Potassium tantalate substrates for neutron experiments on antiferromagnetic perovskite films

H M Christen,1,* G J MacDougall,2 H-S Kim,1 D H Kim,1,3 L A Boatner,1 C J Callender Bennett,1 J L Zarestky,2 and S E Nagler2

1 Oak Ridge National Laboratory, Materials Science and Technology Division, PO Box 2008, Oak Ridge, TN 37831, USA
2 Oak Ridge National Laboratory, Neutron Scattering Science Division, PO Box 2008, Oak Ridge, TN 37831, USA
3 Tulane University, Department of Physics and Engineering Physics, New Orleans, LA 70118, USA

E-mail: christenhm@ornl.gov

Abstract. For the study of antiferromagnetism in thin-film materials, neutron diffraction is a particularly important tool, especially since magnetometry experiments are often complicated by the substrate’s strong diamagnetic or paramagnetic contribution. However, the substrate, by necessity, has a lattice parameter that is very similar to that of the film, and in most cases is over 1000 times more massive than the film. Therefore, even weak structural distortions in the substrate crystal may complicate the analysis of magnetic scattering from the film. Here we show that in contrast to most other perovskite substrates (including SrTiO$_3$, LaAlO$_3$, etc.), KTaO$_3$ provides a uniquely appropriate substrate platform for magnetic diffraction experiments on epitaxial oxide films.

1. Introduction
Epitaxial perovskite films have been studied extensively due to their interesting ferroelectric (FE), magnetic, and multiferroic properties [1]. Due to the possibility of forming precisely controlled interfaces and heterostructures [2,3], the coupling between dissimilar materials at well-defined length scales can be studied, with the goal of developing new materials whose properties are determined by effects occurring at the interfaces.

One of the mechanisms leading to a coupling of adjacent layers in a multi-layer structure is the exchange interaction between an antiferromagnetic (AFM) and a ferromagnetic (FM) material. Understanding and enhancing this coupling may provide a means to create composite materials with a strong magneto-electric effect at room temperature: combining a room-temperature multiferroic (AFM+FE) with a FM layer could yield macroscopic properties that, to date, have not been found in a single-phase material [4].

In order to understand and maximize the coupling between AFM and FM layers, the spin order in the AFM material needs to be known. While significant progress has been made in using x-ray dichroism techniques to probe magnetism in thin films [5], neutron diffraction remains the method-of-
choice for a quantitative analysis of the entire volume of a film, and several studies have shown the power of neutron methods for understanding AFM in epitaxial perovskite layers [6].

Epitaxial growth of high-quality films typically requires a substrate material with a similar lattice parameter to that of the film, and thus, the film’s nuclear scattering positions are necessarily close to those of the substrate. However, when indexed in the perovskite’s pseudocubic notation, AFM magnetic diffraction occurs at half-integer positions [i.e. (½ ½ ½) for G-type and (0 0 ½) for the layered A-type], at which no nuclear diffraction from the substrate should occur if the substrate is cubic. However, as we show here, this is not the case for most of the commercially available perovskite substrates, and structural distortions yield nuclear diffraction from the substrate at positions that overlap with the AFM diffraction from the film. Considering that the typical substrate (0.5mm to 1mm thick) is 1000 times more massive than the actual material of interest (i.e. the film, with a thickness that is typically below 1 μm), this significantly complicates the data analysis. However, we find that KTaO₃ substrates remain cubic at all temperatures and, thus, are an ideal platform for such experiments.

2. Neutron diffraction of epitaxial BiCrO₃ films on LaAlO₃ and SrTiO₃

BiCrO₃ films are used here as a test system, since this AFM material [7] is readily grown by pulsed-laser deposition on various perovskite substrates [8], having a distorted perovskite structure that can be approximated as pseudo-cubic with \( a = b = c \approx 3.90 \) Å [7]. Layers with thicknesses of 1.5 – 2 μm were deposited as described in our previous work [8], and the substrates were obtained commercially. Buffer layers [SrRuO₃ on SrTiO₃, (La,Ca)MnO₃ on LaAlO₃] with thicknesses of 4 – 8 nm were used since they led to better crystallinity of the BiCrO₃. These buffer layers are too thin to be observed in these neutron experiments and thus do not contribute to the observed scattering. Elastic neutron scattering measurements were performed at Oak Ridge National Laboratory’s High Flux Isotope Reactor (HFIR) on beamline HB1A, using PG(002) monochromator and analyzer, collimations 48-48-40-136, and a fixed incident neutron energy of 14.64 meV.

![Figure 1](image)

**Figure 1.** BiCrO₃ film on LaAlO₃ substrate. a) Radial scan through the film and substrate’s (0 0 2) diffraction peak at 200K. b) Radial scan at the (½ ½ ½) position at 20K, showing the LaAlO₃ substrate’s large contribution due to its non-cubic nature.

Figure 1a shows a radial scan through the film and the substrate (0 0 2) peaks. Note that pseudocubic notation is used throughout this manuscript with indices referenced according to the substrate lattice parameters). The weak film peak (\( h \approx 1.95, c \approx 3.90 \) Å) is clearly separated from the strong substrate reflection at \( h = 2 \). Figure 1b depicts a scan at the (½ ½ ½) position at 20 K (i.e. well below the Néel temperature of BiCrO₃, \( T_N \approx 110K \)). A strong substrate contribution, largely masking the diffraction from the thin film, is clearly observed as a consequence of this material’s non-cubic structure (\( R \overline{3}m \) [9], which can be approximated as pseudocubic below room temperature, where \( a = b = c = 3.788 \) Å and \( \alpha \approx 89.93^\circ \)).
The lattice mismatch between the film and the substrate helps to distinguish between the different contributions, however, the weakness of the magnetic scattering combined with the large mass of the substrate make this distinction difficult. This therefore complicates the extraction of quantitative data.

In the case of the better-matched (more appropriately chosen) SrTiO₃ substrate (Fig. 2), the lattice parameter difference between the film and the substrate (a = 3.905 Å at room temperature) is too small for a distinction to be made between the different components (Fig. 2a). More importantly, SrTiO₃ undergoes a structural phase transition at T ≈ 105 K [10], which nearly coincides with the T_N of BiCrO₃. Below 105 K, SrTiO₃ is tetragonal and shows nuclear scattering at peak positions that overlap those of the magnetic scattering from BiCrO₃. As has been pointed out, some of this scattering persists at temperatures well above 105 K [11].

A number of other substrates are commercially available for the epitaxial growth of perovskite materials, including the orthorhombic perovskites NdGaO₃, DyScO₃, GdScO₃, the K₂NiF₄-structure materials SrLaGaO₄ and SrLaAlO₄, and the tetragonal alloy LSAT [(LaAlO₃)₀.₃(Sr₂AlTaO₆)₀.₇]. Similar experiments as those described above were also performed on LSAT substrates (data not shown), for which strong scattering was observed at those half-integer positions that lie close to the film’s peaks for G-type AFM. Clearly, for the present studies, a material that is cubic across the entire temperature range is required.

Figure 2. BiCrO₃ film on SrTiO₃ substrate. a) Radial scan at the (½ ½ ½) position at 150 K (above the SrTiO₃ structural phase transition and the BiCrO₃ Néel temperature) and at 20 K, where the film’s (magnetic) and the substrate’s (nuclear) contributions cannot be separated due to the small difference in lattice parameters. b) Temperature-dependence of the intensities of the (½ ½ ½), (½ ½ ½), (½ ½ ½) and (½ ½ ½) peaks, dominated by the SrTiO₃ structural phase transition at 105 K.

3. BiCrO₃ films on KTaO₃

KTaO₃ retains the prototype cubic perovskite symmetry down to the lowest temperatures investigated [10] and, therefore, promises to be an ideal substrate material for this work. Its room-temperature lattice parameter is 3.989 Å. KTaO₃ crystals were grown by spontaneous nucleation [12] and polished with a KOH-buffered solution of colloidal silica. BiCrO₃ films were grown as described above using a SrRuO₃ buffer layer.

Figure 3a shows a radial scan through the film and substrate (1 1 1) peak, allowing us to identify the positions where the corresponding half-integer peaks (resulting from structural distortions or magnetic scattering) are expected. As is seen in Fig. 3b, no intensity is detected at the substrate’s (½ ½ ½) position. This result clearly allows us to determine quantitatively the scattering from the film. It is important to note that such quantitative experiments are, therefore, not only possible for films with lattice parameters that are well separated from those of the KTaO₃ substrate, but also for well-matched layers, due to the complete absence of substrate peaks at half-integer positions (experiments were also performed for (½ ½ ½), (½ ½ ½), (½ ½ ½), and (½ ½ ½), data not shown).
Figure 3. BiCrO$_3$ film on KTaO$_3$ substrate at 20 K. a) Radial scan at the (1 1 1) position showing the substrate at $h = 1$ and the film at $h \approx 1.03$. b) Radial scan at the ($\frac{1}{2} \frac{1}{2} \frac{1}{2}$) position. Corresponding to the data in (a), the film’s ($\frac{1}{2} \frac{1}{2} \frac{1}{2}$) peak is observed at $h \approx 0.515$, while no intensity is seen at $h = 0.5$ (i.e., no substrate contribution).

4. Conclusions
Due to its perfect cubic symmetry at all investigated temperatures, KTaO$_3$ is an ideal substrate for the study of antiferromagnetism in epitaxial perovskite films. Our work demonstrates that quantitative analysis of the magnetic diffraction is possible for epitaxial layers, which will lead to a better understanding of the properties of thin-film materials that are being studied both for their fundamental properties as well as for a broad range of potential applications in oxide electronics and for sensors.

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