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SUPERCONDUCTING (Rb,Ba)BiO₃ THIN FILMS GROWN BY MOLECULAR BEAM EPITAXY

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The simple cubic perovskite (Rb,Ba)BiO₃ can be grown by molecular beam epitaxy using an RF plasma oxygen source. Films with superconducting onsets in resistivity as high as 27K are obtained without annealing. The epitaxy proceeds in the normal (1 0 0) orientation on (1 0 0) SrTiO₃, despite a 10% lattice mis-match. (1 1 0) epitaxy is obtained on (1 0 0) MgO substrates, despite the good lattice match for (1 0 0) growth. The films with the lowest normal state resistivity are those grown on SrTiO₃ at 300±10°C and are Bi deficient despite excess Bi flux during growth. The temperature dependence of the resistivity for these films is metallic down to T_c. H_{c2} for a T_c=20K film is 10±1T.

The discovery of superconductivity at 30K in the simple cubic perovskites (K,Ba)BiO₃ and (Rb,Ba)BiO₃¹ has shown that high temperature superconductivity can occur in materials other than layered cuprates. In addition to fundamental interest in the mechanisms of superconductivity in these materials, they are of interest because their comparatively simple structure may facilitate the modification and control of their properties in thin films. The low growth temperatures typical of thin film epitaxy may be particularly useful for doping of BaBiO₃ materials with alkali metals, which volatilize at low temperatures. Recently, Sato et. al. have reported on films of (K,Ba)BiO₃ made by sputtering, followed by an anneal.² This paper reports the successful *in-situ* growth of epitaxial (Rb,Ba)BiO₃ thin films on MgO and SrTiO₃ substrates by molecular beam epitaxy (MBE). The best films exhibit transport properties superior to material synthesized by bulk techniques, despite significant non-stoichiometry.

Films were grown in a Riber MBE system with an RF plasma atomic oxygen source which has been described previously.³ Barium, bismuth and Rb₂O were evaporated from standard effusion cells. Films are grown with at least 30% excess flux of bismuth. Reflection high-energy electron diffraction (RHEED) patterns are monitored to determine the surface structure of the growing film. Growth rates are about 20Å/min and total film thicknesses are 1000-4500Å.

RHEED patterns obtained from (Rb,Ba)BiO₃ grown on SrTiO₃ (1 0 0) substrates typically show

patterns of spots and streaks consistent with an a=4.3Å cubic perovskite. The in-plane orientation has the same orientation as the substrate. This orientation and lattice constant are established within the first 5 monolayers of deposition; the substrate streaks vanish by the second monolayer. X-ray diffraction studies confirm the oriented texture of the films. For epitaxy on MgO (1 0 0) substrates, RHEED patterns indicate a mixture of two orientations with film(1 1 0) ||MgO(0 0 1) (the in-plane orientations are film

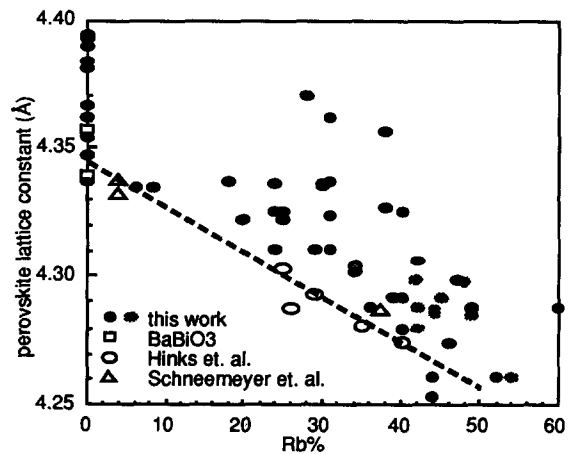


FIGURE 1
The perovskite lattice constant measured by x-ray diffraction plotted as a function of the Rb/(Rb+Ba) percentage measured by RBS. Grey dots denote verified superconducting films. Compositional inhomogeneity may cause some of the observed scatter.

($u\ u\ 1$)||MgO(1 0 0) and film(0 0 1)||MgO(0 1 0)). Since MgO is an excellent lattice match to (Rb,Ba)-BiO₃ in the normal (1 0 0)|| (1 0 0) orientation it is odd that the perovskite grows the way it does.

The perovskite lattice constant from the films is plotted as a function of the Rb/(Rb+Ba) percentage in Fig. 1. Lattice constants for BaBiO₃ and (K,Ba)BiO₃ from the literature⁴ are shown for comparison. While Rb (compared to K) doping and oxygen deficiency are expected to result in slightly larger lattice constants, many of the films have lattice constants which are still larger than would be expected. The (Ba+Rb): Bi ratios for these films suggest that non-stoichiometry may be accommodated in the perovskite structure, causing much of the lattice expansion. Ba-Bi-O films in this composition range did have enlarged lattice constants. These may correspond to the perovskite-like solid-solutions reported by Scholder et. al.⁵.

All of the films which exhibited superconductivity had (Ba+Rb)/Bi ratios between 1 and 1.7. Resistivity vs. temperature for one of the best *in-situ* films is shown in Fig. 2. Note that the slope of the resistivity curve for this sample is positive over the full temperature range. Previously reported transport measurements of (K,Ba)BiO₃ have all shown semiconductor-like resistivity slopes in at least some temperature ranges. No transport measurements have been reported for (Rb,Ba)BiO₃. Fig. 3 shows resistance (plotted on a logarithmic scale) vs. temperature for different magnetic fields (0,1,3 and 7.5T). The resistance drops exponentially below T_C with no hint of the "foot" often present when there is poor coupling between grains. This is remarkable considering that the

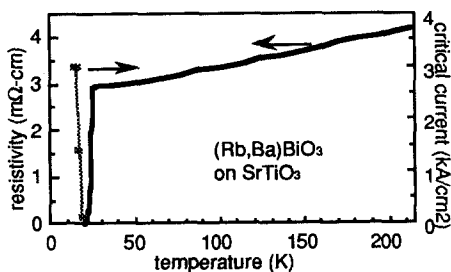


FIGURE 2

Resistivity measured by the van der Pauw technique and critical currents vs. temperature for an *in-situ* film.

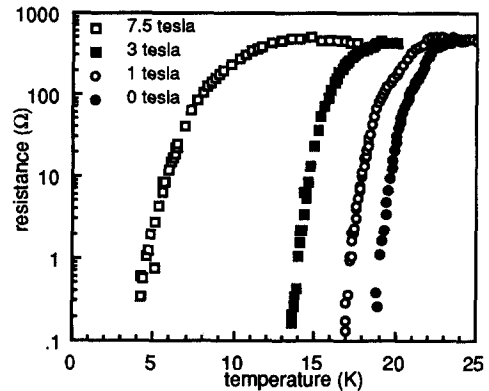


FIGURE 3

Resistance (on a log scale) vs. temperature for a 1200Å *in-situ* film grown on SrTiO₃ for magnetic fields parallel to the sample.

composition of this sample, measured by HBS, is (Rb_{0.45}Ba_{0.55})Bi_{0.58}O_x. Evidently, the Bi deficient impurity phases do not disrupt the superconductivity. The transition does not broaden much in magnetic field, suggesting that flux flow is of minor importance. The extrapolated H_{C2} for this sample, 10T, is similar to that measured by Welp et. al.⁶

In summary, (Rb,Ba)BiO₃ epitaxial films with good transport properties can be grown *in-situ* by MBE.

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