

CHEMICAL PASSIVATION OF UNSTABLE FeO - A MÖSSBAUER STUDY*

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Highly unstable FeO is chemically passivated by incorporating Cr³⁺ ions by solid solution technique and forming Fe_xO:Cr³⁺ single phase material. XRD, chemical analysis and Mossbauer spectroscopy are used for the characterization of the freshly prepared as well as samples aged in the desiccator for nearly three months. Optimum concentration range - 0.25 to 0.75 mole% - of Cr₂O₃ has been found to be necessary for stabilizing Fe_xO:Cr³⁺. x is determined by chemical analysis. Mossbauer and XRD studies have confirmed the chemical passivation of unstable FeO.

1. INTRODUCTION

FeO has a rock-salt (NaCl) type structure with cation vacancies and proportional Fe³⁺ ions for electroneutrality of FeO i.e. Fe²⁺_{1-3x}Fe³⁺_{2x}□_xO, x being governed by preparation conditions of the material /1/. However, this simple model seems unlikely for the following reasons: (i) High defect concentration and (ii) coulombic attraction between Fe³⁺ and the virtual negative charge on the cation vacancy, □. On the basis of neutron diffraction experiments, the basic defect unit of 4:1 cluster is proposed /2/ with four vacancies tetrahedrally coordinating one interstitial Fe ion; and that the larger clusters are formed from the aggregation of these units. Relation between the defect structure and the magnetic properties of Fe_{1-x}O for a wide range of compositions is reported using neutron diffraction technique, by Akimitsu et al /3/. They have proposed a model consisting of ferromagnetic moments directed along <111> direction in each Koch-Cohen Cluster, arranged antiferromagnetically in the matrix. Greenwood and Howe /4/ have reviewed four such defect cluster models to explain the structure of Fe_{1-x}O and its disproportionation to Fe and Fe₃O₄ by Mossbauer studies. Stabilized MnO and FeO have been prepared earlier in this laboratory following a novel and well-proven preparation route of incorporating other cations /5/ such as Zn²⁺ and Mn²⁺ respectively. This paper reports preparation of FeO:Cr³⁺ system following an identical route, its characterization via ⁵⁷Fe Mossbauer effect studies, XRD and chemical analysis.

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2. EXPERIMENTAL

Five compositions of FeO:Cr₂O₃ (Table 1) solid solutions are prepared by in situ decomposition of FeC₂O₄.2H₂O and Cr₂O₃. Ferrous oxalate and chromium sesquioxide were mixed together in the required proportion for the compositions given in Table 1. The mixture was decomposed in a closed system reported elsewhere /5/ at 200°C in a flowing current of oxygen-free N₂ obtained by passing cylinder nitrogen gas through a column of reduced copper pellets heated at 200°C. Carbon monoxide, evolved during the decomposition, was disposed off completely by burning off to carbon dioxide. After the evolution of gases ceased, the powder was degassed at 800°C to remove traces of CO chemisorbed on the surface of FeO. The material was cooled to room temperature and the powder was pressed into pellets for calcining at 1100°C/24 hrs in static vacuum so as to form FeO:Cr₂O₃ solid solutions. Same procedure was followed to prepare a sample of pure FeO without any Cr₂O₃ doping. Five solid solutions and the pure undoped FeO sample were characterized using XRD, chemical analysis and Mossbauer spectroscopy for comparative evaluation.

2.1 Characterization

X-ray diffraction patterns were obtained using Philips PW 1730 x-ray generator with CuK_α radiation, for freshly prepared as well as samples aged for about three months. Standard analytical methods were followed for the estimation of the total iron and Fe²⁺ iron content in the solid solutions and pure Fe_xO sample which gave the value of x in all the Fe_xO:Cr³⁺ compositions. Mossbauer spectra were recorded with a conventional constant acceleration electro-mechanical drive coupled to ND 100 multichannel analyser operating in time mode. A 25mCi⁵⁷ Co:Rh source was used to record the spectra at room temperature. A metallic iron foil (25μm) was used to calibrate the spectrometer and all isomer shifts were measured with respect to that of metallic iron. All the hyperfine (hf) interaction parameters were computed using an iterative least square MOSFIT programme on ICL 1409S computer. Table 1 describes all the computed Mossbauer and cubic lattice parameters along with chemical analysis results.

3. RESULTS AND DISCUSSION

XRD pattern of pure FeO showed a multiphase consisting of FeO, Fe₃O₄ and metallic Fe, as expected, due to its disproportionation. Single phase of FeO for compositions 3 to 5 indicates miscibility of Cr₂O₃ in FeO in this range of compositions. This observation was reproducible even after a period of three months from the date of preparation of the solid solutions. However, XRD data of compositions 2 and 6 showed additional lines of Fe₃O₄, Fe metal and FeCr₂O₄ besides those of FeO indicating multiphase compositions due to their instability. This implies that there is an optimum concentration of Cr³⁺ ions needed to stabilize FeO. Lattice parameters of these compositions showed that (i) one with minimum concentration of Cr₂O₃ (0.25 mole %), a = 4.298 Å, matches well with that reported earlier /6/ and

Table 1
Experimental data on Mossbauer, XRD and chemical analysis

S. No.	FeO:Cr ₂ O ₃ (Cr ³⁺) mole %	x in Fe _x O	Cubic lattice parameter 'a'	δ mm/sec w.r.t. Fe metal (± 0.02)	Δ E mm/sec (± 0.02)
1	100.00 : 0.00	0.861	multiphase	1.05	Broad-non-Lorentzian spectrum
2	99.90 : 0.10	0.894	multiphase	1.04	Broad non-Lorentzian spectrum
3	99.75 : 0.25	0.911	4.298	0.90	0.60
4	99.50 : 0.50	0.914	4.289	0.93	0.70
5	99.25 : 0.75	0.910	4.281	0.91	0.73
6	99.00 : 1.00	0.884	multiphase	0.90	Broad non-Lorentzian spectrum

(ii) there is a progressive decrease in 'a' with the increasing concentration of Cr³⁺ ions in the lattice. The decrease can be attributed to smaller ionic radius of Cr³⁺ (0.55Å) than that of Fe²⁺ (0.76 Å). Chemical analysis of the samples was done immediately after preparation and on keeping the samples for about three months. The analysis clearly indicated that x in Fe_xO:Cr³⁺ remains unchanged for composition Nos 3 to 5 and decreases for remaining three. A slight asymmetry is seen in Mossbauer spectra due to the presence of a small concentration, less than 2-3% of Fe³⁺ species. It is well-known that the presence of Fe³⁺ distorts the local site symmetry (even though the overall crystallographic phase is cubic) resulting in a small temperature dependent quadrupole splitting (ΔE). Unstable compositions (1 and 2) gave broad non-Lorentzian spectrum superimposed on magnetically split three sextets of Fe₃O₄ and metallic iron, while the stabilized Fe_xO:Cr³⁺ composition (3 to 5) gave ΔE ranging from 0.6 to 0.73 mm/sec, in good agreement with that reported by Johnson /7/. Isomer shift (δ) values range from 0.90 to 1.05 mm/sec which confirm the presence of Fe²⁺ in all the compositions. The small ΔE at RT can be attributed to the local distortion of the lattice due to Cr³⁺ ions incorporated in the lattice. The Mossbauer results of stabilized Fe_xO:Cr³⁺ compositions are reproducible even after three months of the date of preparation confirming their stability. It could be explained on the model proposed for the stabilization of MnO with ZnO wherein we have observed by XPS studies that a mixed phase of ZnO/Mn₂O₃ formed on the surface protects the bulk MnO from its oxidation /8/. In case of FeO, we expect FeO/Cr₂O₃ phase on its surface resulting in the surface passivation and hindrance to the disproportionation of FeO.

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