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Electrochemical Synthesis of the Perovskite $\text{Ba}_{1-x}\text{Cs}_x\text{BiO}_3$ from Molten Salts

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Abstract. Single crystals of the perovskite $\text{Ba}_{1-x}\text{Cs}_x\text{BiO}_3$ with $x = 0.22$ have been successfully synthesized by the electrochemical method from molten salts. The electrodeposition of $\text{Ba}_{1-x}\text{Cs}_x\text{BiO}_3$ from $\text{CsOH} \cdot \text{H}_2\text{O}$ flux containing $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ and Bi_2O_3 was performed in a Teflon crucible under a water-saturated argon atmosphere at 270 °C. Single crystals of high quality were grown up to $1 \times 1 \times 1 \text{ mm}^3$ in size. The crystal symmetry was cubic at room temperature. However, no superconductivity was observed above 2 K in the magnetic susceptibility measurements.

Keywords: $\text{Ba}_{1-x}\text{Cs}_x\text{BiO}_3$, electrochemical method, molten salts, single crystal

PACS: 74.62.Bf, 74.75.Dd, 82.45.Aa

In the perovskite BaBiO_3 with the monoclinic symmetry, the BiO_6 octahedron is on the tilt because of the size mismatch between the shorter Ba-O bond length and the longer Bi-O bond length. According to the simple electron-band theory, BaBiO_3 has a half-filled band of 6s electrons of Bi^{4+} , leading to a metallic behavior. However, the valence state of Bi^{4+} with $6s^1$ is unstable, so that Bi^{4+} disproportionates into Bi^{3+} with $6s^2$ and Bi^{5+} with $6s^0$, leading to a CDW insulator [1].

The tilt of the BiO_6 octahedron is alleviated by the hole doping through the partial substitution of K for Ba in BaBiO_3 . The crystal structure of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ changes from monoclinic to cubic via orthorhombic with increasing x . There is no tilt of the BiO_6 octahedron in the cubic phase. The metal-insulator transition coincides with the structural phase transition from orthorhombic to cubic. The cubic $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ shows superconductivity with the superconducting transition temperature $T_c = 30 \text{ K}$ [2], which is the highest T_c among oxides free of copper.

So far, some carrier-doped compounds based on BaBiO_3 have been reported: for example, hole-doped superconductors, $\text{Ba}_{1-x}\text{A}_x\text{BiO}_3$ ($A = \text{K}, \text{Rb}$) [3], and electron-doped insulators, $\text{Ba}_{1-x}\text{Bi}_x\text{BiO}_3$ [4]. The purpose of this research is to synthesize a new hole-doped compound of $\text{Ba}_{1-x}\text{Cs}_x\text{BiO}_3$ through the partial substitution of Cs^+ for Ba^{2+} in BaBiO_3 . The substitution of Cs is more effective in alleviating the tilt of the BiO_6 octahedron than that of K, because the ionic radius of Cs^+ is much larger than that of K^+ . Therefore, a higher T_c than 30 K is expected in the cubic $\text{Ba}_{1-x}\text{Cs}_x\text{BiO}_3$ with a small x value because of the large density of states at the Fermi energy.

Single crystals of $\text{Ba}_{1-x}\text{Cs}_x\text{BiO}_3$ were synthesized

by the electrochemical method from molten salts. All electrodepositions were performed under water-saturated flowing argon gas using a three-electrodes cell. Pt wires with the diameter of 0.5 mm were used as the working electrode and the counter electrode. A rod of Bi (5N) was used as the reference electrode. $\text{CsOH} \cdot \text{H}_2\text{O}$ (3N) was placed in a Teflon crucible and melted at 270 °C. The CsOH solution was stirred for about 2 h. $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (2N) and Bi_2O_3 (3N) were then slowly added to the solution. The molar ratio of the melt was Cs : Ba : Bi = 17.5 : 0.33 : 1. After 24 h, cyclic voltammograms of the quiescent solution were run to determine the electrocrystallization potential. Upon application of the chosen potential, the electrocrystallization process was instantly initiated. Crystals were grown for 48 h. Grown crystals were taken out of the solution, washed with the distilled water and then dried.

The crystal structure and composition of the products were determined by the powder x-ray diffraction using $\text{Cu K}\alpha$ radiation and the inductively coupled plasma atomic emission spectrometry (ICP-AES), respectively. Magnetic susceptibility measurements were performed using a SQUID magnetometer (Quantum Design, Inc).

The cyclic voltammogram obtained in the $\text{Ba}(\text{OH})_2\text{-Bi}_2\text{O}_3\text{-CsOH}$ solution is shown in Fig. 1. The initial potential of the voltammetric scan (400 mV vs. Bi) was set at a value where no apparent electrochemical processes occur; the potential range was swept first anodically up to 900 mV vs. Bi, cathodically to -400 mV vs. Bi and then anodically up to the initial potential. Around the peak at 560 mV vs. Bi, the oxidation from Bi^{3+} to Bi^{4+} is expected to occur. Taking the low diffusion velocity of the ions in the solution into consideration, the applied potential for the electrocrystallization of $\text{Ba}_{1-x}\text{Cs}_x\text{BiO}_3$

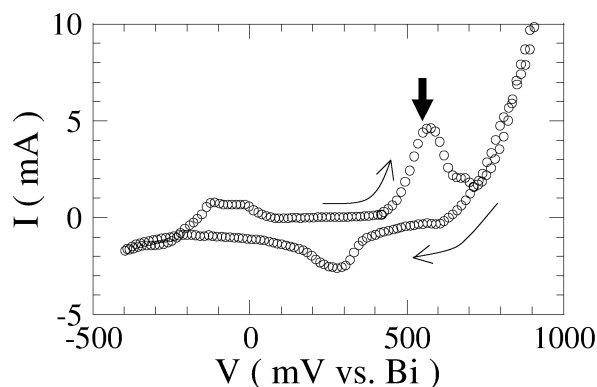


FIGURE 1. Cyclic Voltammogram from -400 mV vs. Bi to 900 mV vs. Bi in the $\text{Ba}(\text{OH})_2\text{-Bi}_2\text{O}_3\text{-CsOH}$ solution. The sweep rate is 5 mV/sec. The big downward arrow exhibits the potential in which the electrodeposition was performed.

was determined to be 550 mV vs. Bi which was somewhat lower than the peak potential. Single crystals of $\text{Ba}_{1-x}\text{Cs}_x\text{BiO}_3$ were successfully electrodeposited on the Pt wire. As-grown crystals are shown in Fig. 2. The typical dimensions of a single crystal were $1 \times 1 \times 1$ mm³.

The powder x-ray diffraction pattern of the grown crystal at room temperature is shown in Fig. 3. All the peaks can be indexed on the basis of the simple cubic Pm $\bar{3}$ m lattice, which is the same structure as the superconducting $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ ($x \geq 0.37$). The Cs content x of the grown crystal is determined to be $x = 0.22$ by ICP-AES. This x value in the grown crystal of $\text{Ba}_{1-x}\text{Cs}_x\text{BiO}_3$ with the cubic symmetry is much smaller than the minimum K content ($x = 0.37$) required for the dissolution of the tilt of the BiO_6 octahedron in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ [2]. The lattice parameter is determined to be $a = 4.341$ Å, which is much larger than $a = 4.283$ Å in the superconducting $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ [2]. However, the cubic $\text{Ba}_{0.78}\text{Cs}_{0.22}\text{BiO}_3$ showed no superconductivity above 2 K in the magnetic susceptibility measurements as opposed to the superconducting $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ with the cubic symmetry.

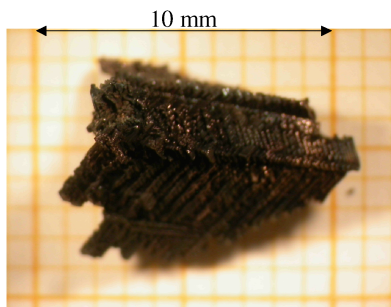


FIGURE 2. As-grown crystal of $\text{Ba}_{1-x}\text{Cs}_x\text{BiO}_3$ by the electrochemical method.

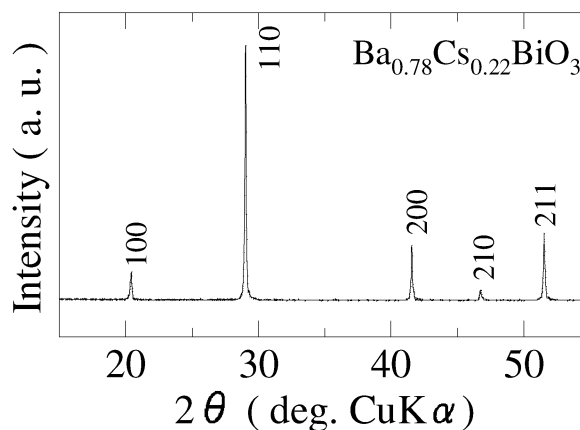


FIGURE 3. Powder x-ray diffraction pattern of the grown crystal $\text{Ba}_{0.78}\text{Cs}_{0.22}\text{BiO}_3$ at room temperature. The diffraction peaks are indexed on the basis of the cubic symmetry.

The possibility that the tilt of the BiO_6 octahedron exists at low temperatures is considered as a reason of non-superconductivity in the grown crystal, as follows. That is, in general, the thermal expansivity of the ionic bond tend to be larger than that of the covalent bond. Accordingly, the size mismatch in the present system would increase at low temperatures because the ionic Ba-O bond is expected to shrink more than the covalent Bi-O bond, leading to the tilt of the BiO_6 octahedron at low temperatures.

In summary, single crystals of the perovskite $\text{Ba}_{0.78}\text{Cs}_{0.22}\text{BiO}_3$ with $1 \times 1 \times 1$ mm³ in size have been successfully synthesized by the electrochemical method from molten salts. The electrodeposition of $\text{Ba}_{1-x}\text{Cs}_x\text{BiO}_3$ from $\text{CsOH} \cdot \text{H}_2\text{O}$ flux containing $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ and Bi_2O_3 was performed in a Teflon crucible under a water-saturated argon atmosphere at 270 °C. The lattice parameter was 4.341 Å with the cubic symmetry at room temperature. However, no superconductivity was observed above 2 K.

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