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ABSTRACTS
**CW-05. Study of site occupancy in single crystalline Zn$_x$Fe$_{3-x}$O$_4$ microspheres based on Mössbauer analysis.**

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The 3d-transition metal-oxide nano/microparticles have been considered to be an ideal candidate for biological applications with unique physical properties [1, 2]. A series of monodispersed Zn$_x$Fe$_{3-x}$O$_4$ ($x=0, 0.05, 0.1, 0.2, 0.4$) microspheres have been prepared by the solvothermal reaction technique. From the Rietveld refinement analysis, the crystal structure was determined to be cubic spinel with lattice constant and X-ray density, linearly increasing from $8.3956$ to $8.4315$ Å , and $5.1971$ to $5.2158$ g/cm$^3$, with the Zn concentration. HR-TEM measurements showed that the size of the monodispersed particles was around $200$–$300$ nm as well as diffraction patterns with single crystalline spots. From the saturation magnetization ($M_s$) and coercivity ($H_c$) as a function of Zn concentration $x$ in Fig. 1, we observed that $M_s$ and $H_c$ values at $295$ K increase with $x$ up to $x=0.05$ and then decrease monotonously as $x$ increases above $0.4$. We have analyzed the Mössbauer spectra as 4 sets with six-lines of tetrahedral $A$ site and octahedral $B_1$ and $B_2$ sites as well as including paramagnetic phase of a doublet at $295$ K, as shown in Fig. 2. The values of the hyperfine field at $A$, $B_1$, and $B_2$ sites decrease from $488$ to $453$ kOe, $458$ to $412$ kOe, and $452$ to $369$ kOe with Zn concentration. From the isomer shift values, the valance state of $A$, $B_1$ sites and doublet were determined to be ferric, while the $B_2$ site was ferrous. The corresponding area ratio of $A$ site decreased by $40$–$25$ % while that of $B_1$, $B_2$ site and doublet sets increased by $60$–$63$ %, and $0$–$12$ %, as the Zn concentration changed from $x=0$ to $0.4$. Here, the changes in the area ratios of $A$, $B$ sites and doublet set are originated from the site preference of cation in Zn$_x$Fe$_{3-x}$O$_4$ microspheres. This site preference, depending on the amount of Zn$^{2+}$ ion substituted in $A$ site, affects the hopping between Fe$^{2+}$ and Fe$^{3+}$ ions, and the super-exchange interaction $A$-$B$ and $B$-$B$ between $A$ and $B$ sites [2, 3].