

Preferential exposure of certain crystallographic planes on the surface of spinel ferrites: a study by LEIS on polycrystalline spinel ferrite surfaces

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Spinel ferrites are commercially important because of their excellent magnetic and catalytic properties. The study by Low Energy Ion Scattering (LEIS) can reveal atomic scale information on the surface. The surface of selected spinel ferrites was investigated by LEIS. It has been found that it is the octahedral sites which are preferentially exposed on the surface of the spinel ferrites. So the probable planes which are exposed on spinel ferrite surfaces are D(110) or B(111). This prediction using LEIS gives scope for tailor-making compounds with catalytically active ions on the surface for various catalytic reactions.

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1. Introduction

Compounds exhibiting spinel structures belong to the class of inorganic materials resemble the crystal structure of the naturally occurring mineral (MgAl_2O_4) [1]. The spinel structure has a cubic symmetry consisting of a face centred cubic lattice of oxygen ions which accommodates the cations in interstitial positions, of which are of two types. In the former, the cation is surrounded by four oxygen ions located at the corners of a tetrahedron and in the later by six oxygen ions located at the vertices of an octahedron (cf. Fig. 1a and b). These are called tetrahedral and octahedral sites respectively and are often referred to as A and B sites [1].

A host of compounds exhibiting spinel structures are commercially important materials [2]. For example spinel like ferrites find extensive applications in the form of passive components in devices such as transformers, loud speakers, TV, Radio and as microwave and storage devices. These materials are also active catalysts used for a variety of reactions. For instance polycrystalline ferrites are increasingly being used for the production of alkenes [3].

The study of surfaces by Low Energy Ion Scattering (LEIS) is important since it can reveal atomic scale information on the surface. This leads to the evaluation of surface composition and structural details pertaining to the surface. The materials under investigations in the present study by LEIS are spinel ferrites. The compounds selected for the study are the following.

- (1) Magnetite (Fe_3O_4)
- (2) Maghemite ($\gamma\text{Fe}_2\text{O}_3$)
- (3) Zinc ferrite (ZnFe_2O_4)
- (4) Magnesium ferrite (MgFe_2O_4)

It is known that the important factors that determine the structural and magnetic properties of spinel ferrites are the cation arrangement in spinel ferrites, the radius of cations, charge and site preference energy. So knowledge of magnetic properties of these ferrites together with structural data can establish the cation arrangements with respect to the bulk. Moreover they can be synthesized easily and the data on occupation of cations in the interstitial positions namely octahedral and tetrahedral sites are easily available. These are the reasons for the choice of these compounds.

2. Experimental

2.1. Synthesis

Maghemite and Magnetite were prepared from freshly prepared iron oxalate precursors based on a scheme of preparation developed by Anantharaman *et al.* [4]. Zinc and Magnesium ferrites were prepared by employing ceramic technique [5]. Appropriate amounts of ZnO/MgO were mixed with Fe_2O_3 and pre-fired at 773 K. The final firing (sintering) was carried out at 1473 K for several hours.

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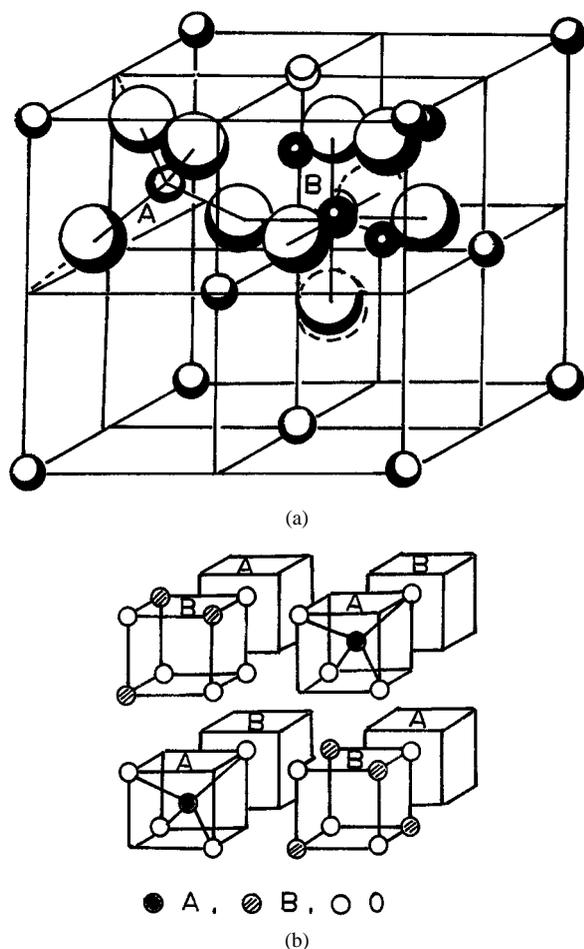


Figure 1 The unit cell of spinel.

2.2. X-Ray diffraction

The X-ray diffraction of these powder samples were recorded on a Philips (PW 1130) X-ray diffractometer using $\text{CuK}\alpha$ radiation $\lambda = 0.15418$ nm. Lattice spacing (d) and lattice parameter (a) were evaluated using the Bragg relation $n\lambda = 2d \sin \theta$, where θ is the glancing angle and n is the order of diffraction.

2.3. Low energy ion scattering (LEIS)

The characteristic feature of LEIS is that it is a powerful tool to probe the outer most layer of atoms on a material. The experiments were performed with the LEIS instrument NODUS of which the design and other details are illustrated elsewhere [6]. In this apparatus it is possible to compensate for surface charging by impinging thermal electrons over the surface from all sides. The base pressure in the UHV system was about 10^{-9} mbar, and during operation it increases to 10^{-8} mbar. The polycrystalline powders were pressed in to pellets in lead holders. A 3 keV $^4\text{He}^+$ ion beam was used for the LEIS measurements.

The scattering conditions were kept constant during measurements in order to facilitate comparison of data on an absolute level on different powder samples having different surface areas. The background in the LEIS spectra is caused by ions that are first neutralised, then the ions penetrate the material where they undergo multiple collisions thus losing energy. When they scatter

back and then collide with an atom such as oxygen, they are reionised. If this occurs during the last collision with the surface, this leads to emission of scattered noble gas ions. It is known that oxygen reionises He atoms at impact energies above 700 eV. Thus peak of the LEIS spectrum relates to ions scattered by atoms in the top layer, while the low-energy background relates to the multiple scattered ions. The energy distribution of the scattered ions is analysed. The high neutralisation probability and large cross section of the inert gas ions ensure monolayer sensitivity.

3. Results and discussions

From the X-ray diffractograms of the powder samples, d -values and lattice parameters (a) were evaluated. The XRD analysis of the samples indicate that the materials prepared as described earlier yielded monophasic compounds exhibiting characteristic features of the spinel phase. This was done by evaluating the lattice spacing and the corresponding relative intensities of the various hkl planes. The comparison of these values with the standard values listed in JCPDS [7–10] confirmed the formation of the spinel phase without any detectable impurities. A typical XRD spectrum of a spinel phase is shown in Fig. 2. The XRD details are cited in Table I–IV.

The findings of LEIS are cited in Table V. Some typical LEIS spectra are shown in Fig. 3. It can be seen that the surface peak of oxygen is similar in the three spectra. It is to be noted that practically no zinc is detected on the surface of zinc ferrite while in the case of magnesium ferrite Mg is detected along with Fe on the surface. The low concentration of zinc on the surface of zinc ferrite cannot be attributed to low sensitivity of

TABLE I XRD results of zinc ferrite

| d (nm) | Relative intensity ($I/I_0 \times 100$) | hkl |
|----------|--|-------|
| 0.48663 | 6.4 | 111 |
| 0.29824 | 36.4 | 220 |
| 0.25453 | 100.0 | 311 |
| 0.24359 | 7.1 | 222 |
| 0.21104 | 17.1 | 400 |
| 0.17232 | 12.1 | 422 |
| 0.16248 | 35.7 | 511 |
| 0.14929 | 42.1 | 440 |

TABLE II XRD results of $\gamma\text{-Fe}_2\text{O}_3$

| d (nm) | Relative intensity ($I/I_0 \times 100$) | hkl |
|----------|--|-------|
| 0.58944 | 6.7 | 110 |
| 0.48088 | 4.2 | 111 |
| 0.37231 | 7.5 | 210 |
| 0.34038 | 7.5 | 220 |
| 0.29374 | 36.7 | 311 |
| 0.25150 | 100.0 | 222 |
| 0.24057 | 5.8 | 400 |
| 0.20849 | 20.0 | 422 |
| 0.17039 | 11.7 | 511 |
| 0.16066 | 25.0 | 440 |

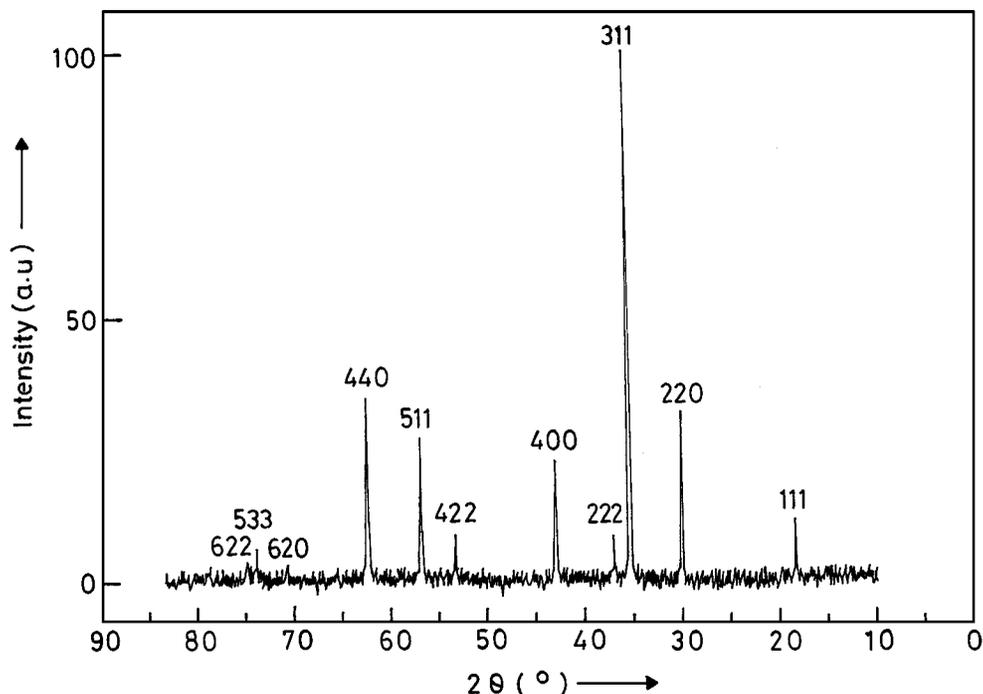


Figure 2 Typical XRD spectrum of a spinel (Fe_3O_4).

TABLE III XRD results of Fe_3O_4 (Prepared by low temperature method)

| d (nm) | Relative intensity ($I/I_0 \times 100$) | hkl |
|----------|--|-------|
| 0.48217 | 8 | 111 |
| 0.29593 | 26 | 220 |
| 0.25286 | 100 | 311 |
| 0.2420 | 5 | 222 |
| 0.20964 | 23 | 400 |
| 0.17112 | 5 | 422 |
| 0.16156 | 23 | 511 |

TABLE IV XRD results of MgFe_2O_4

| d (nm) | Relative intensity ($I/I_0 \times 100$) | hkl |
|----------|--|-------|
| 0.48347 | 4.8 | 111 |
| 0.29669 | 42.9 | 220 |
| 0.25252 | 100.0 | 311 |
| 0.24188 | 3.3 | 222 |
| 0.20964 | 23.3 | 400 |
| 0.17118 | 17.6 | 422 |
| 0.16104 | 19.5 | 511 |
| 0.14796 | 25.2 | 440 |

TABLE V Results of LEIS experiments on various spinel ferrites

| Sample | Method of preparation | LEIS peak area ($\#10^3$) | | | |
|--------------------------------|-----------------------|-----------------------------|------|------|------|
| | | O | Mg | Fe | Zn |
| Fe_3O_4 | Co precipitation | 5.2 | | 24.4 | |
| ZnFe_2O_4 | Ceramic | 4.8 | | 26.5 | <1.7 |
| MgFe_2O_4 | Ceramic | 5.2 | 14.8 | 12.1 | |
| $\gamma\text{-Fe}_2\text{O}_3$ | Co precipitation | 4.1 | | 23.0 | |

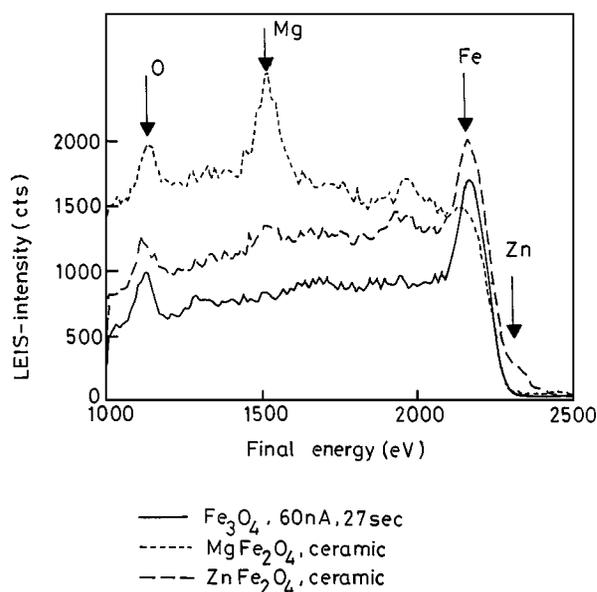


Figure 3 Superimposed LEIS spectra for various ferrites.

LEIS for zinc, because this is not the case for pure zinc where no matrix effects are expected [11]. The iron peak from ZnFe_2O_4 and Fe_3O_4 samples have almost identical peak areas while the iron peak of magnesium ferrite is almost half the size. The amount of iron on the surface of $\gamma\text{-Fe}_2\text{O}_3$ is less with respect to Fe_3O_4 .

ZnFe_2O_4 is a normal spinel where Zn^{2+} is exclusively found on the tetrahedral sites while MgFe_2O_4 is an inverse spinel where Mg^{2+} is found on the octahedral sites [12]. The structure of Fe_3O_4 can be written as $(\text{Fe}^{3+})_A[\text{Fe}^{3+}\text{Fe}^{2+}]_B\text{O}_4$ while $\gamma\text{-Fe}_2\text{O}_3$ is known to be a vacancy ordered spinel having the structure $\text{Fe}^{3+}[(\text{Fe}^{3+})_{5/3}\square_{1/3}]_B(\text{O}^{2-})_4$. The presence of vacancies on the octahedral sites have been confirmed by neutron diffraction studies [13].

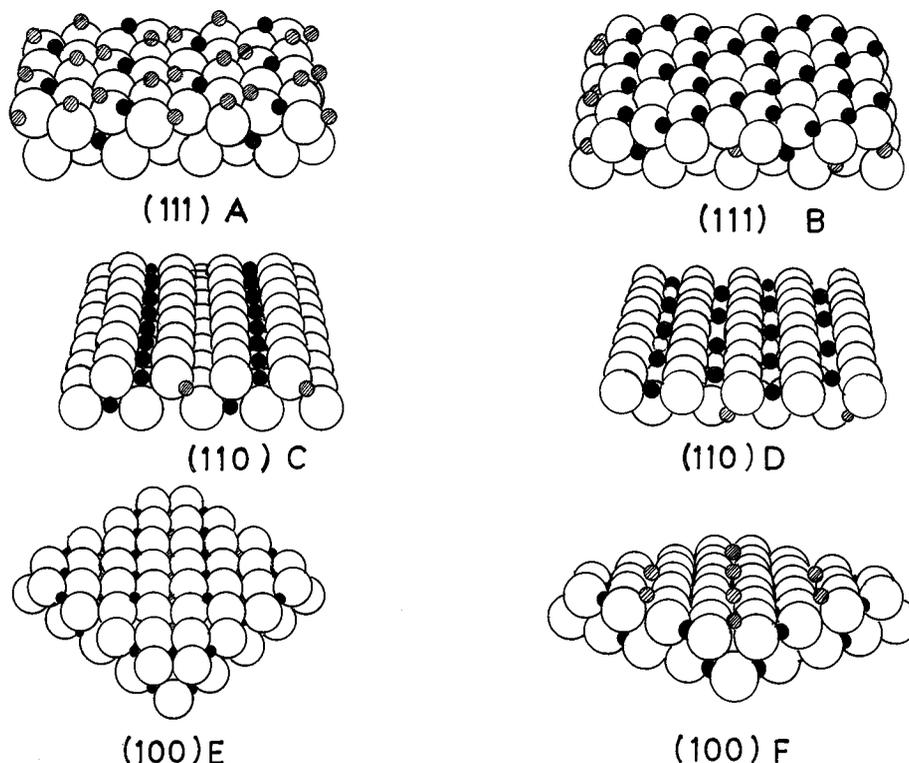


Figure 4 Various planes possible on a spinel surface.

Since LEIS cannot distinguish between Fe^{3+} and Fe^{2+} , the LEIS spectra for ZnFe_2O_4 and Fe_3O_4 can be thought of as the same, atleast for the iron and oxygen signals. The reason for the reduction of Fe on the surface of $\gamma\text{-Fe}_2\text{O}_3$ could be because of the fact that vacancies do appear on the surface of the vacancy ordered spinels like $\gamma\text{-Fe}_2\text{O}_3$. This assumption, though not supported by any other evidence, appears to hold since the precursors used for the preparation of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ were the same and any impurity influence on the LEIS signal is equally applicable for both. In a normal 2-3 spinel structure such as ZnFe_2O_4 , 8 of the 64 sites are occupied by divalent cations and the 32 B sites are filled with trivalent cations. In inverse spinels such as MgFe_2O_4 , 8 Fe^{3+} ions are in A sites and the Mg ions occupy B positions [14]. In a typical spinel 6 different low index planes can be distinguished (cf. Fig. 4). According to Knozinger and Ratnaswamy [15] there are A(111), B(111), C(110), D(110), E(100) and F(100). All planes except B(111) and D(110) have both A and B sites on the surface [15].

Ziolkowski and Barbaux [16] have predicted through semiempirical calculations that in the case of spinels like Co_3O_4 it is the A(111) and D(110) planes which are energetically favoured on the surface, whereas Shelef and Yao [17, 18] with the aid of LEIS concluded that tetrahedral sites are not on the surface despite low resolution of their experiments. The above findings also receive support from the studies done by Beauflis and Barbaux [19, 20] using differential neutron diffraction. They have concluded that in systems like MgAl_2O_4 and Co_3O_4 only D(110) and B(111) planes are exposed on the surface.

The very fact that only Mg is detected on the surface of MgFe_2O_4 and practically no zinc is detected on the

surface of ZnFe_2O_4 confirms the idea that it is the octahedral sites which are exposed on the surface of spinel ferrites. This is based on the fact that the magnetisation of MgFe_2O_4 has been satisfactorily explained based on the idea that Mg^{2+} has a strong octahedral site preference, whereas Zn^{2+} has a strong tetrahedral site preference. Thus by taking into account of all probable planes that are on the surface of the spinels and considering the fact that it is the octahedrally preferred cations that are detected on the surface of the ferrites, it can be concluded that in spinel ferrites it is the octahedral sites that are exposed on the surface. So going by the notation of Knozinger and Ratnaswamy [15] the probable planes are the B(111) and D(110) (cf. Fig. 4). This has been concluded based on the fact that octahedral sites occur only on D(110) and B(111) planes. The above findings by LEIS are in good agreement with the observations made by Jacobs *et al.* on zinc aluminate catalysts [21].

4. Conclusion

The LEIS experiments conducted on spinel ferrites gives clear indication that in spinel ferrites it is the octahedral sites that are exposed on the spinel surface and the prediction that D(110) or B(111) are the preferentially exposed planes on spinel ferrites surfaces gives scope for selecting catalytically active cations in spinel type compounds and this enables tailor making compounds for potential catalytic reactions.

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