Thermodynamic studies on $SrFe_{12}O_{19}(s)$, $SrFe_2O_4(s)$, $Sr_2Fe_2O_5(s)$ and $Sr_3Fe_2O_6(s)$

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Abstract

The citrate–nitrate gel combustion route was used to prepare $SrFe_2O_4(s)$, $Sr_2Fe_2O_5(s)$ and $Sr_3Fe_2O_6(s)$ powders and the compounds were characterized by X-ray diffraction analysis. Different solid-state electrochemical cells were used for the measurement of emf as a function of temperature from 970 to 1151 K. The standard molar Gibbs energies of formation of these ternary oxides were calculated as a function of temperature from the emf data and are represented as

$\Delta_f G_m^\circ$ ($SrFe_2O_4$, s, T)/kJ mol^{-1} (± 1.7) $= -1494.8 + 0.3754 (T/K)$ ($970 \leqslant T/K \leqslant 1151$).
$\Delta_f G_m^\circ$ ($Sr_2Fe_2O_5$, s, T)/kJ mol^{-1} (± 3.0) $= -2119.3 + 0.4461 (T/K)$ ($970 \leqslant T/K \leqslant 1149$).
$\Delta_f G_m^\circ$ ($Sr_3Fe_2O_6$, s, T)/kJ mol^{-1} (± 7.3) $= -2719.8 + 0.4974 (T/K)$ ($969 \leqslant T/K \leqslant 1150$).

Standard molar heat capacities of these ternary oxides were determined from 310 to 820 K using a heat flux type differential scanning calorimeter (DSC). Based on second law analysis and using the thermodynamic database FactSage software, thermodynamic functions such as $\Delta_f H^\circ(298.15\,K)$, $S^\circ(298.15\,K)$ $S^\circ(T)$, $C_p^\circ(T)$, $H^\circ(T)$, $\{H^\circ(T)-H^\circ(298.15\,K)\}$, $G^\circ(T)$, free energy function (*fef*), $\Delta_f H^\circ(T)$ and $\Delta_f G^\circ(T)$ for these ternary oxides were also calculated from 298 to 1000 K.
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Keywords: Magnetic materials; Strontium hexaferrite; Solid-state galvanic cell; Differential scanning calorimetry (DSC); Curie temperature; Thermodynamic properties

1. Introduction

$SrFe_{12}O_{19}(s)$, $SrFe_2O_4(s)$, $Sr_2Fe_2O_5(s)$ and $Sr_3Fe_2O_6(s)$ are few stoichiometric ternary oxides exist in $SrO–Fe_2O_3$ binary system and stable in air [1,2]. In particular, strontium hexaferrite ($SrFe_{12}O_{19}$) crystallizes in the magnetoplumbite hexaferrite structure (*M*-phase) and is widely used as hard ceramic permanent magnetic material and used in high-density recording media, microwave devices and DC motors for the automotive industry and consumer goods [3]. This ferrite crystallizes in a hexagonal structure with 64 ions per unit cell on 11 different symmetry sites ($P6_3/mmc$ space group). The 24 Fe^{3+} atoms are distributed over five distinct sites: three octahedral sites, one tetrahedral site, and one bi-pyramidal site. The magnetic

structure is ferrimagnet with five different sublattices: three parallel and two antiparallels [4]. This *M*-type hexaferrite has a very large saturation magnetization, a large uniaxial magnetic anisotropy, and a high curie temperature, which have been widely used as permanent magnetic materials [5]. Strontium hexaferrite powders can exhibit a high coercivity due to the relatively high magneto-crystalline anisotropy field. Several techniques have been used to prepare strontium ferrites such as ball milling [6], salt melting [7], chemical precipitation [8], glass crystallization [9] and self-propagating high temperature synthesis [10]. A chemical route can be excellent method for the synthesis of high pure multi-component oxide due to better homogeneity, better compositional control and lower processing temperatures which are few potential advantages of this wet chemical route over the conventional solid state reaction method [11]. System Sr–Fe–O has been studied extensively with respect to their preparation, characterization, crystallographic, and magnetic properties [1–12], but very few

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studies has dealt with its thermodynamic and thermal properties of the ternary compounds of the system [1,13]. Rakshit et al. [13] have already reported the standard molar Gibbs free energy of formation and the molar heat capacities of strontium hexaferrite, $SrFe_{12}O_{19}(s)$. Same authors also reported a heat capacity anomaly at 732 K for $SrFe_{12}O_{19}(s)$ due to the magnetic order–disorder transition from ferrimagnetic state to paramagnetic state. Many synthesis techniques such as sputtering, organometallic chemical vapor deposition, laser ablation and liquid phase epitaxy (LPE) have been tested for the growth of high quality thin films of strontium hexaferrite. Most of these synthesis processes use low oxygen partial pressures ($<10^{-6}$ kPa) and moderately high temperature. Hence for reproducible synthesis of magnetic thin films with the desired structure and magnetic properties, information on oxygen potential and standard Gibbs energies of formation of the compounds is required.

Compounds $SrFe_{12}O_{19}(s)$, $SrFe_2O_4(s)$, $Sr_2Fe_2O_5(s)$ and $Sr_3Fe_2O_6(s)$ lie on the tie line joining SrO and Fe_2O_3 phases in pseudo-binary system of $SrO–Fe_2O_3$. Hence, it is possible to setup different electrochemical cells based on $CaF_2(s)$ solid electrolyte to determine the Gibbs free energy of formations of these ternary oxides. In this work, stoichiometric ternary oxides, $SrFe_2O_4(s)$, $Sr_2Fe_2O_5(s)$ and $Sr_3Fe_2O_6(s)$ of Sr–Fe–O system were synthesized by citrate–nitrate gel combustion route and characterized by X-ray diffraction (XRD) analysis and thermodynamic studies have been carried out using solid-state electrochemical technique and differential scanning calorimetry.

2. Experimental

2.1. Materials preparation

Different stoichiometric proportions of $Fe(NO_3)_3 \cdot 9H_2O$ (Qualigens Fine Chemicals, mass fraction 0.995) and $SrCO_3$ (LEICO Ind., USA, mass fraction 0.9999) were dissolved in dilute nitric acid to prepare $SrFe_2O_4(s)$, $Sr_2Fe_2O_5(s)$ and $Sr_3Fe_2O_6(s)$. Excess amount of citric acid (E. Merck, India, mass fraction 0.995) was added to the solution to assist complete dissolution. The resultant solutions were heated on a hot plate around 375 K to remove water and oxides of nitrogen. A gel was formed which was further heated at 450 K to dryness. The residues were ground in an agate mortar and pestle and heated at 1273 K in dry air for 100 h with two intermediate grindings. The resultant products were identified as pure phases of $SrFe_2O_4(s)$, $Sr_2Fe_2O_5(s)$ and $Sr_3Fe_2O_6(s)$ by XRD analysis using a STOE powder X-ray diffractometer with $CuK\alpha$ radiation using JCPDS file no. 48–0156, 33–0677 and 82–0426, respectively. Preparations of powder samples of $SrFe_{12}O_{19}(s)$ were described in details by Rakshit et al. [13]. Powder samples of these oxides were used for heat capacity measurements. Phase mixtures of $\{SrFe_2O_4(s) + SrFe_{12}O_{19}(s) + SrF_2(s)\}$, $\{Sr_2Fe_2O_5(s) + SrFe_2O_4(s) + SrF_2(s)\}$ and $\{Sr_3Fe_2O_6(s) + Sr_2Fe_2O_5(s) + SrF_2(s)\}$ were mixed

homogeneously using agate mortar and pestle and palletized using a steel die at a pressure of 100 MPa into a 10 mm dia and 3 mm thick pellet and sintered at 1100 K in purified argon gas atmosphere for 24 h and preserved inside a desiccator for emf measurements.

2.2. Solid-state electrochemical cell with CaF$_2$ as solid electrolyte

A schematic diagram of a fluoride cell used in this study is shown in Fig. 1. Optical grade single crystal CaF_2 pellet of 6 mm diameter and 3 mm thick (supplied by Solon Technologies, Inc., USA) was used as an electrolyte. It is a single compartment cell with provisions for passing argon gas during the experiment and to measure the temperature of the cell near the electrode/electrolyte interface. High purity argon containing 10 ppm $O_2(g)$ gas at 10^5 Pa was allowed to pass through successive traps of oxidized form of BTS catalysts, molecular sieves, silica gels and anhydrous magnesium perchlorate for removal of traces of hydrogen and moisture. The reference electrode, the electrolyte and the measuring electrode stacked one over the other, was kept in the isothermal zone of a Kanthal wire wound resistance furnace. The furnace temperature was controlled within ± 1 K by using a PID controller. The experimental setup and the cell assembly used in this study have been explained in details in an earlier publication [13].
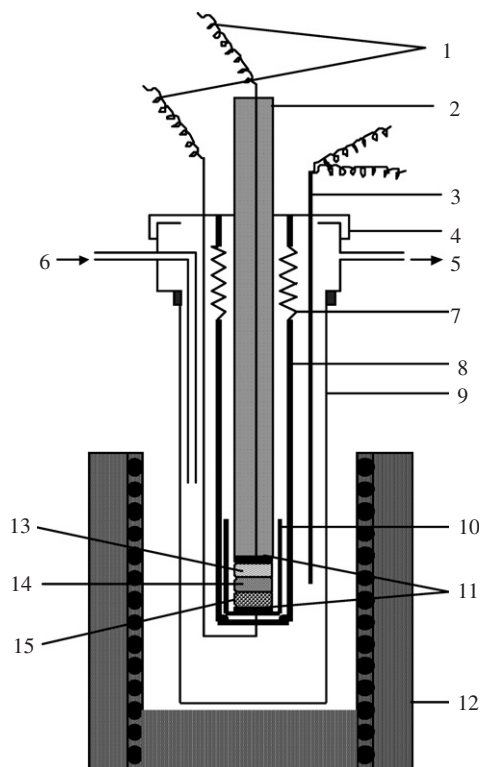

Fig. 1. Schematic diagram of the fluoride cell 1: Pt wires; 2: alumina pressing tube; 3: thermocouple; 4: stainless steel flange; 5: gas inlet; 6: gas outlet; 7: spring; 8: quartz holder; 9: quartz tube; 10: alumina cup; 11: Pt discs; 12: Kanthal wire wound furnace; 13: reference electrode; 14: CaF$_2$ electrolyte; 15: sample electrode.