However, tetragonal-phase barium titanate
20 transducers were largely displaced from use when lead-based piezoelectric materials
(*e.g.*, lead zirconate titanate, a.k.a., PZT) were discovered due to the superior
performance in terms of the much higher strain levels and the higher piezoelectric
coefficient of the lead-based materials relative to traditional tetragonal-phase barium

titanate. Quartz is also used as a piezoelectric material. However, the magnitude of the piezoelectric effect exhibited by quartz is negligible in comparison to that exhibited by the lead-based materials that are used.

SUMMARY OF THE INVENTION

5 Notwithstanding the advantages of using lead-based materials, such as PZT, as piezoelectric transducers, use of these materials can cause significant problems. Because lead is toxic, its use often presents serious health and environmental hazards. Additionally, lead has a high vapor pressure and is highly reactive. Consequently, processes for fabricating a material with the desired lead-based
10 piezoelectric composition are very unpredictable and unreliable, and the defect rates of the resulting product are very high.

In contrast to known lead-based piezoelectric transducers, a piezoelectric transducer of this invention has a barium-titanate-based composition in a poled, rhombohedral structure. In preferred embodiments, the piezoelectric material is
15 stable at room temperature (and atmospheric pressure). The rhombohedral structure of the barium-titanate-based material can be stabilized at room temperature by doping the barium titanate with an appropriate concentration of KNbO_3 , BaHfO_3 , BaSnO_3 , BaZrO_3 or KTaO_3 .

The transducer can further include electrical contacts configured to allow for
20 transmission of a voltage to or from the barium-titanate-based piezoelectric material. Where the transducer is used as an actuator, a voltage source coupled with the transducer can supply a voltage to the transducer to generate physical displacement, or strain, in the piezoelectric material. Further, a processor programmed to determine the voltage necessary to produce a particular strain in the barium-titanate-
25 based material and further programmed to instruct the voltage source to generate that voltage can be put in communication with the voltage source to perform this function. In preferred embodiments, the barium-titanate-based material exhibits an absolute peak strain of at least about 0.1% when actuated by a voltage source. Where the transducer is used as a sensing device, a sensor can be coupled with the
30 transducer and used to detect the electric field generated by the barium-titanate-

based piezoelectric material under strain. Further, a processor programmed to calculate displacement as a function of the generated electric field can be put in communication with the sensor to calculate the displacement of the barium-titanate-based piezoelectric material.

5 The apparatus and methods of this invention offer a number of advantages over the prior art. A piezoelectric transducer of this invention offers relatively-high strain levels and piezoelectric constants far higher than those of tetragonal-phase barium titanate and comparable to those of PZT and other lead-based piezoelectrics without the toxicity and unpredictability that plague the use of lead-based materials.

10 Moreover, barium titanate is inexpensive and the know-how required to process it for piezoelectric applications is already in place due to the known use of conventional, tetragonal-phase barium titanate. Further, the addition of a respective percentage of a dopant, such as BaZrO_3 , BaHfO_3 , KNbO_3 , BaSnO_3 or KTaO_3 , within a particular concentration range in accordance with aspects of this invention results

15 in a barium-titanate-based material that can exist in a rhombohedral crystalline structure at or above room temperature and ambient atmospheric pressure, thereby facilitating its use for room-temperature transducer applications.

BRIEF DESCRIPTION OF THE DRAWINGS

20 The foregoing and other objects, features and advantages of the invention will be apparent from the following more-particular description of preferred embodiments of the invention, as illustrated in the accompanying drawings in which like reference characters refer to the same parts throughout the different views. The drawings are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the invention.

25 FIG. 1 is a phase diagram of a barium-titanate-based composition doped with varying percentages of KNbO_3 .

 FIG. 2 is a phase diagram of a barium-titanate-based composition doped with varying percentages of BaHfO_3 .

30 FIG. 3 is a phase diagram of a barium-titanate-based composition doped with varying percentages of BaSnO_3 .

FIG. 4 is a phase diagram of a barium-titanate-based composition doped with varying percentages of BaZrO₃.

FIG. 5 is a graph illustrating the strain level of a pair of rhombohedral-phase barium-titanate-based compositions of this invention and that of a pair of PZT
5 compositions of the prior art.

FIG. 6 is a drawing, partially schematic, of a piezoelectric actuator apparatus of this invention.

FIG. 7 is a drawing, partially schematic, of a piezoelectric sensor apparatus of this invention.

10 DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

A description of preferred embodiments of the invention follows. These embodiments are provided by way of example and not as limitations of the invention.

A piezoelectric transducer of this invention comprises a barium-titanate-
15 based piezoelectric material having a poled, rhombohedral structure.

The term, "poled," is used herein to describe a structure with a net polarization. During "poling," an electric field is applied to the material at high temperature (but below the Curie temperature of the material) to preferentially align the "domains" (wherein one or more domains are formed in each grain of the crystal
20 structure) toward the direction of the applied field. Poling serves an important function in piezoelectric materials and generally distinguishes piezoelectric materials from similar materials used in other applications, such as those used as capacitors where the structure of the composition is not poled. A poled composition will have an effectively lower dielectric constant at low fields compared to an unpoled sample.
25 In the case of high-strain materials, poling increases the maximum possible strain of the material.

A "rhombohedral" crystal lattice can be characterized in that the three axes of a unit cell are of equal length, and the three angles between axes are the same, and are not right angles. The rhombohedral structure is further defined by its location on

the phase diagrams of FIGS. 1-4 for various compositions of barium-titanate-based materials.

In addition to barium titanate (BaTiO_3), the transducer can also include other compositions in the form, for example, of dopants, substitutions, and additives for controlling properties such as resistivity, microstructure, sintering temperature, etc. However, the rhombohedral-phase barium titanate provides the essential structure for providing the desired piezoelectric properties. Accordingly, the term, "barium-titanate-based," is intended to include compositions with other ingredients and is not limited to pure barium titanate. Moreover, preferred embodiments of this invention include at least one dopant in the barium-titanate-based composition.

In a pure barium titanate composition, the crystalline phase will transform from rhombohedral to orthorhombic when the temperature of the composition rises above about -90°C . Accordingly, the rhombohedral phase cannot ordinarily be maintained in a barium titanate composition at or near room temperature (approximately 25°C). With the addition of a suitable concentration of any of a number of selected dopants, however, the rhombohedral structure of the barium-titanate-based composition can be maintained at or above room temperature at atmospheric pressure (approximately 101 kPa). Dopants selected for this purpose include potassium niobate (KNbO_3), barium hafnate (BaHfO_3), barium stannate (BaSnO_3), barium zirconate (BaZrO_3) and potassium tantalate (KTaO_3).

Phase diagrams for several barium-titanate-based compositions including KNbO_3 , BaHfO_3 , BaSnO_3 or BaZrO_3 are provided in FIGS. 1-4, respectively. In each of the phase diagrams, the molar percentage of the dopant is provided on the horizontal axis, with temperature in $^\circ\text{C}$ plotted on the vertical axis. The phase diagram for KTaO_3 , not illustrated, is very similar to that for KNbO_3 (FIG. 1). Consistent with FIGS. 1-4, approximate ranges of molar concentrations of each dopant that will produce a rhombohedral structure at room temperature and to temperatures above 50°C are shown in the table, below.

Material	Doping for rhombohedral phase at room temp.	Range of particular interest (rhomb@T>50C)
KNbO ₃	3.5-12%	4.5-8.5%
KTaO ₃	3.5-12%	4.5-8.5%
BaHfO ₃	7-22%	9-16%
BaZrO ₃	6-21%	8-15%
BaSnO ₃	7-14%	9.5-10.5%

Alternatively, these and other dopants can be used in combination, wherein lesser amounts of each of two or more dopants can generally be added to preserve the rhombohedral crystalline structure in the barium-titanate-based composition at room temperature and above.

In a preferred method for forming a poled, rhombohedral-phase, barium-titanate-based transducer of this invention, powders of barium titanate and the selected dopant are mixed and ball milled. The mixed composition is then sintered at a temperature in a range between about 700°C and about 1200°C. The sintered composition is then crushed and ball milled again. Next, the composition is pressed to form the desired shape and re-sintering at about 1200°C. The pressed composition is then poled at an elevated temperature below the Curie temperature of the composition. The conductive contacts can then be painted on the finished piezoelectric transducer.

A chart comparing the electromechanical behavior of a pair of barium-titanate-based compositions (one doped with BaZrO₃ and the other doped with KNbO₃) with the electromechanical behavior of a pair of PZT compositions is provided in FIG. 5. In the chart, the applied electric field is represented on the horizontal axis and is expressed in kV/cm, while strain is represented on the vertical axis in units of 10⁻⁴. The observed strain in a barium-titanate-based composition doped with 7% BaZrO₃ is represented by plot 12. Meanwhile, the observed strain in a barium-titanate-based composition doped with 3.8% KNbO₃ is represented by plot 14. For comparison, the strain behavior of a pair of PZT compositions reported in Park *et al.*, "Ultrahigh Strain and Piezoelectric Behavior in Relaxor Based

Ferroelectric Single Crystals," *Journal of Applied Physics* 82(4), 15 August 1997, 1804-1811, are provided as plots 16 (soft PZT-5H) and 18 (hard PZT-8). As is evident in the chart of FIG. 5, the strain rates for the two doped, rhombohedral, barium-titanate-based compositions (shown in plots 12 and 14) were competitive
5 with the strain levels for the two PZT compositions (shown in plots 16 and 18).

The piezoelectric transducer of this invention can be operated either as an actuator or as a transducer. A piezoelectric actuator apparatus of this invention is illustrated in FIG. 6. The apparatus includes a poled, rhombohedral-phase barium-titanate-based transducer 22; a voltage source 24 in electrical contact with contacts
10 26 on the transducer for supplying a voltage to the transducer 22; and a processor 28 in communication with the voltage source 24 and programmed to determine the voltage necessary to produce a particular strain in the barium-titanate-based piezoelectric material and to instruct the voltage source 24 to generate that voltage. Accordingly, the processor 28 governs displacement of the transducer 22 by sending
15 commands to the voltage source 24. The voltage source, in turn, supplies a voltage to the barium-titanate-based piezoelectric transducer 22 to produce the desired strain in the transducer 22.

A piezoelectric sensor apparatus of this invention is illustrated in FIG. 7. The apparatus includes a poled, rhombohedral-phase barium-titanate-based
20 transducer 22; a sensor 30 coupled with the transducer 22 for detecting an electric field generated by the barium-titanate-based piezoelectric material when the transducer 22 is strained; and a processor 28 coupled with the sensor 30 and programmed to calculate displacement (or strain) of the transducer 22 as a function of the generated electric field. Accordingly, when stress is applied to the barium-titanate-based piezoelectric transducer 22, the strain of the barium-titanate-based
25 piezoelectric material produces a voltage that is detected by the sensor 30, which communicates that voltage to the processor 28, which calculates the degree of displacement therefrom.

Representative applications for which the piezoelectric transducers of this
30 invention can be used include applications in optics, photonics and measuring technology; disk drives; microelectronics; precision mechanics and mechanical

engineering; and life science, medicine and biology. Specific applications in each of these fields are outlined, below.

In optics, photonics and measuring technology, a piezoelectric transducer of this invention can be used for image stabilization, scanning microscopy, auto-focus
5 systems, interferometry, fiber optic alignment and switching, fast mirror scanners, adaptive and active optics, laser tuning, mirror positioning, holography, and simulations of vibrations.

In disk drive applications, a piezoelectric transducer of this invention can be used for MR head testing, pole tip recession, disk spin stands, and vibration
10 cancellation.

In microelectronics, a piezoelectric transducer of this invention can be used for nano-metrology, wafer and mask positioning, critical dimensions measurement, microlithography, inspection systems, and vibration cancellation.

In precision mechanics and mechanical engineering applications, a
15 piezoelectric transducer of this invention can be used for vibration cancellation; structural deformation; out-of-roundness grinding, drilling and turning; tool adjustment; wear correction; needle valve actuation; micro pumps; linear drives; piezo hammers; knife edge control in extrusion tools; micro-engraving systems; and shock wave generation.

In life science, medicine and biology applications, a piezoelectric transducer
20 of this invention can be used for patch-clamp drives, gene technology, micro manipulation, cell penetration, micro dispensing devices, audiophysiological stimulation, and shock wave generation.

Note, however, that the list of applications, above, is far from exhaustive in
25 terms of the technologies in which the piezoelectric transducer of this invention can be used.

While this invention has been particularly shown and described with
references to preferred embodiments thereof, it will be understood by those skilled
in the art that various changes in form and details may be made therein without
30 departing from the scope of the invention encompassed by the appended claims.

CLAIMS

What is claimed is:

1. A piezoelectric transducer comprising a barium-titanate-based piezoelectric material having a poled, rhombohedral structure.
- 5 2. The piezoelectric transducer of claim 1, wherein the rhombohedral structure of the barium-titanate-based piezoelectric material is stable at or above ambient room-temperature conditions.
3. The piezoelectric transducer of claim 2, wherein the barium-titanate-based piezoelectric material includes KNbO_3 dopant
- 10 4. The piezoelectric transducer of claim 3, wherein the KNbO_3 dopant forms about 3.5 mol% to about 12 mol% of the barium-titanate-based piezoelectric material.
5. The piezoelectric transducer of claim 3, wherein the KNbO_3 dopant forms about 4.5 mol% to about 8.5 mol% of the barium-titanate-based piezoelectric
15 material.
6. The piezoelectric transducer of claim 2, wherein the barium-titanate-based piezoelectric material includes BaHfO_3 dopant.
7. The piezoelectric transducer of claim 6, wherein the BaHfO_3 dopant forms about 7 mol% to about 22 mol% of the barium-titanate-based piezoelectric
20 material.

8. The piezoelectric transducer of claim 6, wherein the BaHfO₃ dopant forms about 9 mol% to about 16 mol% of the barium-titanate-based piezoelectric material.
9. The piezoelectric transducer of claim 2, wherein the barium-titanate-based piezoelectric material includes BaSnO₃ dopant.
10. The piezoelectric transducer of claim 9, wherein the BaSnO₃ dopant forms about 7 mol% to about 14 mol% of the barium-titanate-based piezoelectric material.
11. The piezoelectric transducer of claim 9, wherein the BaSnO₃ dopant forms about 10 mol% of the barium-titanate-based piezoelectric material.
12. The piezoelectric transducer of claim 2, wherein the barium-titanate-based piezoelectric material includes BaZrO₃ dopant.
13. The piezoelectric transducer of claim 12, wherein the BaZrO₃ dopant forms about 6 mol% to about 21 mol% of the barium-titanate-based piezoelectric material.
14. The piezoelectric transducer of claim 12, wherein the BaZrO₃ dopant forms about 8 mol% to about 15 mol% of the barium-titanate-based piezoelectric material.
15. The piezoelectric transducer of claim 2, wherein the barium-titanate-based piezoelectric material includes KTaO₃ dopant.
16. The piezoelectric transducer of claim 15, wherein the KTaO₃ dopant forms about 3.5 mol% to about 12 mol% of the barium-titanate-based piezoelectric material.

17. The piezoelectric transducer of claim 15, wherein the KTaO_3 dopant forms about 4.5 mol% to about 8.5 mol% of the barium-titanate-based piezoelectric material.
18. The piezoelectric transducer of claim 2, wherein the barium-titanate-based
5 piezoelectric material exhibits an absolute peak strain of at least about 0.1% when actuated by a voltage source.
19. The piezoelectric transducer of claim 2, further comprising electrical contacts configured to allow for transmission of a voltage to or from the barium-titanate-based piezoelectric material.
- 10 20. An apparatus including the piezoelectric transducer of claim 19, the apparatus further comprising a voltage source electrically coupled to the contacts of the barium-titanate-based piezoelectric material.
21. The apparatus of claim 20, further comprising a processor programmed to determine the voltage necessary to produce a particular strain in the barium-titanate-based piezoelectric material and to instruct the voltage source to
15 generate said voltage.
22. An apparatus including the piezoelectric transducer apparatus of claim 19, the apparatus further comprising a sensor coupled with the contacts of the barium-titanate-based piezoelectric material for detecting an electric field
20 generated by the barium-titanate-based piezoelectric material under strain.
23. The apparatus of claim 22, further comprising a processor in communication with the sensor, the processor programmed to calculate displacement as a function of the generated electric field.

24. A method for actuation comprising:
coupling a voltage source with a poled, rhombohedral-phase, barium-titanate-based piezoelectric material; and
supplying a voltage to the poled, rhombohedral-phase, barium-titanate-based piezoelectric material to generate a physical displacement of the piezoelectric material.
25. The method of claim 24, wherein the poled, rhombohedral-phase, barium-titanate-based piezoelectric material undergoes a strain of at least about 0.1% when the voltage is supplied to the piezoelectric material
26. The method of claim 24, wherein the poled, rhombohedral-phase, barium-titanate-based piezoelectric material is at or above room temperature.
27. A method for sensing displacement comprising:
providing a rhombohedral-phase, barium-titanate-based piezoelectric material;
applying stress to the rhombohedral-phase, barium-titanate-based piezoelectric material to generate strain in said material; and
measuring the voltage generated by the strained rhombohedral-phase, barium-titanate-based piezoelectric material.
28. The method of claim 27, wherein the poled, rhombohedral-phase, barium-titanate-based, piezoelectric material is at or above room temperature.
29. A method for forming a barium-titanate-based piezoelectric material comprising:
thermally processing a precursor composition comprising barium titanate to obtain a rhombohedral-phase, barium-titanate-based crystalline structure; and

poling the rhombohedral-phase, barium-titanate-based crystalline structure to obtain a rhombohedral-phase piezoelectric material.

30. The method of claim 29, wherein the rhombohedral crystalline structure of the barium-titanate-based piezoelectric material is maintained at or above room temperature and atmospheric pressure.
- 5
31. The method of claim 29, wherein the precursor composition further includes at least one dopant that shifts the phase-transition temperatures of the composition to allow a stable rhombohedral phase to exist at or above room temperature and atmospheric pressure.
- 10 32. The method of claim 31, wherein the dopant is selected from the group consisting of KNbO_3 , KTaO_3 , BaHfO_3 , BaSnO_3 and BaZrO_3 .
33. The method of claim 31, wherein the barium-titanate-based piezoelectric material has a peak strain of at least about 0.1% when actuated by a voltage source.

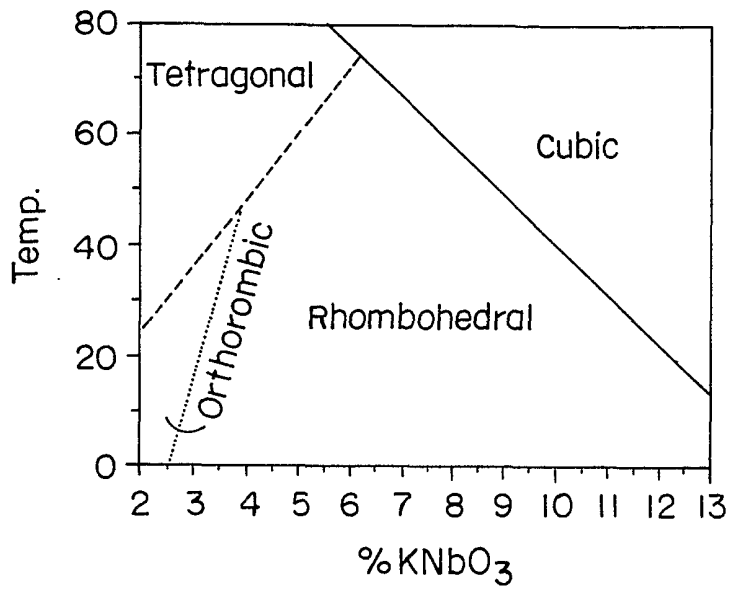


FIG. 1

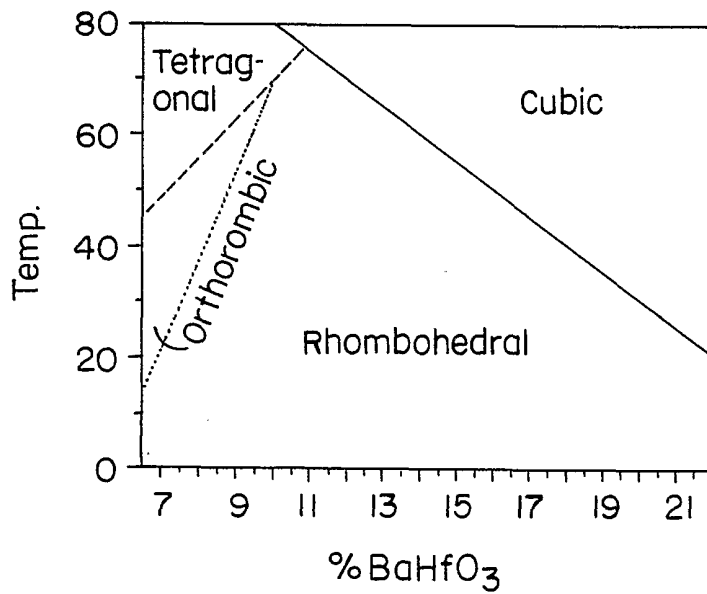


FIG. 2

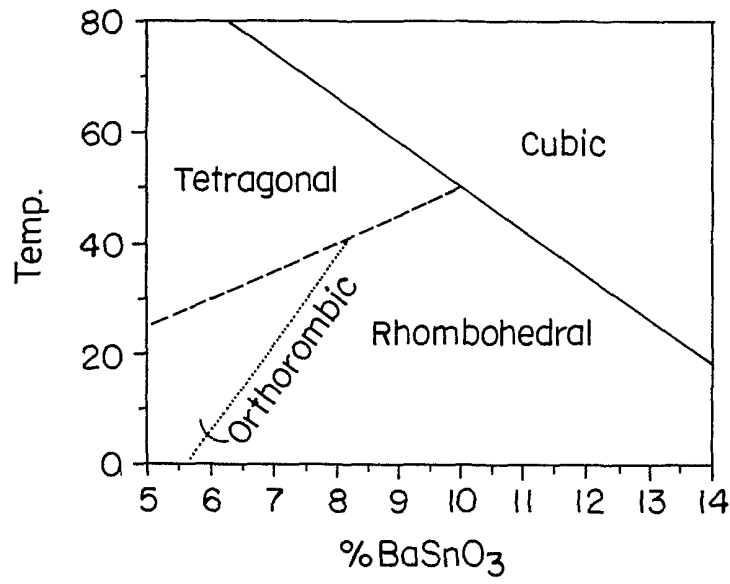


FIG. 3

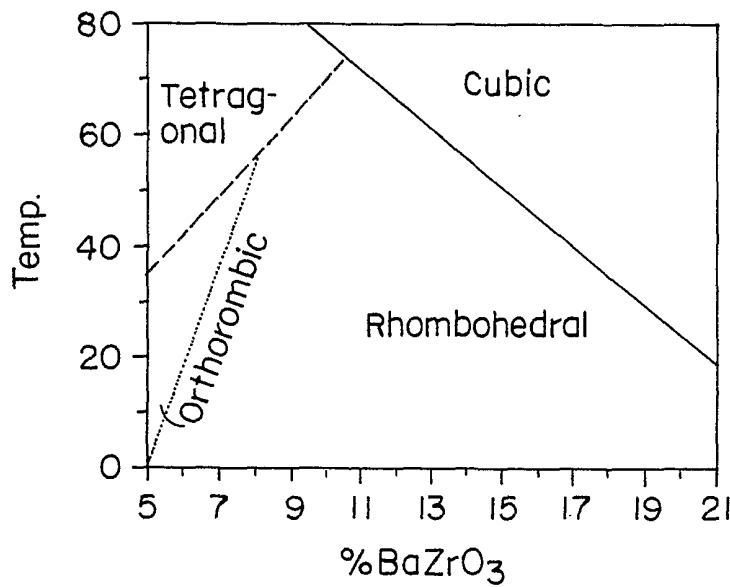


FIG. 4

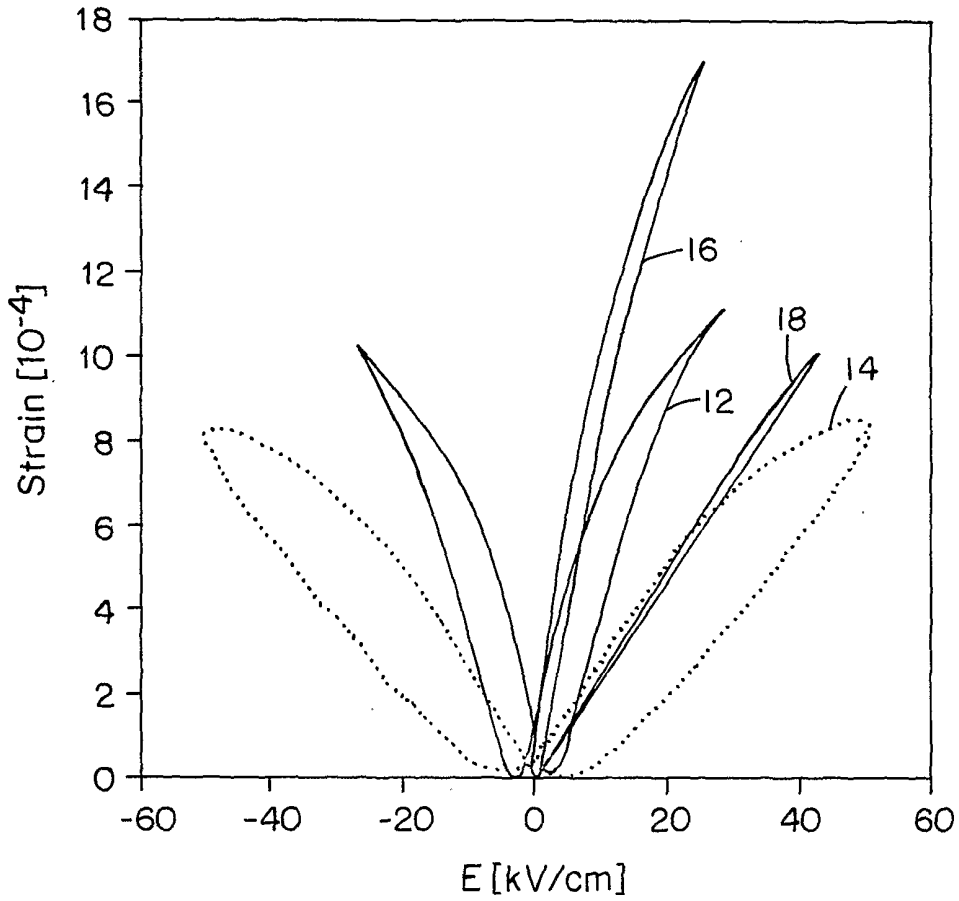


FIG. 5

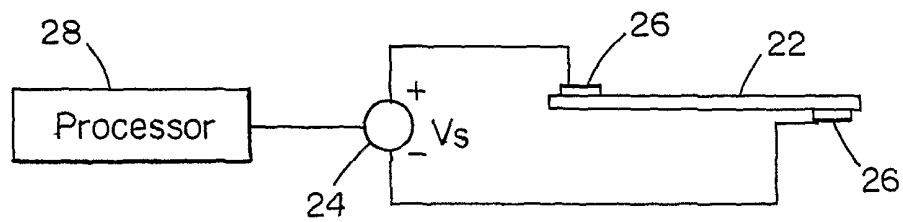


FIG. 6

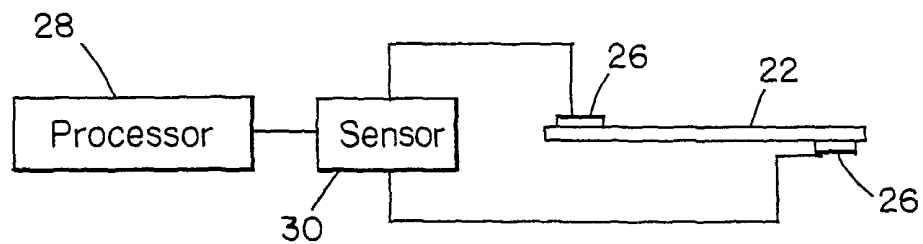


FIG. 7