High pressure crystal structure and electronic properties of bismuth silicate Bi$_2$SiO$_5$ from synchrotron experiment and first principle calculations.

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The high pressure structural properties of bismuth oxide Bi$_2$SiO$_5$ have been investigated up to 28 GPa using in situ powder synchrotron X-ray diffraction and up to 50 GPa with DFT calculations. The monoclinic structure is found to persist up to $\approx$ 20 GPa, where a notable change in the compressibility occurs. The DFT data imply that this is due to a second-order phase transition from the ambient condition monoclinic structure with space group $Cc$ to an orthorhombic polymorph with space group $Cmcm$. This transition involves the straightening of the chains formed by corner-connected SiO$_4$ tetrahedra, that suppresses the ferroelectricity in the high pressure, centrosymmetric phase of Bi$_2$SiO$_5$. The stereo-chemical activity of the Bi$^{3+}$ lone electron pair is found to decrease with increasing pressure, but it can still be identified in the calculated electron density difference maps at 50 GPa.

I. INTRODUCTION

Currently, there is a considerable interest in ferroelectric lead-free oxide materials with high transition temperatures. In this context, Bi$_2$SiO$_5$ (BSO) has emerged as a promising lead-free oxide, after the finding of high transition temperature ferroelectricity with a transition from the $Cc$ to the $Cmcm$ phase at the Curie temperature $T_C = 670$ K $\cite{1,2}$. Apart from ferroelectricity, another interesting electronic feature in BSO is the lone electron pair located at the irregularly coordinated Bi atom. In contrast to other lone-pair-electron-driven displacive-type ferroelectrics $\cite{3}$ or multi- and ferroelectric compounds with perovskite-type structures, where the spontaneous polarization arises from the cation off-centering (BiFeO$_3$ $\cite{4}$, BiMnO$_3$ $\cite{5}$, PbTiO$_3$), the ferroelectricity in BSO is primarily driven by the tilt of the SiO$_4$ units $\cite{6}$ within the 1D tetrahedral chains, characteristic for this structure. These findings have triggered numerous experimental and theoretical studies making BSO a benchmark system for ferroelectrics based on polymerized tetrahedra as an alternative to perovskite-type ferroelectrics.

At ambient conditions BSO is stable in the monoclinic $Cc$ space group, see structure in Fig.1. A very small monoclinic distortion of the crystallographic angle $\beta$ from 90° to 90.0695° was reported based on transmission electron microscopy measurements and Rietveld refinements $\cite{7}$.

Characteristic for the BSO structure at ambient conditions are chains of corner-sharing SiO$_4$-tetrahedra aligned along the $c$-axis. These chains are located in layers parallel to the $(b,c)$-plane. Bi atoms are also located on planes parallel to the $(b,c)$-plane, and are irregularly coordinated by six oxygens located on one side of Bi atom, while the lone electron pair is located at the other side. Based on ab initio calculations Park et al. $\cite{8}$ concluded that the spontaneous polarisation along the $c$-axis was overwhelmingly due to tetrahedral tilting. A systematic tuning of the ferroelectric phase transition is possible by element substitution, where Pb was successfully substituted for Bi up to 20 % $\cite{9}$.

Besides the importance of BSO as a benchmark system to design new tetrahedra-based ferroelectrics, this compound is also interesting as a model system to study the interplay between ferroelectric and antiferroelectric ordering. It was observed by Taniguchi et al. $\cite{1}$ that the ferroelectric – paraelectric phase transition at $T_C$ is driven by the freezing of an optical phonon at the $\Gamma$ point $\cite{1}$, as is usually observed in ferroelectric materials $\cite{5}$. However in a recent study an additional dynamical anomaly at the Brillouin zone edge was reported $\cite{9}$, where the $Y$ point optical phonon substantially softens down to $\sim$50 % when approaching the $T_C$. The phonon softening was observed along the whole $\Gamma – Y$ optical branch, presumably producing a collapse of the transverse acoustic branch due to TO – TA mode coupling. Because the $Y$ point phonon is intrinsically associated with antiferroelectric displacements, the simultaneous observation of a zone center and a zone bound-

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ary dynamical anomaly is evidence for a competition between ferroelectric and antiferroelectric ordering in BSO. The outcome of such competition can strongly depend on an external field, such as pressure. However, the pressure dependence of BSO has not been reported yet, which was the main motivation for carrying out the present study.

In this paper we report a high pressure structural study of BSO based on in situ powder diffraction synchrotron experiments and density functional theory (DFT) calculations. We address the activity of the stereo-chemically active lone electron pair on the Bi$^{3+}$ ion under pressure and the compression mechanisms of the ferroelectric Cc structure with an emphasis on the evolution of the 1D tetrahedral chains responsible for the ferroelectric properties of BSO.

II. EXPERIMENTAL

Bi$_2$O$_3$ and SiO$_2$ powders were mixed in an agate mortar in a stoichiometric ratio and heated in a Pt crucible at 1373 K over 2 h. The resulting polycrystalline melt was subsequently cooled to ambient temperature and crushed to obtain fine powders.

High pressure diffraction data were recorded at the Extreme Conditions Beamline P02.2 at PETRA III, Hamburg, Germany. The beam was focused to a spot size of $8 \times 2.4 \mu$m (FWHM, H $\times$ V) using compound refractive lenses. The incoming photon energy was 42.66 keV (corresponding to 0.29063 Å) and the detector to sample distance was 400 mm.

The BSO powder was loaded into the symmetric type diamond-anvil cell (DAC) with 300 $\mu$m culet size diamonds. Rhenium plate pre-indentated to 35$\mu$m thickness was used as the gasket, in which a 150 $\mu$m diameter hole was drilled with an excimer laser. Au was used as pressure marker and neon was employed as a pressure transmitting medium.

The pressure was increased in steps of 1 to 2 GPa. Before commencing with the data collection we waited for pressure equilibration. We collected data at two positions at each pressure. The maximum pressure achieved was 29 GPa. Data collection was performed in oscillation mode (10° rotation in 10 seconds) to increase the number of crystallites in diffraction condition. The two-dimensional XRD images were converted to one-dimensional diffraction pattern using the DIOPTAS program. For data analysis, Le Bail and Rietveld refinements were carried out with the Jana2006 software. Additional ambient pressure data were recorded at the ID28 beamline side station from the European Synchrotron Radiation Facility (ESRF) with a wavelength $\lambda = 0.5226$ Å.

III. COMPUTATIONAL DETAILS

First-principles calculations were carried out within the framework of density-functional theory (DFT), the PBE exchange correlation functional and the plane wave/pseudopotential method using the CASTEP simulation package. "On the fly" norm-conserving pseudopotentials from the CASTEP data base were employed in conjunction with plane waves up to a kinetic energy cutoff of 800 eV. A Monkhorst- Pack grid was used for Brillouin-zone integrations with a distance of <0.023 Å$^{-1}$ between grid points. Convergence criteria included an energy change of $<5 \times 10^{-6}$ eV/atom for scf-cycles, a maximal force of $<0.008$ eV/Å, and a maximal component of the stress tensor $<0.02$ GPa. Phonon frequencies were obtained from density functional perturbation theory-based calculations as implemented in the CASTEP package.

IV. RESULTS AND DISCUSSION

A selection of powder diffraction patterns measured at ambient pressure in a capillary and under pressure up to $P = 28.8$ GPa in a DAC are shown in Fig. 2(a). Due to the presence of the strongly scattering Bi atoms, the extraction of reliable positional parameters for the much lighter elements was not possible for the data collected in a DAC. Hence, the analysis was restricted to a removal of the background and a subsequent Le Bail fit, from which the pressure dependence of the lattice parameters were obtained. The pressure-induced changes are shown in Fig. 2(b). The compression of the Cc structure is only very slightly anisotropic, with a stronger compressibility of the long a-axis, while the b- and c-axis show a similar variation with pressure. The a-axis compression is almost linear up to $\sim$ 20 GPa while the compressibility decreases above this pressure. Small changes are also observed at about 19 GPa in the evolution of the b- and c-axis, which becomes more obvious by looking the lattice parameters ratios in Fig. 2(c). The ratios $b/a$ and $c/a$ have a very similar behaviour, slightly increasing up to $\sim$ 29 GPa. However, the ratio $c/b$ shows
a more interesting pressure dependence. The c/b ratio continuously decreases up to 17 GPa, where a kink in the pressure dependence is clearly observed. DFT calculations show that these compressibility changes are related to the conformational changes of the chains of Si tetrahedrons in the (b, c)-plane and will be discussed in more details below. The P-V data for the low pressure phase of BSO were fitted with a third order Birch Murnaghan equation-of-state from ambient pressure up to 17 GPa, see Fig. 3 (a). The fit to the experimental P-V data lead to $V_0 = 444.3 \text{ Å}^3$ (fixed), $B_0 = 69.6 \text{ GPa}$ and $B_0' = 7(1)$, where $B_0$ is the Bulk modulus, $B_0'$ its pressure derivative and $V_0$ the volume of the unit cell at ambient conditions (Table II). The fit parameters of the equation-of-state, namely $B_0$ and $B_0'$, are highly correlated, and to facilitate a comparison with other data we plotted confidence ellipses in Fig. 3 (b).

We now turn to our theoretical results. The pressure-dependence of the lattice parameters and their ratios, the equation of state and the resulting bulk modulus obtained from DFT calculations are plotted alongside with the experimental data in Figs. 2 and 3 respectively. Our experimental and calculated lattice parameters at ambient pressure are in reasonable agreement (~2%), see Table I with each other and earlier data. The ambient pressure DFT data deviate in one respect from the structural data published by Taniguchi et al. [1]. In our calculations, the Si-O distances of oxygens coordinating the Bi atoms are about 1.62 Å, i.e. a value typical for Si-O bonds in tetrahedra. However, the Si-O distances to those oxygen which are corner shared with the adjacent tetrahedra are

![Diagram](image-url)

**FIG. 2.** (a) Selection of XRD patterns of BSO measured at various pressures ($T = 300 \text{ K}$, $\lambda = 0.2903 \text{ Å}$). The asterisk indicates a diffraction peak due to neon. (b) Pressure dependence of the lattice parameters of BSO. Filled symbols represent experimental data, continuous lines are results from DFT calculations. (c) Ratios of the lattice parameters highlight the change in the compression mechanism at $\approx 20 \text{ GPa}$.  

![Diagram](image-url)

**FIG. 3.** (a) Pressure dependence of the normalized unit cell volume of BSO. Filled symbols represent experimental data, the red line up to 17 GPa is a fit of an equation-of-state to the experimental data and the black line is data from DFT calculations. (b) Bulk modulus ($B_0$) versus bulk modulus derivative ($B_0'$) values from the PXRD measurement in this study (empty black square) along with the DFT value obtained in this study, see Table II. Dashed lines present confidence ellipses for the fit of $B_0$ and $B_0'$ to the measured $V(P)$ relation.

**TABLE I.** Comparison of BSO unit cell parameters obtained from DFT calculations, from Lebail refinement (this work) and from an earlier study [1].

| Parameter | Exp. this study | DFT this study | Exp. this study |
|-----------|----------------|----------------|----------------|
| a (Å)     | 15.195(1)      | 15.456         | 15.193(1)      |
| b (Å)     | 5.468(2)       | 5.5632         | 5.4435(1)      |
| c (Å)     | 5.315(1)       | 5.4208         | 5.2892(1)      |
| β (°)     | 90.0           | 89.995         | 89.995         |
| $V_0$ (Å³) | 444.3         | 446            | 446            |

**TABLE II.** Bulk modulus $B_0$ (GPa) and its pressure derivative $B_0'$ derived from fits of the $P-V$ data for the low pressure phase of BSO with a third order Birch-Murnaghan equation-of-state from ambient pressure up to 17 GPa, from a fit to the theoretical $P-V$ data and from stress-strain calculations of the elastic stiffness tensor.
FIG. 4. Pressure dependence of the Bi-O and Si-O bond lengths from DFT calculations, which predict that on pressure increase the bismuth coordination polyhedra becomes less distorted, while in the Si-O tetrahedra two longer and two shorter bonds are preserved up to 50 GPa.

unusually long (1.68 Å). At ambient pressure the Si-O-Si and O-Si-O angles in the experimentally determined and computed structure are in very good agreement. A bond population analysis strongly supports the preference for a description of the Bi-atom in six-fold coordination, instead of an alternative description where the Bi-atom is the apex of a pyramid, as there still is an appreciable bond population of about 0.1 eV/Å even for the longest ($d_{\text{max}}(\text{Bi-O}) \approx 2.59$ Å Bi-O distances. The irregular coordination polyhedron is, however, indicative for a stereo-chemical lone electron pair (see below).

The pressure dependence of the lattice parameters obtained from the DFT calculations shows a similar discontinuous change to that observed experimentally around 20 GPa, although the effect is slightly more pronounced in the calculations compared to our observations. The DFT model predicted a structural phase transition to an orthorhombic (space group $Cmcm$) structure, without any discontinuous change in the unit cell volume.

The fit of an equation of state to the theoretical data (Fig. 3) gave $B_0 = 58(11)$ GPa, $B'_0 = 9(3)$ and $V_0=466Å^3$ (fixed), see table II. The fit was carried out below the transition pressure. In order to independently assess the bulk modulus, we carried out stress-strain calculations for the derivation of the complete elastic stiffness tensor. We obtained the following values in GPa: $c_{11} = 108(2)$, $c_{22} = 122(2)$, $c_{33} = 131 (1)$, $c_{44} = 42(1)$, $c_{55} = 42.2(5)$, $c_{66} = 48.0 (4)$, $c_{12} = 45(2)$, $c_{13} = 10(2)$, $c_{23} = 16(2)$, resulting in a bulk modulus $B_0 = 55.6(7)$ GPa. All other tensor components which are allowed to differ from zero in the monoclinic system ($c_{14}, c_{15}, c_{35}, c_{46}$) where zero within the numerical uncertainty.

The DFT-calculations allow us to follow the pressure-induced structural changes in detail. The pressure-dependence of the Si-O and Bi-O bonds are shown in Fig. 4. As has been noted above, the DFT calculations predict that at ambient conditions there are two bonds with the typical Si-O bond length of 1.62 Å, and two bonds which are slightly longer (1.68 Å). At 50 GPa, the bond lengths have decreased substantially to 1.55 Å and 1.60 Å, respectively. This prediction is in good agreement with experimental findings in other silicates. For example, a single crystal high pressure diffraction study of a silicate garnet Bi$_2$Ga$_4$O$_9$ gave a Si-O bond length of 1.58 Å at 50 GPa [17]. The coordination polyhedron around the Bi becomes less distorted on increasing pressure. At 50 GPa there are eight oxygen atoms within 2.8 Å of a Bi atom but a population analysis indicates that along all these distances the population is very low ($<0.08$ e$^-$/Å$^3$ even for the shortest Bi-O distance), and hence there is no well-defined coordination polyhedron around Bi.

The most striking pressure-induced structural effect in BSO is the evolution of the SiO$_4$ tetrahedral chains aligned along the c-axis. The pressure-induced change of the O–O–O angle formed by the corner-sharing oxygen atoms along the chain, and the Si-Si distances are shown in Fig. 5. With increasing pressure, the chains shorten, i.e. the Si-Si distances decrease by an increase of the tetrahedral tilt in the chains. Above 20 GPa, a rotation of the SiO$_4$ units leads to straight SiO$_4$ chains. The compressibility of the chain along the chain axis is signif-
FIG. 6. Slice through the calculated valence electron density difference function of BSO at ambient pressure (top) and 50 GPa (bottom). The maxima of the density difference function with a value of $\approx 0.04 \, e^{-/\text{Å}^3}$ close to the Bi-atoms are typical of stereochemically active lone electron pairs. While the maxima decrease with increasing pressure, they are still discernible at 50 GPa.

icantly smaller for the straight chain than for the tilted chain. The structural changes are reminiscent of those observed at the ferroelectric – paraelectric transition at high temperature [1]. The Bi – O and Si – O bond lengths are only weakly affected by the rotation. The Si tetrahedral volume remains constant across the transition. This structural transition explains the observed anomalies in the compression data.

We also studied the effect of pressure on the Bi$^{3+}$ 6s lone-electron pair. We have evaluated the valence electron density difference function, i.e. the difference between the overlapping non-interacting atomic valence electron densities and the self-consistent electron density up to 50 GPa (Fig. 6). The calculations show clear evidence for a localised stereochemically active lone electron pair at low pressures, with a maximum density of $\approx 0.04 \, e^{-/\text{Å}^3}$ close to the Bi-atoms. At 50 GPa, this maximum is smeared out, but can still be detected, and hence the lone electron pair is still stereo-chemically active. The persistence of stereochemical lone electron pairs at high pressures has been observed in a range of other compounds, including PbO up to 46 GPa [18], Bi$_2$Ga$_4$O$_9$ [19] up to 50 GPa and Bi$_2$S$_3$ [20 21].

As shown by Park et al. [6] the ferroelectricity of BSO at ambient conditions arises mainly from the tilting of the SiO$_4$ chains forming the SiO$_3$ layer, 24.1 $\mu$C/cm$^2$, however a small component originates from the Bi$_2$O$_2$ layer, 1.3 $\mu$C/cm$^2$. They have also shown, that the spontaneous polarization is proportional to the tilting angle, which they defined as an angle complementary to the O–O–O angle defined in this study. This allows us to predict that spontaneous polarization of BSO will increase with pressure, reaching a maximum at $\approx 15$ GPa with a value $\approx 50 \, \mu$C/cm$^2$, two times larger than at ambient pressure. Upon further pressure increase the polarization will decrease, vanishing at $\approx 20$ GPa due to the transition to the centrosymmetric phase.

V. CONCLUSIONS

In summary, we have performed a high pressure study of the structure of BSO by synchrotron X-ray powder diffraction and DFT calculations. The compression mechanism of the structure below 17 GPa is characterized by a continuous rotation of the SiO$_4$ tetrahedra, which leads to a shortening of the Si-Si distances and of the chain length. At 17 GPa we observed a structural phase transition during which the Si tetrahedral chains straighten. The monoclinic angles differs only very slightly from 90° in the low pressure monoclinic phase, and only very small changes in the atomic parameters distinguish the monoclinic phase from the orthorhombic high pressure phase. This transition is not associated with a change of the stereochemical activity of the Bi lone electron pair, as this remains localised up to at least 50 GPa. These results open the route towards dynamical studies of the competition between FE and AFE ordering under high pressure. In particular, the FE soft mode which corresponds to the twisting of the SiO$_4$ tetrahedras, is expected to be strongly affected by the anisotropic compression of the silicate chains.

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