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

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The cubic ($\bar{4}3$ 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 ($\bar{1}\bar{1}\bar{1}$) growth pyramids differ in a systematic way in T_c for each composition. A maximum difference of ~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 ($\bar{4}3$ ml')/monoclinic (m') transition is characterized by a sharp peak of dielectric constant ε', whereas in a strongly absorbing and birefringent (111) sector the anomaly is annihilated.

§1. Introduction

Single crystals of boracites $M_3B_7O_{13}X$, where M stands for Mg^{2+}, Cr^{2+}, Mn^{2+}, Fe^{2+}, etc. and X for OH^-, F^-, Cl^-, Br^-, I^-, 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.[3] An X-ray study[4] was unable to explain the anisotropies.

Growth sectors are common in natural minerals[5] 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 unequivoqual experimental proof of the simultaneous onset of ferromagnetism and ferroelectricity and the comparison of the experimental results with the predictions of Landau theory[7] 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 taken because the sectors in these crystals were known to be better distinguishable visually than those of chlorine boracites.[3] Thin platelets (50–100 μm 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), ($\bar{1}\bar{1}\bar{1}$)

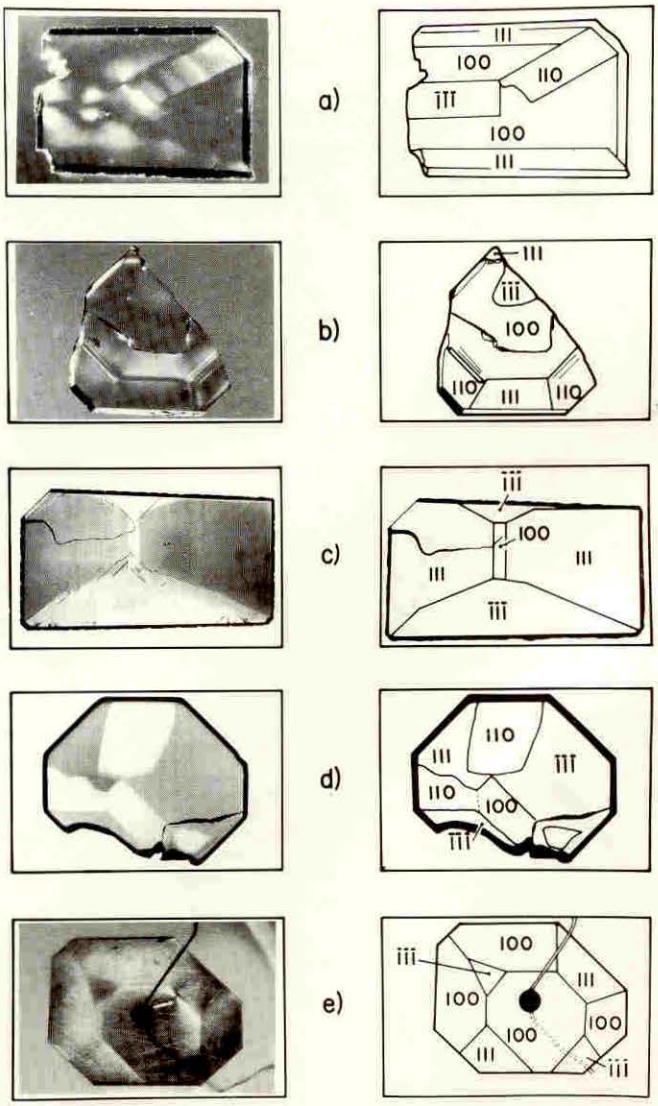

Fig. 1. Photographs and schematic representation of the growth sectors of (100)-cut samples in their cubic phase: a) Mn-I boracite, b) Fe-I boracite, c) Ni-Br boracite, d) Cu-Br boracite, e) Zn-I boracite.

and (110) facets, whereas boracites grown in nature (*e.g.* the mineral $Mg_3B_7O_{13}Cl$) sometimes also developped higher index facets.[8] The occurrence of the mentioned four types of sector is in agreement with the non-centrosymmetric space group F$\bar{4}$3c (at the growth temperature), for which all positive and negative (100) and (110) facets are equivalent, whereas the (111) and ($\bar{1}\bar{1}\bar{1}$) 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 (F$\bar{4}$3c)/orthorhombic ($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 ($\bar{1}\bar{1}\bar{1}$) 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 ($\bar{1}\bar{1}\bar{1}$) 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 ($\bar{1}\bar{1}\bar{1}$) sectors reach the top values. In Cu–Br the ($\bar{1}\bar{1}\bar{1}$) 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 ($\bar{1}\bar{1}\bar{1}$) 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[9] 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 ($\bar{4}$3 ml′) to a monoclinic (m′) ferroelectric/ferroelastic/ferromagnetic phase.[10] This transition temperature is difficult to recognize accurately by visual observation, however, a small but sharp peak of dielectric constant ε' was known to be measurable on a (100)-sector.[10] 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 ε' has been measured with an impedance analyser (HP 4192A)

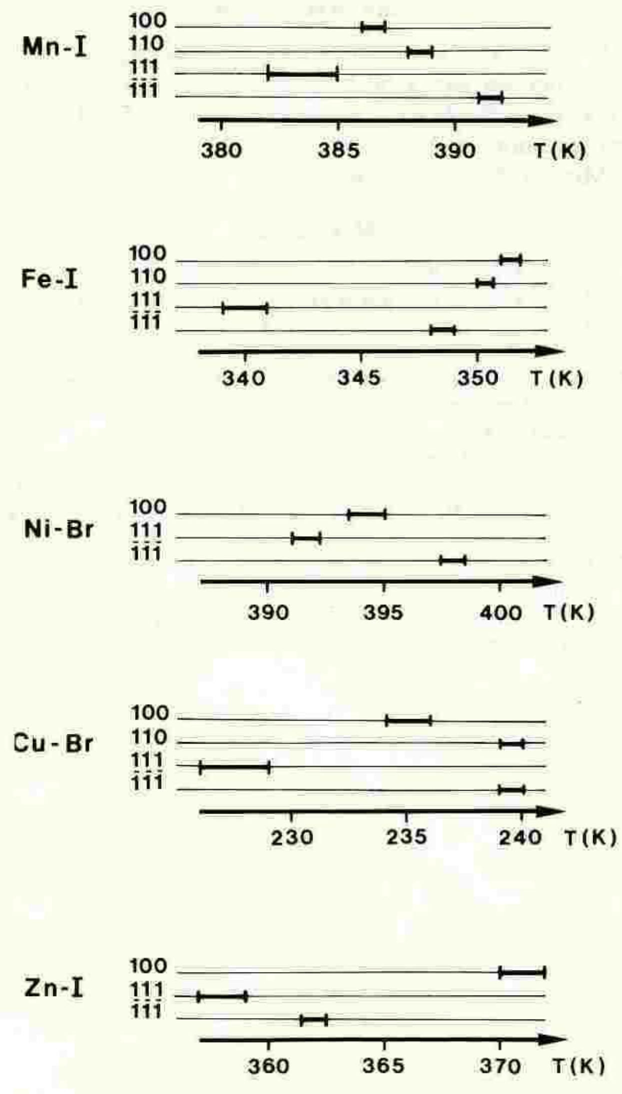

Fig. 2. Cubic ($\bar{4}$3 ml′)/orthorhombic (mm21′) transition temperatures of the pyramidal growth sectors of five different compositions of boracite.

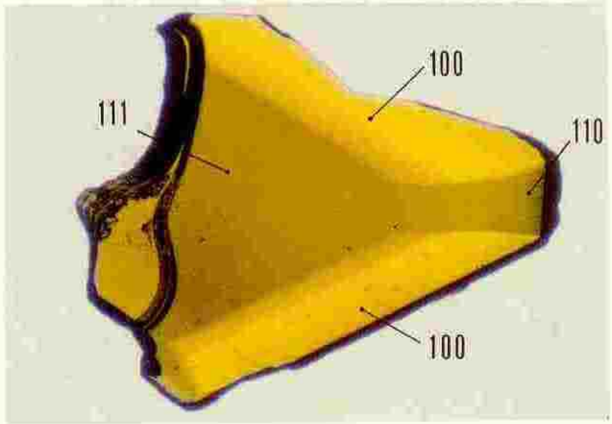

Fig. 3. Photograph of a (111)-cut of Ni–I boracite showing clear-yellow (100) sectors and dark-green (111) and (110) sectors (sample used for measurement of ε', thickness = 115 μm; see Fig. 4b and c).

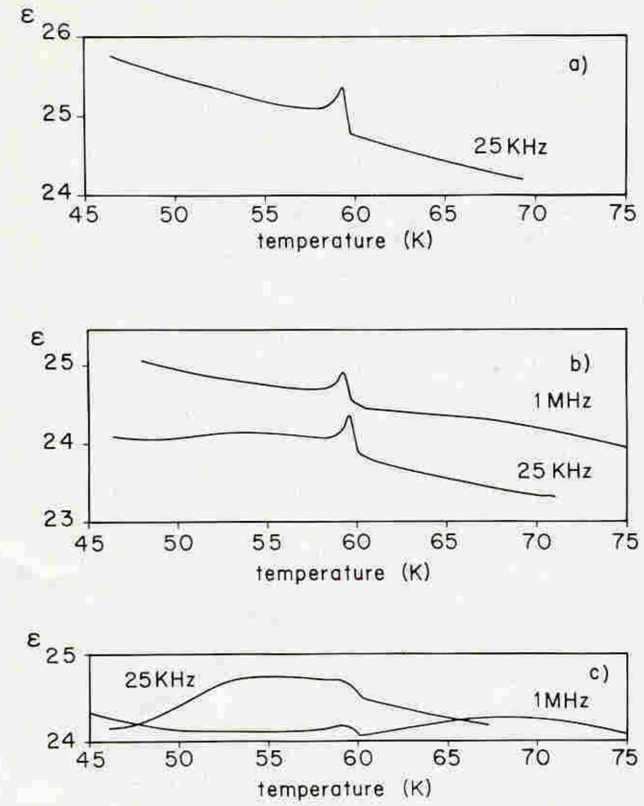

Fig. 4. Dielectric constant ε' of Ni–I boracite in the vicinity of the $\bar{4}3$ ml'↔m' transition. a) (100)-cut (100)-Sector, thickness = 100 μm, b) (111)-cut composed of (100), (110) and (111) Sectors (Fig. 3), thickness = 115 μm, c) same sample as b) but electrodes on (100) sectors removed (small remainder of (100) sectors remains covered with electrode).

at 25 kHz and 1 MHz between 45 K and 75 K. Figure 4a shows the result for the (100)-cut (100)-sector. The peak of ε' is similar to that observed earlier.[10] Figure 4b shows the results on the (111)-cut with silver paint electrodes covering the (111), (110) and (100) sectors. The peak of ε' is essentially located at the same temperature as on the (100)-cut, but an additional broad heap of a relaxation phenomenon centres at about 55 K at 25 kHz but shifts to about 69 K at 1 MHz. After removal of the electrodes on the (100)-sector parts, the peak of ε' disappeared nearly completely (Fig. 4c), only a small anomaly remaining that can be attributed to a small part of (100)-sector on which the electrodes could not be removed. Thus the peak of ε' is only typical of the (100) sector, whereas the phase transition would seem to be suppressed in the (111) sector. (It was not possible to decide whether the measured sector was of the (111) or ($\bar{1}\bar{1}\bar{1}$) type).

§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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References

1) H. Schmid: J. Phys. Chem. Solids, **26** (1965) 973.
2) H. Schmid and H. Tippmann: J. Crystal Growth, **46** (1979) 723.
3) H. Schmid: Rost Kristallov **7** (1967) 32 [Growth of Crystals **7** (1969) 25].
4) R. J. Nelmes and F. R. Thornley: Ferroelectrics **13** (1976) 355.
5) G. G. Lemmlein: *Sektorialnoe Stroennie Kristalla,* Moskva-Leningrad, 1948.
6) G. Winkler: *Magnetic Garnets*, Viehweg & Sohn, Braunschweig/Wiesbaden, 1981.
7) P. Tolédano, H. Schmid, M. Clin et J.-P. Rivera: Phys. Rev. **B32** (1985) 6006.
8) G. H. O. Volger: *Versuch einer Monographie des Borazites*, Carl Rümpler, Hannover, 1855.
9) J.-C. Tolédano: Ann. Télécommun. **39** (1984) 277.
10) J.-P. Rivera and H. Schmid: Ferroelectrics **36** (1981) 447.