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Spectroscopic studies of Ti^{3+} ions speciation inside MgAl_2O_4 spinels

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Abstract: An electron paramagnetic resonance (EPR) investigation on Ti-doped MgAl_2O_4 spinels has been made in order to study the Ti^{3+} sites. The study we present here concerns the angular dependencies of the Ti^{3+} EPR lines and the variations of the EPR spectra due to a modification of the TiO_2 content or of the chemical composition from MgAl_2O_4 to MgAl_4O_7 and $\text{MgAl}_6\text{O}_{10}$. In all the studied samples except one, we observe the presence of both Mn^{2+} and Ti^{3+} ions. No correlation was observed between Ti^{3+} amount and TiO_2 content; the titanium ions are located in three different sites : the octahedral B site of the spinel structure; the tetrahedral A site and a last site which remains unclear. On the contrary, the major part of the Mn^{2+} ions is assumed to be in the tetrahedral A site of the spinel structure and a minor part in the octahedral B site. Our work demonstrates the overall interest of EPR spectroscopy in the study of the paramagnetic optically active ions inside optical materials.

1. Introduction

Among the crystalline compounds, the spinel oxides present a large range of interesting electrical, magnetic and optical properties. The magnesium–aluminum spinel MgAl_2O_4 in particular has been comprehensively studied and previous works point out a high melting point (2135°C [1]), a high hardness (7.5–8 Mohs [2]), and interesting thermal and optical properties [3]. MgAl_2O_4 can crystallize in the “normal” or “inverse” spinel structure. This structure may be described as a cubic closest-packed array of oxygen atoms, with one-eighth of the tetrahedral sites and one-half of the octahedral sites filled. The space group is $\text{Fd}\bar{3}\text{m}$ (O_h^7) and the lattice parameter a equals to 8.08435 Å [4]. In the case of a “normal” spinel structure, Mg^{2+} ions are

located in tetrahedral sites and the Al^{3+} ions are in octahedral sites. Moreover, this compound can be easily doped by transition metal ions such as Ti, Mn [5], Cr [6], Fe [3] or V [7]. In the particular case of Ti-doped MgAl_2O_4 spinel, a strong visible blue emission around 455–490 nm under excitation at 280 nm was observed and attributed to a charge transfer between the Ti^{4+} and Ti^{3+} ions which replaced some of the Al^{3+} ions in octahedral sites [8,9]. This large Stokes shift ($\approx 40,000 \text{ cm}^{-1}$ from 280 to $\approx 500 \text{ nm}$) was understood as the consequence of a large lattice distortion around the titanium ion [8]. Nevertheless, the precise distortions of the environment of the Ti^{3+} ion and the presence of trivalent titanium remain to be explained. Thus, the aim of this work is to determine the nature and the site of the different paramagnetic ions present in Ti-doped MgAl_2O_4 spinel and to study the distortions of the Ti^{3+} ion environment. For that purpose, we used electron paramagnetic resonance (EPR), a very sensitive tool for the analysis of paramagnetic species in crystals and glasses.

2. Experimental procedure

Samples were prepared by Jouini et al. [5] using the modified μ -pulling down method (μ -PD) which has been detailed elsewhere [5, 8]. Synthesis was conducted in a reducing Ar atmo sphere to avoid all oxidation of the special Iridium crucible of the experimental setup and the different samples were Ti-doped at 0.1, 0.4, 0.5, 0.6, 0.8 and 1 mol%. The samples are cylindrical with the c-axis parallel to the direction of the sample. After synthesis, X-band EPR spectra have been recorded at 5K using an OXFORD He cryostat on a EMX Brücker EPR spectrometer. The microwave power used for the experiments is 0.01mW in order to avoid saturation of Ti^{3+} EPR lines. This power was determined in relation with the saturation properties of Ti^{3+} EPR lines at 5K. Angular dependencies of the different Ti-doped MgAl_2O_4 samples EPR spectra were recorded by rotating the samples from a reference EPR spectrum (0°) corresponding to a magnetic field B_0 parallel to the c-axis to a B_0 in the (ab) plane (90° sample). The different EPR spectra presented in this report have been normalized to the receiver gain and to the sample weight in order to obtain quantitative comparison of the EPR lines intensities between the different samples. Moreover, it is worth reminding that EPR spectroscopy allows the absorbance spectra (i.e. the experimental spectrum integrated once) of all EPR lines corresponding to one paramagnetic ion

in a specific site to coincide directly with the number of spins of this paramagnetic ion inside the sample [10].

3. Results

3.1. Influence of TiO_2 content

Fig. 1 presents the reference (c-axis parallel to B_0) X-band EPR spectrum of 0.1 TiO_2 - $MgAl_2O_4$ sample recorded at 5K with a power of 0.01mW and a frequency of 9.490 GHz. We observe a set of six strong and 10 weak lines correlated to the Mn^{2+} ions (electronic spin $S = \frac{5}{2}$, nuclear spin $I = \frac{5}{2}$) diluted inside the spinel structure. This spectrum is very similar to the spectrum obtained by Tomita et al. [11] into crystal manganese-doped spinel $Mn:MgAl_2O_4$. By calculating the spin Hamiltonian of the Mn^{2+} ion into $MgAl_2O_4$ powders, Shaffer et al. [12] predicted the presence of six sharp main lines corresponding to the hyperfine components of the $\Delta MS = \pm 1$, $\Delta MI = 0$ allowed transitions and 10 sharp $\Delta MS = \pm 1$, $\Delta MI = \pm 1$ forbidden transitions. So as a result, the different lines observed in Fig. 1 may be correlated either to a small zero field splitting (ZFS) due to high symmetry around Mn^{2+} ions or to three different Mn^{2+} environments inside the $MgAl_2O_4$ spinel structure. As Tomita et al. have observed before, we do not find any angular dependency of the EPR lines attributed to Mn^{2+} ions (cf. Fig. 4). Tomita et al. concluded to the existence of Mn^{2+} ions into two different spinels sites, a tetragonal one and an octahedral one. In our case, further EPR studies and simulation on Mn-doped $MgAl_2O_4$ spinels are required to discriminate between these two hypotheses. Fig. 2 presents the EPR spectra recorded with the c-axis parallel to the applied magnetic field B_0 of different spinels samples ($MgAl_2O_4$, $MgAl_4O_7$, $MgAl_6O_{10}$) doped with different amounts of titanium from 0.1 to 1mol%. We observe the presence of Mn^{2+} ion EPR lines in all studied samples. Moreover, there is no correlation between the increase of the TiO_2 content introduced inside the crystals and the Mn^{2+} EPR lines intensity. This result could be correlated to two different points. First, Mn^{2+} is mainly an impurity of the MgO powders used for the synthesis. Second, the TiO_2 doping content plays a role upon the redox couple between Mn^{2+} and Mn^{3+} ions inside the spinel crystal. But Mn^{3+} ions are diamagnetic and cannot be studied by EPR spectroscopy; however, optical measurements could be used to analyze Mn^{3+}

ions inside these samples. In addition to Mn^{2+} impurity EPR lines, for all samples except the $0.1\text{TiO}_2\text{-MgAl}_2\text{O}_4$ sample, we observe in Fig. 2 different EPR lines attributed to Ti^{3+} ions diluted inside these samples. The spin Hamiltonian of Ti^{3+} ion ($S = \frac{1}{2}$) is only described by a Zeeman effect without influence of crystalline field observed for paramagnetic species with electronic spin strictly higher than $\frac{1}{2}$ like Mn^{2+} ions [13]. This result means that each line observed on the spectrum can be directly attributed to a different Ti^{3+} environment inside the spinel structure. We will go further later in this study on the different environment around Ti^{3+} ions as a function of Ti content and the nature of the spinel. However, Fig.2 clearly shows that there is no correlation between the Ti^{3+} content and the amount of TiO_2 inserted inside the spinel matrix. Moreover, we observe that the higher Ti^{3+} content in these samples are always associated with the lower Mn^{2+} impurity content in the EPR spectra. This result could show the influence of the different ion redox couples in a reducing atmosphere synthesis.

3.2. Calculated EPR powder spectra from mono crystal experiments

These experiments make it difficult to directly compare EPR spectra because the shape of the Ti^{3+} EPR lines (position and intensity) depends on the orientation of the samples relatively to the applied magnetic field. The cylindrical shape in the (ab) plane of the different samples limits therefore the direct comparison of the EPR spectra on one orientation. A convenient way to compare the nature of different Ti^{3+} sites is to average the different EPR spectra recorded at different orientations. The resulting spectrum is equivalent to an EPR powder spectrum. In Fig. 3, we present the resulting calculated and normalized powder EPR spectra of different Ti-doped spinel samples. In this figure, two different types of EPR powder spectra of Ti^{3+} can be observed. The first Ti^{3+} powder EPR spectrum corresponds to the Ti-doped MgAl_2O_4 samples. As a function of TiO_2 doping content, the Ti^{3+} spectra seems to be equivalent even if the EPR spectra are the sum of two components related to Ti^{3+} and Mn^{2+} ions. On the contrary, calculated EPR powder spectra of $0.4\text{TiO}_2\text{-MgAl}_6\text{O}_{10}$ and $0.4\text{TiO}_2\text{-MgAl}_4\text{O}_7$ are similar and clearly different from $\text{TiO}_2\text{-MgAl}_2\text{O}_4$ samples. This result shows the presence of different Ti^{3+} sites and can be correlated either to the appearance of a new site or to a modification of the Ti^{3+} site speciation when the chemical composition is modified from MgAl_2O_4 to MgAl_4O_7 and $\text{MgAl}_6\text{O}_{10}$.

3.3. Angular dependencies of Ti^{3+} and Mn^{2+} EPR lines

Fig. 4 shows the EPR spectra of the $0.5TiO_2-MgAl_2O_4$ and $0.8TiO_2-MgAl_2O_4$ samples recorded under the same conditions as before but at different orientations (from 0° to 90°) of the sample's c-axis in regard to the magnetic field B_0 . First, we observe that the EPR lines of the Mn^{2+} ions show no angular dependencies. But as mentioned earlier, we observe on the spectra of $0.5TiO_2-MgAl_2O_4$ the presence of a combination of EPR lines corresponding to both Mn^{2+} and Ti^{3+} ions. Due to this combination, it is difficult to follow the angular dependencies of the different Ti^{3+} EPR lines. By contrast, the most Ti-doped samples present the lowest Mn^{2+} impurities content (cf. Section 3.1). Thus, it is easier to follow the evolution of the Ti^{3+} EPR lines during the rotation of the sample on the spectra of $0.8TiO_2-MgAl_2O_4$. We observe here at least three different Ti^{3+} sites inside the spinel structure.

3.4. EPR spectra of the $0.6TiO_2-MgAl_2O_4$ sample annealed at high temperature

The influence of annealing at $1400^\circ C$ in air for 30h is shown for the $0.6TiO_2-MgAl_2O_4$ sample in Fig. 5. With this heat treatment, we observe by EPR spectroscopy a complete disappearance of the EPR lines attributed to Ti^{3+} lines. By contrast we only observe a slight decrease of the Mn^{2+} EPR lines. This confirms the results of Jouini et al. [8] who observe a complete disappearance of the bluish color of the same sample. They attribute this disappearance to (i) a redistribution of the cation sites in the spinel crystal and/or (ii) to the oxidation of the transition metal ions ($Ti^{3+}-Ti^{4+}$) [8]. As will be discussed in the next section, we attribute part of the different Mn^{2+} EPR lines to a redistribution of Mn^{2+} ions in the different sites in the spinel structure. Since we do not observe any modification of the EPR lines attributed to the Mn^{2+} ions we conclude that the disappearance of the bluish color of the sample and the disappearance of the Ti^{3+} EPR line is due to the oxidation of the transition metal ions.

4. Discussion

4.1. Sites of Ti^{3+} ions

We observed by EPR spectroscopy in $0.8\text{TiO}_2\text{-MgAl}_2\text{O}_4$ and $0.4\text{TiO}_2\text{-MgAl}_4\text{O}_7$ samples the presence of, at least, three different sites of Ti^{3+} into the spinel structure. However, previous studies by optical absorption [5], luminescence [6,8] or optically detected magnetic resonance (ODMR) [9] on Ti-doped MgAl_2O_4 samples attributed the observed optical properties to a trivalent titanium in an unique site which consists of a Ti^{3+} in the Al^{3+} octahedral site of the spinel structure (B site). To explain this apparent inconsistency between our EPR observations and the results of previous studies we will consider first the spinel structure and second the possible unusual position of some atoms in the crystal structure. First, as previously mentioned, only one-eighth of the tetrahedral and one-half of the octahedral sites in the spinel structure are occupied respectively by Mg^{2+} or Al^{3+} ions. When heated, some Al^{3+} and Mg^{2+} ions may change their sites, giving rise to a more random distribution of the cations. The fraction of Al^{3+} ions in the Mg^{2+} sublattice is usually denoted by i and it was demonstrated by nuclear magnetic resonance (NMR) and infrared absorption that i takes values from 0.1 to 0.6 in synthetic MgAl_2O_4 spinels [14]. Thus, we speculate that one of the Ti^{3+} sites observed by EPR spectroscopy is linked with a Ti^{3+} in the octahedral B site while another one is linked with an ‘‘inverted’’ Ti^{3+} in a tetrahedral A site of the spinel structure. Second, the spinel structure may contain a part of ions in insertion site which corresponds to unoccupied sites in a pure spinel structure. Due to the different neighbor’s nature and position, the environment’s distortions of these ions into insertion sites will be very different from the distortions of the spinels A or B sites. Thus, we speculate that the third EPR lines attributed to Ti^{3+} originate from trivalent titanium ions in such insertion sites. In that case the important variations of the EPR spectra between $0.5\text{TiO}_2\text{-MgAl}_2\text{O}_4$, $0.4\text{TiO}_2\text{-MgAl}_4\text{O}_7$ and $0.4\text{TiO}_2\text{-MgAl}_6\text{O}_{10}$ samples results from O^{2-} or Mg^{2+} vacancies and will constitute another type of Ti^{3+} site. Sato et al. [9] have already attributed an emission band at 720 nm observed in Ti-doped MgAl_2O_4 spinel under excitation at 280 nm to Mg^{2+} vacancy. However, to confirm these hypotheses and to analyze the difference in the site population as a function of the spinel matrix, more detailed EPR experiments and simulations are required.

4.2. Sites of Mn^{2+} ions

In this work, the observed EPR signal due to Mn^{2+} ions maybe attributed either to three different Mn^{2+} environments inside the MgAl_2O_4 spinel structure or to a ZFS due to high symmetry around

Mn²⁺ ions. Considering absorption [5], luminescence [6, 15] or EPR measurements [15], previous research has concluded to the presence of the Mn²⁺ ion in the A site of the spinel structure, i.e. in the tetrahedral site. However, as said before, Tomita et al. [11] pointed out that the spinel has two types of sites for a metal ion (the tetragonal A site and the octahedral B site). They assign a major part of the Mn²⁺ ions in the A site (tetrahedral) and a minor part in anti sites, i.e. in the B site (octahedral). As with titanium ions we assume that one of the EPR lines is linked to the Mn²⁺ ions in the A site and another one to the Mn²⁺ ions in the B site. However, we only observe a reduction of the intensity of the EPR signal when the number of oxygen and magnesium vacancies increase (Figs.2 and 4). To this day, some general characteristics of Mn²⁺ site linked with the third observed EPR line remain unspecified.

4.3. Relation between the TiO₂ and Ti³⁺ concentrations.

As mentioned in Section 3, we saw no correlation between the amount of TiO₂ inserted into the spinel matrix and the Ti³⁺ content observed by EPR spectroscopy. This inconsistency requires more studies to be fully understood. Electron microprobe analysis will determine the repartition and the concentration of trivalent titanium in the sample and EPR, in addition to a reference sample with a known spin concentration, will be useful to study the number of Ti³⁺ in each different sites.

5. Conclusion

Thanks to EPR spectroscopy, we observed the presence in Ti-doped MgAl₂O₄ spinels of different sites of trivalent titanium and manganese ions. To attribute these different lines to different environments, we considered some previous works based on luminescence, absorption and ODMR experiment and we also considered the variations of the EPR spectra when the chemistry of the sample is modified. For Ti³⁺ ions, we conclude that the major part of the ions is located in the octahedral B site of the spinel structure. A minor part of the Ti³⁺ ions are in tetrahedral sites and one of the sites is assumed to be correlated to some ions in insertion sites. Concerning the Mn²⁺ ions, we conclude that a major part of the ions are in the tetrahedral A site of the structure while a minor are in the octahedral B site. Nevertheless more EPR experiments and simulations

are required to confirm these attributions. However, this work demonstrates the interest of the EPR measurement in the study of the environment of the active ions in optical materials.

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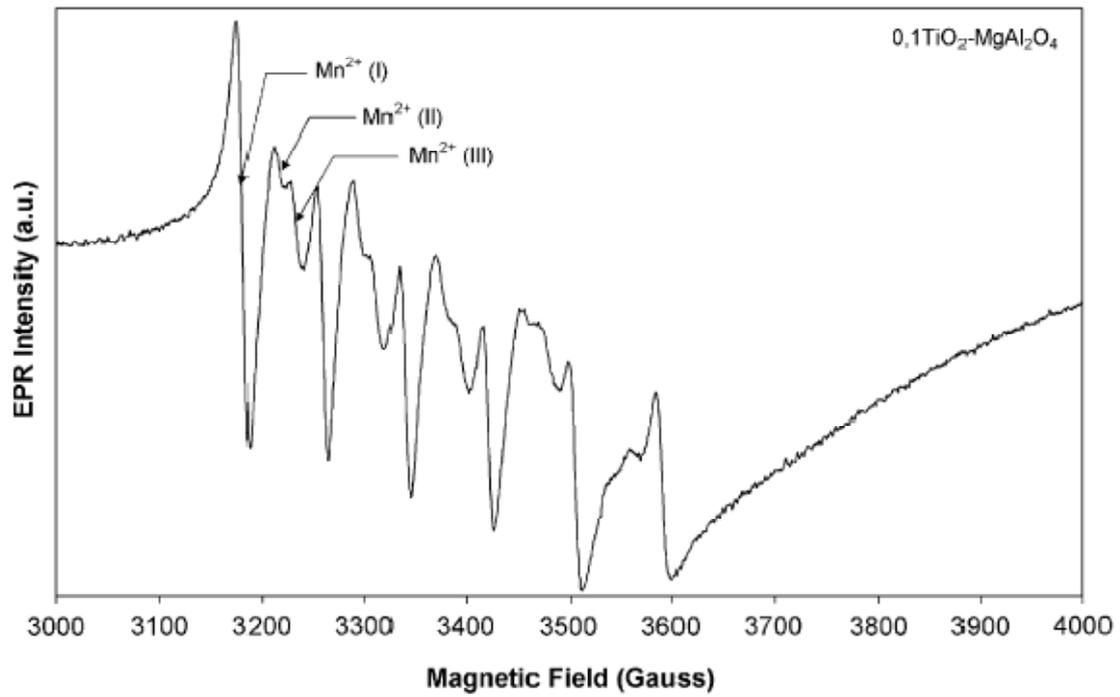


Fig. 1. EPR spectrum of the 0.1TiO₂-MgAl₂O₄ sample recorded with *c*-axis parallel to the direction of the applied magnetic field B_0 ($T = 5$ K, $\nu = 9.490$ GHz, $p = 0.01$ mW).

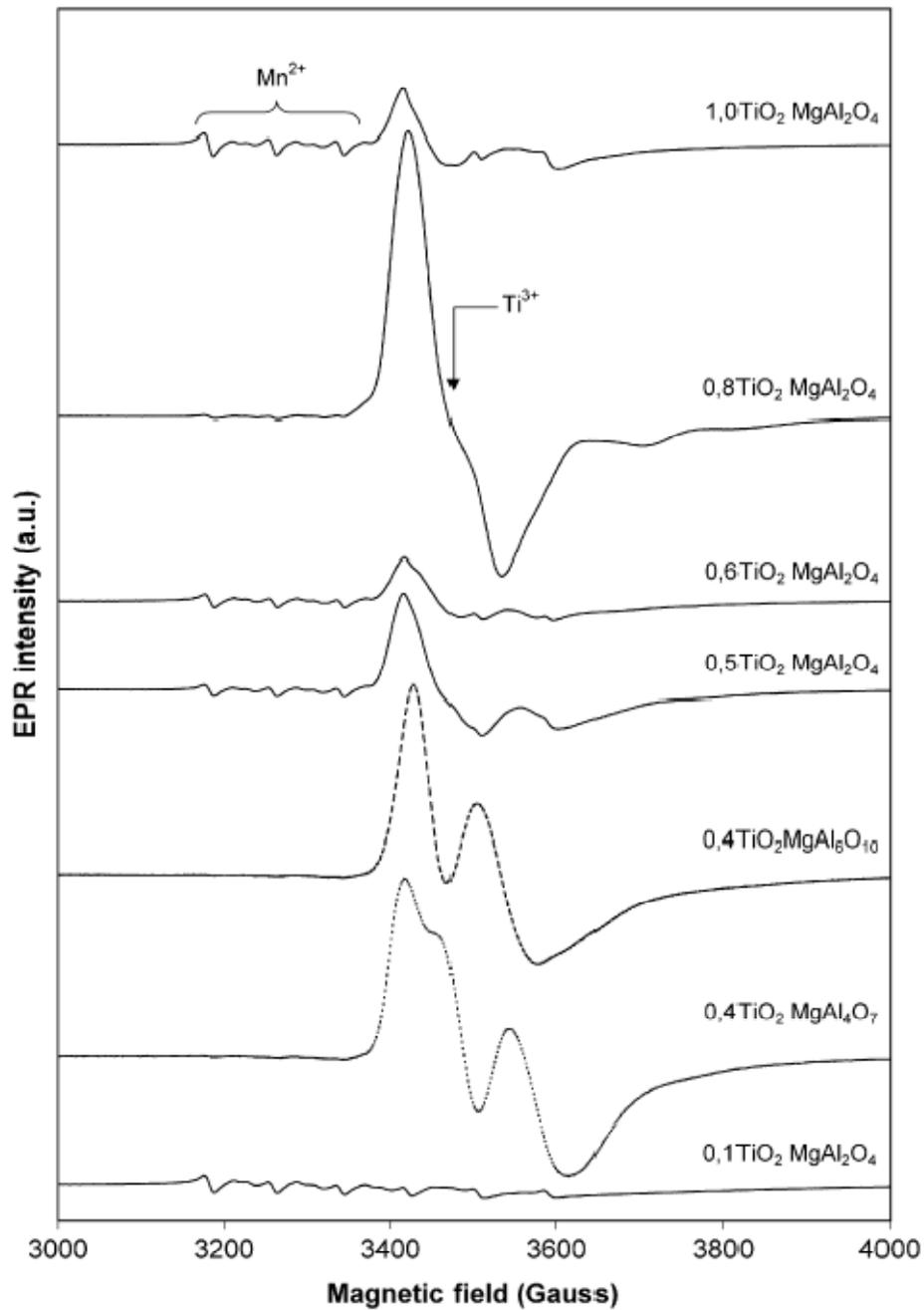


Fig. 2. EPR spectra of different spinel samples doped with different amounts of titanium from 0.1 to 1.0 mol% recorded with *c*-axis parallel to the direction of the applied magnetic field B_0 ($T = 5$ K, $\nu = 9.490$ GHz, $p = 0.01$ mW).

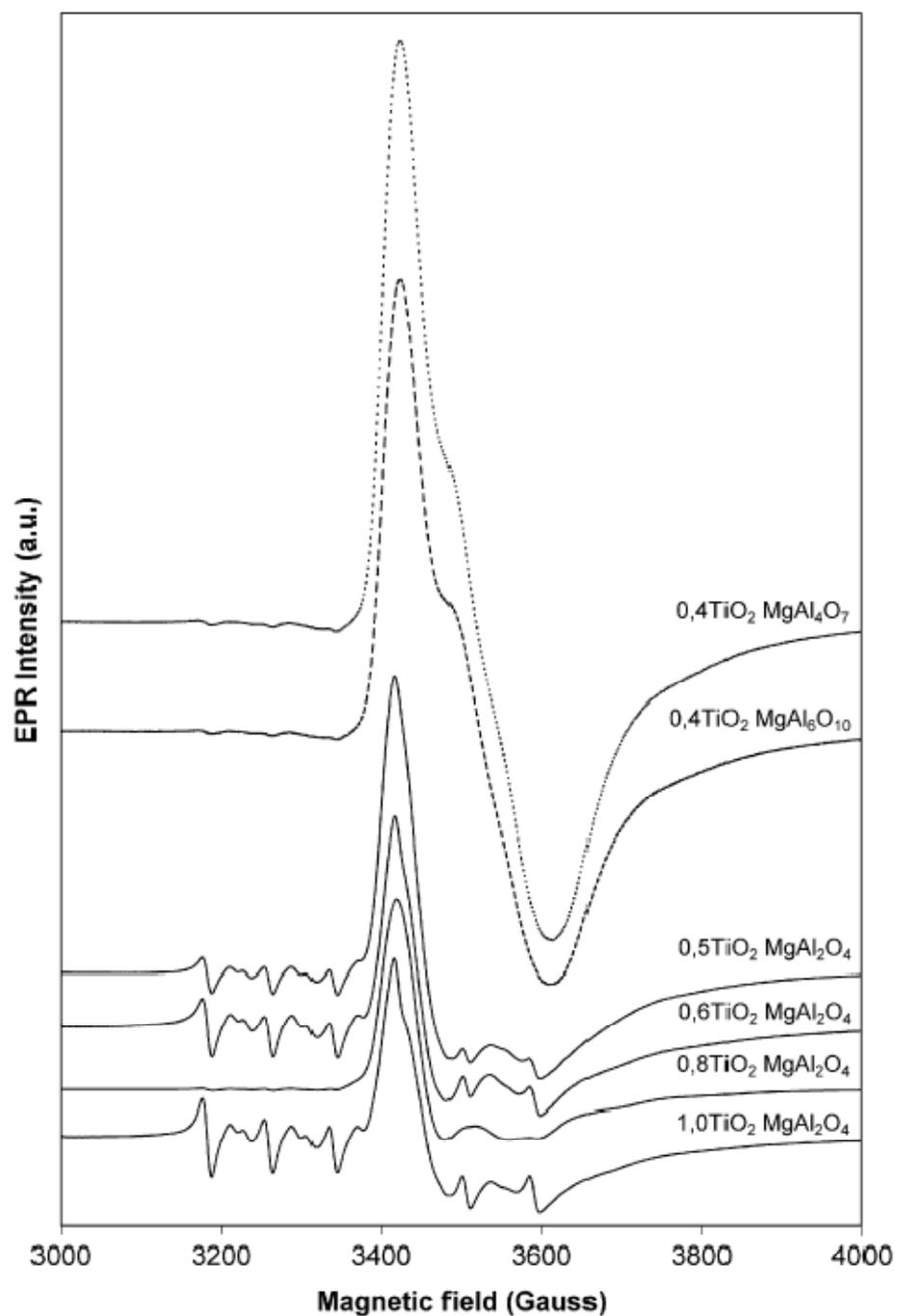


Fig. 3. Calculated and normalized EPR powder spectra for different spinel samples doped with different amount of titanium from 0.1 to 1.0 mol% ($T = 5$ K, $\nu = 9.490$ GHz, $p = 0.01$ mW).

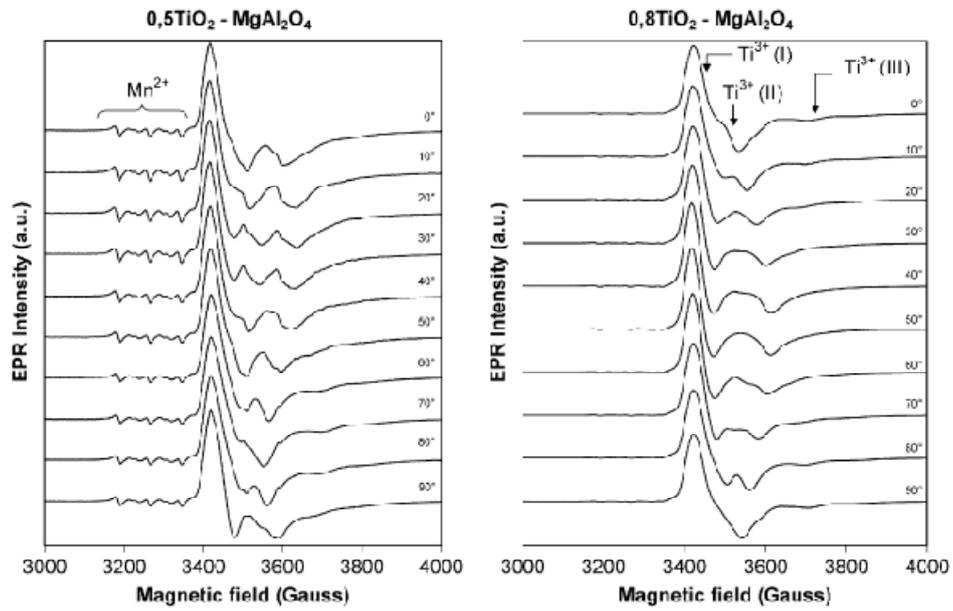


Fig. 4. EPR spectra angular dependencies of the 0.5TiO₂-MgAl₂O₄ and 0.8TiO₂-MgAl₂O₄ samples ($T = 5$ K, $\nu = 9.490$ GHz, $p = 0.01$ mW).

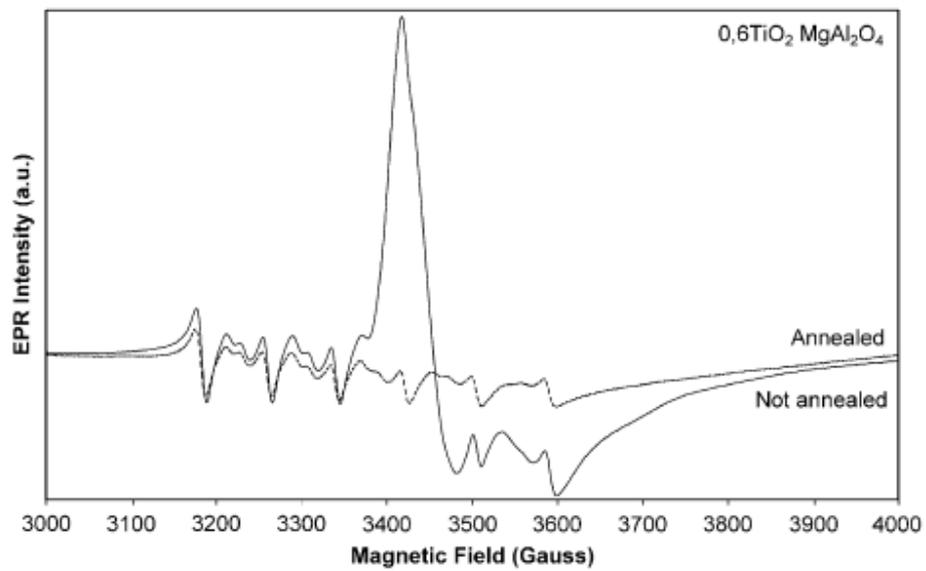


Fig. 5. Calculated and normalized EPR powder spectra of $0.6\text{TiO}_2\text{-MgAl}_2\text{O}_4$ spinel sample before and after heat treatment in air at 1400°C during 30 h ($T = 5\text{ K}$, $\nu = 9.490\text{ GHz}$, $p = 0.01\text{ mW}$).