

# Ferroelastic Phase Transition in a Layered Bismuth Oxychloride Single Crystals

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We report the results of low-temperature specific-heat, magnetization, and X-ray diffraction measurements on a bismuth oxyhalide (BiOCl) single crystal. We conclude that BiOCl in temperature region 150–230 K shows “antiferroelastic–paraelectric” phase transitions at critical temperatures  $T_{c1} = 167.5$  K and  $T_{c2} = 214.6$  K, respectively.

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## 1. Introduction

Bismuth oxychloride BiOCl single crystals are very interesting materials which find various applications in photonics. The great interest for these materials is strongly related to the influence of dimensionality on the behaviour of physical properties, polymorphic and phase transformations [1].

## 2. Experimental details

The BiOCl compound was prepared by dissolving 99.99 pure bismuth oxides in hydrochloric acid, evaporating to form the hydrated chlorides, dehydrating the latter under the vacuum, heating at  $\approx 380$ – $700$  °C in a Cl<sub>2</sub> atmosphere, cooling to room temperature, and washing the product to remove BiCl<sub>3</sub>. The products was BiOCl. The BiOCl single crystal was grown up using the vapour gas transport reaction method in closed volume. The lattice parameters are  $a = 3.887$  Å and  $c = 7.354$  Å. A Laue photograph taken parallel to the large face of the platelets showed clearly a fourfold symmetry axis characterizing (001) planes of a matlockite tetragonal PbFCl-like structure. An examination of the platelets using a polarizing microscope shows no extinction, thus indicating that the tetragonal  $c$ -axis is perpendicular to the plane of the platelets [1]. The specific heat was measured

in the temperature range from 2 to 50 K in zero and 8 T magnetic field. The measurements were performed in a Physical Properties Measurement System (PPMS) from Quantum Design.

## 3. Results and discussion

BiOCl structure consists of O–Bi–Cl–Cl–Bi–O layers and belongs to space group of  $P4/nmm$ . The structure exhibits a cleavage plane perpendicular to the  $c$  axis where the bonding between the neighboring Cl layers is weaker [1]. On the basis of the structure we concluded that the origin of the dipole moment was due to the induced atomic dipole of the halogen, aligned antiparallel with the  $c$  axis [2].

For the analysis of specific heat we have chosen the approximation described in detail in the paper of Martin [3]. In this approximation the phonon spectrum is again divided into the acoustic and optical branches and those are described by the modified Debye and Einstein formulae, respectively. The resulting isobaric phonon specific heat can be then written in the form

$$(C_p)_{\text{calc}} = R \left( \sum_{i=1}^n \frac{1}{1 - \alpha_{E_i} T} \frac{x_{E_i}^2 \exp(x_{E_i})}{[\exp(x_{E_i}) - 1]^2} + \frac{n-3}{1 - \alpha_D T} \left( \frac{1}{x_D} \right)^3 \int_0^{x_D} \frac{x^4 \exp(x)}{[\exp(x) - 1]^2} dx \right),$$

where  $\alpha_D$  and  $\alpha_{E_i}$  are the anharmonic correction coefficients for acoustic and optical branches, respectively;  $n$

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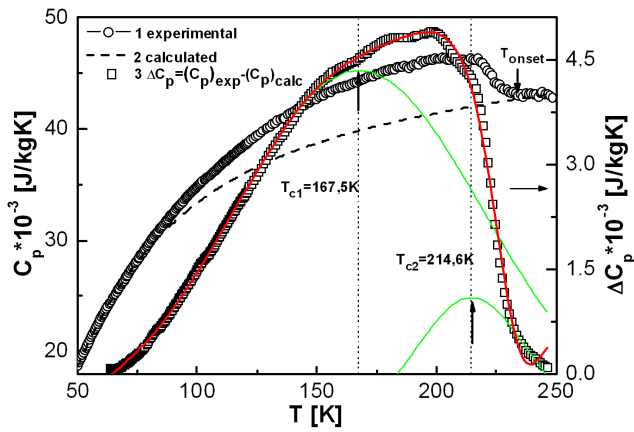


Fig. 1. Temperature dependence of experimental (curve 1), calculated (curve 2) specific heat and their difference (curve 3) in region of phase transitions BiOCl single crystal. Green curves indicate the temperature areas of existence of the ferroelastic domains.

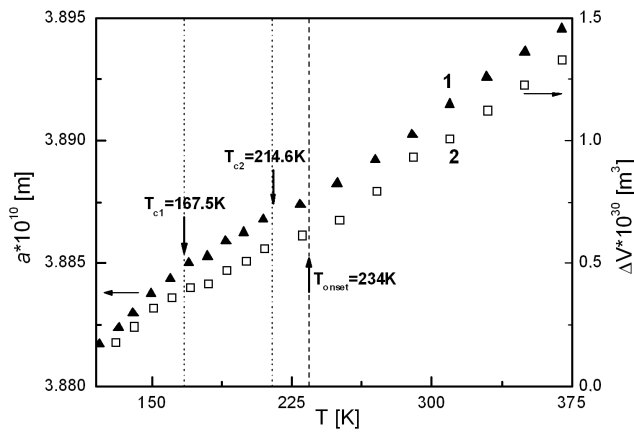


Fig. 2. The temperature dependence of lattice parameter  $a$  (curve 1) and change of elementary cell volume of unit cell  $\Delta V$  (curve 2) in phase transitions region of BiOCl.

— number of acoustic and optical branches ( $n = 18$  for BiOCl);  $R$  is the gas constant. The temperature dependence of the experimental  $(C_p)_{\text{exp}}$  and calculated  $(C_p)_{\text{calc}}$  specific heat of BiOCl in both  $C$  vs.  $T$  is present in Fig. 1. The  $\Delta C_p$  value is difference between  $(C_p)_{\text{exp}}$  and  $(C_p)_{\text{calc}}$ .

From the dielectric constant, specific heat, magnetic susceptibility and X-ray diffraction studies on BiOCl as a function of temperature, we report the wide maximum in the dielectric constant and specific heat (Fig. 1) and breaks in the X-ray diffraction in temperature region 150–230 K (Fig. 2). They testify that “antiferroelastic(AFE)–paraelectric(PE)” phase transitions are present possibly by order–disorder mechanism [4] at critical temperatures  $T_{c1} = 167.5$  K and  $T_{c2} = 214.6$  K, respectively. The mechanism of “AFE–PE” phase transition in BiOCl is caused by possible existence of ferroelastic domains on basis of Bi–O coordination polyhedron [2].

The results discussed above reveal that it is highly desirable to study the inelastic neutron scattering on BiOCl to be able to directly measure the dispersion relation of phonons and domains structure.

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