ELECTRICAL SWITCHING IN CADMIUM BORACITE SINGLE CRYSTALS

Tatsuo Takahashi and Osamu Yamada
RCA Research Laboratories, Inc., Machida City, Tokyo, Japan

Abstract - Cadmium boracite single crystals at high temperatures ($\gtrsim$ 300°C) were found to exhibit a reversible electric field-induced transition between a highly insulative and a conductive state. The switching threshold is smaller than a few volts for an electrode spacing of a few tenth of a millimeter corresponding to an electric field of $10^2 \sim 10^3$ V/cm. This is much smaller than the dielectric break-down field for an insulator such as boracite. The insulative state reappears after voltage removal. A pulse technique revealed two different types of switching. Unstable switching occurs when the pulse voltage slightly exceeds the switching threshold and is characterized by a pre-switching delay and also a residual current after voltage pulse removal. A stable type of switching occurs when the voltage becomes sufficiently high. Possible device applications of this switching phenomenon are discussed.

Introduction

A series of compounds having a chemical formula $M_3B_7O_{13}X$ (M = divalent metal, X = halogen) have been known to be isostructural with the mineral magnesium chlorine boracite ($Mg_3B_7O_{13}Cl$).[1-3] These compounds have an orthorhombic C_{2v}^5-Pca structure at room temperature and transform to a cubic T_d^5-$F\bar{4}3c$ structure at a higher temperature. Extensive investigations of physical properties of boracite compounds were made in the past and some boracites were found to be ferroelectric and ferromagnetic simultaneously at low temperatures.[5-9] Recently, we have successfully grown single crystals of Cd boracites, $Cd_3B_7O_{13}X$; X = Cl or Br, by a chemical vapor transport method.[10] The crystallographic transition temperatures were 520 ± 5°C for the Cd-Cl boracite and 430 ± 5°C for the Cd-Br boracite. During measurements on these crystals, we found that the crystals abruptly became conductive when a dc bias voltage was applied at above 300°C, temperatures considerably below the transition temperature. The switching was reproducible and closely resembled that observed in chalcogenide glasses.[11] However, the critical field strength required for such switching ($10^2 \sim 10^3$ V/cm) was at least one or two orders of magnitude smaller than that in the case of amorphous semiconductors. The results of dc and pulse measurements of this interesting switching phenomenon are described below. Possible device applications of this phenomenon will also be discussed.

Sample Preparation and Measuring Technique

The Cd boracite crystals were grown by a method described elsewhere.[10] The crystals (max. edge length ~5 mm) were cut into slices having a simple crystallographic face such as (100), (110), and (111) in pseudo-cubic indices. Each slice was ground and polished with diamond paste. Electrodes of Au/Cr film were evaporated. The Cr inner layer adheres rigidly to boracite surface to make a good supporting film for the Au overlayer. Gold lead wires were attached to the electrodes with Ag-conducting paste. In the dc measurements, the sample was connected in series with a large protective load resistance R_L (10 ~ 100 KΩ). A voltage across the sample (X) and a current through the load resistance (Y) were recorded on an X-Y recorder.

In the pulse measurements, the pulse generator (Toyo Telesonics) was capable of delivering a square pulse of maximum amplitude 10 V with various pulse lengths (1 μsec ~ 10 msec) and pulse repetition rates (single sweep ~10^6 pulses/sec). Both the dc pulse and the current through a 50 KΩ load resistance were recorded via a storage oscilloscope (Tektronix type 564).

DC Measurement

When a crystal was heated to above a certain critical temperature T_c, the crystal could be made conductive upon the application of a dc voltage. Figure 1 is a schematic illustration of current-voltage characteristics for such switching. As can be seen, the switching is symmetrical with respect to voltage polarity. Before switching, the current is determined by the sample resistance since it is much larger than R_L.

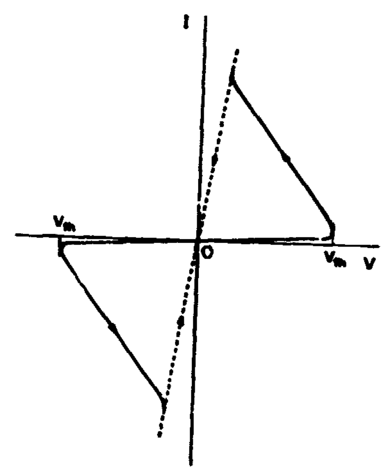

Fig. 1. dc current-voltage characteristics of a Cd-X boracite crystal (X = Cl or Br) at $T \geq T_c$.

After the threshold is exceeded, a negative resistance region appears. In the 'on' state, the dynamic resistance of the sample dV/dI takes a small positive or zero value. Unlike the case of threshold switching in amorphous semiconductors, there does not exist a critical current, or a so-called holding current at which the sample abruptly switches back to the 'off' state.[11] It seems that the sample gradually returns to the 'off' state as the current is decreased. Therefore, the sample resistance in the 'on' state cannot be clearly defined. The threshold voltage V_{th} is dependent upon temperature and decreases with temperature increase. In Fig. 2, the temperature variation of V_{th} for Cd-Cl boracite sandwich electrode samples of two different thickness are shown. Figure 3 is a similar result for a Cd-Br boracite sandwich electrode sample that shows the presence of temperature hysteresis on cooling. An apparent critical temperature T_c, obtained by extrapolating V_{th} to infinity, is dependent upon sample thickness. The thicker the sample, the higher T_c. The threshold voltage V_{th} is not a linear function of thickness; the critical field increases with thickness. The V_{th} vs temperature curve does not show any anomaly at the crystallographic transition temperature T_{tr} at which the peculiar twin lamellar structure disappears.[10] It may be pointed out that T_c for thinner samples is indeed very close to the inflexion temperature which appeared in differential thermal analysis (DTA) curves of the crystal which are believed to show the existence of a higher order phase transition. Much the same results were obtained in the case of coplanar electrode samples.

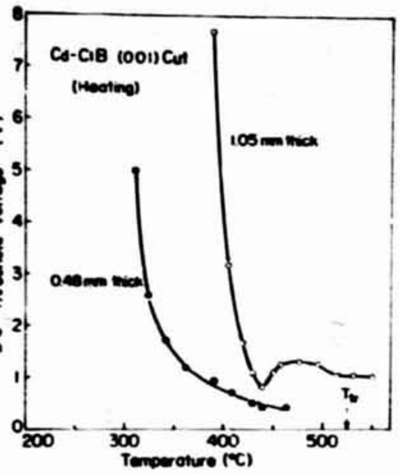

Fig. 2. Threshold voltage V_{th} as a function of temperature for two Cd-Cl boracite sandwich electrode samples with different electrode spacings.

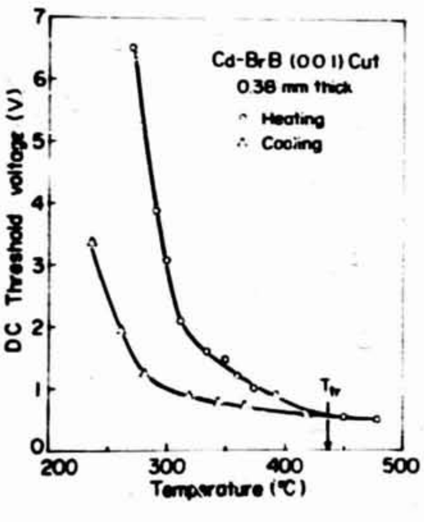

Fig. 3. Threshold voltage V_{th} as a function of temperature for a Cd-Br boracite sandwich electrode sample.

When a sample is kept in the 'on' state at a certain temperature, stabilization of the conductive state seems to set in. That is, if the 'on' state is maintained for a short time, V_{th} measured immediately afterwards is considerably smaller than its previous value. After repeated switchings, the 'on' state is temporarily stabilized. The stabilization of the 'on' state, or 'memory switching,' is always preceded by threshold switching in Cd boracites, just as in the case of memory switching in chalcogenide glasses.[11] The stabilized 'on' state in Cd boracites eventually returns to the 'off' state after the removal of a dc voltage. Complete recovery requires times ranging from seconds to hours. The occurrence of stabilization of an 'on' state makes interpretation of dc measurements somewhat ambiguous. Accordingly, pulse measurements were carried out with results as next discussed below.

Pulse Experiments

Threshold switching was clearly observed in the pulse experiments. The critical temperature for switching was comparable to that observed in the dc experiments. However, there occurred several other peculiar phenomena not observed in the dc experiments.

Two different types of switching were distinguished in the pulse experiments. The first type appears near the voltage switching threshold and is characterized by a time delay before switching and by an unstable current. There also exists residual current after the pulse is removed. In Fig. 4, an example of such 'unstable' switching is shown. The photograph was taken by multiple exposures at various pulse voltages.

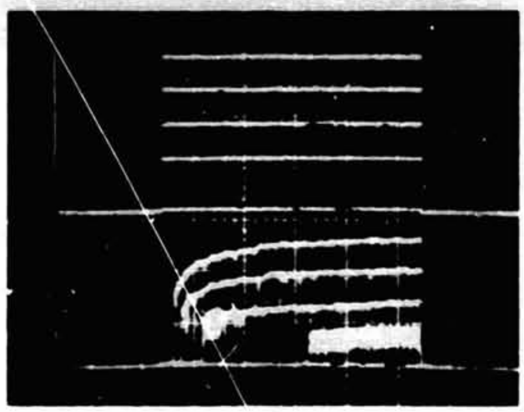

Fig. 4. Scope trace of unstable switching pulse (multiple exposure). Cd-Br boracite sandwich electrode sample with electrode spacing 0.38mm; voltage (upper trace) of 2V/div; current (lower trace) of 40μA/div; time of 2 msec/div; single sweep trace; and temp of 340° ± 2°C.

As can be seen, the delay time shortens as the voltage increases. After the removal of the pulse, the current disappears with a decay time of 15 ∿ 20 μsec. An example of such a decaying current is shown in Fig. 5. When the applied voltage becomes much larger than the threshold voltage for unstable switching, the switching begins to take place with almost no delay. The current is stable and disappears instantaneously after the removal of voltage (Fig. 6). Typical threshold voltage values for unstable switching V_{th}(USSW) and threshold voltage values for stable switching V_{th}(SSW) for various pulse lengths are shown in Table I. These voltage data were taken under constant duty operation, i.e., pulse length (sec) X pulse repetition (sec^{-1}) = 0.1. As can be seen, both V_{th}'s increase as the pulse length decreases. V_{th}(SSW) is at least 3 ∿ 4 times V_{th}(USSW). When the applied voltage is kept constant, there exists a critical pulse repetition rate at which unstable switching takes place. The critical pulse repetition rate increases with decreasing pulse length as expected. In all cases, little or no stabilization effect was observed after repeated applications of voltage pulses.

Fig. 5. Scope trace of unstable switching pulses. Cd-Cl boracite sandwich electrode sample with electrode spacing of 0.48mm; voltage (upper trace) of 5V/div; current (lower trace) of 40 μA/div; time of 5 μsec/div; pulse repetition rate of 2 KPPS; and temp of 345° ± 2°C.

Fig. 6. Scope trace of stable switching pulses. The sample is the same as in Fig. 5 with voltage (upper trace) of 2V/div; current (lower trace) of 40μA/div; time of 5 μsec/div; pulse repetition rate of 10 KPPS; and temp of 345° ± 2°C.

Table I
V_{th}'s for Constant Duty Operation

Pulse Width (sec)	Pulse Repetition (Pulses/sec)	V_{th}(USSW) (V)	V_{th}(SSW) (V)
10^{-6}	10^5	2	7 ∿ 8
10^{-5}	10^4	1.2	3
10^{-4}	10^3	0.2 ∿ 0.4	4
10^{-3}	10^2	0.2 ∿ 0.3	4
10^{-2}	10	0.3 ∿ 0.4	3

Sample: Cd-Cl boracite (001) cut, 0.48 mm thick, T = 340 ± 2°C.

Throughout the present switching experiments, dc or pulse, the aforementioned switching characteristics changed little with crystallographic orientation of the sample.

In the present experiment, Au lead wires were attached to the sample with Ag-conducting paste. In this case, a Ag-boracite contact is presumably formed at high temperatures by the diffusion of Ag through the Au/Cr film. It was found that the sample did not switch when a Au lead wire was thermally bonded onto the Au/Cr film. It seems that Ag is indispensable to form a good electric contact to a boracite crystal. However, little is understood about the electrode effect as well as the switching phenomenon in general at present. Several mechanisms that had been proposed to account for the other switching phenomena have been discussed in connection with the switching in Cd-boracite crystals elsewhere.[12]

Device Applications

A number of functional devices can be fabricated by making use of the newly found threshold switching in Cd-boracite single crystals. Since the switching takes place only at high temperatures ($\gtrsim$ 300°C), such devices may be found to be useful in the fields where a high ambient temperature or a lack of workable heat sink prevents the use of ordinary solid state devices. Such devices include:

1. Current controlling devices having non-blocking Ag electrodes for dc, dc pulse and ac circuits (symmetric devices).
2. Current controlling devices having one blocking and one non-blocking electrode (asymmetric devices). Such asymmetric electrode devices can be used in a logic circuit for dc and dc pulse voltages.
3. Current rectifiers for low frequency ac.

Since the operative principle of devices of first and second categories are obvious from the foregoing discussion, only the current rectifiers will be described in some detail. Figures 7 and 8 show the circuits for half-wave and full-wave rectifiers, respectively. The half-wave rectifier of Fig. 7 consists of an ac source, a load resistance R_L, a blocking capacitance C_b, a boracite crystal element, and a dc

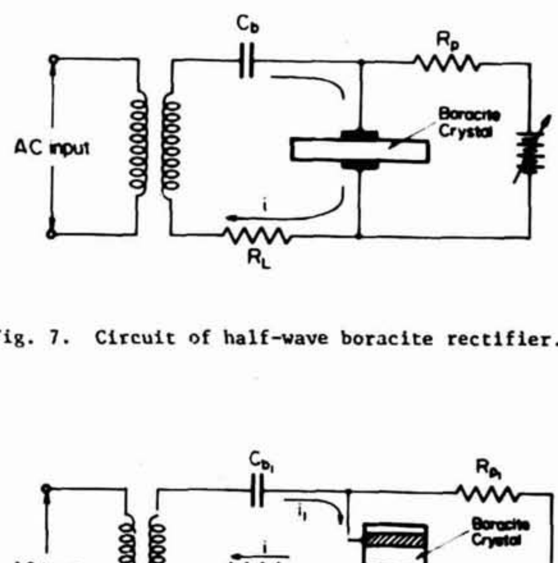

Fig. 7. Circuit of half-wave boracite rectifier.

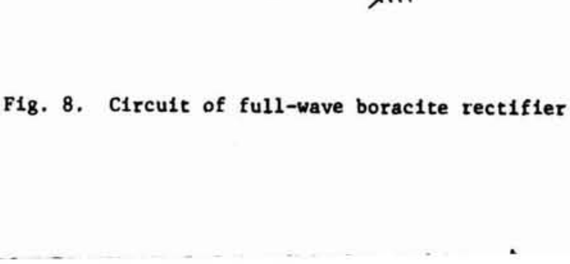

Fig. 8. Circuit of full-wave boracite rectifier.

control circuit. The boracite element in this case can be either a symmetric or asymmetric device. The dc control circuit consists of a variable dc voltage source and a large protective resistance R_p to block ac current. When a small ac voltage is applied followed by a dc voltage, a regulated current begins to flow at a critical dc voltage. Figure 9 shows a scope trace of such a regulated current. Because of

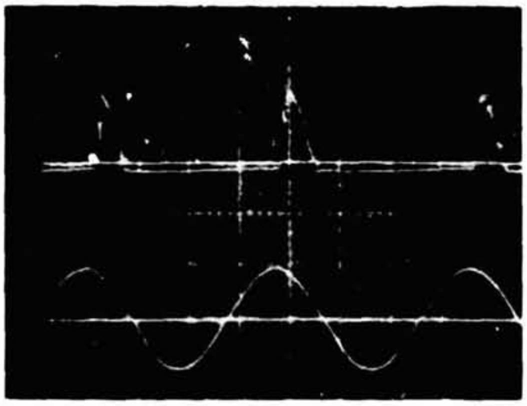

Fig.9. Scope trace of ac half-wave rectified current. Cd-Br boracite sandwich electrode sample with electrode spacing = 0.30mm, R_L = 100 Ω, R_p = 100KΩ, C_b = 10 μF, V_{dc} = 8.0V, and temp = 395° ± 2°C. Ac rectified current (upper trace): 0.05V/div. Applied 50Hz ac voltage (lower trace): 0.5V/div. Time: 5msec/div.

the threshold switching characteristics of boracite crystal, the current appears in the form of regularly repeated pulses. The direction of current is reversed when the polarity of dc voltage (V_{dc}) is reversed. For stable operation of the half-wave rectifier, an upper limit (maximum) exists for both V_{dc} and V_{ac}. For V_{dc}, it is about ten times the minimum voltage. The maximum of V_{ac} is much smaller than that of V_{dc}. The bias dc voltage, both minimum and maximum, required for the rectifying effect to take place increases with increasing current or power in the ac circuit. This observation cannot be explained but it seems that the response of the Cd boracite element is different when ac and dc are applied simultaneously as compared to the case of dc or ac used alone.

The full-wave rectifier of Fig. 8 consists of an ac source, a load resistance R_L, two blocking capacitances

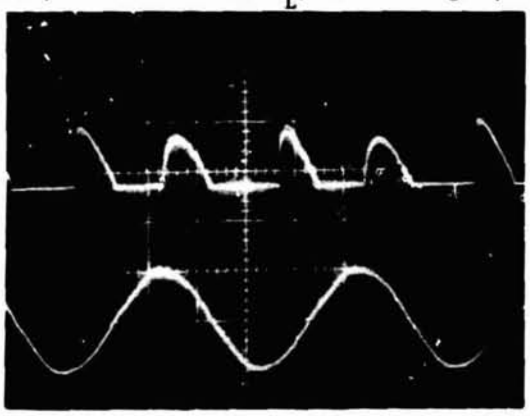

Fig.10. Scope trace of ac full-wave rectified current. Cd-Br boracite coplanar trielectrode sample with electrode spacing = 0.20mm; R_L=100Ω, R_p=100KΩ; C_{bI}, C_{bII}=10μF; V_{dc}=15V; and temp = 301° ± 2°C.
Ac rectified current (upper trace): 0.1V/div. Applied 50 Hz ac voltage (lower trace): 0.5V/div.
Time: 5 msec/div.

C_{bI}, C_{b2}, a boracite element, and a dc controlling circuit. The boracite element in this rectifier has three electrodes. In Fig. 8, the two side electrodes are positively biased with respect to the middle one. The current through R_L will be i_1 in the first half cycle of ac and i_2 in the next half cycle so that the full-wave rectification will be completed. The direction of current through R_L reverses when the polarity of side and middle electrodes is reversed. Figure 10 shows a scope trace of such a rectified current obtained by the circuit of Fig. 8. As in the case of half-wave rectification, the minimum dc bias voltage increased with increasing ac voltage.

The above examples are illustrative of potential usefulness. Other circuit applications of the Cd boracite switching devices seem possible.

Acknowledgments

The authors wish to thank E. O. Johnson for his continuous encouragement and many helpful discussions during the course of this work.

References

1. F. Jona, J. Phys. Chem., 63, 1750 (1959).
2. F. Heide, G. Walter and R. Urlau, Naturwissenschaften, 48, 97 (1961).
3. H. Schmid, J. Phys. Chem. Solids, 26, 973 (1965).
4. T. Ito, N. Morimoto and R. Sadanaga, Acta Cryst., 4, 310 (1951).
5. E. Ascher, H. Schmid and D. Tar, Solid State Commun., 2, 45 (1964).
6. E. Ascher, H. Rieder, H. Schmid and H. Stossel, J. Appl. Phys., 37, 1404 (1966).
7. J. Kobayashi, H. Schmid and E. Ascher, Phys. Status Solidi, 26, 277 (1968).
8. G. Quezel and H. Schmid, Solid State Commun., 6, 447 (1968).
9. F. Smutny and J. Fousek, Phys. Status Solidi, 40, K13 (1970).
10. T. Takahashi and O. Yamada, J. Cryst. Growth, 33, 361 (1976).
11. S. R. Ovshinsky, Phys. Rev. Lett., 21, 1450(1968).
12. T. Takahashi and O. Yamada, J. Appl. Phys., 48, 1258 (1977).