Boosting optical nonreciprocity: surface reconstruction in iron garnets: supplement

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We report significant differences in the ionic structure between surface and bulk in bismuth-substituted iron garnet materials. The study was motivated by recent evidence of large near-surface enhancement in the magneto-optic response in these materials. It is found that the unit cell is elongated normal to the surface, making the separation between Fe$^{3+}$ ions active in the optical response larger. A marked displacement of Fe ions creates gaps at the surface that are populated in the bulk. Concomitantly, surface- and bulk-sensitive measurements of spin-polarized 3d Fe$^{3+}$ states show significant differences in the magnitude of L2 edge x-ray magnetic circular dichroism, as well as differences in L3 edge dichroism which in the presence of spin-orbit coupling in 3d states can be assigned to high-energy states. An increase in magnetic circular dichroism correlates with larger Faraday rotation. Bi-substituted iron garnet films are extensively used in the fabrication of nonreciprocal devices such as optical isolators and circulators. A deeper understanding of the role of the surface in the electronic transitions to excited Fe$^{3+}$ 3d states, responsible for these nonreciprocal phenomena, is technologically important to advance the on-chip integration of nonreciprocal devices in optical circuits. © 2014 Optical Society of America

Figure S1 shows the HAADF S-TEM image from the bulk of the film, oriented along the [001] zone axis. The inset shows the fast Fourier transform (FFT) of the image. We have indexed the FFT with space group $Ia3d$, and a lattice parameter 1.25 nm. The crystallographic parameters of rare-earth substituted garnets can be found in [1].

We have performed an energy dispersive spectroscopic mapping at the atomic scale to quantify further the atomic arrangements at the bulk and surface. Figure S2 shows the HAADF image, Fe, and Lu elemental maps from the bulk and the surface of the sample. The compositions from the bulk and surface regions are presented in Table I, below. There is approximately a 6-at.-percent decrease in Fe content at the surface compared to bulk and similar amount of increase in O content. All other elements show no significant variation.

Figure S3 shows the lines-cans drawn along the red, blue and green lines of the EDS maps. The top and bottom rows show the HAADF, Fe (magenta), and Lu (orange) scans from the bulk and surface respectively. We have presented here the net intensity X-ray counts that is independent of sample thickness as a function of distance. The net intensity maps help comparing compositions at two different parts of the sample with varying thickness. As evident from the scans here, the regular arrangement of Fe and Lu in the bulk has changed at the surface. There is considerable amount of overlap between Fe and Lu positions, indicating movement of these elements from their original sites at the surface. This
is also corroborated by comparing the change in intensities of Fe and Fe-Lu sites at the bulk and the surface. Figure S4 shows a detailed cross-sectional image of the surface area.

Fig. S1. HAADF image of the Fe Garnet thin film and its corresponding FFT. The FFT is indexed with Ia3d space group and a lattice parameter of 1.25 nm.

Fig. S2. The EDS elemental maps of Fe and Lu from the bulk and the surface of the sample.
Fig. S3. EDS line scans along the red, blue and green lines of the HAADF image. The magenta and orange colors indicate the Fe and Lu net intensity maps. The black lines show the corresponding HAADF line scans with arbitrary intensity. The top (c-e) and bottom (f-h) rows show the line scans from the bulk and the surface of the sample.

Figure S4 shows a cross-sectional image of the near-surface region, with a larger field of view. A tabulation of elongated and contracted inter-ionic distances at the surface for Fe$^{3+}$ over 12 unit-cells is presented in Table II. This table is based on Fig. S4, and the data encompasses the first 2-3 nm from the surface. The standard deviation for both elongation and contraction measurements is found to be 0.007 nm, whereas the mean difference between elongated and contracted interionic distances (0.027 nm) is close to four standard deviations.

Fig. S4. Cross-sectional image showing detail of the surface region.
### TABLE I

| Element | Atomic Fraction (%) | Atomic Error (%) |
|---------|---------------------|------------------|
|         | Bulk | Surface | Bulk | Surface |
| O       | 58.0 | 64.4    | 5.0  | 5.2     |
| Fe      | 25.0 | 19.4    | 4.0  | 3.0     |
| Ga      | 3.7  | 4.0     | 0.6  | 0.6     |
| Gd      | 0.3  | 0.2     | 0.0  | 0.0     |
| Lu      | 9.7  | 9.6     | 1.4  | 1.3     |
| Bi      | 3.3  | 2.4     | 0.5  | 0.3     |

### TABLE II

| Contracted distance (nm) | Elongated distance (nm) |
|--------------------------|-------------------------|
| 0.283                    | 0.324                   |
| 0.292                    | 0.316                   |
| 0.300                    | 0.324                   |
| 0.292                    | 0.316                   |
| 0.300                    | 0.316                   |
| 0.300                    | 0.332                   |
| 0.283                    | 0.332                   |
| 0.283                    | 0.316                   |
| 0.300                    | 0.316                   |
| 0.300                    | 0.316                   |
| 0.292                    | 0.316                   |
| 0.300                    | 0.332                   |

Mean: 0.294  Mean: 0.321
Std. Deviation 0.007  Std. Deviation 0.007

Measurements showing the elongated and contracted inter-atomic distances at the surface of the Bi-substituted Fe Garnet films.

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