NUKLEONIKA 2015;60(1):143–145
doi: 10.1515/nuka-2015-0024

ORIGINAL PAPER

DE GRUYTER
OPEN

Position of Fe ions in MgO crystalline structure

**Jacek Szczerba,
Ryszard Prorok,
Paweł Stoch,
Edyta Śnieżek,
Ilona Jastrzębska**

Abstract. Magnesium oxide (MgO) is one of the most important raw materials in many branches of industry. Magnesium oxide is a popular refractory raw material because of its high refractoriness and high resistance to basic slags and environment. In many cases, use of MgO is limited by its properties, especially the presence of secondary phases like iron oxides. The amount and distribution of iron oxides can strongly influence the technological properties of MgO and depend on the manufacturing method, particularly the heat-treatment process. The aim of the study was to evaluate the influence of the heat-treatment process on amount and distribution of iron ions in a magnesium oxide lattice. The ^{57}Fe Mössbauer effect measurements of fused and sintered magnesium oxide samples doped by the iron oxide were conducted. Investigation reveals in both cases the presence of Fe^{2+} as well as Fe^{3+} ions. Fe^{2+} ions occupy Mg^{2+} octahedral sites in the MgO lattice, whereas the Fe^{3+} ions are located in highly distorted octahedral coordination. The amount of Fe^{2+} varies from around 66% for fused samples to 30% for sintered samples.

Key words: Mössbauer spectroscopy • MgO • Fe ions • crystal structure

Introduction

Magnesium oxide is a substance with versatile applications, but use of MgO for specific and advanced application is limited by its purity. One of the most common admixtures coexisting with magnesium oxide are iron oxides, whose amount and distribution strongly influence the properties of MgO, such as melting point, mechanical properties at high temperatures, corrosion resistance, and others. This is particularly important in the case of refractory materials, which work under hard conditions, such as high temperatures, reducing or oxidizing conditions, and so on.

The refractory industry uses a relatively high-purity magnesium oxide called magnesia; amount and distribution of iron oxides in magnesia depend on quality and type of starting raw materials and, on the other hand, on the manufacturing process. Magnesia during commercial production is usually subjected to sintering or melting techniques. These two types of heat treatment processes strongly influence the properties of magnesia with respect to amount and distribution of iron oxides. This is the reason why determination of heat treatment in terms of amount and location of iron oxides in an MgO crystal structure is very important.

MgO crystallizes in the regular system with an *Fm*3*m* space group. Iron in MgO mainly occurs as Fe^{2+} and Fe^{3+} ions. The ion radius of Mg^{2+} (0.72 Å [1]) is close enough to the ion radius of Fe^{2+} (0.63 Å [1]) that enables Fe^{2+} to easily substitute Mg^{2+} ions

J. Szczerba, R. Prorok✉, P. Stoch, E. Śnieżek, I. Jastrzębska
Department of Ceramics and Refractories, Faculty of Material Science and Ceramics, AGH – University of Science and Technology, 30 A. Mickiewicza Ave., 30-059 Kraków, Poland,
Tel.: +48 12 617 2462, Fax: +48 12 633 4630,
E-mail: rprorok@agh.edu.pl

Received: 18 June 2014
Accepted: 2 November 2014

and creates with MgO unlimited solid solutions called magnesiowüstite, whereas Fe^{3+} located in octahedral positions can highly distort the MgO lattice and at a higher amount can undergo clustering in a new magnesioferrite phase ($MgFe_2O_4$). $MgFe_2O_4$ belongs to the spinel group in which Fe^{3+} cations can occupy both octahedral and tetrahedral sites [2]. Formation of magnesiowüstite in an MgO lattice is observed at high temperatures, and during slow cooling, it transforms to magnesioferrite [3]. Therefore, depending on cooling rates, different amounts of both phases are observed [4, 5]. The influence of synthesis conditions on crystal phase formation in the MgO-FeO-Fe_2O_3 system has been studied earlier [4, 5], but sample-preparation methods were significantly different from those implemented in industry. Taking this into account, this work was focused on the behavior of iron ions in an MgO lattice in materials synthesized under conditions corresponding to those used in industry.

Materials and methods

Chemically pure magnesium oxide (Chempur) and iron (III) oxide (Avantor) were used as starting materials. The samples were prepared by mechanical mixing of MgO with Fe_2O_3 at 0.5 wt% addition in relation to MgO. The mixed powder was pressed into pellets under the pressure of 100 MPa and divided into two groups; one was sintered at 1800°C, and the second one was fused in an electric arc furnace. The sintered sample was designated as S and the fused sample as F.

After the heat treatment, samples were examined by the XRD analysis in order to determine phase composition. The measurements were carry out in a range of 2θ° = 5–90° (Panalytical X'Pert-Pro diffractometer).

Investigation of the Mössbauer effect was conducted by a transmission technique on ^{57}Fe nuclei at room temperature. Masses of the samples were selected according to approximation of the thin absorber model. As the source of radiation ^{57}Co in an Rh matrix of 15-mCi activity was used. The obtained spectra were fitted by the least square method in order to determine hyperfine interaction parameters. The spectra were processed using Gaussian distribution of quadrupole splitting (QS). Paramagnetic doublets were fitted using two different components, the first corresponding to Fe^{2+} and the second to Fe^{3+}.

Results and discussion

The results of phase compositions of the S and F samples, obtained from XRD analysis, are presented in Figs. 1 and 2. The studies revealed the presence of magnesium oxide as the only crystal phase.

The ^{57}Fe Mössbauer spectra of the S and F samples are shown in Figs. 3 and 4. Hyperfine parameters corresponding to them are presented in Table 1.

The obtained spectra of the S and F samples were fitted by two independent density probability

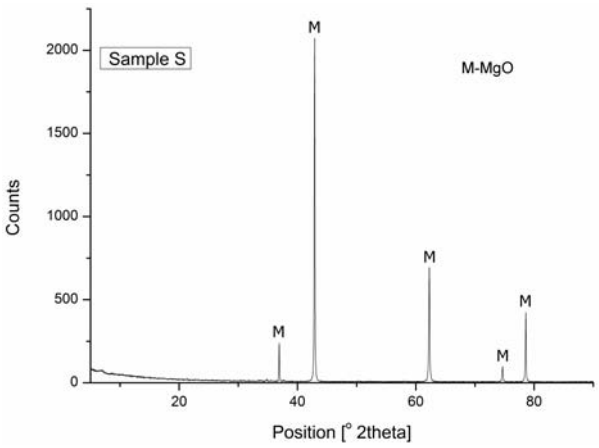

Fig. 1. Results of XRD analysis of the S sample.

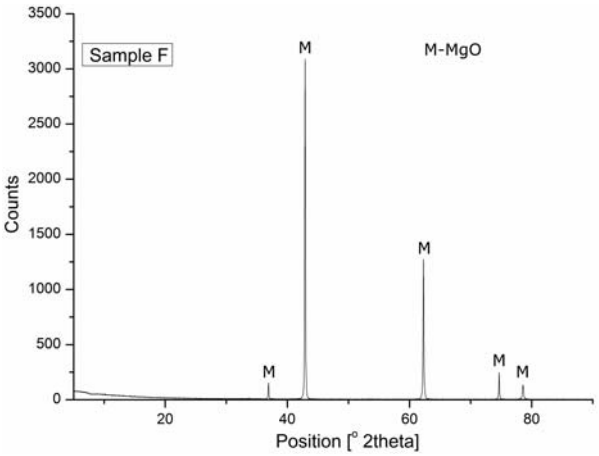

Fig. 2. Results of XRD analysis of the F sample.

distributions of QS. First of them (component 1 in Table 1) was modeled by a single Gaussian distribution. Isomer shift (IS) in this case corresponds to Fe^{2+} in octahedral coordination. Taking into account the high sensitivity of Fe^{2+} on changing the electric field gradient at the atomic nucleus, the determined QS parameter of approximately 0.0 mm/s indicates an almost ideal octahedral symmetry of Fe^{2+} in an MgO lattice. This was also confirmed by the narrow width of the QS distribution, δQS of approximately 0.2 mm/s.

The second distribution (component 2 in Table 1) with the lower value of IS of approximately 0.3 mm/s

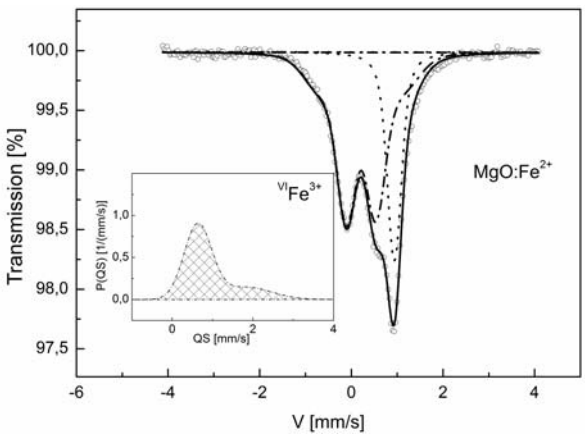

Fig. 3. ^{57}Fe Mössbauer spectrum of the S sample at 300 K and quadrupole splitting distribution.

Table 1. Hyperfine interaction parameters of the S and F samples at 300 K (A – surface area; Pp – distribution probability; IS – isomer shift; QS – quadrupole splitting; and δQS – width of the quadrupole split distribution)

Sample	Component	A [%]	Pp [%]	IS [mm/s]	QS [mm/s]	δQS [mm/s]
S	1	29	100	1.04	0.001	0.217
	2	71	76	0.32	0.633	0.343
			24		1.822	0.645
F	1	66	100	1.03	0.002	0.216
	2	34	56	0.33	0.577	0.299
			44		1.612	0.667

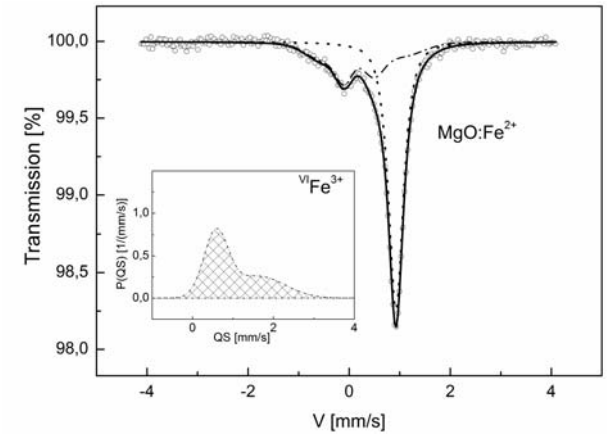

Fig. 4. ^{57}Fe Mössbauer spectrum of the F sample at 300 K and quadrupole splitting distribution.

corresponds to Fe^{3+} ions. In this case, satisfactory fit of the experimental data to the theoretical model was obtained by presentation of this site as the sum of two Gaussian distributions, which could correspond to two sites of iron in the spinel structure. The higher QS of approximately 1 mm/s corresponds to Fe^{3+} ions in a highly distorted octahedral coordination, causing creation of a strong gradient of electric field in the location of the atomic nucleus. Additionally, strong broadening of QS above 0.5 mm/s indicates significant disorder of this position. The second Gaussian distribution with a lower value of QS indicates a higher order and better symmetry of this position of iron.

According to the obtained results, it could be concluded that all Fe^{2+} ions substitute Mg^{2+} in cationic sublattices of MgO. The Fe^{3+} ions can also substitute Mg^{2+}, but in this case, in order to maintain the neutrality of crystal charge, it must create an Mg^{2+} vacancy. The Mg^{2+} vacancy incorporated with a Fe^{3+} ion causes a strong distortion of this position in the crystal lattice, which is associated with the strong gradient of electric field. The position of Fe^{3+} ion that is not incorporated with Mg^{2+} vacancy has a higher symmetry. Both these effects could be related to reorganization of the MgO lattice due to early-stage formation of $MgFe_2O_4$ clusters. A similar effect was observed previously [5].

We could also notice the absence of magnetic coupling among Fe^{3+}-O-Fe^{3+}, which indicates a very limited clustering of iron ions associated with creation of magnesioferrite [4, 6].

Conclusions

The investigation revealed, in both cases, the presence of three subspectra, which indicated a presence of iron ions in different locations in an MgO lattice. In both cases, fused as well as sintered samples, Fe^{2+} ions showed an almost ideal symmetry of charge distribution at the iron site, which was possible only when Fe^{2+} substituted Mg^{2+} in the MgO lattice. In this case, the content of Fe^{2+} ions varied from 66% for fused samples and approximately 30% for sintered samples. The Fe^{3+} ions are located in highly distorted octahedral coordination, which was evidenced by hyperfine interaction parameters.

Acknowledgments. This work was supported by the grant no. NCBIR-INNOTECH-K2/IN2/16/181920/NCBR/13 of the Polish Government.

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