Pyroelectricity of Fe-I and Cu-Cl boracite

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Abstract
The pyroelectric coefficient (p) of the mm2 phases of Fe-I and Cu-Cl boracites were measured from 20 Deg up to their Curie temperatures by the quasistatic technique of R. L. Byer and C. B. Roundy (1972). For Fe-I boracite at 20 and 63 Deg, p = 0.02 * 10^-8 and 0.1 * 10^-8 C/cm2 K, resp. For Cu-Cl boracite at 20 and 86 Deg, p = 0.55 * 10^-8 and 2.5 * 10^-8 C/cm2 K, resp. A dynamic measurement method applied to Cu-Cl boracite at 20 and 60 Deg gave p = 0.36 * 10^-8 and .apprx.1.3 * 10^-8 C/cm2 K, resp.

Reference

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PYROELECTRICITY OF Fe-I AND Cu-Cl BORACITE

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Abstract --- The pyroelectric coefficient $p$ of the mm$^2$ phase of Fe-I and Cu-Cl boracite has been measured from 20°C upwards. The quasistatic Byer-Roundy technique applied to Fe-I boracite yielded $p = 0.01 \times 10^{-8}$ Ccm$^{-2}K^{-1}$ at 20°C, rising to $0.1 \times 10^{-8}$ Ccm$^{-2}K^{-1}$ at 63°C; the extrapolated value for $T_c(72°C)$ is $\approx 1.9 \times 10^{-8}$ Ccm$^{-2}K^{-1}$. For Cu-Cl boracite the same method yielded $p = 0.55 \times 10^{-8}$ Ccm$^{-2}K^{-1}$ at 20°C, rising to $2.5 \times 10^{-8}$ Ccm$^{-2}K^{-1}$ at 86°C. For Cu-Cl boracite a dynamic method yielded $p = 0.36 \times 10^{-8}$ Ccm$^{-2}K^{-1}$ at 20°C and $\approx 1.3 \times 10^{-8}$ Ccm$^{-2}K^{-1}$ at 60°C.

INTRODUCTION

The use of ferroelectric boracites as targets for pyroelectric vidicons or single element detectors is tempting because these materials unite several physical properties favorable for pyroelectric performance: small dielectric constant ($\varepsilon \approx 20$), high electric resistivity, small piezoelectric coefficient, good chemical and physical stability, and a maximum of absorption coefficient centering around 10 μm. Most published data on pyroelectricity of boracites are unreliable because simultaneous visual control of the domain state has been neglected so far (see Table III of ref. 6). In this paper pyroelectric measurements on Fe-I and Cu-Cl boracite under visual control of the domain state are described. Cu-Cl boracite was selected because of its "nearly second order type" behaviour which is e.g. reflected by the spontaneous orthorhombic distortion versus temperature and by the steep slope of the spontaneous birefringence $\Delta n_s(1,2) \perp P_s$ versus temperature, letting foresee a similar steep slope of spontaneous polarization $P_s$ and hence a high pyroelectric coefficient.

EXPERIMENTAL

Crystal growth was performed by gas phase transport. The samples were (100)cub cut wafers with one natural surface. After deposition of transparent gold electrodes the edges of the platelets were ground off parallel to (100)cub in order to minimize nucleation of "180°" spikes. The poling fields at 20°C were 9-10 kVcm$^{-1}$ and up to 50 kVcm$^{-1}$ for Fe-I and Cu-Cl boracite, respectively. Quasistatic measurements of the pyroelectric coefficient were made by the Byer-Roundy technique, using a Cary 31 vibrating electrometer and a load resistor variable between $10^8$ and $10^{12}$ Ω, a linear temperature sweep of 3.3s K$^{-1}$, giving potential differences of 10-100 mV and a reproducibility of ± 5 %. For every sample the temperature change of resistance was measured and taken into account. As integration constant

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the spontaneous polarization at 20°C was taken: $P_s = 3.9 \times 10^{-6} \text{Ccm}^{-2}$ for Fe-I boracite, determined both by the Sawyer-Tower and Camlibel technique and $P_s = 1.85 \times 10^{-6} \text{Ccm}^{-2}$ for Cu-Cl boracite, measured by Camlibel's technique in this work.

The dynamic measurements of the pyroelectric coefficient - with visual domain control in polarized light - were performed on Cu-Cl boracite only. The method was in principle that of Chynoweth but the salient feature was the use of the intrinsic resistivity change with temperature for "self-calibrating" the temperature excursions. The details of the method will be reported elsewhere but the essentials can be summarized in the following: the expression for the pyroelectric coefficient $p$ is

$$p = \frac{dP_s}{dT} = \frac{dP_s}{dt} \frac{dt}{dT} \approx \frac{i \Delta t}{A \Delta T}$$

(1)

(where $i =$ measured pyroelectric current, $A =$ sample area, $\Delta t =$ half-period of the light chopping, $\Delta T =$ corresponding change in temperature). The exact determination of $\Delta T$ is usually difficult. In the present case a permanent bias field was applied in order to suppress self-depolarization on upheat. Because of the light chopping the bias induced resistive current had a dynamic component (periodic triangular function) of a level permitting its measurement independently of the pyroelectric current (rectangular function). The temperature excursion $\Delta T$ can be extracted from the relationship

$$\frac{I_{\text{res}}}{\Delta T} = \frac{dI_{\text{res}}}{dT} = \frac{d(V/R)}{dT} = \frac{V}{R} \frac{d(lnR)}{dT}$$

(2)

where $I_{\text{res}} =$ DC resistive current, $V =$ DC applied voltage, $R =$ resistance of crystal). For cross checking the dynamically determined resistance, $R(T,V)$ can be compared with the $R$ values obtained from the continuous component of the current. The advantage of the method resides in the fact that an intrinsic property of the crystal is used to monitor its temperature excursions; its disadvantage resides in the fact that it can only be used in a restricted range of resistivity (compatible with the magnitude of the pyroelectric signal).

RESULTS

In Figure 1 the quasistatically measured pyroelectric coefficient of Fe-I boracite is represented. From 63°C to $T_c$ the curve is extrapolated because the observation of depoling did not warrant the use of the too high data measured in that range. Figure 2 shows $P_s$ of Fe-I boracite versus temperature as calculated from the pyroelectric coefficient and the measured $P_s$ at 20°C.

In figure 3 three curves of the pyroelectric coefficient of Cu-Cl boracite versus temperature are represented. Curve a shows the result of the quasistatic measurement up to 86°C; above that temperature depoling set in and did not allow to obtain reliable data. Curve b shows the results of the dynamic measurements up to 60°C and curve c has been calculated by supposing the same temperature dependence for $P_s$ and spontaneous birefringence $\Delta n_s(1,2)$ and taking $P_s = 1.85 \times 10^{-6} \text{Ccm}^{-2}$ at 20°C. It is noteworthy that the order of magnitude of all three curves is the same, but more work is still necessary in order to obtain reliable data up to the Curie point.

An attempt to measure the temperature dependence of $P_s$ by Camlibel's pulse technique was successful up to to 45°C only (Figure 4). Above that temperature observation with the microscope showed that the sample was partially depolarized before and after applying the voltage pulse for switching. This explains the too low drop out value obtained for $P_s$ at 46°C. The broken line curve was calculated by assuming the same temperature dependence of $P_s$ and $\Delta n_s(1,2)$. 
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FIGURE 1 Pyroelectric coefficient of Fe-I boracite versus temperature; Byer-Roundy technique

FIGURE 2 Spontaneous polarization of Fe-I boracite versus temperature; calculated from $P_s(20^\circ\text{C})$ and $\partial P_s/\partial T$

FIGURE 3 Pyroelectric coefficient of Cu-Cl boracite versus temperature

DISCUSSION

For further work the use of stress annealed samples and careful stressfree mounting is recommended in order to avoid spontaneous depoling on upheat.

The pyroelectric coefficient of Cu-Cl boracite is indeed higher than that of Fe-I boracite as was expected from the $\partial \Delta n_s/\partial T$ curves. Close to $T_c$ the pyroelectric coefficient of Cu-Cl boracite approaches that of TGS at room temperature. Although this fact for itself would not yet justify the use of Cu-Cl boracite as a target, it is remarkable that the figure of merit $p/\varepsilon_0 C_v$ ($\varepsilon$ = dielectric constant, $\varepsilon_0$ = dielectric constant of free space, $C_v$ = volume specific heat) of Fe-I and Cu-Cl boracite is increasing with temperature (Fig. 5) in contrast to that to TGS which goes to zero on approaching $T_c$. These results warrant further careful study of the pyroelectric properties of boracites.

On the basis of thermodynamic phase stability arguments the upper bound of the pyroelectric coefficient at constant magnetic field and pressure is given by

$$P_{Hp} < (T^{-1} C_{EHP} \kappa_{\text{ii}})^{\frac{1}{2}}$$

where $T$ = temperature, $C_{EHP}$ = the specific heat at constant electric field, magnetic field and pressure and $\kappa_{\text{ii}}$ = the electric susceptibility at constant temperature, magnetic field and pressure. By assuming for Cu-Cl boracite the values $\varepsilon$ =15,3 (1Mc) $^2$, $C_{EHP}$ = 3,58 Jcm$^{-3}$K$^{-1}$ at 90°C and for Fe-I boracite $\varepsilon$ = 15 (1Mc) $^1$ and $C_{EHP}$ = 3,62 Jcm$^{-3}$K$^{-1}$ at 63°C one obtains in both cases $P_{Hp} < \approx 11 \times 10^{-8}$ Ccm$^{-2}$K$^{-1}$

The limit at $T_c$ will be somewhat higher, however, it cannot be calculated at present correctly because the so far available specific heat data close to $T_c$ are not free of the contribution of the latent heat of transition. These upper limits are consistent with, but do not explain, the measured data.
FIGURE 4 Spontaneous polarization of Cu-Cl boracite versus temperature; data points by Camlibel’s technique, broken line: calculated from $\Delta N_s(1,2)$ and $P_s(20^\circ C)$.

FIGURE 5 Pyroelectric figure of merit $p/\varepsilon_0 c_v$ of Fe-I and Cu-Cl boracite, compared with that of TGS 13 (used data: $c_{Fe-I-B}1$, $c_{Cu-Cl-B}2$, $c_v Fe-I-B1$, $c_v Cu-Cl-B5$).

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