Huge differences in ferroelectric Curie temperature between growth sectors of boracite crystals

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Abstract

The cubic (\(\overline{4}3\ m\))/orthorhombic (mm2) phase transition temp. Tc of Mn-I, Zn-I, Ni-Br, and Cu-Br boracite was measured by polarized light microscopy in the pyramidal growth sectors. In either of the 5 compns. the (100), (110), (111), and (\(\overline{1}\overline{1}\overline{1}\)) growth pyramids differ in a systematic way in Tc for each compn. A max. difference of \(\sim 15\) K between inequivalent sectors was obsd. in the same sample of both Zn-I and Cu-Br boracite. In a (100) growth sector of Ni-I boracite the cubic (\(\overline{4}3\ mL')/monoclinic (m') transition is characterized by a sharp peak of dielec. const. \(\varepsilon'\), whereas in a strongly absorbing and birefringent (111) sector the anomaly is annihilated.

Reference


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Huge Differences in Ferroelectric Curie Temperature between Growth Sectors of Boracite Crystals

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The cubic (43 m)/orthorhombic (mm2) phase transition temperature \( T_c \) of Mn-I, Fe-I, Zn-I, Ni-Br and Cu-Br boracite has been measured by polarized light microscopy in the pyramidal growth sectors. In either of the five compositions the (100), (110), (111) and (111) growth pyramids differ in a systematic way in \( T_c \) for each composition. A maximum difference of \( \sim 15 \) \( K \) between inequivalent sectors has been observed in a same sample of both Zn-I and Cu-Br boracite.

In a (100) growth sector of Ni-I boracite the cubic (43 m')/monoclinic (m') transition is characterized by a sharp peak of dielectric constant \( \varepsilon' \), whereas in a strongly absorbing and birefringent (111) sector the anomaly is annihilated.

§1. Introduction

Single crystals of boracites \( \text{M}_{2}\text{B}_{2}\text{O}_{5}\text{X} \), where \( \text{M} \) stands for \( \text{Mg}^{2+}, \text{Cr}^{3+}, \text{Mn}^{2+}, \text{Fe}^{2+}, \text{etc.} \) and \( \text{X} \) for \( \text{OH}^{-}, \text{F}^{-}, \text{Cl}^{-}, \text{Br}^{-}, \text{I}^{-}, \text{etc.} \), are grown by the chemical vapour transport (CVT) method.\(^1\)\(^2\) Such crystals often show a variety of defects formed during the growth process and that can influence significantly the physical properties, in particular in the vicinity of the phase transitions. Most of the defects are related to a sectorial structure of growth pyramids that have been described phenomenologically\(^3\) and studied by X-rays\(^4\) for Ni-I boracite. The sectors can be seen by transmission microscopy. In unpolarized light more or less strong differences in coloration may reveal the sectors, but sometimes they are invisible and can only be recognized in polarized light owing to anomalous birefringence and dichroism in the "cubic" phase.\(^5\) An X-ray study\(^6\) was unable to explain the anisotropies.

Growth sectors are common in natural minerals\(^7\) but they are also typical of artificial crystals grown by a process permitting the free development of equilibrium growth facets (flux growth, CVT, hydrothermal growth, etc.). The effects of growth sectors on the physical properties of a crystal may even find technical applications like the growth induced uniaxial magnetic anisotropy in garnets used for bubble devices,\(^6\) but they may also represent a severe handicap in determining the intrinsic properties of a material like Ni-I boracite, where the unequivocal experimental proof of the simultaneous onset of ferromagnetism and ferroelectricity and the comparison of the experimental results with the predictions of Landau theory\(^8\) requires careful consideration of the growth sectors.

The present paper tries to draw more attention to the problem by showing up the strong dependence of the paraelectric/ferroelectric-ferroelastic transition temperature \( T_c \) on the type of sector.

§2. Experimental

2.1 Samples. The choice of Mn-I, Fe-I, Zn-I, Ni-Br and Cu-Br boracite for the measurement of \( T_c \) in the different sectors is rather arbitrary and corresponds to the availability of samples. Only bromine and iodine boracites were known to be better distinguishable visually than those of chlorine boracites.\(^9\) Thin platelets (50-100 \( \mu m \) thick) of the crystals have been prepared in such a way that they contained a maximum of different sectors.

2.2 Types of sector. Boracite crystals grown by CVT are found to show one or more of the (100), (111), (111) types.

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Fig. 1. Photographs and schematic representation of the growth sectors of (100)-cut samples in their cubic phase: a) Mn-I boracite, b) Fe-I boracite, c) Ni-Br boracite, d) Cu-Br boracite, e) Zn-I boracite.
and (110) facets, whereas boracites grown in nature (e.g. the mineral Mg₃BBr₂O₆Cl) sometimes also developed higher index facets. The occurrence of the mentioned four types of sector is in agreement with the non-centrosymmetric space group F43c (at the growth temperature), for which all positive and negative (100) and (110) facets are equivalent, whereas the (111) and (111) are not. Assuming that all four sectors incorporate different amounts and types of defects, four different values of $T_c$ can be expected.

2.3 Optical measurement of the cubic (F43c)/orthorhombic (Pca2$_1$) transition temperature, $T_c$. For the compositions with $T_c$ above room temperature (Mn–I, Fe–I, Zn–I and Ni–Br) a hot stage and for Cu–Br a quartz Dewar tube with optical windows, combined with a polarizing microscope, were used. The relative temperature was controllable to ±0.1 K. For all samples photographs and schematic sketches of the sectors in the cubic phase have been prepared (Fig. 1a–1e). The phase transition in the different sectors has been measured several times on heating and cooling. An overview of the results is given in Fig. 2 where the streaks represent the width of thermal hysteresis, the low temperature end corresponding to the onset of the transition on cooling and the high temperature end to that on heating.

Figure 2 shows the following major results:

i) A remarkably high difference in $T_c$ is found between (111) and (111) sectors reaching ~ 10 K in Mn–I and Fe–I and ~ 15 K in Cu–Br boracite. The indices (111) have been arbitrarily assigned to the octahedral face pyramid with the lower $T_c$ and (111) to that with the higher $T_c$. No correlation with the absolute configuration of the structure has been made sofar.

ii) In the Fe–I and Zn–I boracites the (100) sectors have the highest $T_c$, whereas in Mn–I, Ni–Br and Cu–Br the (111) sectors reach the top values. In Cu–Br the (111) and (110) sectors have the same $T_c$ value.

iii) Whereas the sequence of types of sector transforming on upheat or cooling is not the same for different boracite compositions, the $T_c$ values of pyramids with equivalent indices are identical in a same specimen.

iv) The (111) pyramids that were found to have the lowest $T_c$, have most probably the highest defect concentration, however, one cannot claim that the sectors with the highest $T_c$ are necessarily the most perfect ones. For example, the (111) pyramids of Cu–Br boracite are strongly coloured-indicating point defects—and have none-the-less the higher $T_c$ than the clear (100) sectors, considered so far as the most perfect ones.

Depending on the type of defect, theory predicts the possibility of either a decrease or an increase of $T_c$. At present we can therefore only say that we ignore the true $T_c$ of a hypothetic high quality boracite crystal.

2.4 Dielectric characterization of growth sectors of Ni–I boracite. Various physical measurements on a (100)-cut (100)-sector showed that Ni–I transforms at 61.5 K from a cubic (43 m$^3$) to a monoclinic (m$^1$) ferroelastic/ferroelectric/ferromagnetic phase. This transition temperature is difficult to recognize accurately by visual observation, however, a small but sharp peak of dielectric constant $\varepsilon'$ was known to be measurable on a (100)-sector. Therefore measurements of dielectric constant were chosen to characterize different growth sectors. From a same crystal, a (100)-platelet made up of a pure (100) sector and a (111)-platelet composed of (100), (111) and (110) sectors (Fig. 3) have been prepared and $\varepsilon'$ has been measured with an impedance analyser (HP 4192A).

Fig. 2. Cubic (43 m$^3$)/orthorhombic (mm21$'$) transition temperatures of the pyramidal growth sectors of five different compositions of boracite.

Fig. 3. Photograph of a (111)-cut of Ni–I boracite showing clear–yellow (100) sectors and dark-green (111) and (110) sectors (sample used for measurement of $\varepsilon'$, thickness=115 $\mu$m; see Fig. 4b and c).
§3. Conclusions

The observation of huge differences of the paraelectric/ferroelectric-ferroelastic transition temperature in inequivalent growth sectors of bromine and iodine boracites should be taken as a warning for the experimentalist desiring to study the physical properties of boracites, in particular in the vicinity of phase transitions. Erroneous conclusions will be avoided in future if type and properties of the sector of the sample will be specified and characterized clearly. In this respect the observed annihilation of the dielectric anomaly $T_c$ of (111) sectors of Ni-I boracite, is particularly instructive. One can also expect that the magnetic domains will be strongly affected by the sector structure.

It remains a major challenge to find out the nature and origin of the defects causing the sectorial anomalies and to conceive new adequate synthesis methods to produce more perfect crystals.

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