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POLYCRYSTALLINE PYROELECTRIC DETECTOR IN WHICH THE
CRYSTALS ARE BOUND TOGETHER WITH A PLASTIC CEMENT
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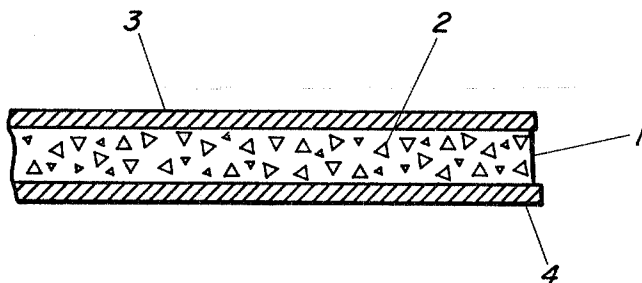


Fig-1

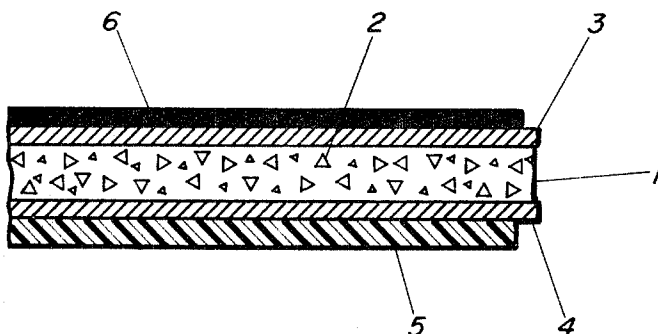


Fig-2

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POLYCRYSTALLINE PYROELECTRIC DETECTOR IN WHICH THE CRYSTALS ARE BOUND TO- GETHER WITH A PLASTIC CEMENT

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U.S. Cl. 250—83

8 Claims

ABSTRACT OF THE DISCLOSURE

Pyroelectric detectors are prepared with microcrystalline triglycine sulfate held together with a binder between metallic electrodes, one of the electrodes being preferably blackened to increase absorption of radiant energy. The size of the microcrystals can vary typically from 3 to 100 microns and can be prepared by wet grinding larger single crystals in acetone, or by precipitating the microcrystals by rapid cooling of the aqueous solution followed by filtering.

RELATED APPLICATIONS

This application is a continuation in part of my co-pending application Ser. No. 704,554, filed Feb. 12, 1968, now abandoned.

BACKGROUND OF THE INVENTION

Up to the Curie point the change in spontaneous polarization with temperature and dielectric constant of a pyroelectric material is increased. This effect is large enough in certain pyroelectric materials such as triglycine sulfate (hereinafter abbreviated in the specification as TGS) to be used as a temperature readout mechanism and is particularly attractive because no biasing current or voltage is required beyond a one-time application of a D.C. voltage of 10 kv./cm. of crystal thickness. TGS has been formed in single crystals, which have been difficult to grow and which are strongly limited in the size which can be practically produced. For some purposes pyroelectric detectors of fairly large size, for example one or more centimeters on a side, are desirable, but it has been impractical to produce them in the form of homogeneous crystals. Similarly, detectors of single crystals less than 0.5 x 0.5 mm. are difficult to produce because they require a reduction in thickness to maintain a minimum capacitance of 10 picofarads needed for the preamplifier input capacitance. Single crystal pyroelectric detectors use only non-transparent metallic electrodes, one of which is blackened to increase the absorption of radiant energy.

Another manufacturing problem is that the single crystal must be accurately cut with the planes of the electrode faces perpendicular to the ferroelectric axis of the crystal.

SUMMARY OF THE INVENTION

The present invention is based on the use of microcrystalline addition salts of TGS or lithium sulfate monohydrate as a material for pyroelectric detectors. The tiny microcrystals of course cannot be used as a powder, and in the present invention they are cemented together with a binder. This binder is a thermoplastic, such as cellulose acetate, cellulose acetate butyrate, cellulose nitrate, or polystyrene. The binder in solution in an essentially anhydrous organic liquid, such as acetone, amyl acetate, methylethyl ketone, benzene, toluene, etc., is mixed with the microcrystals as will be described below. The microcrystals are in sizes from about 3 μ to 100 μ in diameter, and produce highly sensitive pyroelectric detectors. While

the thermoplastic binder is present in smaller amounts than the microcrystals, it is possible to think of the material after solvent evaporation as the microcrystals embedded in a plastic matrix, though normally such a concept would be used where the matrix was present in larger amounts than the embedded material. In the present case, after solvent evaporation the thermoplastic binder is present in a range from 1% to 25% by weight of the microcrystals. Excellent results are obtained near the middle part of the range, for example about 10%, but the exact figure is not sharply critical, and useful detectors can be produced throughout the range, although at the two extremes they are of somewhat less desirable physical characteristics. Responsively is a function of being able to align the ferroelectric axes of the microcrystals perpendicular to the plane of the detector by a single application of a polarizing DC voltage. A pyroelectric detector is generally limited by the amplifier noise and the loss tangent of the crystal material.

The microcrystal layer, cemented together with the binder, can be quite thin, for example 10 μ to 250 μ , and in most cases is not sufficiently strong to be self-supporting. The film or layer is therefore preferably laid down on a stronger substrate, which should be electrically insulating. In general a conductive film is formed on the substrate to form one electrode of the detector, which, as in all pyroelectric detectors, may be considered as a variable capacitor. This electrode may be of any desired conductive material which does not oxidize at ambient temperatures to form an insulating compound. It may be a metal such as gold, nickel, Nichrome, platinum, and the like, or where the substrate can withstand a sputtering operation, it is also possible to lay down an electrode of certain conductive oxides such as cadmium oxide. The pyroelectric layer with the microcrystals either of the certain TGS addition salts, which will be set out below, or lithium sulfate monohydrate, is normally sprayed onto the electrode on the substrate while the microcrystals are suspended in a solution of the binder. The solvent evaporates, and the thin layer of cemented microcrystals remains. On top of this another electrode has to be deposited, and it is impractical to deposit this other than by vacuum deposition. This limits the material somewhat to metals such as gold, platinum, palladium, Nichrome, and the like. While the electrode on top of the layer of microcrystals must be vacuum deposited, it is often desirable to deposit both of the electrode layers, that is to say on the substrate and then on the layer, by vacuum deposition and this may be considered preferred.

Essentially the electrode films have to fulfill certain requirements. In the first place, there must be a continuous film of the conductor over the area of each detector. As the surface of the layer of microcrystals cemented together by the plastic binder is not perfectly smooth when viewed under high magnification, the requirement for continuity of the electrode film sets a limit on the thickness of this film, and films which have to be transparent to radiation of certain wavelengths are often too thin to produce a continuous film.

The film on the microcrystal layer must not reflect excessive amounts of the radiation to be detected by the detector. With a film so thin as to be transparent, this is ordinarily not a serious problem, but when somewhat thicker films, which are needed for continuity, are used, reflection may be a problem and therefore the surface of the film can advantageously be blackened with a thin layer of a black, for example a layer of silicon carbide pigments in fine sizes where blackness into far infrared is important. Other blackenings, such as gold black and the like, may be used where the detector is to be employed with radiations which are highly absorbed. The blackening layer is

relatively thin and must not be so thick that it has excessive thermal capacity. Otherwise, when used with high-frequency radiation the heating up of the blackening will not be transferred efficiently to the microcrystalline layer.

The substrate is not particularly critical, and well known detector substrates can be used. In some cases glass or fused aluminum oxide, known in the art as sapphire, may be used, and in other cases a thin but strong layer of polyglycol terephthalate, which is available under the trade name "Mylar," is desirable. Because of the versatility of such a tough film, the use of a thin film of thermoplastic, particularly Mylar, is preferred, although the invention is not limited thereto.

The pyroelectric microcrystals used in the present invention are triglycene sulfate, triglycene fluoroberyllate, triglycene selenate, and lithium sulfate monohydrate. The microcrystals of the three triglycene addition salts referred to above normally require polarization before the detector is used, as will be described below. Lithium sulfate monohydrate, however, will function even without polarization.

The method by which the microcrystals are prepared is not critical, and apparently the quality of the resulting pyroelectric detectors is substantially unaffected by the method used in preparing the microcrystals of TGS. One way is to take single crystals, for example small single crystals or waste from larger ones, and grind them wet, for example in acetone with a small amount of a solution or film-forming substance such as a cellulose alkanoate. It is also possible to produce the microcrystals direct by rapidly cooling down a saturated aqueous solution of TGS so that the crystals come down initially in very small size. In such a case, of course, the microcrystals may be ground and dispersed in the plastic film, if desired with some wet grinding in a solvent for the film-forming material.

The single application of a polarizing electromotive force to the polycrystalline detector serves only to improve the alignment of the electric dipoles parallel to the ferro-electric axes of the detector crystals. It was found that a polarizing voltage greater, such as five times greater, than for single crystal material was needed. Thus, for polycrystalline TGS layers 60 kv./cm. for 2 to 5 minutes at ambient temperature was suitable. If the Curie temperature of 47° to 49° C. is ever exceeded, polarizing must be repeated below the Curie point to realign the dipoles.

A typical microcrystalline TGS detector requires a capacitance, after polarization, of 10 to 500 picofarads. The responsivity is within a factor of 3 of the expected responsivity for a single crystal detector of equivalent area and capacitance. Since ultimately thinner layers of microcrystalline material can be formed than with single crystal material, the responsivity of the microcrystalline layer will therefore improve to equal or even exceed that of single crystal detectors.

Leakage resistance of the microcrystalline layer after polarizing was typically 10^{10} ohms which compares favorably with single crystal material.

For use in the infrared at wavelengths from 2μ to at least 35μ , the absorption of TGS crystals is quite high, so that one transparent metallic electrode without further blackening to enhance absorption of radiation may be employed. As has been pointed out above, transparent electrode layers can only be used if they are continuous. Suitable transparent metallic electrodes, as for example of Nichrome, must be of a thickness so that the resistance of a square area measures in the range from 500 to 5000 ohms. For example, a 1000 ohm per square Nichrome film itself absorbs about 20% of the incoming energy, transmits 70% to be absorbed by the TGS layer, and reflects about 10%. It is only the reflected energy which may be lost. This transparent electrode on the TGS, whether single crystal or polycrystalline, serves to obtain uniform spectral response from 2 to at least 35μ . For wavelengths where the transparency of TGS is greater, as for example below 2μ , blackening of the electrode en-

countering radiation is necessary, but in any event can be used even where a wavelength range is such that the TGS microcrystals are quite absorbent. In the case of long wave infrared, where ordinary blackening is not sufficiently absorptive, blackening from a dispersion of silicon carbide may be used, especially silicon carbide which has been ground down to an average particle size of 5–25 μ and which produces uniform black films of satisfactory thinness. These preferred blackenings are effected by wet grinding suspensions of larger silicon carbide pigment particles, for example up to 50 μ in average particle size, in a dispersion of a resin such as a thermoplastic alkyd resin in a suitable solvent. In general the present invention is not concerned with the use of any particular kind of blackening, and it is an advantage that where blackening is considered desirable, any known type, suitable for the radiation, may be used.

If a spectrally selective detector is required, a selective absorber, as for example Teflon at 9.2 μ , may be sprayed on top of a highly reflective gold electrode.

The uniform dispersion of the TGS microcrystals in a solution of the film forming substance can be obtained in a viscosity suitable for spraying. This makes it possible to spray through a very fine mask to form a mosaic of tiny areas so that a large detector surface suitable for an infrared vidicon tube is produced. Discharging by the conventional scanned electron beam can produce a video signal in the usual manner. Since the pyroelectric detector is sensitive out to the far infrared, this makes possible for the first time a practical infrared vidicon tube, and is a further important field for which the present invention is useful. This field was not practical with other infrared thermal detectors.

The tremendous advantages of the present invention, which permits forming pyroelectric detectors of any desired size, and also mosaic detectors, are obtained with only a very slight loss in sensitivity as compared to single crystals of TGS which are not practical for large detector areas or for mosaics.

TGS is the preferred material for use with ambient temperatures from 10° to 45° C. Other pyroelectric materials may be used and in some cases are needed, for example since the Curie point of TGS is between 47° and 49° C., if operation at a higher temperature is desired, a different addition salt such as a fluoberyllate may be used. For lower temperatures a selenate may be used. As has been stated above, lithium sulfate monohydrate is also useful. In general, responsivity is greatest at or slightly below the Curie point.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a section through a pyroelectric detector using only a plastic matrix, and

FIG. 2 is a similar section through a detector in which the matrix has been formed on a second plastic film.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The pyroelectric detectors are illustrated in FIGS. 1 and 2. In FIG. 1 the finely divided microcrystals 2 of the TGS are dispersed through a plastic matrix 1. On one side there is an electrode 3 and on the other side an electrode 4. These electrodes are very thin metal films such as thin films of gold or a partially transparent thin metal film such as Nichrome.

FIG. 2 illustrates a modification in which the matrix 1 is formed on a gold-plated, thin film of Mylar 5. This figure also illustrates an upper gold electrode 3 which is coated with a coating 6 of a thin suspension of silicon carbide particles. The thicknesses of the various layers are of course enormously exaggerated for clarity. The following description sets forth details of the formation of the plastic matrix containing the TGS microcrystals and also use of blackening for one electrode.

A suspension of polycrystalline TGS microcrystals 2 having an average size of 3μ to 100μ was produced by grinding down larger single crystals in a solution of 100 grams TGS in 200 cc. acetone, 100 cc. amyl acetate, the solution containing 10 grams of the cellulose alkanoate in ordinary commercial fingernail polish. This forms the dispersion containing the TGS crystals, and after spraying the layer, as described below, and evaporation of the solvents, forms the film 1 in which the microcrystals are embedded, or cemented together. The grinding can be in stages, removing the finest material each time. The suspension was then sprayed on gold-coated Mylar 5, the gold layer being shown at 4. The thickness of the coated Mylar is of the thickness of $\frac{1}{4}$ mil or less, the gold electrode layer 4 being very thin and produced by vacuum deposition. The uniform suspension is then allowed to set, to form a matrix 1 in which the TGS microcrystals 2 are held, and a second electrode 3 vacuum deposited on the matrix. Two different sizes of detectors were prepared, one being about 4×10^{-2} cm.² and about 160μ in thickness. The second electrode was sprayed with a thin coating 6 of a suspension of silicon carbide particles from $5-25\mu$ in diameter in a solution of a thermoplastic alkyd resin. The larger detector was polarized with 600 volts and showed a D.C. leakage resistance of 6.5×10^{11} ohms and a D.C. responsivity of 113 v./w. was measured. The smaller sample, when polarized with 300 volts D.C., showed a leakage resistance of 1×10^4 ohms.

The smaller detector was measured with infrared radiation from a black body source of 1000° K., which peaks just under 3μ . Responsivity at two different frequencies, together with detectivity and noise, were measured and are shown in the following table:

R	D* (cm. cps. $\frac{1}{2}$ w.-1)	Noise/1 cycle band width (μ v.)
15 c.p.s. 113 v./w-----	1.5×10^7	1.26
90 c.p.s. 16 v./w-----	1.5×10^7	0.20

It will be seen that while the responsivity varied, the detectivity did not, as the noise changed substantially in

proportion. The capacity of the pyroelectric detector was measured at 11 pf.

What is claimed is:

1. A pyroelectric detector comprising a pair of thin but continuous electrodes between which is a layer of pyroelectric microcrystals cemented together with from 1% to 25% dry weight of the crystals of a thermoplastic cement, the microcrystals being selected from the group consisting of triglycine sulfate, triglycine fluoberyllate, triglycine selenate, and lithium sulfate monohydrate, the particle size of the microcrystals being from 3μ to 100μ , one of the electrodes being mounted on an insulating substrate.

2. A pyroelectric detector according to claim 1 in which the microcrystals are of triglycine sulfate.

3. A pyroelectric detector according to claim 2 in which both of the electrodes are continuous vacuum-deposited metal films.

4. A pyroelectric detector according to claim 3 in which the substrate is a sheet of polyglycol terephthalate.

5. A pyroelectric detector according to claim 1 in which the substrate is a sheet of polyglycol terephthalate.

6. A pyroelectric detector according to claim 2 in which the substrate is a sheet of polyglycol terephthalate.

7. A pyroelectric detector according to claim 5 in which one of the electrodes is blackened with a thin film of plastic having uniformly embedded therein silicon carbide pigment particles of $5-25\mu$ diameter.

8. A pyroelectric detector according to claim 1 in which one of the electrodes is blackened with a thin film of plastic having uniformly embedded therein silicon carbide pigment particles of $5-25\mu$ diameter.

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