

## Electronic Structure Characterization of the Bi-YIG by EELS-STEM

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The present study monitored the electronic structure (multiplet structure) of a ceramic material with garnet structure  $\text{BiY}_2\text{Fe}_5\text{O}_{12}$  (Bi-YIG) that has important magneto-optical properties [1,2]. There are few studies regarding the electronic structure characterization obtained by electron energy loss spectroscopy (EELS). The motivation of this work is to present the EELS of Bi-YIG and its interpretation of the local electronic structure through the Fe  $L_{2,3}$  -edge. This interpretation is based on the multiplet calculation using the modified Hartree-Fock method that includes the crystal field and charge transfer effects [3].

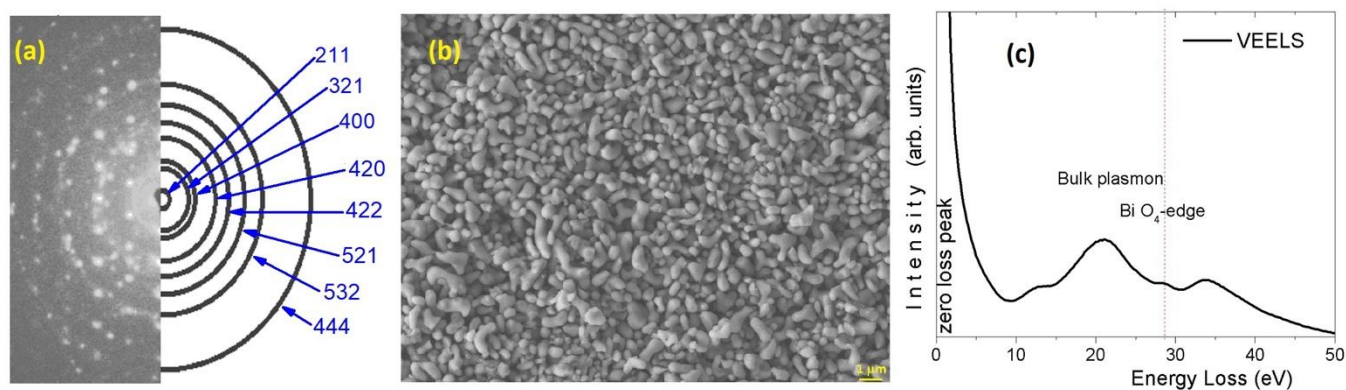
The Bi-YIG was prepared by the sol-gel method via combustion and heat treated at 1000 °C [4]. The powders were dispersed in isopropanol and deposited on the lacey carbon films on a 300mesh copper TEM grid. A JEM-2200FS microscope operated at 200 kV was used for a microstructural and structural study. The last one was determined by the selected area of electron diffraction (SAED) characterization using the ICSD No. 2012; for the average grain size and shape was obtained with the analysis on five field emission scanning electron (FE-SEM model JSM-7401F) micrographs through the ImageJ software [5]. The EELS spectra were collected in a Phillips CM200 microscope that has a PEEL766 system worked at 200 kV. Figure 1(a) shows SAED pattern with its indexing using the Process diffraction software [6]. The results are associated with a garnet-type structure with cubic phase and spatial group Ia-3d (No. 230). The SEM characterization reveals non-uniform faceted grains with polygonal shape with an average grain size around 3 microns as one can observe in panel (b) of Figure 1. The EELS spectra were analyzed in the valence region (VEELS) as well as in the core region (CEELS). Figure 1(c) shows the VEELS spectrum. It can be observed the elastic peak and the bulk plasmon centered at 21 eV. It can be notice also, the  $O_{4,5}$ -edge of bismuth is centered at 28 eV. Figure 2(a) shows the core region and the respective Y  $M_{4,5}$ -edge and Y  $M_{2,3}$ -edge. The O K-edge (530 eV) is presented in panel b.

The crystal field value used in the calculations takes into account  $10Dq = 1.2$  eV for octahedral sites and  $10 Dq = -0.6$  for tetrahedral sites. The core-hole lifetime for  $L_3$  and  $L_2$  edge were broadened by Lorentzian of  $\Gamma = 0.36$  and  $0.37$ , respectively. The resulting spectrum was convoluted with a Gaussian function width of 1.0 eV to take into account the instrumental broadening. The comparison between the  $L_{2,3}$ -edge of iron with calculated spectrum related to the sum of the contributions of  $\text{Fe}^{2+}$  in octahedral  $O_h$  ( $d^6O_h$ ) symmetry,  $\text{Fe}^{3+}$ ,  $O_h$  ( $d^6O_h$ ) and  $\text{Fe}^{3+}$  tetrahedral  $T_d$  ( $d^5T_h$ ) symmetry is shown in panel c. The present results agree with those reported that the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  cations at the octahedral sites are

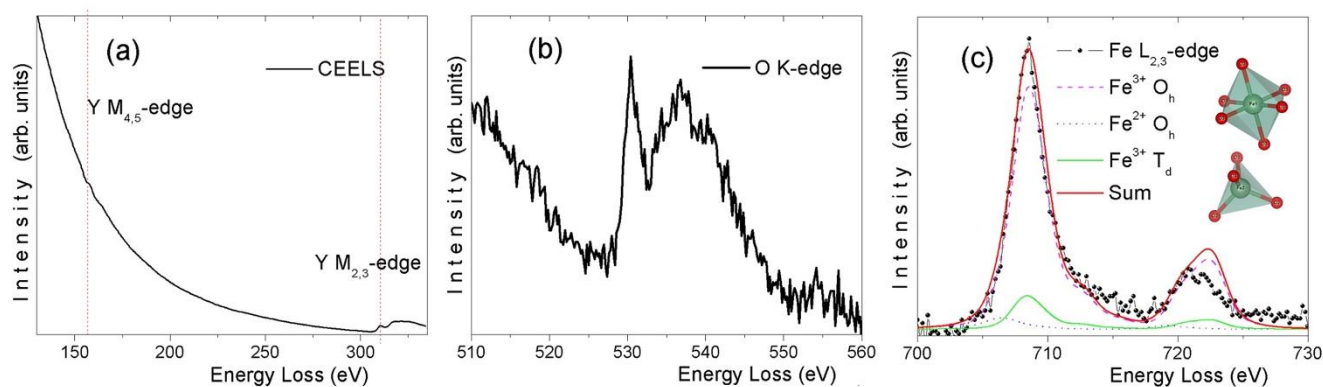
ferromagnetically aligned, and the  $\text{Fe}^{3+}$  ions at the tetrahedral sites are antiferromagnetically coupled [6]. The calculated component contributions for the multiplets of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ( $\text{O}_h$ ) are 5% and 84%, respectively, whereas  $\text{Fe}^{3+}$  ( $\text{T}_d$ ) is 11%. In summary, the main contribution of this work is to present the experimental EELS in combination with the calculated spectrum for the Fe  $L_{2,3}$  edge. The multiplet structure is important to understand the electronic structure of smart ceramics such as Bi-YIG.

#### References:

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**Figure 1.** (a) Indexing the SAED pattern of Bi-YIG. (b) A representative FE-SEM micrograph that shown the microstructure of Bi-YIG. (c) Valence EELS region for the Bi-YIG.



**Figure 2.** (a) Core EELS region for the Yttrium. (b) Oxygen K-edge in the core-region of EELS. (c) Comparison between experimental Fe  $L_{2,3}$ -edge EELS and calculated spectrum.