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Exploring the effects of silica and zirconia additives on electrical and redox properties of ferrospinels

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ABSTRACT

The interplay of unique cation arrangement and redox coupling in ferrospinels offers a wide range of magnetic and catalytic properties, evaluated mostly for low and intermediate temperature applications. This work focuses on high-temperature properties of magnesium-substituted magnetite, for prospective high temperature applications such as electrodes for pyroelectrolysis, energy conversion, catalysis, etc. The effects of silica and zirconia additions to $(Fe,Mg)_3O_4$ are studied, with emphasis on structural, electronic transport and redox properties. Up to at least 2% Zr^{4+} can be dissolved in the spinel lattice by sintering in inert atmosphere at 1773 K, resulting in a moderate conductivity decrease and lower tolerance against oxidative decomposition. Silica additions are accommodated by magnesium exsolution and formation of $(Fe,Mg)_2SiO_4$ and (Mg,Fe)O phase impurities rather than by the substitution in spinel lattice, as confirmed by combined structural, microstructural and electrical conductivity studies. Minor amounts of silica in ferrospinels do not result in the conductivity decrease and apparently provide more stable thermo-chemical expansion behaviour, being favourable for prospective high-temperature applications, including anode materials in silicate-based melts.

1. Introduction

Spinel-type ferrites represent a large family of oxides which possess the structure of natural spinel $MgAl_2O_4$. From these, magnetite Fe_3O_4 is one of the commercially most important and probably the oldest magnetic material with practical applications [1]. Applications of magnetite and magnetite-based spinels are still mainly determined by attractive magnetic properties, including recording media, magnetic fluids and waste water treatment [2,3]. Multifunctional nanoparticles composed of a magnetite nanocrystal core have a great potential for simultaneous bio-imaging and drug delivery [4]. Magnetite also possesses high electrical conductivity reaching up to 100 S/cm [3]. Such versatile properties are provided by the inverse spinel crystal lattice built from the oxygen ions in a cubic close-packed array with two types of interstices for residing cations, coordinated tetrahedrally and octahedrally. The presence of the redox-active couple Fe^{3+}/Fe^{2+} creates the conditions for electron hopping, which proceeds mainly in the octahedral sublattice [5–7]. On the other hand, remarkable electronic conductivity of magnetite and magnetite-based spinels is complemented with high refractoriness, enabling a broader range of electroceramics applications [8]. As an example, ferrospinels were proposed as consumable anode materials in a pyroelectrolysis process for iron extraction from oxide-silica melts [9], a carbon-lean alternative to traditional steelmaking [10–12]. In such melts even noble metals are not truly inert under anodic and also under cathodic polarization [10,12]. Magnetite-based anodes are expected to have a moderate dissolution rate [9], while also being cheap and chemically compatible with the molten electrolyte. High electrical conductivity is essential for the anode and can be only maintained by retaining the spinel structure and avoiding oxidative decomposition. However, in many cases a reasonable compromise between electrical and redox properties becomes a challenge, especially taking into account that anodic polarization also promotes the oxidation.

High-temperature electrical properties and redox stability of magnetite can be widely tuned by various substitutions, including magnesium, aluminium and transition metal cations [6,13–15]. To meet the requirements of high-temperature applications, a ferrospinel composition can be even designed by

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multiple simultaneous co-substitutions [16], which introduce desired functionalities. As an example, substitution with magnesium increases the refractoriness [14], Al^{3+} improves the redox stability without significant deterioration of the conductivity [14], while additions of higher-valence transition metal cations like Ti^{4+} facilitate the electronic transport [15]. In general, the oxidation state of the transition metal cation is one of the key factors determining the electrical conductivity and redox tolerance. The hopping is facilitated in the case of metal cations, having the oxidation state higher than three, by increasing the concentration of Fe^{2+} and the hopping probability $[Fe^{3+}]_{oct}[Fe^{2+}]_{oct}$ [14,15].

This work aims to explore the possibilities for substitutions of tetravalent cations Si^{4+} or Zr^{4+} in $(Fe,Mg,M)_3O_4$ ferrospinels, with M = Si, Zr, and their impact on high-temperature electrical and redox properties, based on the expected effects of Fe^{2+}:Fe^{3+} ratio. According to phase diagrams, some minor solubility of these cations in the spinel lattice at high temperatures is foreseen [17–19]. The impact of silicon is also extremely important if considering pyroelectrolysis application, where one may expect the formation of Si-containing spinel at the surface of consumable anode, immersed in the molten silicate electrolyte. Magnesium-substituted magnetite was used as a model system, to maintain sufficient redox stability upon the substitution with high-valent cations and to provide suitable refractoriness, as the addition of silica decreases the temperature of the liquid phase formation [17,18].

2. Experimental

The list of nominal chemical compositions of the studied materials includes: $Fe_{2.8}Mg_{0.2}O_4$ as a reference, Si-containing $Fe_{2.77}Si_{0.03}Mg_{0.2}O_4$, $Fe_{2.75}Si_{0.05}Mg_{0.2}O_4$ and $Fe_{2.45}Si_{0.05}Mg_{0.5}O_4$, and Zr-containing $Fe_{2.77}Zr_{0.03}Mg_{0.2}O_4$, $Fe_{2.45}Zr_{0.05}Mg_{0.5}O_4$. The precursor powders were prepared via standard solid state route by mixing the stoichiometric amounts of $FeC_2O_4{\cdot}2H_2O$ (99%, Sigma-Aldrich), $Mg(NO_3)_2{\cdot}6H_2O$ (99%, Avocado Research Chemicals), ZrO_2 (Tosoh TZ-0) and SiO_2 (99.6%, Sigma Aldrich), followed by several annealing steps at 1173–1373 K with multiple intermediate grindings, to enhance homogeneity. The powders were uniaxially compacted and sintered at 1673–1773 K for 10 h in flowing argon atmosphere ($p(O_2)$~10 Pa). Combined scanning electron microscopy/energy dispersive X-Ray spectroscopy (SEM/EDS) were performed on fractured ceramic samples. For measurements of the electrical conductivity and thermal expansion the sintered ceramics were cut into $\sim 3 \times 4 \times 12\,mm^3$ rectangular bars. The experimental density was measured for ceramic disk-shaped samples, from geometrical dimensions and weight. X-ray diffraction (XRD) and thermogravimetry (TG) studies were performed on the powders, prepared by grinding corresponding ceramics in a mortar.

The phase composition and unit cell parameters were determined from the room-temperature XRD patterns (Rigaku D/Max-B diffractometer, CuK_α, $2\Theta = 10–80°$, step 0.02°, exposition 2 s), using a profile matching method in Fullprof software [20]. Microstructural studies were performed by SEM (Hitachi SU-70 instrument) and EDS (Bruker Quantax 400 detector). Thermogravimetry (TG, Setaram SetSys 16/18 instrument) was used to evaluate the redox behavior under constant heating/cooling rate of 2 K/min in argon and dry air atmospheres. The impact of redox interactions on the ceramics expansion/contraction was evaluated by dilatometry (vertical alumina dilatometer Linseis L70/2001) on heating up to 1350 K (3 K/min) in argon and air atmospheres. Total electrical conductivity (σ) was measured by 4-probe DC method in argon at 1140–1773 K, using stepwise (50 K) cooling with corresponding dwells for thermal and redox equilibration.

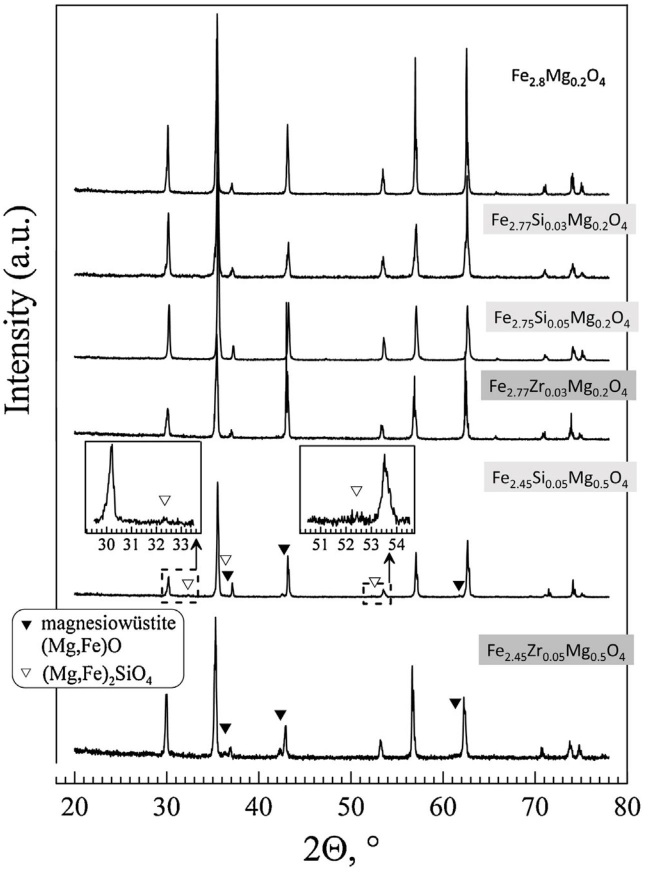

Fig. 1. Room-temperature XRD patterns of $Fe_{2.8}Mg_{0.2}O_4$, and Si- and Zr-containing compositions. The insets emphasize the peaks corresponding to minor amounts of the $(Mg,Fe)_2SiO_4$ phase.

3. Results and discussion

The results of XRD analysis (Fig. 1) suggest apparently single-phase spinel composition (space group $Fd\bar{3}m$) for the samples with minor magnesium substitution level, namely, the reference $Fe_{2.8}Mg_{0.2}O_4$ and Si- and Zr- containing samples $Fe_{2.77}Si_{0.03}Mg_{0.2}O_4$, $Fe_{2.75}Si_{0.05}Mg_{0.2}O_4$ and $Fe_{2.77}Zr_{0.03}Mg_{0.2}O_4$.

Corresponding phase composition, lattice parameters and densities of the sintered ceramic samples are listed in Table 1.

The obtained values for spinel lattice parameters of $Fe_{2.8}Mg_{0.2}O_4$, $Fe_{2.77}Si_{0.03}Mg_{0.2}O_4$, $Fe_{2.75}Si_{0.05}Mg_{0.2}O_4$ are scattered around 0.840 nm and do not provide any clear guidelines regarding effective solubility and effects of silicon additions. Actually, the effects of substitution on the unit cell size in spinels can be quite complex and are often determined by a combination of contributions from cation sizes of the divalent and tetravalent additives (Mg^{2+}, Si^{4+}), their influence on the Fe^{2+}:Fe^{3+} ratio, induced by charge compensation, their preferred coordination, either tetrahedral or octahedral, or even a combination thereof, with hardly predictable final impacts on the bond length [21]. Additional contributions provided by other point defects such as interstitial cations and vacancies also should be considered [15]. Still, the ionic radii of Si^{4+} with tetrahedral (0.026 nm) and octahedral (0.04 nm) coordination are significantly below those for high-spin Fe^{3+} (0.049 and 0.0645 nm) and Fe^{2+} (0.063 and 0.078 nm, respectively) [22]. Therefore, in the case of the Si substitution in spinel one should rather expect unit cell contraction, which is not observed.

In the case of Zr^{4+}, with expected ionic radii of 0.059 nm in tetrahedral coordination and 0.072 nm in octahedral coordination,