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Reference


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CHARACTERIZATION OF COPPER BROMINE BORACITE Cu$_3$B$_7$O$_{13}$Br

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Abstract Dielectric constant, spontaneous polarization and birefringence have been measured between 10 K to 290 K on single domain samples of Cu$_3$B$_7$O$_{13}$Br.

INTRODUCTION
At about 243 K the Cu-Br boracite (Cu$_3$B$_7$O$_{13}$Br) undergoes an improper ferroelectric/ferroelastic phase transition from a cubic Fd$ar{3}$c$^1$ to an orthorhombic phase mm2$^2$. Up to now, dielectric investigations (spontaneous polarization (P$_s$) and dielectric constant ($\varepsilon$)) have only been performed on polydomain crystals$^3$ or by means of point by point techniques$^4$ and have failed to give reliable measurements, in particular near the phase transition. In this paper, dielectric measurements versus temperature of Cu-Br boracite have been re-examined on single domain samples, especially P$_s$ and the dielectric constant $\varepsilon_{33}$, the behaviour of which near the ferroelectric transition has been specified. The temperature dependence of the spontaneous birefringence on the three principal sections is also reported.

EXPERIMENTS AND RESULTS

Single crystals were grown by chemical vapour transport. On a (100)$_c$ cut platelet, semi-transparent gold on chromium electrodes were evaporated, and a field of 13 KV/cm was applied during cooling through the ferroelectric transition in order to yield a ferroelectric single domain. A low frequency impedance analyzer (HP 4192A) connected
to a computer for automated data acquisition was used. A preliminary measurement of the capacity of the sample versus frequency at 12 K and 293 K (Fig.1) was realized in order to determine a frequency range where neither piezoelectric resonance nor relaxation mechanism could alter the results. At 100 KHz, $\varepsilon_{33}$ has been measured (Fig.2) from 11 K to 290 K. Values are systematically smaller than previous results$^3$ obtained at 1 KHz$^4$ (also in agreement with Fig.1). At the ferroelectric transition, $\varepsilon_{33}$ shows a discontinuity which corresponds to an upward jump on cooling. This behaviour, also encountered in certain other boracites, has been discussed$^5$ in the framework of a Landau phenomenological approach using a single six dimensional order parameter related to the X point ($k=00\pi/a$) of the cubic phase centered Brillouin zone surface. The temperature dependence of $P_s$ has been measured using an electrometer (Keithley 642) (Fig.3). The values obtained are about five times higher than those reported for a polydomain sample$^3$. At low temperature, where a ferromagnetic phase transition has been observed at 11 K by means of hysteresis loops$^6$, careful high resolution measurements of $P_s$ have been performed. However, contrary to other ferromagnetic/ferroelectric boracites$^7$$^8$, no drastic change of slope was detected (Inset of Fig.3). The spontaneous birefringence $\Delta n_s$ of the mm2 phase has been measured on a (100)$_c$ cut ($\perp P_s$) and a (110)$_c$ cut, corresponding to two of the three indicatrix principal sections. The difference in $T_c$ of about 10 degrees between (100)$_c$ and (110)$_c$ cuts (Fig.4) can be attributed to different growth sectors$^9$. By admitting that $\Delta n_s$ ($\perp P_s$) represents $n_\gamma-n_\alpha$, in analogy to all other known bromine boracites, $\Delta n_s$ of the third section (no available sample) was calculable (Fig.4). As can be seen on figure 4, premonitory effects of magnetic ordering seem to affect $\Delta n_s$ already at about 60 K. Moreover high resolution plot below 20 K (Inset of Fig.4) shows a pronounced minimum, coinciding with the ferromagnetic Curie point. A more detailed report will be given elsewhere.

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FIGURE 1 Capacity vs. frequency; sample (100) thickness 0.040 mm, surface 3.51 mm².

FIGURE 2 Dielectric constant vs. temperature at 100 KHz; sample: (100) c-cut, thickness 0.040 mm, surface 3.51 mm².

FIGURE 3 Spontaneous polarization vs. temperature; sample (100) thickness 0.040 mm, surface 3.51 mm².

FIGURE 4 Spontaneous birefringence vs. temperature; sample: (100) thickness 0.122 mm; (110) c thickness 0.048 mm.
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