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Humidity response of Li-substituted magnesium ferrite

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Abstract

Humidity sensitivity of $Mg_{1-x}Li_xFe_2O_4$ ($0.0 \leq x \leq 0.6$) samples prepared by solid-state reaction of inorganic precursors has been studied. Specimens prepared by this method were confirmed to exhibit spinel structure by X-ray diffraction studies and FT-IR spectral absorption peaks observed in mid IR spectroscopic analysis at $\upsilon_1 = 580–600\ \text{cm}^{-1}$ and $\upsilon_2 = 400–436\ \text{cm}^{-1}$. Distribution of nano-size grains was observed by scanning electron micrographs. It was observed that the grain size further decreased from 200 nm to 110 nm with substitution of lithium ions. The sensitivity factor increased from 165 for pure magnesium ferrite to 2080 for lithium substitution in the range 10–80% RH. The shortest response time was measured to be 180 s for the $x = 0.4$ composition sample.

Keywords: Magnesium–lithium ferrite; Porosity; Grotthuss chain reaction; Protonic conduction; Humidity sensing; Magnesium ferrite FT-IR spectra

1. Introduction

Oxide ceramics are widely used for humidity sensing. Many interesting chemical and physical phenomena that take place on the surface of metal oxide ceramics rely on the electronic surface conduction and its porous structure. For most metal oxides this functionality is connected to the degree of non-stoichiometry and the presence of structural defects. The structure of spinel compounds contains tetrahedral framework always even with high density of defects and is semiconductive in nature. Polycrystalline magnesium ferrite is a porous assembly of an n-type oxide [1]. When water vapors are brought to an n-type oxide surface, electron near to the surface are transferred from the conduction band to the electron accepting level of H_2O, giving a chemisorbed layer of OH^- ions. Further adsorption leads to formation of H_3O^+ ions. Conduction occurs when H_3O^+ releases a proton to a neighboring water molecule, which accepts it while releasing another proton and so forth. This is known as Grotthuss chain reaction. It is the basic conduction mechanism in liquid water as well as in the surface aquatic layers on humidity-sensitive metal oxides [2]. At high relative humidity, water vapors condense in the capillary-like pores and electrolytic conduction takes place in addition to the protonic conduction in the adsorbed layers. This is known as physisorption of water vapors. Due to high electrostatic fields in the chemisorbed layer, physisorbed water dissociates with a factor of 10^6, which is greater than that in liquid water:

$$2H_2O \Leftrightarrow H_3O^+ + OH^-$$

In present work humidity sensing properties of Li^+-substituted magnesium ferrite samples prepared by solid-state reaction of inorganic reagents are reported. The purpose of substituting smaller Li^+ ions for Mg^{2+} ions was to create more defects and porosity in the structure. The results suggested that lithium ion substitution enhanced the formation of smaller grains of magnesium ferrite, leading to an increase in surface area and improved humidity sensing properties. It was observed that the distribution of wide-open pores shortened the response time. The humidity responses of the samples were examined on the basis of microstructure and conduction mechanism of such porous spinel ferrite materials.

2. Experimental

2.1. Material preparation

N-type polycrystalline samples of $Mg_{1-x}Li_xFe_2O_4$ ($x = 0.0$, 0.2, 0.4 and 0.6) were prepared by solid-state reaction of inor-

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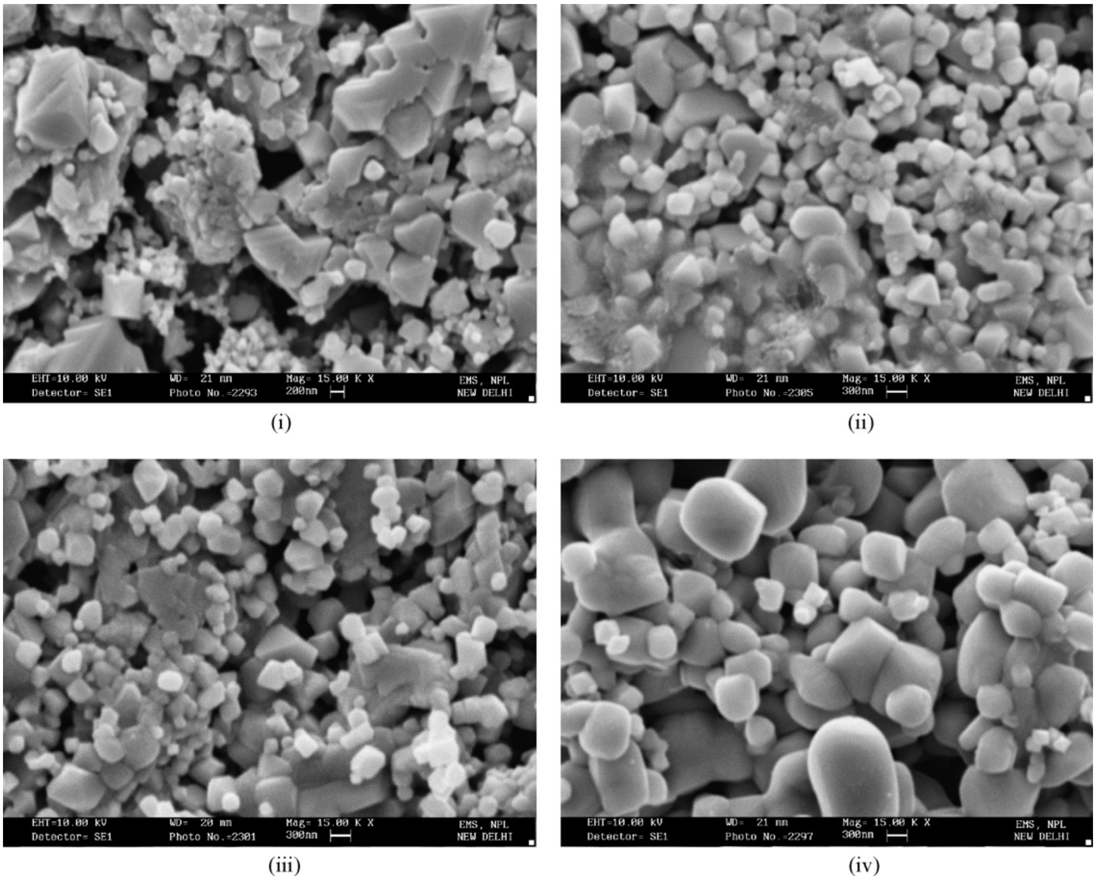

Fig. 1. SEM micrographs of (i) pure $MgFe_2O_4$, (ii) $Mg_{0.8}Li_{0.2}Fe_2O_4$, (iii) $Mg_{0.6}Li_{0.4}Fe_2O_4$, and (iv) $Mg_{0.4}Li_{0.6}Fe_2O_4$.

ganic reagents $MgSO_4$, $LiNO_3$, Fe $(NO_3)_3 \cdot 9H_2O$, NaOH and NaCl [3]. All the chemicals used were of analytical grade. The NaOH was added to convert metal nitrates and sulfates into hydroxides, whereas NaCl restricted the growth of grains to keep the size as small as possible. The reagents were mixed in the ratio of $1-x$:x:2:8:10 and ground in an agate mortar with a pastel for 50–60 min. An exothermic reaction proceeded during grinding, and a dark red aqueous mixture initially formed gradually transformed into brown paste. The paste was taken in a quartz crucible and prefired at 750 °C for 3 h in a box furnace. The prefired mixture was washed several times with deionized water to leach out the sodium salts and was subsequently dried at 120 °C overnight in a furnace. The dried powder was pelletized in rectangular shape of dimensions 5 mm × 3 mm × 2 mm. The rectangular pellets were then sintered at 850 °C in air for 2 h. For making ohmic electrical contacts silver paste was applied on the parallel opposite faces (3 mm × 2 mm) of the rectangular pellets and was annealed at 300 °C for 30 min. The electrodes were soldered on the silvered faces.

2.2. Characterization

The characterization of the samples was carried out by SEM, XRD and IR spectroscopy. Grain size distribution, distribution of pores and surface layer morphology were analyzed by scanning electron micrographs. The spinel phase confirmation and lattice constants were calculated by X-ray diffraction peaks of the samples. Electrical resistivity response to relative humidity of the samples was measured by a two-probe method in the range 10–80% RH at 25 °C. The relative humidity generator used was based on two-pressure technique. The FT-IR spectra of the series were measured using model 5700 Thermo Nicolet instrument in the range 400–800 cm^{-1}. Each sample was mixed with KBr and pressed into pellets to record their FT-IR spectra. The electrical resistivity was calculated by using the formula

$$\rho = \frac{RA}{L} \tag{1}$$

where R is the dc resistance of the sample at room temperature at a particular relative humidity, L is the length of the pellet, and A is the electrode area on a rectangular pellet.

The sensitivity factor of the samples was calculated by the following equation:

$$S_{\mathrm{f}} = \frac{R_{80\%}}{R_{10\%}} \tag{2}$$

The lattice constant was determined by equation:

$$a = d\,x(h^2 + k^2 + l^2)^{1/2} \tag{3}$$

where $(h\,k\,l)$ is the miller indices and d is the interplaner spacing obtained by the XRD pattern.