Applications of Sn4+ and Zr4+ Substituted Nanoscale Calcium Hexaferrites in Microwave Absorbers and Storage Devices

Asmita D. Deshpande, Sharad N. Sable, Vivek M. Nanoti, Kishor G. Rewatkar

a Department of Applied Physics, Priyadarshini College of Engineering, Nagpur (India)
b Department of Physics, Dr. Ambedkar College, Deekshabhumi, Nagpur (India)

ABSTRACT
The industrial applications of substituted nanoscale hexaferrites are of immense importance because of their versatile utility in modern technical and scientific world. It has been observed that Sn4+ and Zr4+ Substituted Nanoscale Calcium Hexaferrites have unique feature that their structural and magnetic properties can be tailored and manipulated to the practical extent. This salient feature makes them very useful in the design of microwave absorbers, switching devices and storage devices. Also, by virtue of their nano sized grain structure and improvised magnetic characters over those of earlier reported ferrites, they are not only found to be more economical but also more resolute. Therefore this class of hexagonal ferrites has been reported to be the promising candidate for electronic gadgets like high density recording media, microwave absorption devices, magneto-optic recording media, etc.

In our exhaustive research module, base of calcium hexaferrite is substituted with Sn4+ and Zr4+ with stoichiometric proportions for x ranging for 0 to 5 in the generic formula Ca(Co-Sn)xFe12-2xO19 and Ca(Co-Zr)xFe12-2xO19. But for the present research module, only one combination for x = 2 is taken into explanation as it has shown to be more useful for aforementioned applications. The synthesis of Ca(Co-Sn)2Fe8O19 and Ca(Co-Zr)2Fe8O19 is carried out by recently reported technique i.e. Microwave Induced Sol-Gel Combustion Route. The morphological and structural parameters of the samples are studied by scanning electron microscopy and further by transverse electron microscopy which leads to confirm these samples into category of nanoscale ranging from 11.52 nm to 36.28 nm. The space group for the samples is observed to be p63/mmc as confirmed by Reitveld quantitative analysis. The magnetic characterization of the samples is done by vibrating sample magnetometry. The saturation magnetization (Ms), coercivity (Hc) and retentivity (Mr) of the samples are found in the ranges which are aptly suitable for microwave absorbers, switching as well as storage devices. Further investigation is underway to tailor their properties to fit them for these more demanding applications in the modern technology.

RESULT & DISCUSSION
The diffraction patterns of samples are taken with Phillips X’pert Diffractometer and Cu-Kα radiation with wavelength, λ=1.542A0. The data is analyzed by using computer softwares. By comparing the patterns with JCPDS standards, the phases in the different samples are determined. It is being observed that most of the hexagonal grains are of same size (2, 5). Using 20, observed d-values and intensity calculations, d-value is recalculated and (hkl) planes are finalized. These values confirm the formation of single phase hexagonal ferrites. The lattice parameters a and c are found to be 5.8421 Å and 21.5378 Å respectively for Ca(Co-Zr)2Fe8O19 and 5.8758 A0 and 22.6089 A0 for Ca(Co-Sn)2Fe8O19 respectively. The space group for the samples is observed to be p63/mmc as confirmed by Reitveld Analysis as shown in the figure 1. Further it is observed that the internal structure of M-type hexaferrite accommodates three different types of interstitial Fe+3 cation positions: tetrahedral, octahedral and bipyramidal.

The transverse electron micrographs given in the figure 2 reveal the remarkable changes in the microstructure, grain size, porosity and homogeneous particle size distribution obtained as a perturbation of many dependant parameters like time of synthesis, temperature, process of annealing, intermittent quenching, grinding, etc. It is also come to the notice that the presence of the large crystalline agglomerations is composed of very small discrete crystallites in the samples at the temperature of synthesis (7). The particle size is determined with the help of TEM studies. The size is found to be about 11.52 nm to 36.28 nm respectively confirming the nanoparticle size of these samples as shown in the figure 2. The grains are found to be hexagonal platelets. It is reasonable to confirm that the doping of tetravalent ions does remain responsive to the grain size of these substituted hexa ferrites (7, 8).
Figure 1 (a): Reitveld Qualitative Analysis for Ca(Co-Sn)$_2$Fe$_8$O$_{19}$
Figure 1 (b): Reitveld Qualitative Analysis for Ca(Co-Zr)$_2$Fe$_8$O$_{19}$

Figure 2 (a) TEM for Ca(Co-Sn)$_2$Fe$_8$O$_{19}$
Figure 2 (b) TEM for Ca(Co-Zr)$_2$Fe$_8$O$_{19}$

Figure 3 (a) Hysteresis Curve for Ca(Co-Sn)$_2$Fe$_8$O$_{19}$
Figure 3 (b) Hysteresis Curve for Ca(Co-Zr)$_2$Fe$_8$O$_{19}$
The magnetic properties of the two samples synthesized are tabulated in Table (1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Saturation Magnetization ($M_s$)</th>
<th>Remanant Magnetization ($M_r$)</th>
<th>Coercivity ($H_c$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(Co-Sn)$_2$Fe$<em>8$O$</em>{19}$</td>
<td>17.087 emu/g</td>
<td>8.758 emu/g</td>
<td>9209 G</td>
</tr>
<tr>
<td>Ca(Co-Zr)$_2$Fe$<em>8$O$</em>{19}$</td>
<td>11.613 emu/g</td>
<td>5.997 emu/g</td>
<td>2143 G</td>
</tr>
</tbody>
</table>

Table (1): Magnetic Properties of Ca(Co-Sn)$_2$Fe$_8$O$_{19}$ and Ca(Co-Zr)$_2$Fe$_8$O$_{19}$

From the hysteresis curves and magnetic parameters of the samples, it can be attributed that with the substitution of Sn$^{4+}$, Ms, Mr and Hc are found to be more than those for the substitution of Zr$^{4+}$ into the pure base of CaFe$_2$O$_{19}$. The application of a magnetic sample for a specific device depends on the relevant properties of such sample (9). One of these properties is the coercivity of the magnetoplumbites. The coercivity of the material Hc should be reduced as low as possible. High coercivity is the demand of a hard magnet while low coercivity is the need of a soft magnet (3, 9). The former is needed for data storage applications. The later is needed for information storage recording media. The origin of coercivity lies in the magnetic anisotropy, which is particularly uniaxial for the hexagonal close packing of the hexaferrites. In view of improvisation of the hexaferrites testing various magnetic properties is of great importance. The stoichiometry of the sample is so chosen that the desired improvement in the coercivity, remanence as well as saturation magnetization is expected (10).

CONCLUSION:
The substitution of Sn$^{4+}$ and Zr$^{4+}$ in Calcium hexaferrites by replacing Fe$^{3+}$ is found to be successful by recently reported technique i.e. Sol Gel Combustion Route (11). The Reitveld qualitative analysis of the samples confirms the formation of hexaferrites and ‘a’ & ‘c’ values of the sample ensure them into the category of hexaferrites (12). Further, the morphological and structural studies have confirmed the space group of samples to be p63/mmc (7, 12). The transverse electron microscopy of the samples has cataloged them as nanoscale hexaferrites. The significant aspect of the samples is their structural and magnetic properties can be tailored and modulated within the practical limits from the point of view of applications (13). On the firm background of structural and magnetic parameters of Ca(Al-Sn)$_2$Fe$_8$O$_{19}$ and Ca(Al-Zr)$_2$Fe$_8$O$_{19}$, it can be attributed that former is more useful for switching devices as its hysteresis curve is more thin like saw tooth wave between logic 0 and logic 1 state (14, 16). Similarly, later can be used in storage devices as its coercivity (Hc) can be manipulated as per the maximum volume of the data to be stored (5, 15). But it is evident that both can be used for microwave absorbers with some tailoring in their structural as well as magnetic properties (16).

REFERENCE