

COMMENTS

Comment on “Lattice deformation and magnetic properties in epitaxial thin films of $\text{Sr}_{1-x}\text{Ba}_x\text{RuO}_3$ ” [Appl. Phys. Lett. 73, 1200 (1998)]

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Recently, Fukushima *et al.*¹ reported the epitaxial growth of (001) BaRuO_3 films with the perovskite structure on (001) SrTiO_3 substrates. Based on BaRuO_3 films we have grown by both 90° off-axis sputtering and pulsed laser deposition,² however, we believe that the x-ray patterns that they attributed to the growth of the metastable perovskite³ polymorph of BaRuO_3 are actually due to the stable nine layer (9L) hexagonal polymorph of BaRuO_3 ,⁴ with a $(20\bar{2}5)$ orientation. As has been shown for other materials systems,⁵ these polymorphs have nearly degenerate peaks in 2θ , χ , and ϕ

with each other and would give rise to x-ray patterns consistent in both peak positions and peak intensities with those shown by Fukushima *et al.*¹

In studying the epitaxial growth of BaRuO_3 films on (001) SrTiO_3 , we observed very similar θ - 2θ x-ray diffraction (XRD) patterns to those reported by Fukushima *et al.*¹ An example is shown in Fig. 1(a). This θ - 2θ plot alone is inconclusive for phase determination, since the 002 peak of the perovskite polymorph occurs at a nearly identical 2θ value as the $20\bar{2}5$ reflection of the 9L polymorph (see Table I). The small discrepancy between the observed and calculated position of the $20\bar{2}5$ reflection is most likely due to strain and film inhomogeneity.⁷ Additionally, the ϕ scan reported by Fukushima *et al.*¹ is insufficient to discriminate the 101 reflection of the perovskite polymorph from the $11\bar{2}0$ reflection of the 9L polymorph (see Table I). Using four-circle x-ray diffraction and performing a ϕ scan [Fig. 1(b)] at $2\theta \approx 27.2^\circ$ and $\chi \approx 43.0^\circ$ ($01\bar{1}5$ reflection of 9L BaRuO_3) we have found the phase in our films to be consistent with the 9L BaRuO_3 polymorph, and inconsistent with the growth of the metastable perovskite polymorph.⁷ This and other ϕ scans, i.e., a scan of the $11\bar{2}0$ reflection of the 9L polymorph, lead us to believe that each of the “very

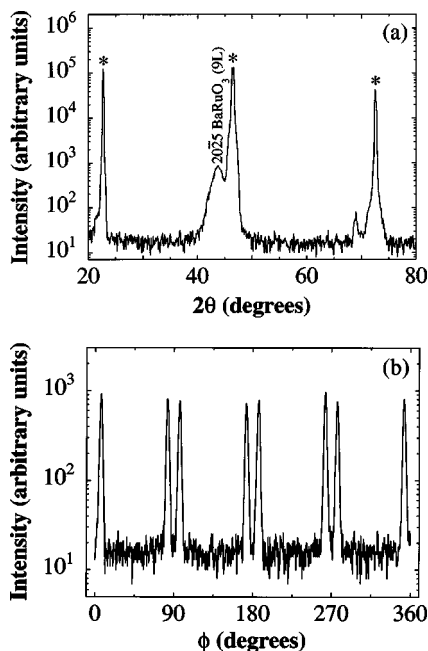


FIG. 1. X-ray diffraction patterns of a film grown under similar conditions as Fukushima *et al.* that is not BaRuO_3 with the perovskite structure, but rather the 9L polymorph of BaRuO_3 (see Ref. 7): (a) θ - 2θ at $\chi = 90^\circ$ [substrate peaks are labeled as (*)] and (b) ϕ scan of the $01\bar{1}5$ reflection of the 9L polymorph of BaRuO_3 at $2\theta \approx 27.2^\circ$ and $\chi \approx 43.0^\circ$.

TABLE I. Calculated XRD peak positions of the perovskite and the 9L hexagonal polymorph of BaRuO_3 .^a

Phase	Peaks	2θ (deg)	χ^b (deg)	ϕ (deg)
BaRuO_3 (001)-oriented perovskite	002	45.17	90	—
	101	31.51	45	0
	202	65.79	45	0
BaRuO_3 ($20\bar{2}5$)-oriented (nine layer hexagonal)	$20\bar{2}5$	41.83	90	—
	$11\bar{2}0$	31.07	48.62	$\pm 1.4^\circ$
	$22\bar{4}0$	64.79	48.62	$\pm 1.4^\circ$
	$01\bar{1}5$	27.29	41.38	$\pm 6.9^\circ$

^aThe values are based on $\text{Cu } K\alpha_1$ radiation, bulk lattice constants (see Refs. 3 and 4), and $\phi = 0^\circ$ chosen to be parallel to the in-plane $[100]$ direction of the (001) SrTiO_3 substrate.

^b $\chi = 90^\circ$ is perpendicular to the plane of the substrate.

^cAssuming degenerate epitaxy (see Ref. 6).

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broad peaks of the XRD'' patterns reported by Fukushima *et al.*¹ in their ϕ scan of the ''BaRuO₃(101)^{tetragonal} peak'' may be explained as broad and overlapping 11 $\bar{2}$ 0 peaks of the 9*L* polymorph (see Table I). Our results are in full agreement with previous unsuccessful attempts to grow metastable BaRuO₃ by epitaxial stabilization on (100) KTaO₃.⁸

It should be noted that the results presented by Fukushima *et al.*¹ are *not* inconsistent with the perovskite polymorph of BaRuO₃, yet they are ambiguous given the demonstrated near overlap of all the peaks reported by them with peaks of the 9*L* (and 4*L*) polymorph. Despite our attempts to replicate their work, we cannot synthesize the metastable perovskite polymorph of BaRuO₃ and we would suggest additional, definitive scans for unambiguous corroboration of their interpretation of their results.

¹N. Fukushima, K. Sano, T. Schimiza, K. Abe, and S. Komatsu, Appl. Phys. Lett. **73**, 1200 (1998).

²M. K. Lee, I. W. Scrymgeour, J. Lettieri, D. G. Schlom, and C. B. Eom (unpublished).

³J. M. Longo and A. J. Kafalas, Mater. Res. Bull. **3**, 687 (1968). The lattice

constants of the metastable perovskite polymorph of BaRuO₃ (pseudocubic with $a \approx 4.01$ Å) have been estimated by extrapolating the lattice constants reported in this work for Ba_xSr_{1-x}RuO₃ to $x = 1$.

⁴*Powder Diffraction File* (International Centre for Diffraction Data, Swarthmore, PA, 1995), JCPDS card 45-529. This reference states that the 9*L* polymorph of BaRuO₃ has lattice constants $a = 5.749$ Å and $c = 21.608$ Å.

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⁶S.-W. Chan, J. Phys. Chem. Solids **55**, 1137 (1994).

⁷Our films showed evidence of a mixture of both the four layer (4*L*) and 9*L* hexagonal polymorphs. Discrimination of the 4*L* polymorph from the perovskite phase is equally as difficult since the 20 $\bar{2}$ 3, 11 $\bar{2}$ 0, and 22 $\bar{4}$ 0 reflections of the 4*L* structure also exhibit a near overlap of peak position and intensity with the perovskite polymorph (and with the 20 $\bar{2}$ 5, 11 $\bar{2}$ 0, and 22 $\bar{4}$ 0 reflections of the 9*L* polymorph). A ϕ scan of the 01 $\bar{1}$ 5 reflection of the 9*L* polymorph or the 01 $\bar{1}$ 2 reflection of the 4*L* polymorph is sufficient to distinguish between these two phases. Nevertheless, in none of our films grown under a wide range of growth conditions by both sputtering and pulsed laser deposition was the perovskite polymorph evident.

⁸H.-M. Christen, L. A. Boatner, J. D. Budai, M. F. Chisholm, L. A. Gea, D. P. Norton, C. Gerber, and M. Urbanik, Appl. Phys. Lett. **70**, 2147 (1997).