X-ray study on the phase transition of Cu-Cl boracite

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Abstract
The temperature and electric field dependences were measured of the lattice strains in Cu-Cl boracite. The spontaneous pure shear is 8 times larger than that of Fe-I boracite, whereas spontaneous dilation strains are .apprx.1/2 those of Fe-I boracite. The electrostrictive constants show anomalous temperature variations near the transition temperature. The results were explained by the theory of improper ferroelectrics.

Reference

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X-RAY STUDY ON THE PHASE TRANSITION OF Cu—Cl BORACITE

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Temperature and electric field dependences of lattice strains of Cu—Cl boracite were accurately measured. The spontaneous pure shear $x_{12}$ of Cu—Cl boracite is 8 times as large as that of Fe—I boracite, while spontaneous dilatation strains are about half of those of Fe—I boracite. Electrostrictive constants $Q_1^1$ and $Q_3^3$ show anomalous temperature dependences near the transition temperature. These peculiarities have been successfully explained by our theory of improper ferroelectrics.

INTRODUCTION

Boracite crystals are regarded as typical improper ferroelectrics. They undergo a sequence of phase transitions. Especially the ferroelectric phase transition from cubic $T_h$ to orthorhombic $C_{2v}^2$ is of interest, because of peculiar physical properties. We are interested in relating the strength of coupling between an order parameter and polarization to peculiar physical properties of boracites. For this reason, we studied lattice strains of Cu—Cl boracite under an electric field.

EXPERIMENTAL RESULTS

We used a c-plate specimen with the dimension of $1.5 \times 0.5 \times 0.037 \text{ mm}^2$. The specimen was held in a vacuum of $10^{-4} \text{ torr}$ at $200^\circ \text{C}$ during 120 hours and cooled gradually. This treatment diminished a broad spread of X-ray spectra.

Lattice strains of Cu—Cl boracite were measured by using high precision x-ray strainmeter with the accuracy of $10^{-6}$ combined with the two-dimensional reciprocal lattice method. Figure 1 shows the temperature dependence of lattice constants of Cu—Cl boracite along the orthorhombic $A$, $B$ and $C$ axes. From these results, we obtained deformation strain $D = x_1 - x_2$ and dilatation strains $S = x_1 + x_2$, and $S_3 = x_3$. The pure shear $x_{12} = D/2$ of Cu—Cl boracite is found to be 8 times as large as that of Fe—I boracite, while dilatation strains $S_1$ and $S_3$ are about half of those of Fe—I boracite. It is interesting to note that Cu—Cl boracite is similar to KH$_2$PO$_4$ as far as lattice strains are concerned.

The electric field dependences of $D$ and $S$ were measured in the vicinity of $T_0$. $D$ increases with increasing (+) electric field both in paraelectric and ferroelectric phases, with steeper slopes in the vicinity of $T_0$. On the other hand, the electric field dependence of strain $S_1$ is quite unusual as shown in Figure 2(a): the spontaneous $S_1$ is positive showing the dilation of the lattice, while the induced $S_1$ changes its sign and becomes positive immediately above $T_0$. Electrostrictive constant $Q_1^1$ is shown in Figure 2(b) as a function of temperature. $Q_3^3$ has a strong dependence upon temperature: it changes sign at $98.8^\circ \text{C}$ and has a pronounced peak at $T_0$. The same anomaly has been also observed in the strain $S_3$. These peculiar behaviours of electromechanical properties of Cu—Cl boracite have been explained by our theory of improper ferroelectrics as discussed below section.
DISCUSSIONS

According to this theory, strain $S$ is described by polarization $P$ and an order parameter $\theta$ as:

$$S = 2Q_{31}P_3 + 2R_{31}\theta_3^2.$$  

(1)

These expressions provide for ad hoc strains, that is, latent lattice strains, which come from the mechanical coupling with $\theta$. From these equations, we derive the following expressions for electrostrictive constants.

For spontaneous strain,

$$Q_{31} = Q_{31}^0 + (\omega^2 f)^2 R_{31}.$$  

(2)

For induced strains,

$$Q_{31}^d = Q_{31} - (f/\beta)^2 R_{31}/(T - T_0)^2 \text{(in para).}$$  

(3)

$$Q_{31}^f = Q_{31} - (\omega/2\beta)R_{31}/(T - T_f) \text{(in ferro).}$$  

(4)

Experimental results shown in Figure 2a and b are explained if the constant $R_{31}$ is positive and $Q_{31}$ negative. The electric field dependence of $S$ and temperature dependence of $Q^d$ predicted from the theory are schematically depicted in Figures 2c and d, respectively, which clearly manifest that the peculiar electromechanical properties of Cu–Cl boracite can be explained by the theory. Comparison with the result of Fe–I boracite indicates that the strength of the coupling $f$ between $P$ and $\theta$ for Cu–Cl boracite is stronger than that for Fe–I boracite.

REFERENCES