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Revealing structural distortion and dielectric relaxation in $Ga_{1-x}Sc_xFeO_3$ $(0 \leq x \leq 0.3)$

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ABSTRACT

Polycrystalline samples of $Ga_{1-x}Sc_xFeO_3$ (x=0, 0.1, 0.2, and 0.3) were prepared by solid state reaction method. The monophasic compounds were found to crystallize in the orthorhombic space group $Pna2_1$, confirmed from Rietveld refinement of the XRD patterns. The lattice constants were found to increase with increasing Sc content. Mössbauer measurements carried out at room temperature (RT) showed four paramagnetic doublets. Isomer shift values show that iron is in Fe^{3+} high spin state for all four Fe sites in all the compositions. Quadrupole splitting increases with Sc content which means that there is an increase in local structural distortion with Sc substitution. That Sc resides in the Ga2/Fe site was confirmed by Mössbauer spectroscopy. Low temperature Mössbauer study also shows a similar trend. Hyperfine magnetic field decreases with increasing Sc content. Sc substitution causes a reduction of magnetic ordering. The dielectric constant was found to decrease with increasing Sc content. The activation energies, obtained by the temperature dependence of dielectric relaxation as well as the conductivity, showed almost equal values around 0.3 eV.

1. Introduction

Multiferroic compounds which show a coexistence of at least two types of ferroic order (ferroelectric, ferromagnetic or ferroelastic) and continue to attract a lot of attention due to their scientific interest as well as their potential for technological applications [1,2]. The coupling due to the magnetic and electric properties in these materials could lead to interesting magnetoelectric (ME) effects where the magnetization can be controlled by application of an electric field and vice-versa [3–5].

The magnetoelectric properties of $GaFeO_3$, a compound first synthesized by Remeika [6] have been studied in recent years by Sun et al.[7] and Naik et al. [8] $GaFeO_3$ crystallizes in an orthorhombic structure conforming to the space group $Pna2_1$ (space-group No.33). The compound shows a spontaneous electric polarization along the c axis, and is reported to be a ferrimagnet below room temperature as reported by Frankel et al. [9] though theoretical studies suggest that it should be an A-type antiferromagnet [10,11]. The observed ferrimagnetism is attributed to the considerable cation site disorder in this compound as reported by Arima et al. [12]. The low temperature neutron diffraction measurements on $GaFeO_3$ showed a weak magnetic moment arising from the difference in effective magnetic moments of Fe^{3+} at Fe1, Fe2 and Fe3 sites as reported by Rana et al. [13]. Another interesting study by Rana et al. [14]. demonstrates how a simple ball-milling and annealing could bring about interesting transformations of $GaFeO_3$ and $AlFeO_3$ from the chiral orthorhombic ($Pna2_1$) structure to rhombohedral (R-3c) structure. In another detailed study by Mishra et al. [15]. of high temperature structure of $GaFeO_3$, in the temperature range 296–1368 K, the authors found no change in cation disorder up to the highest measured temperature of 1368 K which was a significant finding in order to understand the origin of its magnetoelectric coupling and its multiferroic nature.

Since $GaFeO_3$ contains only trivalent metals, it is an attractive system for investigating isovalent substitutions. Some reports exist in the literature on studies of trivalent doping at the Fe site in $GaFeO_3$ [16]. However, very few reports exist on the effect of doping at the Ga site, especially the effect of ionic size at the Ga-site on the magnetic and dielectric properties of such interesting systems. Moreover, recently, a spin glass-like phase has been reported in single crystal of $GaFeO_3$ below 210 K by Wang et al. [17],

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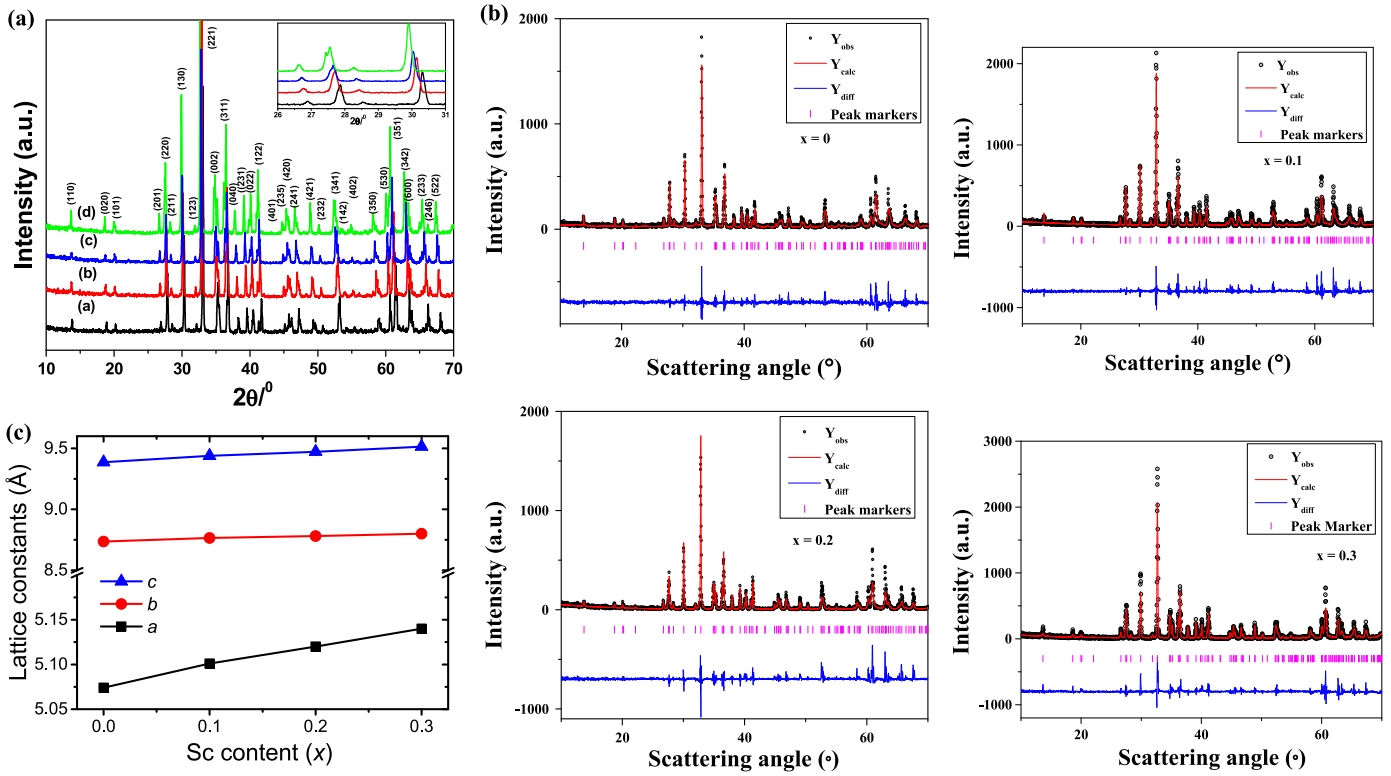

Fig. 1. (a): XRD patterns of $Ga_{1-x}Sc_xFeO_3$ at room temperature. Inset shows the decrease in 2θ values (for a given Bragg peak position) on increasing x. Fig. 1(b) Rietveld refined x-ray diffraction patterns recorded at room temperature for $Ga_{1-x}Sc_xFeO_3$ with $x=0$, 0.1,0.2 and 0.3; observed (open black circles), calculated (continuous red curve) difference (continuous blue curve) and solid magenta bars peak markers. Fig. 1(c): Variation of lattice constant with Sc content in $Ga_{1-x}Sc_xFeO_3$ ($x=0$, 0.1, 0.2, and 0.3) samples. (For interpretation of the references to color in this figure legend,the reader is referred to the web version of this article.)

Table 1
The lattice parameters of various nominal compositions for the system $Ga_{1-x}Sc_xFeO_3$ ($0.0 \le x \le 0.3$) from XRD at room temperature (space group $Pna2_1$).The numbers in the brackets denote the standard deviations in the respective values.

Composition $Ga_{1-x}Sc_xFeO_3$	a (Å)	b (Å)	c (Å)
$x=0$	5.074 (2)	8.736 (6)	9.386 (4)
$x=0.1$	5.101 (2)	8.765 (5)	9.439 (3)
$x=0.2$	5.120 (3)	8.781 (7)	9.472 (5)
$x=0.3$	5.140 (3)	8.800 (7)	9.514 (5)

with a ferrimagnetic background whereas, $ScFeO_3$ has been found to be a cluster spin-glass possessing a cubic crystal structure as reported by Breard et al. [18]. It is already confirmed from our earlier neutron diffraction study on the same compounds that there are three Fe magnetic sites (all having octahedral symmetry) with one site (Fe1) having oppositely oriented magnetic moment with respect to the other two sites (Ga/Fe and Fe2), thus exhibiting a ferrimagnetic structure [19]. We also found that the magnetization and the magnetic transition temperatures decrease with increasing Sc content, hinting at a greater anti-site disorder. However to reveal the exact oxidation states of Fe in all the sites and the effects of Sc content on the Mössbauer parameters we present here the results of our Mössbauer spectroscopic study.

In order to understand the evolution of dielectric response as a function of temperature, and composition we have investigated the dielectric properties of $Ga_{1-x}Sc_xFeO_3$ with increasing Sc concentration ($x=0$, 0.1, 0.2, and 0.3), frequency and temperature.

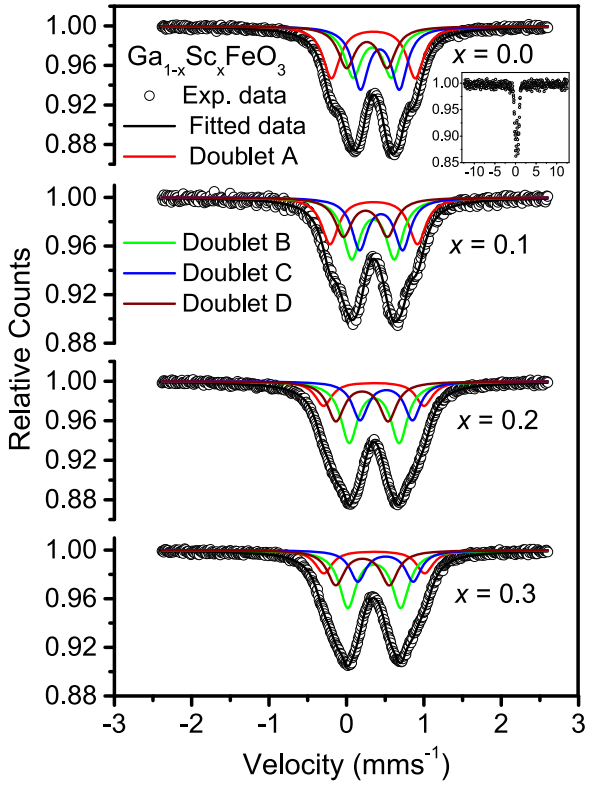

Fig. 2. Room temperature Mössbauer spectra of $Ga_{1-x}Sc_xFeO_3$ ($x=0$, 0.1, 0.2, and 0.3) samples. Inset shows the Mössbauer spectrum of composition $x=0$ at higher velocity.