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^{57}Fe and ^{151}Eu Mössbauer study of charge disproportionation and magnetic properties in $Eu_{1/3}Sr_{2/3}FeO_3$

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ABSTRACT

In this work, the study on charge disproportionation and magnetic property in perovskite sample, $Eu_{1/3}Sr_{2/3}FeO_3$, is presented. The sample was prepared by conventional method of solid-state reaction and was found as a single phase with orthorhombic structure. ^{57}Fe and ^{151}Eu Mössbauer spectra have been measured at the temperatures ranging from 360 K to 15 K. The intensity ratio of the ^{57}Fe Mössbauer spectra corresponding to the Fe^{3+} and Fe^{4+} at paramagnetic state is found with the ratio 60:40, and a typical ratio corresponding to Fe^{3+} and Fe^{5+} is observed as about 70:30 below 90 K, which indicates charge disproportionation (CD) as $2Fe^{4+} \rightarrow Fe^{3+} + Fe^{5+}$ and a typical magnetic relaxation phenomenon have taken place between 270 K and 90 K. Also, the much broadened absorption peaks with decreasing temperature at ^{151}Eu Mössbauer spectra provide another evidence of magnetic relaxation properties in this compound.

The iron perovskite-type oxides with rare earth and alkaline earth atoms are interesting because of their unique properties such as charge disproportionation(CD) [1–8], charge and orbital ordering [2,4,9,10] and cluster glass behaviors [11–13]. The first example of CD transition in perovskite was $CaFeO_3$ at 290 K at which the Fe^{4+} discrete as Fe^{3+} and Fe^{5+}, accompanied by a structural transition from *Pbnm* in the normal state to *P*2/*n* [6]. In other iron perovskite related compounds, such as $La_{1/3}Sr_{2/3}FeO_3$, $Sr_3Fe_2O_7$ and $LaSr_3Fe_3O_{10}$, the CD effect was also observed [7,14]. This phenomenon was generally ascribed to electronically driven mechanism, and the oxygen holes play an important role. Moreover, phase separation in these systems usually occurs, which leads to cluster glass behavior and the corresponding superparamagnetism or magnetic relaxation behaviors [8,14]. The dynamics of cluster glass behavior and the relationship between the phase separations, cluster properties and CD in these systems are still open questions. In this paper we report the charge disproportionation, and magnetic relaxation properties in $Eu_{1/3}Sr_{2/3}FeO_3$. X-ray diffraction (XRD), magnetic measurement, ^{57}Fe and ^{151}Eu Mössbauer spectra are used in this investigation.

The compound was prepared by conventional solid-state reaction method. The structure and phase purity of the sample were checked by XRD and its pattern is shown in Fig. 1. A single phase with orthorhombically distorted structure (space group: *Pbnm*) was observed. By applying GSAS [15], the Rietveld refinement was used to determine the lattice constants and the atomic positions, which are listed in Table 1.

The magnetization curves and hysteresis loops were recorded by using a SQUID magnetometer. The magnetic-field variations of magnetization at 10 K, 180 K and 300 K are shown in Fig. 2. The hysteresis loops can be observed at the curves of the three temperatures, which indicate a typical characteristic of weak ferromagnetism between 10 K and 300 K. The coercivity and remanence are both very small. It can be seen that even under a field of 50 kOe, the magnetization does not saturate. It still has a tendency to increase, which is corresponding to the main antiferromagnetic ordering of spins [7,8]. It was reported that the Fe–O bond length and the Fe–O–Fe angel are two important structural properties which affect the weak ferromagnetism in iron perovskite [4,5]. From the calculation of GSAS refinement of the XRD pattern of $Eu_{1/3}Sr_{2/3}FeO_3$ at room temperature, shown in Table 1, an orthorhombically distorted structure was observed and that the O^{2-} ions have two inequivalent sites, and the corresponding Fe–O band lengths are different, and the Fe–O–Fe band angles are 134.0(4)° and 175.6(2)° respectively. And the weak ferromagnetism

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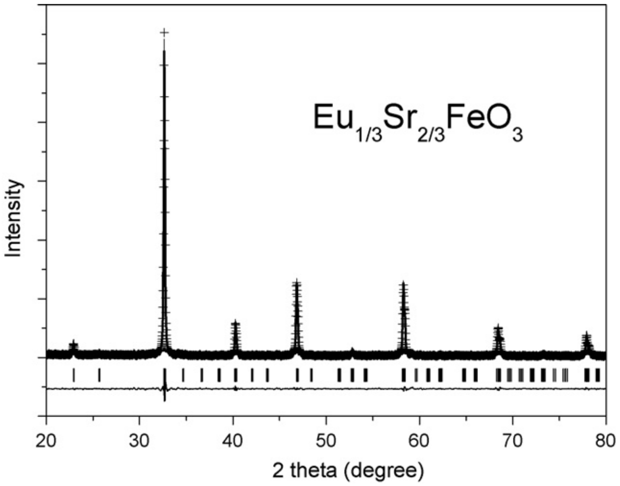

Fig. 1. XRD pattern of $Eu_{1/3}Sr_{2/3}FeO_3$.

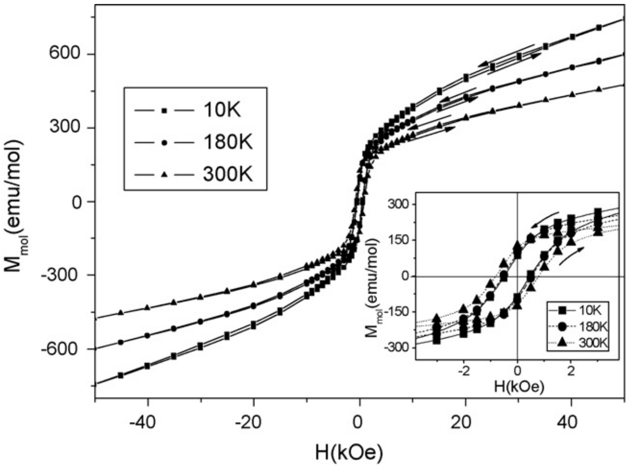

Fig. 2. Magnetic-field dependence of magnetization M_{mol} of $Eu_{1-x}Sr_xFeO_3$.

may originate from the uniaxialy antiferromagnetic-coupled spins in the orthorhombic distortion of crystal structure.

The Mössbauer spectra were collected on a conventional spectrometer with constant-acceleration mode at various temperatures by using a vibration-isolated helium closed-cycle refrigerator (below room temperature) or a vacuum heating furnace (above room temperature). The sources are $^{57}Co/Pd$ (~25 mCi) and $^{151}SmF_3$(~80 mCi) for ^{57}Fe and ^{151}Eu Mössbauer spectra, respectively. The spectra were fitted in Lorentzian line shapes with MossWinn 3.0 software [16]. All spectra were calibrated by using natural α-Fe at room temperature. The central shifts of the ^{57}Fe and ^{151}Eu Mössbauer spectra are relative to the spectrum center of α-Fe and EuF_3 at room temperature, respectively.

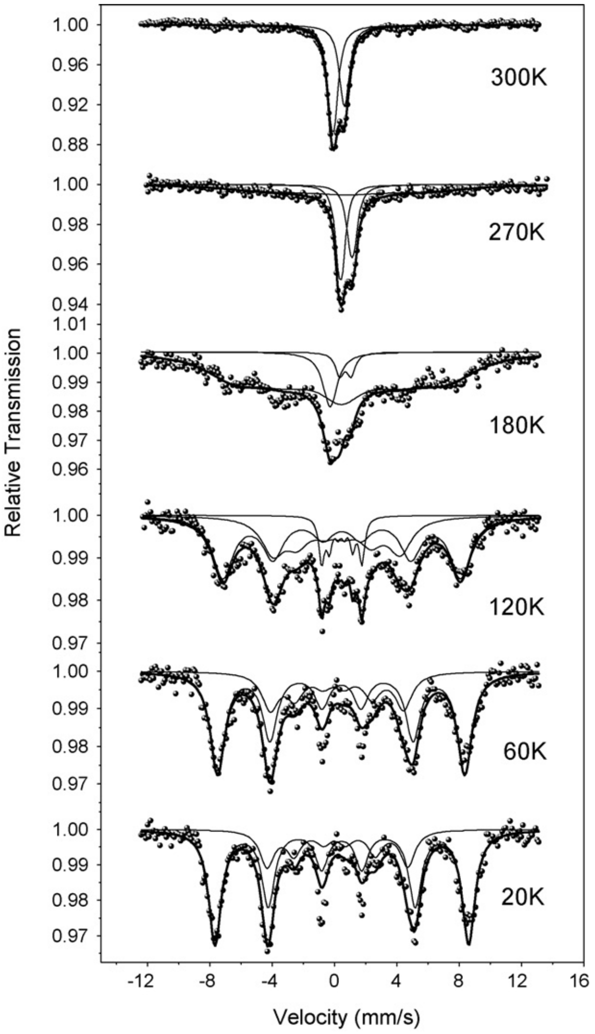

Fig. 3. ^{57}Fe Mössbauer spectra of $Eu_{1/3}Sr_{2/3}FeO_3$ obtained at selected temperatures.

The selected ^{57}Fe Mössbauer spectra are shown in Fig. 3. All ^{57}Fe Mössbauer spectra above 300 K consist of superposition of paramagnetic doublets, and no obvious magnetic sextets components are observed. From the spectrum at 300 K, two doublets with CS = −0.11(5) mm/s, QS = 0.23(5) mm/s and CS = 0.63(5) mm/s, QS = 0.18(5) mm/s are resolved, which are corresponded to the typical values of Fe^{4+} and Fe^{3+}. The ratio of the relative intensities of the two components is about 60:40. It has been known that the Fe^{4+} cations exist in the perovskite-related ferrates. So the two doublets could be assigned to Fe^{4+} and Fe^{3+} respectively. The oxygen deficiencies are calculated as 0.033 and the molecular formula can be deduced as $Eu_{1/3}Sr_{2/3}FeO_{2.967}$ for charge balance consideration. The analysis receives support from the Mössbauer study of similar perovskites [7–10,13]. The Mössbauer spectra measured below 90 K are

Table 1
Refinement parameters of $Eu_{1/3}Sr_{2/3}FeO_3$ at room temperature*

Lattice constants (Å)	Lattice coordinate (Å)				Fe–O (Å)		Fe–O–Fe (°)	
	Atom	x	y	z	$Fe–O_I$	$Fe–O_{II}$	$Fe–O_I–Fe$	$Fe–O_{II}–Fe$
a = 5.4768(1)	Eu/Sr(4c)	0.998(2)	−0.004(6)	1/4	2.11(3)	1.99(3)	134.0(4)	175.6(2)
b = 5.4914(2)	Fe(4a)	0.500	0	0		1.88(3)		
c = 7.7469(1)	O_I(4c)	0.650(1)	−0.000(3)	1/4				
	O_{II}(8d)	0.266(6)	0.252(4)	−0.002(6)				

* The reliability factor was found as R_{wp} = 9.51, R_p = 6.63, χ^2 = 1.223.