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Construction of Prototypes of a New Class of Infrared Detectors

NASA Grant NSG 1173

Final Report

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Report

The proposal requested funds to build and test a new kind of infrared detector constructed from LaF_3. The detectors worked well. A preprint of a paper submitted to Applied Physics Letters is the content of Appendix A. A talk on this subject will also be presented at the March 29 - April 1. A.P.S. Meeting in Atlanta, Georgia. A patent disclosure entitled "Pyroionic Infrared Detector" was submitted to the Langley Research Center patent department. A NASA Tech. Brief is scheduled to appear on this subject.

In addition, though it was not included in the original proposal, we tested some infrared detectors constructed from V_2O_3. They worked too. A patent disclosure entitled "Infrared Detector Constructed from Metal to Insulator Transition Materials" was also submitted to the Langley Research Center patent department. The data collected on these devices was too tenitive to warrent publication.

Appendix

A LaF_3 INFRARED DETECTOR*

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ABSTRACT

A new class of infrared detectors is proposed and experimental results are presented for a prototype device. The material used is LaF_3, an ionic conductor with a capacitance that varies exponentially with temperature. The detectivity of a prototype detector is estimated from measured signal voltages and incident power, and a Johnson noise voltage calculated from the measured resistance. At a modulation frequency of 20 Hz the estimated detectivity is $\sim 2 \times 10^6$ cm $Hz^{1/2}$ W^{-1}. For the parameters characterizing this device the estimated detectivity is consistent with a theoretical prediction. The theory further predicts an optimum detectivity of $\sim 10^9$ cm $Hz^{1/2}$ W^{-1} for much thinner devices than the prototypes.

Crystalline rare earth trifluorides, in particular LaF_3, have been observed to exhibit activated ionic conduction[1] and an exceptionally large temperature sensitive surface polarization.[2,3] These effects have also been observed in thin (100 - 10,000 Å) amorphous layers.[4-7] In LaF_3 over the temperature range 300° to 400°K the series resistance and "fast" capacitance vary approximately as $R \alpha C^{-1} \alpha e^{+E/kT}$, where the activation energy E is $E \cong 0.5$ eV. This temperature sensitivity can be used as the basis of an infrared detector that operates at room temperature much like pyroelectric detectors. In order to have a compact name for the new class of detectors and to distinguish them from pyroelectric devices that are constructed from ferroelectric materials, they will be referred to as "pyrionic detectors".

The previously observed [1,2,3] electrical characteristics of LaF_3 that are important in this application are:

1) There is a very low activation energy for the formation of Schottky defects $E_S \cong 0.08$ eV, so there is a large number of fluorine vacancies at room temperature even though the melting point is 1497°C.

2) The resistivity is dominated by the activated hopping of the fluorine vacancies. Below the Debye temperature $T_D \cong 360°K$,[8] the resistivity varies roughly as $\rho(T) = 1.35 \times 10^{-4}\, Te^{+E/kT}$, but at higher temperatures varies as $Te^{+E/kT}(T/T_D)^9$.

3) Two distinct kinds of capacitive effects are observed. Both are independent of sample thickness and the choice of metal electrodes:

a) there is a slow phenomena, with a typical time constant of minutes, where charges as large as 1 μ C/cm^2 are stored for applied voltages of $\sim$ 10 volts (effective dielectric constant $\sim 10^6$), which is probably a result of electro-chemical reactions taking place at the crystal surface, and

b) a faster phenomena with characteristic times of $\sim$ 1 ms, associated with the variation of a permanent dipole layer just below the surface of a thickness $\sim$ 2 μm at room temperature, corresponding to a capacitance of $\sim$ 7.3 nF/cm^2.

4) For applied voltages larger than $\sim$ 5 volts, independent of sample thickness, the material breaks down and metal dendrites appear.

Two crude devices were fabricated from LaF_3. The samples were polished to a thickness of $\ell \sim 125$ μm, then thin silver electrodes were deposited, wires connected with silver epoxy, and flat black paint sprayed on them. Sample number 1 had black paint on both sides, and number 2 was covered only on one side. Both samples total thickness was about 200 μm. The samples were charged at 3 volts for several hours before they would function well as detectors. Following their prolonged virgin charge, they could be recharged in a few minutes. Once charged, the battery was removed and the detectors functioned for periods of $\sim$ 24 hours without changing sensitivity. A detector that had been set aside for a week regained its sensitivity after a 5 minute charge. Just after charging a detector the noise is approximately ten times greater than the ambient level. This excess noise can be eliminated by shorting the terminals of the device for a few seconds. When the short is removed, the signal is unaffected, but the noise is gone. Presumably the excess noise is an effect associated with the surface electrochemical reactions.

To explain the data a simple thermal model[9] is assumed in which the detector is treated as a lumped heat capacity (paint plus LaF_3), and the rate of heat loss to the surroundings is proportional to the difference between the sample and ambient temperatures. For a chopped incident beam of radiation, the explicit temperature dependence of the series equivalent (fast) capacitance and resistance is used to solve the electrical circuit equations. The small signal equivalent circuit for the fundamental frequency component is found to be a resistance (R_0) in series with a parallel combination of a current source and the fast capacitance (C_0). The peak current amplitude is given by

$$I_m = \frac{\alpha_0 V_0 C_0}{\sqrt{1+(f_T/f)^2}} \quad ,$$

where

$$\alpha_0 = \frac{1}{2\pi}\frac{E}{kT_0}\frac{P_1}{C_v \mathcal{V} T_0} \quad ,$$

V_0 is the potential to which the sample is charged, C_0 is the fast capacitance, T_0 is the ambient temperature, C_v is the specific heat, $\mathcal{V}$ is the sample volume, f_T is the thermal relaxation frequency = $(2\pi\tau_T)^{-1}$, τ_T is the thermal time constant = $(C_v\mathcal{V}/\gamma)$, γ is the heat loss proportionality factor, and P_1 is the fundamental frequency component amplitude of the power absorbed from the incident beam. The rms open circuit signal voltage is

$$V_s = \frac{\alpha_0 V_0}{\sqrt{2(f^2+f_0{}^2)}}$$

where f_0 is temporarily identified with the thermal relaxation frequency f_T. Contributions due to mixing of the frequency components of the capacitance and resistance are small, and the lowest harmonics are essentially driven by the harmonic content of the absorbed power signal as partly evidence by the inability to detect a first harmonic.

The particular type of black paint used in this fabrication did not absorb in the infrared. In order to obtain a meaningful calibration of responsivity, a tungsten source was used with filters to attenuate the infrared wavelengths and the power in the resulting beam was measured by a Hewlett-Packard radiant flux meter and detector.

Optical phonon modes should not be excited in LaF_3 at room temperature, since their characteristic temperatures are > 650°K.[10] Therefore, in the Debye approximation based on the formula unit, the specific heat is estimated to be 0.74 joules$(cm)^{-3}$ $^oK^{-1}$, which is slightly less than the Dulong and Petit limiting value. We have set the specific heat of the entire device (LaF_3 plus black paint) equal to the above value. This underestimates the specific heat of the black paint, and overestimates the predicted detectivity since in the black paint layers were thick. Finally, for the measured incident beam power (P_1 = 140 μW), and assuming and absorptivity of unity for the portion of the spectrum used, α_0 is obtained.

The solid curve, marked theory, in Fig. 1 corresponds to the theoretical estimate for the open circuit signal voltage as a function of chopping frequency with $f_0 = 0$. It exhibits a 1/f drop off. The experimental results of the measurements with a Hewlett-Packard 3580A spectrum analyzer on the two samples are shown as data points in Fig. 1. The solid curves represent visual fits of the theoretical expression for V_s to the data found by scaling the value of $\alpha_0 V_0$ and adjusting f_0. In a somewhat unusual occurrence, sample number 1 has a measured signal voltage that exceeds the theoretical prediction. This happens despite the fact that we have overestimated the predicted signal by using a low specific heat, and under estimated the measured signal by supposing that all the incident power is absorbed by the black layer.

However, the material used in the present fabrication[11] is obviously different from that reported previously.[1,2] We find a resistivity for sample 1 that is a factor of ten smaller and an effective fast capacitance a factor of ten larger than expected based on the earlier work. The differences are probably due to the presence of divalent oxygen or other impurities in our samples. Sample 1 came from the end of the boule and looked cloudy; sample 2 came from the middle and where the material looked clear. While it was not reported in Refs. (1 & 2), it was observed that impure materials had diffusion activation energies greater than those of pure samples. Thus we speculate that in sample 1 the carrier concentration is extrinsic and higher, while the conduction activation energy (E) is larger than for sample 2. Also (E) is probably larger for sample 1 than we used in the theoretical estimate. Evidently one wants "poor" material for this application.

For sample number 1 the signal voltage appears to decrease faster than 1/f as the chopping frequency is increased toward 1kHz. These frequencies are too low for shunt capacitive loading to be significant. One possible cause for this deviation is a distributive effect arising from the finite thickness of the black paint coating and the LaF_3. Attenuation of the thermal wave becomes more pronounced for increasing frequencies.

The values of f_0 for both samples, i.e. 50 Hz and 90 Hz, are larger than can be explained based on the simple thermal relaxation effect that originally motivated the insertion of f_0 into the theory. These thermal relaxation frequencies would correspond to large values of the heat loss proportionality factor γ that cannot be reconciled with our estimates of heat loss. But in the simple model no account has been taken of the slow capacitances or slow charge capacity effect.[2] Pursuing a semiconductor surface state analogy, f_0 can be accounted for as arising from long time constant electrical process rather than a thermal relaxation effect.

A detector figure of merit[9] frequently used is the normalized detectivity, D*, defined here by the relation

$$D^* = \frac{V_s}{V_n} \cdot \frac{(\Delta f)^{1/2} A^{1/2}}{P_1}$$

where V_s/V_n is the signal-to-noise ratio, Δf is the system bandwidth, A is the active detector area, and P_1 is the incident radiant power. We did not have satisfactory means of making a noise measurement because it was so low. A semi-experimental D* was obtained by assuming that the dominant detector noise mechanism is the Johnson noise due to the series resistance, R_0, which is a measurable quantity. Although R_0 has a weak frequency dependence, we used a mean value of 15 kΩ, A = 0.374 cm^2, for sample number 1. This corresponds to a normalized noise voltage of 16 nV/(Hz)$^{1/2}$, which is clearly less than most low noise amplifiers ($\sim$ 30 nV/(Hz)$^{1/2}$). But since D* for the present case is independent of area, we can envision a physical device having a sufficiently small area that the Johnson noise component is dominant. A semi-empirical D* ranges from $\sim 2 \times 10^6$ cm Hz$^{1/2}$ W^{-1} at 20 Hz to $\sim 7 \times 10^4$ cm Hz$^{1/2}$ W^{-1} at 10^3Hz. Since in the Johnson noise limit, D* varies as $\ell^{-3/2}$

(ℓ = sample thickness), an improvement in D* can be expected by decreasing the device thickness. Supposing a physically realizable device 5 μm thick and holding all other parameters fixed, the projected D* ($f_0 = 0$) ranges from $\sim 10^9$ cm Hz$^{1/2}$ W^{-1} at 20 Hz to $\sim 2 \times 10^7$ cm Hz$^{1/2}$ W^{-1} at 1 kHz. These speculative values for D* compare favorably with currently available pyroelectric detectors for which detectivities in the range of 10^9 cm Hz$^{1/2}$ W^{-1} have been measured at chopping frequencies of 10 Hz.[12]

Practical pyroelectric devices detectivities are often limited by piezoelectric noise.[1,2] Based on an unsuccessful attempt some years ago at Varian to measure the piezoelectric coefficient, we believe it is quite small. Thus piezoelectric noise is unlikely to be a problem with LaF_3 detectors.

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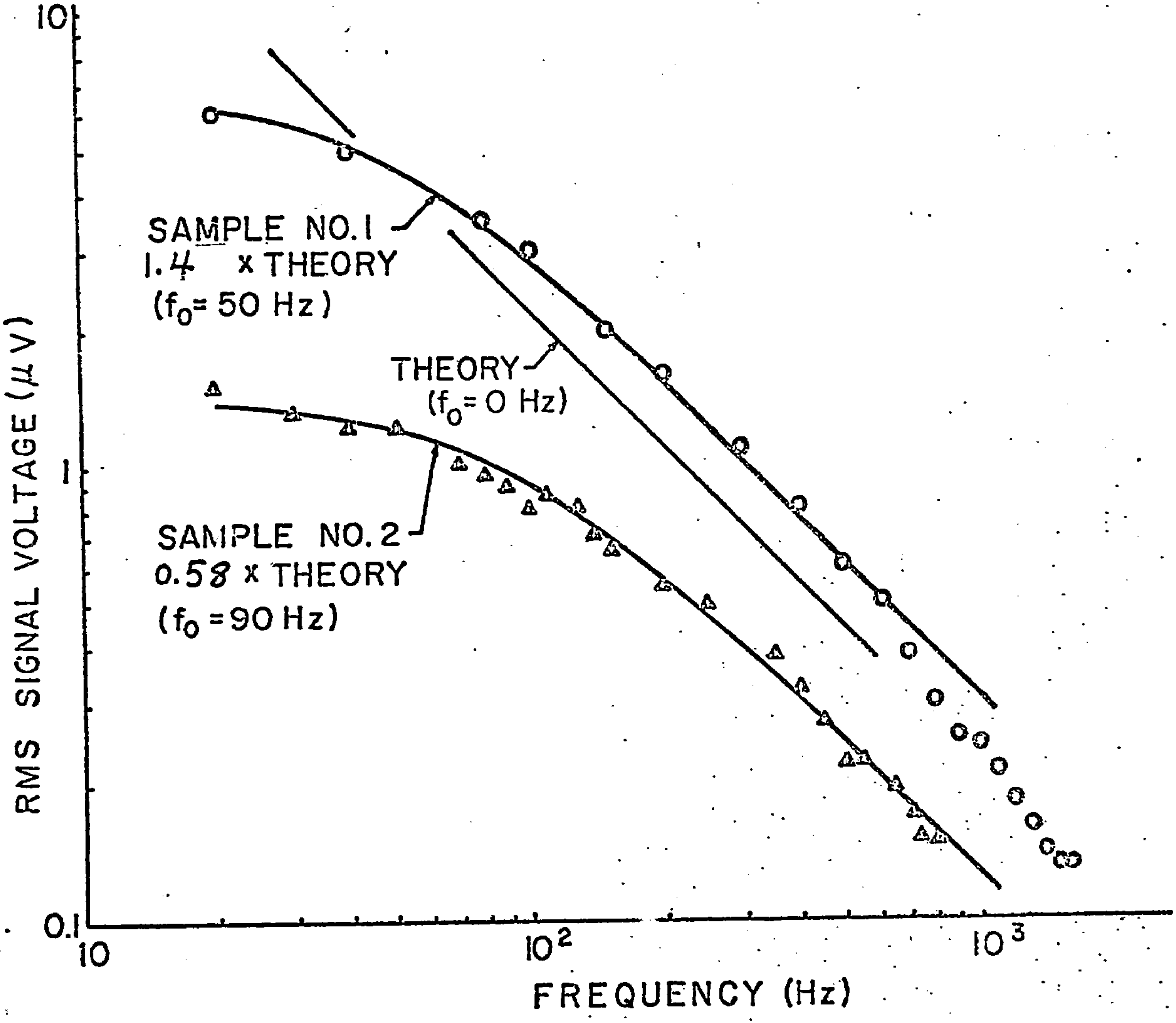
REFERENCES

1. A. Sher, R. Solomon, K. Lee, and M. W. Muller, Phys. Rev. 144, 593 (1966).
2. R. Solomon, A. Sher, and M. W. Muller, J. Appl. Phys. 37, 3427 (1966).
3. A. Sher, R. Solomon, K. Lee, and M. W. Muller, "Lattice Defects and Their Interactions", Ed. by R. R. Hasigati (Gordon and Breach, 1967), p. 361.
4. C. O. Tiller, A. C. Lilly, and B. C. LaRoy, Phys. Rev. B 8, 4787 (1973).
5. B. C. LaRoy, A. C. Lilly, and C. O. Tiller, J. Electrochem. Soc., 1668 (1973).
6. A. C. Lilly, Jr., B. C. LaRoy, C. O. Tiller, and B. Whiting, J. Electrochem. Soc. 120, 1673 (1973).
7. A. C. Lilly and B. C. LaRoy, Gas Pulse Experiments Indicative of Space Charge Limited Conduction in Rare Earth Fluorides, private communication.
8. W. M. Yen, W. C. Scott, and A. L. Schawlow, Phys. Rev. 136, 271 (1964).
9. E. H. Putley, Semiconductors and Semimetals, Vol. 5 Ed. R. K. Willardson and A. C. Beer (Academic Press, 1970) p. 259.
10. H. H. Caspers, H. A. Buchanan, and H. R. Marlin, J. Chem. Phys. 41, 94 (1964).
11. The crystal was grown by Alfa-Ventron.
12. N. E. Byer, S. E. Stokowski, J. D. Venables, Appl. Phys. Letters 27, 639 (1975).

FIGURE CAPTION

Fig. 1. RMS signal voltage as a function of chopping frequency.


SAMPLE NO.1
1.4 x THEORY
(f_0= 50 Hz)
THEORY
(f_0= 0 Hz)
SAMPLE NO.2
0.58 x THEORY
(f_0 =90 Hz)
RMS SIGNAL VOLTAGE (μV)
FREQUENCY (Hz)
10
1
0.1
10
10^2
10^3