Solid State Communications Vol. 2, pp. 45-49, 1964. Pergamon Press, Inc. Printed in the United States.

DIELECTRIC PROPERTIES OF BORACITES AND EVIDENCE FOR FERROELECTRICITY

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(Received 17 January 1964 by G. Busch)

The dielectric constants of Ni-Cl, Ni-Br, Co-Br and Co-I boracites have each a maximum at a temperature which coincides with that of a phase transformation we have observed optically. Motion of ferroelectric domain walls under an applied electric field has been sought for in Ni-Cl boracite and found to occur at temperatures as far as 80° below that of the phase transition.

Introduction

BORACITES are compounds with the composition $M_3B_7O_{13}X$ where M stands for one of the divalent ions Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and X denotes one of the halogens Cl, Br, I. Solid solutions of these compounds exist. We have also indications that boracites may be formed with other divalent ions than those mentioned above and that halogens may be replaced by OH.

Ito and collaborators[1] have determined the crystal structure of the mineral called boracite: $Mg_3B_7O_{13}Cl$; there exists a piezoelectric, optically isotropic high temperature phase with space-group T_d^5 ($F\bar{4}3c$) and a pyroelectric, optically anisotropic low-temperature phase with space group C_{2v}^5 (-Pca).

Boracites have been investigated already for more than one century; recently Le Corre, Jona, and Sonine and Zheludev[2] have investigated whether boracites are ferroelectric.

With a view to verifying a working hypothesis on the existence of electric polarization in paramagnetic crystals, we have prepared single crystals of boracites and measured their electric, magnetic and optical properties. Here our principal aim is to report our first findings concerning the dielectric properties of boracites. Other questions will be taken up in subsequent papers.

Dielectric constant

FIG. 1 shows the dielectric constants of the Ni-Cl, Ni-Br, Co-Br, Co-I boracites as a function of temperature. In all these cases we find a maximum of the dielectric constant. The temperature at which the maximum occurs for each of these compounds is indicated in Table 1. In two cases (Ni-Br, Co-I) we observe a thermal hysteresis. Ni-I boracite was also investigated; the dielectric constant shows no maximum between 80° and 500° K.

Phase transition

WE have investigated whether there is a phase transition corresponding to the maximum of the dielectric constant. The phase transition can be observed optically, because the low temperature phase is optically anisotropic, whereas the high temperature phase is not. The temperatures of the phase transition are reported in Table 1 together with data obtained by Heide[3] and Jona[2].

From this table it may be seen that the maximum of the dielectric constant occurs at

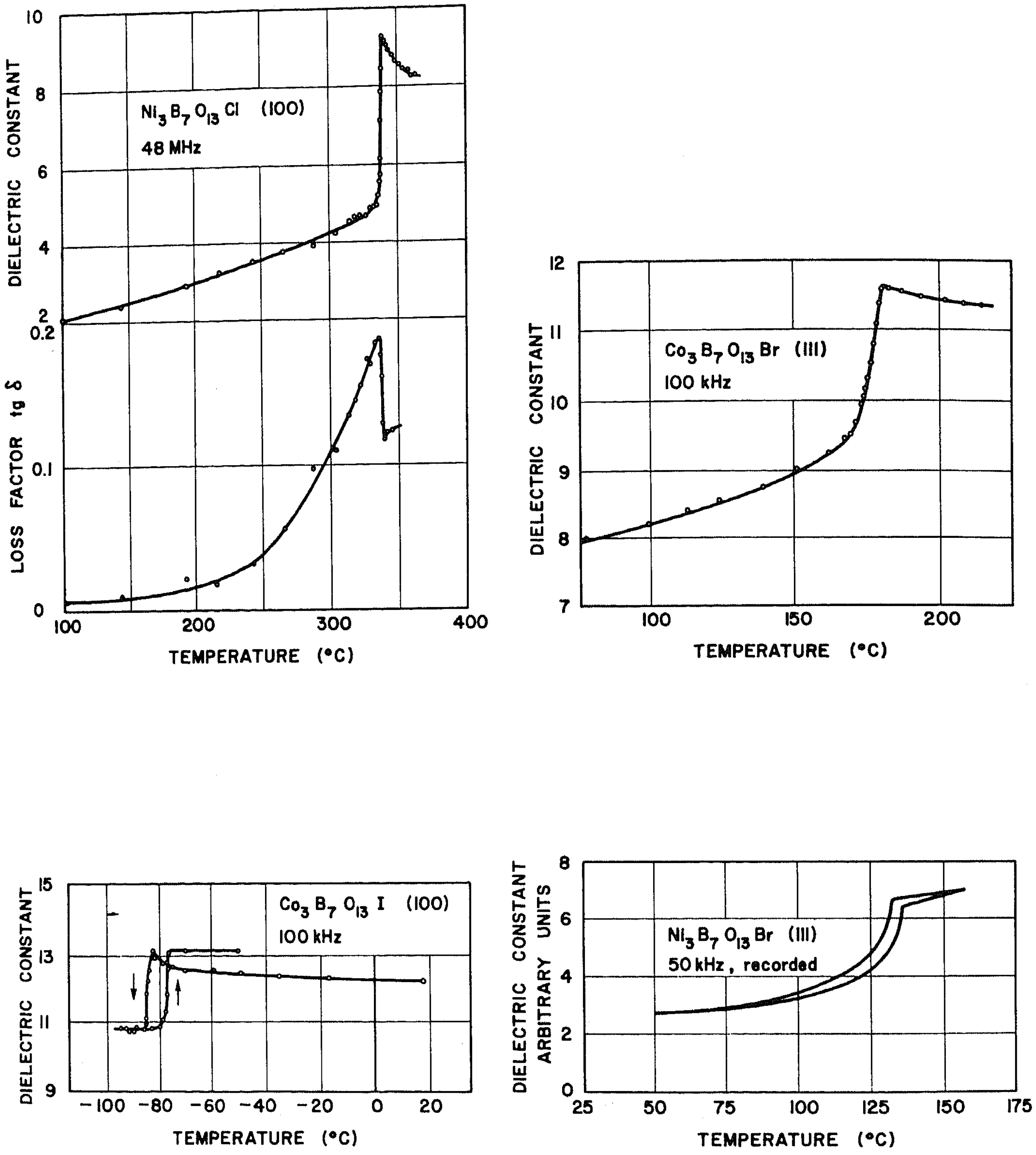
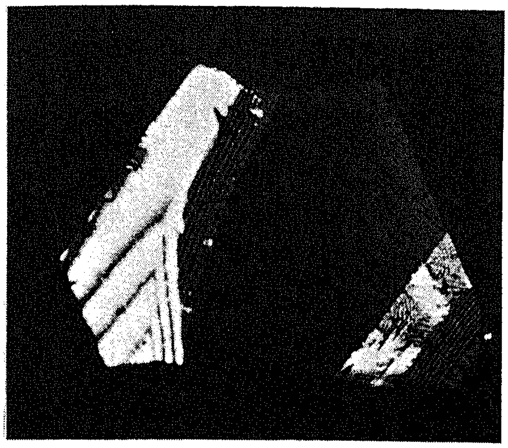
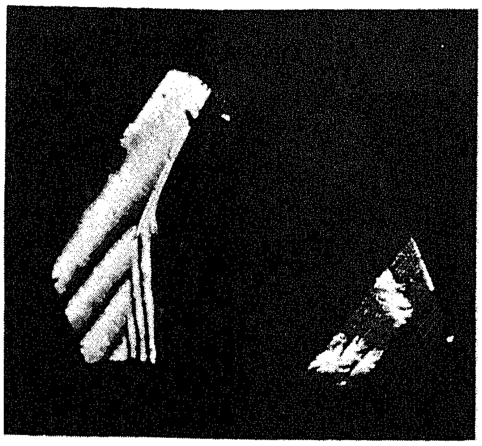


FIG. 1

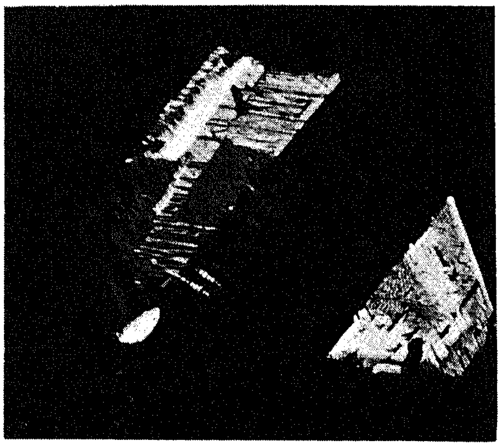
Dielectric constants of some boracites



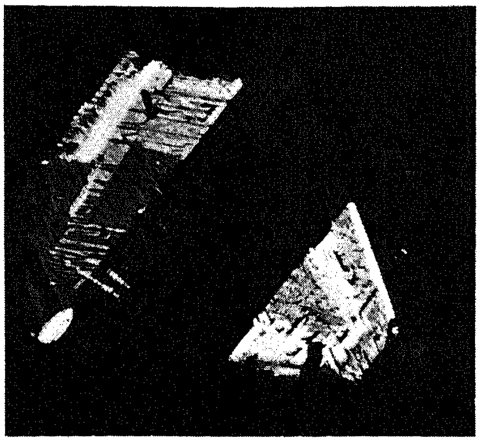
a) $E = +3,6 \frac{kV}{cm}$



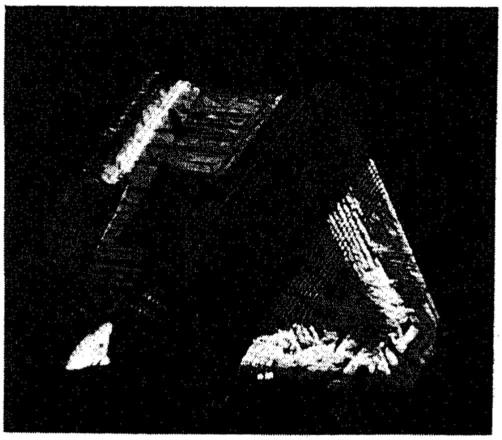
b) $E = 0$



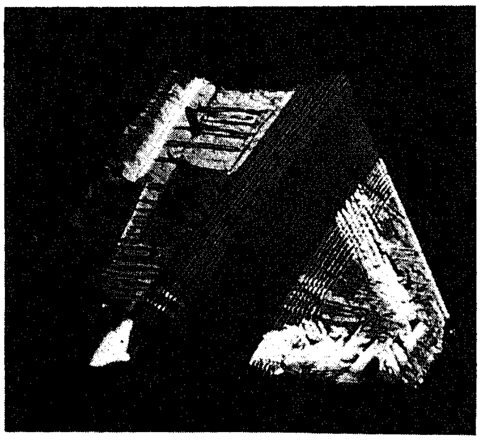
c) $E = -3,5 \frac{kV}{cm}$



d) $E = 0$



e) $E = -5,3 \frac{kV}{cm}$



f) $E = 0$

FIG. 2

Motion of ferroelectric domain walls in $Ni_3B_7O_{13}Cl$

TABLE 1

	Cl		Br		I	
	phase transition °K	maximum of ε °K	phase transition °K	maximum of ε °K	phase transition °K	maximum of ε °K
Mg	538*		291-294			
Cr	251-257		<10		<10	
Mn	680*		564-567ˣ		411-413	
Fe	607, 603*		499		345	
Co	623*		458	457	193-201	190-195
Ni	610, 610*	612	398	399-400	<80	<80
Cu	365*		222-226			
Zn	723*		584-587		681-693	
Cd	798+		732-737		611-623	

*HEIDE[3], +JONA[2], ˣfor some specimens : 523-533

the transition between a polar and a non-polar phase.

Domain wall motion

WE have looked for domain wall motion in Ni-Cl boracite under an applied electric field and found this phenomenon in several cases, of which an example is shown in Fig. 2.

The specimen was prepared as a (111) plate with a surface of about 4 mm^2 and a thickness of 0.22 mm. The wall movement was observed at 527 ±1°K, i.e. well below the temperature of phase transition (610° K).

In the photographs one sees essentially three domains that are separated by two (100) planes which appear as bands of interference fringes. The angle which these planes make with the free surface (as calculated from the width of the bands and the thickness of the crystal) is, within experimental error, equal to the theoretical value of 54°44'.

The direction of polarization is that of one of the six [100] directions; thus the polarization is either perpendicular or parallel to the domain wall and makes an angle of 15°16' with the surface.

The photographs 2a to 2f are given in chronological order. The voltage is applied in the plane of the plate, to its upper and lower edges. The average field strength is indicated, a plus sign meaning that the positive voltage is applied to the lower edge.

Conclusion

WE have shown that Ni-Cl boracite is ferroelectric. Experiments in progress lead us to believe that this is also the case for most of the other boracites.

Acknowledgement

We wish to thank Prof. A. Janner and Prof. B. Elschner for their decisive help in the initial stages of our research on boracites.

References

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Les constantes diélectriques des boracites de Ni-Cl, de Ni-Br et de Co-I passent par un maximum à une température qui coïcide avec celle d'un changement de phase observé par voie optique. Dans la boracite de Ni-Cl, les parois de domaine se déplacent sous l'effet d'un champ électrique appliqué, jusqu'à des températures inférieures de 80^{0} à celle du changement de phase.