March 31, 1953

G. N. HOWATT

2,633,543

BIMORPH ELEMENT

Filed April 19, 1948

Fig. 1.

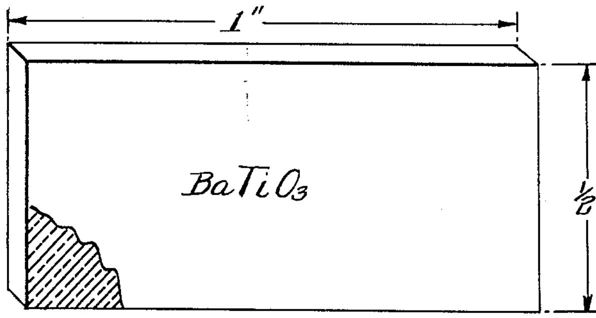


Fig. 2.

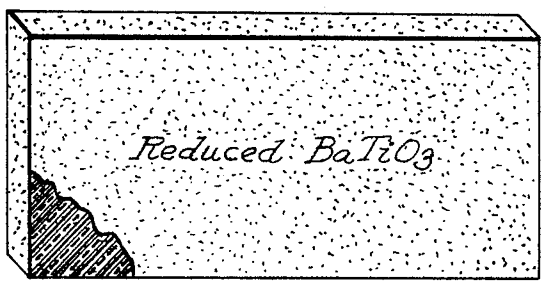


Fig. 3.

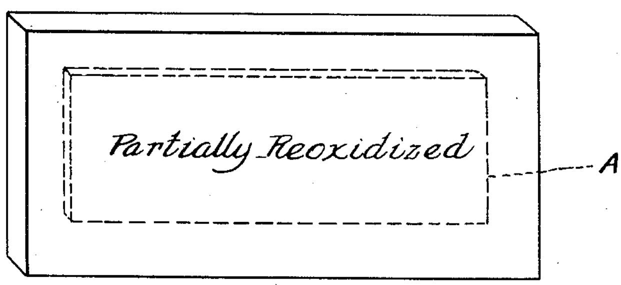


Fig. 4.

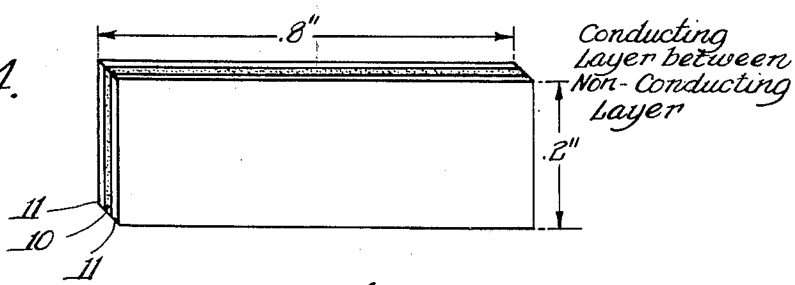
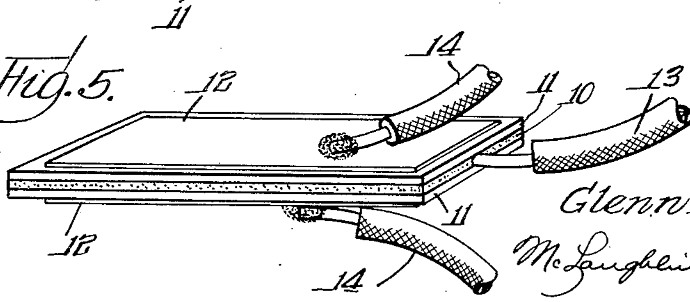


Fig. 5.



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UNITED STATES PATENT OFFICE

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BIMORPH ELEMENT

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15 Claims. (Cl. 310—9.8)

1

The present invention relates to a bimorph element and method of making the same and, more in particular, to a bimorph barium titanate transducer element.

It is known that if polygranular ceramics of the class comprising alkali earth metal titanates are subjected to an electro static charge they become active as piezoelectric elements. Barium titanate, particularly, has been used successfully as a transducer element. When so used, the element is supported in such a way as to be vibrated mechanically as by a phonograph needle and the alternating potential developed is picked up from signal electrodes carried on the large area flat surfaces of a thin sheet of the ceramic body. Various expedients have been employed to avoid a cancelling-out effect caused by the production of opposing stresses, and one such means comprises the use of two flat ceramic bodies with opposite charges and so secured together as to vibrate as a single body.

The principal object of the present invention is the provision of an improved bimorph titanate ceramic element particularly adapted for use in a transducer.

In carrying out the invention, an alkali earth metal titanate is first produced in the form of a thin sheet and this thin sheet is then partially reduced by heating the same to a relatively high temperature in a reducing atmosphere until the flat sheet becomes uniformly partially conducting. The reduced sheet is then heated for a shorter period of time in an oxidizing atmosphere to oxidize the exterior portions of the sheet and leave a conducting layer in the center thereof. By applying electrodes to the opposite large area surfaces and making an electric contact to the center conducting area the portions of the element on opposite sides of the conducting center area may be oppositely charged and vibration of the element so produced and so charged generates a voltage after the manner of conventional transducer elements. The details of the manner of carrying out the invention will be supplied hereinbelow in connection with the accompanying drawing where—

Fig. 1 is an enlarged perspective view, partly broken away, showing the ceramic before reduction thereof;

Fig. 2 is a similar view of the reduced ceramic;

Fig. 3 is a perspective view of the oxidized ceramic with dotted lines indicating one manner of trimming the so reduced and oxidized element;

Fig. 4 is a perspective view showing the trimmed element and indicating the center conducting layer; and

2

Fig. 5 is a perspective view showing the complete transducer with the signal leads and the center charging lead attached thereto.

In carrying out the process and producing the element, desirable results have been obtained with barium titanate ceramic and the drawing is prepared to show the steps of the process. In accordance with the example indicated by the drawing, a sheet of substantially pure barium titanate ceramic was first produced 1'' long by ½'' wide by 0.010'' thick. This sheet, shown in Fig. 1, was fabricated by suitable thin sheet techniques such as disclosed in my copending application Serial No. 554,294, filed September 15, 1944, now Patent No. 2,442,524 granted June 1, 1948, and the thin sheet fired to density in accordance with practices common in the art. The sheet so produced was of the type used for production of polygranular piezo crystals but generally of considerably greater dimension than commonly used for such purpose.

The barium titanate ceramic shown in Fig. 1 was then placed in a refractory porcelain plaque and reheated to a temperature of 1300 degrees C. in a hydrogen atmosphere for ten minutes. The resulting partially reduced body, shown in Fig. 2, is much darker in color than the pure barium titanate starting material and has a much lower electrical resistance than the original material. In general, the resistance of the reduced material will be found to be of the order of 100 ohms (the total resistance of the element shown in Fig. 2 measured from end to end is about 890 ohms), while the resistance of the original barium titanate ceramic unreduced is of the order of about 10^{12} ohms. Resistance measurements have not been accurately determined and have been made and are referred to only for the purpose of explaining that the material definitely becomes conductive when subjected to the high temperature reducing treatment. A piece of ten mil thickness will be found to be substantially uniformly reduced throughout its mass by ten minutes' treatment at the temperature disclosed.

The partially reduced ceramic shown in Fig. 2, having first been permitted to cool, was then reheated at a temperature of 1000 degrees C. for a period of five minutes in an oxidizing atmosphere, suitably air. This treatment re-oxidizes the surface portion of the sample but leaves a conductive strip or layer on the inside portion. By cutting the so partially re-oxidized element along the broken line A of Fig. 3, a strip 0.8'' long by 0.2″ wide by 0.010″ thick was produced, as shown in Fig. 4. By so trimming the material, the reduced center layer 10 is exposed around the edges leaving two outside layers 11 of totally oxidized substantially pure barium titanate ceramic.

Electrodes 12 were then applied to the opposite large area surfaces as shown in Fig. 5 by painting a conductive silver paste thereon, taking care not to make a contact between either of such electrodes and the center blackish reduced conducting layer in the center. A spot of silver was then placed on one end of the body and a charging lead 13 secured thereto. Signal leads 14 were soldered to the electrodes 12. The element was then charged by means of a direct current potential of 200 volts, the charging lead 13 being connected to the positive pole of the two leads 14 connected to the negative pole. Charging was continued for six minutes. The signal leads were then connected to an electronic galvanometer and the element stressed between rubber pads. The particular sample showed that a voltage of approximately 0.4 volt was generated under these circumstances, thus showing that the element had piezoelectric properties and comprised an active transducer element.

Those skilled in the art will understand that the features of the invention may be employed in various ways. The significant feature is the production of a conducting center layer by successive reducing and oxidizing procedures in which the re-oxidization is so limited as to extend only part way through the body of the reduced material. The center conductive layer constitutes the center electrode and the signal electrodes are applied by conventional methods such as painting with conductive paint, sputtering, or the like. Instead of partially reoxidizing the ceramic body and then applying the signal electrodes, the reduced material may be treated to apply the silver electrodes by spraying, dipping, painting, or the like, after which the element is dried and then sintered. If the sintering operation is carried out in an oxidizing atmosphere, it has the effect not only of bonding the silver to the ceramic but also of producing the oxidized surface layers in the same operation.

In the specific example given, the material treated was barium titanate, but one may practice the invention using other alkali earth metal titanates or mixtures of the same as, for example, a desirable mixture of strontium and barium titanate. Those skilled in the art will understand that barium titanate is much preferred for many purposes because of its relatively high Curie point. The elements have been produced in various sizes and shapes and embodied in operable devices where they performed satisfactorily as transducer elements, as, for example, in phonograph pick-ups and the like.

While the ceramic body is advantageously treated by the method described to reduce and then re-oxidize the same, other oxidation and reduction methods, or combinations thereof, may be employed. For example, the ceramic may be the cathode of an electrolytic cell during reduction and the anode during oxidation, as when the electrolyte comprises potassium perchlorate dissolved in sulfuric acid and maintained at 100 degrees C. during electrolysis. A molten body of sodium or potassium nitrate may also be employed as the electrolyte. Direct chemical treatment at temperatures below those employed in the hydrogen and oxygen reduction and oxidation, respectively, may be used. One advantageous method is to reduce the ceramic in a hydrogen atmosphere and carry out the oxidation electrolytically so that the thickness of the fully oxidized layers may be more readily controlled.

The use of a 200 volt charging potential for six minutes is, of course, illustrative, and is made possible because of the extreme thinness of the effective piezo layer. Usual times and charging voltages may be employed, depending on the results desired.

The bimorph element of my invention is not limited to use as a transducer. It may, for example, be a unit of a capacitor, and is extremely effective because of the high dielectric constant of the fully oxidized layer. It has a dielectric constant of the order of 1200 to 1400, for example, for $BaTiO_3$, as contrasted with a dielectric constant of 6 for aluminum oxide layers which are used in electrolytic condensers. When my process is used to produce a capacitor or like body, any portion of the surface not desired to be oxidized may be covered with a protective layer during the re-oxidation procedure.

When employing the bimorph element of my invention as a transducer it is desirable that it be an alkaline earth metal titanate, and barium titanate is particularly effective for this purpose. When the bimorph element is a unit in a capacitor or rectifier, however, other metal titanates, including titanium dioxide and mixtures thereof with various titanates, may be used.

What I claim as new and desire to protect by Letters Patent of the United States is:

1. The method of producing a bimorph titanate which comprises forming a strip of ceramic of a class consisting of metal titanates, titanium dioxide, and mixtures thereof, treating the said strip to partially reduce the ceramic body and decrease the electrical resistance thereof, and thereafter oxidizing only a portion of the strip to produce at least two layers having different electrical conductivity.

2. The method of producing a bimorph titanate ceramic element of the character described which comprises heating a strip of the class consisting of titanium dioxide and metal titanate and mixtures thereof, at an elevated temperature in a chemically reducing atmosphere until substantially the entire sheet becomes electrically conducting and then heating the so reduced sheet in an oxidizing atmosphere to oxidize only the surface portion thereof, leaving a conducting unoxidized center portion.

3. The method of producing an improved bimorph element of the character described which comprises heating a flat strip of barium titanate ceramic in a chemically reducing atmosphere until substantially the entire strip becomes electrically conducting, and then heating the so reduced strip in an oxidizing atmosphere to oxidize only substantially the surface portion thereof, leaving a center reduced conducting area.

4. The method defined in claim 2 wherein the temperature of the reducing treatment is of the order of 1250 degrees C. and in which both the time and temperature utilized in the oxidizing treatment are less than the time and temperature utilized in the reducing treatment.

5. The method of producing a barium titanate transducer which comprises forming a relatively thin flat sheet of barium titanate ceramic, heating said sheet in a reducing atmosphere at an elevated temperature until substantially the en-

tire body of the sheet becomes electrically conducting, heating the sheet in an oxidizing atmosphere to oxidize only the surface portion thereof, leaving a center layer of conducting material, cutting a transducer element from said sheet while at the same time exposing the conducting layer at at least one edge of said element, applying conducting electrodes to the opposite flat barium titanate layers to form signal electrodes, and charging the element by connecting the center conducting layer to one pole of the charging source and the two signal electrodes to the opposite pole of the charging source.

6. A bimorph element comprising a single piece alkali earth metal titanate having exterior non-conducting layers and an intermediate electrically conducting layer comprising a partially chemically reduced alkali earth metal titanate.

7. A bimorph element comprising a relatively thin flat sheet of barium titanate having a center layer sufficiently chemically reduced to be electrically conducting.

8. A bimorph element comprising a relatively thin flat sheet of barium titanate having a center layer sufficiently chemically reduced to be electrically conducting, and a pair of signal electrodes on opposite large area flat surfaces of the barium titanate, the layers of barium titanate on opposite sides of the conducting layer being oppositely charged.

9. A bimorph element comprising a ceramic body of the class consisting of titanium dioxide and metal titanate in the form of at least two layers, at least one layer of which comprises a partially chemically reduced layer of the said ceramic.

10. The method of claim 1, which includes the step of oppositely electrically charging the exterior layers on opposite sides of the conducting layer.

11. The method of claim 3, which includes the steps of oppositely electrically charging the exterior layers on opposite sides of the conducting layer.

12. A bimorph element comprising a single piece alkali earth metal titanate having exterior electrically non-conducting layers and an intermediate electrically conducting layer comprising a partially chemically reduced alkali earth metal titanate, said exterior layers on opposite sides of the conducting layer being oppositely electrically charged.

13. A bimorph element, in the form of a relatively thin flat sheet of a ceramic comprising barium titanate, said sheet having a central layer sufficiently chemically reduced to be electrically conducting, and a pair of signal electrodes on the opposite large area flat surfaces of said sheet.

14. A bimorph element comprising a relatively thin flat sheet comprising barium titanate having a center layer sufficiently chemically reduced to be electrically conducting, the exterior layers on opposite sides of the conducting layer being oppositely electrically charged.

15. The method of producing a transducer which comprises forming a relatively thin flat sheet comprising barium titanate, heating said sheet in a reducing atmosphere at an elevated temperature until substantially the entire body of the sheet becomes electrically conducting, heating the sheet in an oxidizing atmosphere to oxidize only the surface portion thereof whereby to leave a center layer of conducting material, applying conducting electrodes to the opposite flat surfaces of said sheet to form signal electrodes, and charging the resulting element by connecting the center conducting layer to one pole of the charging source and the two signal electrodes to the opposite pole of the charging source.

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