Crystal structure
of the ceramic superconductor BaPb$_{0.75}$Bi$_{0.25}$O$_3$

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The ceramic superconductor BaPb$_{0.75}$Bi$_{0.25}$O$_3$ is monoclinic at T<430 K with space group I2/m. Lattice constants and the atomic coordinates result from 20 reflection groups (12 < 20 < 120°, λ = 1.1267 Å) collected with a high resolution powder diffractometer using a synchrotron radiation source and a full neutron powder pattern (6 < 20 < 140, λ = 1.909 Å). Synchrotron and neutron data were simultaneously refined with SIMREF, a new profile refinement program, based on the Rietveld method. Group theoretical analysis of the distortion field leading from the ideal perovskite structure to I2/m exhibits R$_2^1$ symmetry. A comparison is made with the corresponding distortions in nonsuperconducting BaBiO$_3$ where three different symmetry types are identified. The space group I2/m found for BaPb$_{0.75}$Bi$_{0.25}$O$_3$ allows only one type of averaged (Pb/Bi)O$_6$ octahedron in the structure: this may support valence fluctuations and hence contribute to the mechanism of superconductivity in this particular compound.

Introduction

Early evidence for strong electron-phonon coupling in perovskite-like metallic oxides came from the discovery of superconductivity in the BaPb$_1-x$Bi$_x$O$_3$ system [1]. Since then, several models have been suggested for the structure of these perovskite like superconducting compounds. Cox et al. [2] concluded from X-ray and neutron diffraction studies that the room temperature symmetry for the superconducting compositions (0.05 < x < 0.3) is tetragonal. The tetragonal model was the basis for electronic band calculations from Mattheis and Haman [3] and for their assumption of a strong oxygen octahedra breathing mode.

Kahn et al. [4] suggested the space group Cmm2 from X-ray powder data and Oda et al. [5] found orthorhombic symmetry from an analysis of the splitting of the pseudo-cubic (222) reflection peak. The latter work was done with a single crystal and X-ray radiation. From Raman scattering, Sugai et al. [6] observed soft modes, which could not be explained with a tetragonal structure. They concluded, that the crystal structure is lower in symmetry than tetragonal. In a later paper Sleight and Cox [7] confirmed their tetragonal model from a detailed investigation of 4 reflection groups using a synchrotron source with a high resolution powder diffractometer. They suppose that evidence for lower symmetry may arise from two phase mixtures in some compositions of this compounds. Asano et al. [8] found tetragonal, orthorhombic and monoclinic polymorphs of BaPb$_{0.75}$Bi$_{0.25}$O$_3$. The tetragonal structure was obtained by an additional heat treatment of the sample in oxygen gas, the initial sample, orthorhombic at 300 K, is given to be of P2$_1$/m symmetry at 5 K. Referred to the cubic perovskite cell with $a_0=4.3$ Å, the suggested non cubic cells are all given by the edges $a_0=b_0=a_0^*$, and $c_0=2a_0$, with the exception of the cell found by Kahn et al. [4] in which $c_0=a_0$.

However, knowledge of the correct symmetry is the basis for any calculation intended to explain the high electron-phonon coupling in this mixed valent compounds. We decided therefore to reexamine the open questions of symmetry and structure by a new method: the simultaneous refinement of synchrotron-, X-ray and neutron data. The analysis of the different diffraction data was done with the refinement program SIMREF [9]. Several datasets, collected with various methods at a given temperature, are used in one least squares procedure to fit one structural model to all data. Basis of this development is the Rietveld structure refinement program [10] in the version of Wiles and Young [11].

Experimental

 Appropriately weighed starting ingredients (BaCO$_3$, PbO$_2$, Bi$_2$O$_3$) were thoroughly mixed and fired for 24 h at 800 °C. After cooling, with a cooling rate of 100°/h, the sample was remixed and refired for 25 h at 850 °C. After mixing again the material was pressed in pellets.
and finally annealed at 930 °C for 24 h. All treatments were carried out in a Pt-foil in air at atmospheric pressure. A chemical analysis confirmed the stoichiometry of BaPb_{0.75}Bi_{0.25}O_3. Superconductivity was tested by the onset of diamagnetic repulsion at T_c ~ 10 K with a torsion magnetometer.

The synchrotron X-ray data were collected on a makeshift three-circle powder diffractometer at HASYLAB/DESY at 308 K [12]. We used the diffraction geometry described by Cox et al. [13] with a Ge-(111) double monochromator and a Ge-(111) crystal plate as “angular receiving slit”. As Cox pointed out, this beam path is adapted to the low divergence (0.2 mrad) of the primary beam and yields high resolution together with insensitivity against misalignments of the sample. In our experiment the cross section of the primary beam was 6 * 10 mm^2.

The BaPb_{0.75}Bi_{0.25}O_3 powder sample with grain size between 5 and 50 μm was fixed to a 20 μm Mylar-foil with silicon oil. The foil, clamped between two rings with diameter of ~80 mm, is rotated around an axis normal to its plane with ~30 rpm during the measurements. The sample rotation turned out to be of great importance for the correct intensity measurements. Data measured with oscillations of the sample plane by 2 to 5 degrees gave poorer profiles due to the reduced amount of powder averaging done by the well collimated beam. For the wavelength calibration a Ge powder sample was prepared in the same way. With the BaPb_{0.75}Bi_{0.25}O_3 20 reflection groups were recorded in an angular range from 10 to 120° with a step size Δ2θ ≤ 0.01°. The 2θ range of each group was between 0.4 and 1.5°. The resolution (full width at half maximum on the 2θ scale) was about 0.02° at 2θ ≈ 20° and 0.08° at 2θ ≈ 80°. All measurements at the synchrotron were done at T = 308 K and with a wavelength λ = 1.1267 Å.

High resolution X-ray data were measured at 12 K and 295 K with a low temperature Guinier diffractometer and camera [14] mounted on a rotating anode generator with CuKα radiation at 14° < 2θ < 92° with a step size of 0.02°. Film lift photographs were taken with this apparatus at 12 < T < 300 K and 280 < T < 430 K.

The neutron powder diffraction data were collected with instrument D1A at the ILL in Grenoble. The wavelength was 1.909 Å, and the step size 0.05° in the scan range 6° < 2θ < 140°. The patterns were recorded with the 10 counter multidetector bench of D1A at 2, 50, 120, 200 and 308 K.

**Data analysis and results**

The low temperature neutron data show uniquely a monoclinic distortion of the unit cell: at T = 2 K the monoclinic angle γ is 90.1402 ± 0.0016 degrees.

The analysis of the room temperature neutron data results in γ = 90.0328 ± 0.0006 degrees. The lattice constants vs. temperature are given in Fig. 1. If we choose a pseudo orthorhombic cell with a monoclinic atom distribution these neutron data give the same atom sites and the same R-factor. It is only when neutron and synchrotron data, both taken at room temperature, are simultaneous treated with SIMREF, that a monoclinic cell is enforced. This observation becomes clear from Fig. 1: if a linear extrapolation were allowed, γ would approach 90° deg at ~420 K. In terms of an idealised perovskite unit cell having lattice constants a_0 = b_0 = c_0 the monoclinic cell found here has a ≈ √2 a_0, b ≈ √2 b_0, c ≈ 2 c_0, γ ≈ γ (a_0 + b_0, a_0 − b_0). In all cases the monoclinic lattice symmetry is extracted from the diffraction pattern as a whole: even with the high resolution of the synchrotron diffractometer shown in Fig. 2 a true monoclinic splitting of single reflections could not be seen. Figure 3 shows parts of the result of a simultaneous refinement of 10 neutron datasets, one from each counter, and some reflection groups measured with synchrotron radiation and with the Guinier diffractometer.