Spontaneous polarization, dielectric constant, D.C. resistivity, and specific heat of orthorhombic boracite Fe$_3$B$_7$O$_{13}$I

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Abstract
Iodo Fe boracite properties are: spontaneous polarization (25°C) 3.9 × 10^{-2} cm^{-2}, dielec. const., ε33, (25°C) 11, d.c. resistivity (71°C) 1.1 × 108 Ω m (mm2) and 3 × 106 Ω m (mmm), vol. sp. heat (25°C) 3.5 × 106 J/m3/K, latent heat 3.1 × 103 J/mol, and transition entropy 8.9 J/mol/K.

Reference

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SPONTANEOUS POLARIZATION, DIELECTRIC CONSTANT, D.C. RESISTIVITY, AND SPECIFIC HEAT OF ORTHORHOMBIC BORACITE Fe$_3$B$_7$O$_{13}$I

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Several properties of ferroelectric orthorhombic Fe-1 boracite have been measured; some individual values are:

- Spontaneous polarization $P_s$ (25°C) = 3.9 ± 0.1 $\times 10^{-2}$ cm$^{-2}$
- Dielectric constant $\varepsilon_33$ (25°C) = 11
- D.C. resistivity $\rho$ (71°C, mm2) = 3 $\times 10^6$ $\Omega$m
- Volume specific heat $C_p$ (25°C) = 3.5 ± 0.3 $\times 10^6$ Jm$^{-3}$ K$^{-1}$
- Latent heat $\Delta Q$ = 3.1 ± 0.3 $\times 10^5$ Jmole$^{-1}$
- Transition enthalpy $\Delta S$ = 8.9 ± 0.5 Jmole$^{-1}$ K$^{-1}$

The spontaneous polarization $P_s$ of Fe$_3$B$_7$O$_{13}$I in its mm2 phase has been measured at 25°C under simultaneous visual control. The Sawyer-Tower method$^1$ at 50 Hz and the Camlibel pulse method$^2$ both gave a value of $P_s = 3.9 \pm 0.1 \times 10^{-2}$ Cm$^{-2}$. At the Curie point $T_c$ (71–72°C) integration of the charge during the first order polarization breakdown yielded $P_s = 3.7 \pm 0.1 \times 10^{-2}$ Cm$^{-2}$.

The temperature dependence of the dielectric constant was measured parallel to $P_s$ in the poled mm2 phase ($\varepsilon_{33}$) and in the 43m phase (Figure 1) using a micromanipulator and evaporated guard ring electrodes.

Following Sailer’s$^3$ fit of $\varepsilon$ of Mg-Cl boracite to Curie laws of the form

$$\varepsilon^f(T) = \varepsilon^0_g + \frac{C^0_p}{T - T_c^p}$$

and

$$\varepsilon^f(T) = \varepsilon^0_g + \frac{C^f}{T_c^f - T}$$

being the para- and ferroelectric temperature independent part of $\varepsilon$, Curie constants and Curie-Weiss temperatures, resp.), the Curie-Weiss law of Fe$_3$B$_7$O$_{13}$I becomes obvious (Figure 2). This behaviour would be consistent with the requirements of the phenomenological theory of Levanyuk and Sannikov.$^4$

FIGURE 1 Electric resistivity of Fe$_3$B$_7$O$_{13}$I vs. reciprocal temperature.

FIGURE 2 Dielectric constant (1 MHz, 15 mV) of Fe$_3$B$_7$O$_{13}$I vs. temperature.

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The temperature dependence of the D.C. resistivity was measured at 4.5 Volts in the $mm_2$ phase and in the $43m$ phase using a guard ring method. Respective activation energies of $E_{mm_2} \approx 1.17$ eV and $E_{43m} \approx 0.52$ eV were observed. At $T_c$ the resistivity jumps abruptly from $\rho_{mm_2} = 1.1 \times 10^8 \ \Omega m$ to $\rho_{43m} = 3 \times 10^6 \ \Omega m$ (Figure 3).

The specific heat was measured from $-80^\circ C$ to $+150^\circ C$ with a differential scanning calorimeter (Perkin-Elmer DSC1) (Figure 4). The volume specific heat at $25^\circ C$ is $C_v = 3.5 \pm 0.3 \times 10^6 \ \text{J mole}^{-1} \ \text{K}^{-1}$ and the latent heat and transition entropy at $T_c$ were found to be $\Delta Q = 3.1 \pm 0.3 \times 10^3 \ \text{J mole}^{-1}$ and $\Delta S = 8.9 \pm 0.5 \ \text{J mole}^{-1} \ \text{K}^{-1}$, respectively. Visual observation of the sample at the scanning speed ($4^\circ \text{mn}$) showed the transition to occur within $0.2^\circ C$. The data points therefore reflect the true behaviour of the specific heat anomaly. The broad peak of $C_p$ observed between $-60^\circ$ and $-80^\circ C$ (Figure 4) corresponds to the transitions $3m \leftrightarrow m \leftrightarrow mm_2$, but resolution was poor owing to sluggishness of these transformations.

FIGURE 3 Curie-Weiss law of Fe$_3$B$_7$O$_{13}$.1.

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REFERENCES