***Example No. A14*—GB1251933**

PIEZOELECTRIC STRUCTURE COMPOSED OF A CERAMIC FERRO-ELECTRIC MATERIAL HAVING A PEROVSKITE ARRANGEMENT OF COMPONENTS

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US3663440 (A1)
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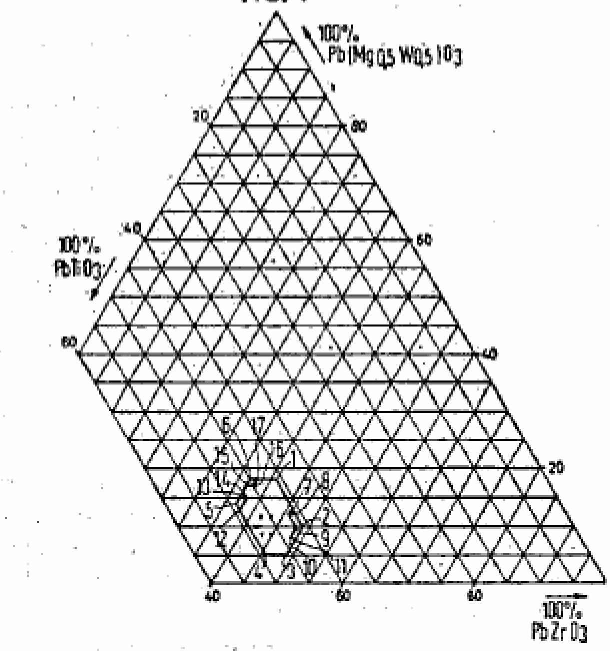
Abstract of GB1251933

1,251,933. Piezo-electric body. SIEMENS A.G. 27 July, 1970 [28 July, 1969], No. 36278/70. Heading C1J. A piezo-electric body having improved K, Q and E factors, is made of ceramic ferro electric material with a perovskite structure belonging to the triple component system X PbTiO 3 - Y PbZrO 3 -Z Pb(Mg 0 . 5 W 0 . 5)O 3 wherein the components are in 41-49, 37-49, 5-18 mol. per cent respectively, and contains 1% MnO 2 and 0À15% Al 2 O 3 based on the total weight of components. In the embodiments X, Y and Z, have the following values :- The compositions lie within the oven 1, 2, 3, 4, 5, 6 of Fig. 1 and E, Q, K factors were measured for compositions within the oven 1, 7, 8, 9,10, 11, 3, 4, 12, 13, 14, 15, 16, 17.

FIG. 1



X	Y	Z
0·465	0·420	0·115
0·450	0·435	0·115
0·480	0·420	0·100
0·480	0·435	0·085
0·465	0·450	0·085

Description of **GB1251933**

PATENT SPECIFICATION

(11) DRAWINGS ATTACHED (21) Application No 36278/70 (22) Filed 27 July 1970 (31) Convention Application No.

P 19 38 318 7 (32) Filed 28 July 1969 in Germany (DT) Complete Specification published 3 Nov 1971

International Classification-C 04 b 35/00 35/46 35/48 Index at acceptance C 1 J 19 2 319 (54) IMPROVEMENTS IN OR RELATING TO PIEZOELECTRIC BODIES (71) We, SIEMENS AKTIENGESELLSCHAFT, a German Company, of Berlin and Munich, Germany, do hereby declare the invention, for which we pray that patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

It) The present invention relates to piezoelectric bodies made of a ceramic, ferroelectric material with a perowskite structure, the components of which belong to the triple element system x Pb Ti O 3-y Pb Zr O 3z Pb(Mgn 5 W O s)O, and which also contain Mn O 2 and A 1203 as additives.

Recently, as piezoelectric bodies for use as elements in the conversion of electrical to mechanical energy and vice versa, (e g. for frequency filters), bodies made of a ceramic, ferroelectric material with a perowskite structure and whose components belong to triple element systems of complex composition have been proposed Whereas, hitherto, bodies of this kind have been manufactured on the basis of lead titanate zirconates, these new materials for piezoelectric bodies can be characterised in that the fundamental triple element system is Pb Ti O 3-Pb Zr OPb(A, B)O Here, for the A component it is possible inter alia to us the chemical elements Mn and Mg, whilst for the B component inter alia the chemical elements Sb Nb Ta, Bi and W can be used.

In this connection, the starting premise is that as far as the overall valency of the elements incorporated into the perowskite lattice is concerned, the valency sum of A+B must compensate for the valency of the tetravalent elements Ti and Zr replaced by them Taking the combination Mn+Sb. for example, it is possible to represent half the valencv of the substituted perowskiteforming elements by Mn 3 +, and the other lPrice 25 pl half by Sb 5 +, so that a triple element system of the form Pb Ti O 3-Pb Zr O 3Pb(Mn O s Sb O)O 03 results.

It is equally possible, however, for only 1/3 of the valency of the substituted ele 50 ments to be replaced by manganese and 2/3 by antimony or other elements of corresponding valency, so that a triple element system of the kind Pb Ti Oa-Pb Zr O 3Pb(Mn O 33 Sb O 67)03 results 55 The same applies to the substitution of Ti and Zr by magnesium and niobium so that a Pb Ti O 3 Pb Zr O 3 Pb(Mg O 33 Nb O 67)O 3 results.

Where this latter system is concerned, it 60 is known, moreover, that by the addition of Mn O 2 in quantities of between 0 2 and 3 %, in particular 1 %, the electromechanical coupling factor k and the mechanical quality factor Q are simultaneously im 65 proved Similar considerations can be produced from the prior art in respect of the sytem Pb Ti O-Pb Zr OQ-Pb(Mg O o W O 5)03, to which the present invention relates.

In considering additives to the above 70 mentioned known systems, as a general rule the starting point is that for the manufacture of piezo-electric bodies particularly pure starting materials must be used, whose impurity level is in fact so low that 75 additives in small quantities further increase the constitutents which may already be present as impurities, with respect to their effect on the electrical properties, or in other words, the starting point must at o 80 the very least be chemically pure starting materials so that piezoelectric and dielectric properties are perceptibly varied by these small quantities of additive materials.

It is an object of the present invention to 85 still further improve the already good characteristics of the Pb Ti OQ-Pb Zr O 3Pb(Mgo 5 W O o 5)O 3 triple-element system, i e.
to achieve an improvement in the electromechanical coupling factor k and the 90 1 251 933 (33) (45) (51) (52) 1 251 933 mechanical quality factor Q, as well as an increase in the e value.

According to the invention, there is provided a piezoelectric body made of a ceramic, ferroelectric material with a perowskite structure, the components of which belong to the triple element system x Pb Ti O-y Pb Zr O 3-z Pb(Mg,, W)O , wherein the components of the triple element systern lie within the ranges Pb Ti O: 41 to 49 Mol %, Pb Zr O, 37 to 49 Mol %, and Pb(Mg,WO 0)O 3 5 to 18 Mol % (the total of the components being 100 %,); wherein said material contains 1 %, by weight of 515 Mn O, based on the total weight of the components, and wherein said material contains about 0 15 % by weight of A 103, based on the total weight of the components.

Preferred embodiments of the invention will be apparent from the Table given below In this Table, the composition of the triple element system x Pb Ti O,-y Pb Zr O:z Pb(Mg, W O 0: is first given, and this is then followed by figures for the parmeters a, k, and Q obtained without the addition of Al Qe and finally figures for the same parameters obtained with the addition of 0.15 % Al Of 3 In drawing up the Table, it has been assumed that in the manufacture 30 of the piezoelectric masses or bodies the Pb O evaporation losses occurring during chemical reaction and sintering have been compensated for by starting with a surplus of 0 4 % by weight of Pb O 35 The manufacture of the bodies can be carried out using individually pre-roasted lead titanates, lead zirconates and lead magnesium tungstates, by sintering the pressed bodies at 1100 to 1250 C for two 40 hours: it is however a better procedure to use the individual components in oxide form or oxide-producing form (e g carbonates), in proportions which correspond to the desired stoichiometric proportions 45 and to react them with one another at around 800 to 1000 C and thereafter to sinter the formed bodies at between 1100 and 1250 C for two hours in order to obtain the end product; for the manu 50 facture of bodies made of materials having a perowskite structure, ceramic process stages which will be quite familiar to those skilled in the art are employed.

Figures for ceramic of the triple element systems x Pb Ti O-y Pb Zr Q,-z Pb(Mg,,5 W,,)O, with a 0 4 % Pb O excess and 1 % Mn OQ content:

without Al O with 0 15 % Al O:

x y z c k Q e k Q 0.465 0 420 0 115 1600 0 46 850 1870 0 62 1150 0.450 0 435 0 115 680 0 43 1250 850 0 54 1550 0.480 0 420 0 100 1420 0 46 850 1700 0 55 1270 0.480 0 435 0 085 1510 0 43 800 1760 0 58 1100 0.465 0

450 0 085 1090 0 49 650 1360 0 61 800 It is evident from the above Table that, by the addition of a relatively small quantity of ALO 3, substantial improvements in terms of electromechanical coupling, mechanical quality factor and even the e value, are achieved This result is surprising because hitherto A 1203 had simply been regarded as an aid to sintering and had been introduced in larger quantities, whilst to improve the electromechanical and electrical properties materials capable of incorporation into the perowskite lattice had been used, e g materials of the kind described above.

The invention, therefore, gives the surprising result that by the simple addition of A 103, substantial improvements are achieved It can be expected that similar improvements would be achieved with the other triple element systems referred to above.

The invention is illustrated by the drawings in which:Figure 1 is a triple diagram for the system Pb Ti O;-Pb Zr O-Pb(Mg,,s W,)_)03, showing the constituent ranges according to the 90 invention; Figure 2 is a part of the diagram of Figure 1 on an enlarged scale showing the dielectric constant e of bodies according to the invention which have been sintered at 95 I 150 C; Figure 3 is a similar diagram to that of Figure 2 showing the quality factor Q of bodies according to the invention which have been sintered at 1150 C; 100 Figure 4 is a similar diagram to that of Figure 3 showing the quality factor Q of bodies according to the invention which have been sintered at 1200 C; Figure 5 is a similar diagram to that of 105 Figures 2 to 4 showing the electromechanical coupling factor k for bodies according to the invention which have been sintered 1 251 933 at 1150 C; and Figure 6 is a similar diagram to that of Figure 5 showing the electromechanical coupling factor k of bodies according to the invention which have been sintered at 1200 C.

In the triple element diagram of Figure 1 relating to the system Pb Ti O 3-Pb Zr OQPb(Mg&,Wo 0)3, the compositions of the bodies of the present invention lie within the irregular hexagon with the corners marked 1, 2, 3, 4, 5, 6 The parameters e, Q, and k have been measured for bodies having compositions lying within the irregular polygon which is defined by the interconnection of the points 1, 7, 8, 9, 10, 11, 3, 4, 12, 13, 14, 15, 16, 17 Particularly preferred compositions are listed in the above Table and are marked by crosses in Figure 1.

In Figures 2 to 6, the hexagonal area 1, 2, 3, 4, 5, 6 of Figure 1 is shown on a much enlarged scale In each of these figures, the particular parameter involved (6, Q or k) is indicated by contours connecting compositions having the particular value of the parameter in question marked alongside the contour line.

The preferred compositions set out in the above Table, can of course be extended to include other compositions which can be determined without difficulty from a comparison of the individual diagrams.

Where this process of selection is concerned, the criteria adopted may differ depending upon whether a high e value or a high mechanical quality factor Q or a high electromechanical coupling factor k, which is required, or again whether optimum values of all three properties at one are desired.

Claims of **GB1251933**

WHAT WE CLAIM IS:-

1. A piezoelectric body made of a ceramic, ferroelectric material with a perowskite structure, the components of which belong to the triple element system x Pb Ti O,-y Pb Zr O 3-z Pb(Mg O 5 W,)30, wherein the components of the triple element system lie within the ranges Pb Ti O 3 41 to 49 50 Mol % Pb Zr O 3 37 to 49 Mol%, and Pb(Mg 05 W O 5)03 5 to 18 Mol % (the total of the components being 100 %); wherein said material contains 1 % by weight of Mn Oz, based on the total weight of the components, and wherein said material contains about 0 15 % by weight of A 1203, based on the total weight of the components.

2. A piezoelectric body as claimed in Claim 1, wherein in the triple element system x Pb Ti O 3-y Pb Zr O 3-z Pb(Mg O 5 W O 5)O 3, x, y, and z have the following values:

x= 0 465, y= 0 420, z= 0 115.

3. A piezoelectric body as claimed in Claim 1 wherein in the triple element system x Pb Ti O 3-y Pb Zr O 3-z Pb(Mgo 5 W O 5)O 3, x, y and z have the following values:

x= 0 450, y= 0 435, z= 0 115.

4. A piezoelectric body as claimed in Claim 1 wherein in the triple element system x Pb Ti O-y Pb Zr Oa-z Pb(Mgo s W O 5)03, x, y and z have the following values:

x= 0 480, y= 0 420, z= 0 100

5. A piezoelectric body as claimed in Claim 1, wherein in the triple element system x Pb Ti O 3-y Pb Zr O-z Pb(Mg O 5 W O 5)03, x, y and z have the following values:

x= 0 480, y= 0 435, z= 0 085.

6. A piezoelectric body as claimed in Claim 1, wherein in the triple element system x Pb Ti O 3-y Pb Zr O,-z Pb(Mg, s W O)03, x, y and z have the following values:

x= 0 465, y= 0 450, z= 0 085.

7. A piezoelectric body substantially as hereinbefore described with reference to the drawings.