Application of INAA for Aluminium Magnesium Oxide Materials Investigation

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APPLICATIONS

**MgO**
- \( T_{\text{melt}} = 2800 ^\circ \text{C} \)
- Cubic fcc
- \( Eg = 7.8 \text{ eV} \)

- **Insulator in industrial cables, heating elements**
- **Substrate for Thin Film Formation**

**MgAl_2O_4**
- \( T_{\text{melt}} = 2135 ^\circ \text{C} \)
- \( E_g = 9 \text{ eV} \)

- **Fireproof Board, Ceiling materials**
- **Gemstone**
- **DOSIMETRIC MATERIALS**
- **LASER MATERIALS**

- **Potential material for fusion reactor application such as dielectric windows for radio – frequency heating systems and insulators for magnetic coils**

- **Candidate materials for unreactive diluent of composite nuclear fuel**
SPINEL APPLICATION

The name "spinel" is derived from the Greek word for "spark," referring to its fiery red color.

Oxide spinels have attracted great attention in the field of Earth science because of their importance as constituent minerals in many igneous and metamorphic rocks.

Natural Spinel Gemstones
OBJECTIVES

- Natural minerals and synthetic materials are not pure and always contain optically active dopant ions. The most common activators found in natural minerals and synthetic materials are transition metal ions (Cr, Mn, Fe). Type, site location and oxidation degree of dopant ions strongly influence the material properties.

- Current understanding of the role of transition metal impurities in the optical absorption and photoluminescence properties of magnesium oxide (MgO) and magnesium aluminium spinel (MgO•nAl$_2$O$_3$) crystals is still incomplete, particularly in relation to the effects of material irradiation with neutrons.
OBJECTIVES

- The report presents study of the structure and phase transitions in natural and synthetic MgO•nAl₂O₃ crystals and MgO containing transition metal ions (Cr, Fe, Mn) and irradiated with fast neutron.

- The INAA method is applied for the analysis of micro (Cr, Mn, Fe) and macro (Al, Mg) components in the MgO, synthetic and natural magnesium aluminium spinel crystals.
SAMPLES

Natural spinel crystals from Ural and Pamir deposits

synthetic magnesium aluminium spinel single crystals with different stoichiometry (\( \text{MgO} \cdot n\text{Al}_2\text{O}_3 \) ) grown by Verneuil and Czochralski methods were used.
METHODS

- For the analysis of macro components (Al and Mg) 15-25 mg sample have been irradiated with neutron flux $1.6 \times 10^{13}$ cm$^{-2}$ s$^{-1}$ for 30 s in the rabbit system.

- Impurities were analysed with irradiation 100-400 mg samples in the neutron flux $3.1 \times 10^{13}$ cm$^{-2}$ s$^{-1}$, time of irradiation – 70 h, cooling time – 5-6 weeks or more.

- Gamma-spectra were measured using the HPGe detector. Analytical $\gamma$-lines: Mg-843.8 keV, Al – 1778.8 keV, Cr – 320.1 keV, Mn – 846.7 keV and Fe – 1099.2, 1291.6 keV.

- The detection limit (ppb) was for Cr – 2, Mn – 100, Fe – 1000.
METHODS

- PLE spectra of Mgo and spinel crystals were measured at the room temperature using conventional equipment consisting of two monochromators and deuterium lamp as a light source with continuous wavelength.

- PL spectra were measured using ANDOR grating monochromator, combined with CCD camera.

- Optical absorption spectra were measured using the “Specord 210” double-beam spectrophotometer operating in the spectral region of 190–1100 nm.

- Chromium ions were used as a sensitive probe for absorption and luminescence spectra analysis.
The impurity concentration was detected by means of the instrumental neutron activation analysis.

Concentration of impurities (in mass%) in MgO

<table>
<thead>
<tr>
<th>Notation</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO (1)</td>
<td>4.4x10^{-3}</td>
<td>5.7x10^{-3}</td>
<td>9.0x10^{-3}</td>
</tr>
<tr>
<td>MgO (2)</td>
<td>2.7x10^{-3}</td>
<td>5.6x10^{-3}</td>
<td>12x10^{-3}</td>
</tr>
<tr>
<td>MgO (3)</td>
<td>3.7x10^{-3}</td>
<td>5.6x10^{-3}</td>
<td>7.3x10^{-3}</td>
</tr>
<tr>
<td>MgO (4)</td>
<td>8.5x10^{-4}</td>
<td>&lt;10^{-5}</td>
<td>7.3x10^{-4}</td>
</tr>
<tr>
<td>MgO (5)</td>
<td>1.75x10^{-4}</td>
<td>5.8x10^{-3}</td>
<td>1.1x10^{-2}</td>
</tr>
<tr>
<td>MgO (6)</td>
<td>1.75x10^{-4}</td>
<td>5.6x10^{-3}</td>
<td>3.7x10^{-3}</td>
</tr>
</tbody>
</table>
The contents of the macrocomponents of MgO·nAl₂O₃

<table>
<thead>
<tr>
<th>Notation</th>
<th>Introduced</th>
<th>Obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO·Al₂O₃ (MA 1:1)</td>
<td>1:1</td>
<td>1:0.9</td>
</tr>
<tr>
<td>MgO·Al₂O₃ (MA 1:1)</td>
<td>1:1</td>
<td>1:1.5</td>
</tr>
<tr>
<td>MgO·2Al₂O₃ (MA 1:2)</td>
<td>1:2</td>
<td>1:1.7</td>
</tr>
<tr>
<td>MgO·2.8Al₂O₃ (MA 1:2.8)</td>
<td>1:2.8</td>
<td>1:2.5</td>
</tr>
</tbody>
</table>
The impurity concentration was detected by means of the instrumental neutron activation analysis.

The concentration of the impurities in the spinel, mass %

<table>
<thead>
<tr>
<th>Notation</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black</td>
<td>1.5x10^{-3}</td>
<td>23</td>
<td>1.2</td>
</tr>
<tr>
<td>Pink</td>
<td>2x10^{-3}</td>
<td>2.9</td>
<td>0.31</td>
</tr>
<tr>
<td>Dark pink</td>
<td>8.0x10^{-2}</td>
<td>0.1</td>
<td>3x10^{-2}</td>
</tr>
<tr>
<td>Middle pink</td>
<td>7.0x10^{-2}</td>
<td>0.1</td>
<td>6x10^{-2}</td>
</tr>
<tr>
<td>Lilac</td>
<td>9.8x10^{-5}</td>
<td>0.02</td>
<td>1.31</td>
</tr>
<tr>
<td>MgO · Al₂O₃ (1)</td>
<td>0.43x10^{-4}</td>
<td>0.3x10^{-4}</td>
<td>1x10^{-3}</td>
</tr>
<tr>
<td>MgO · Al₂O₃ (2)</td>
<td>0.41x10^{-4}</td>
<td>0.16x10^{-4}</td>
<td>8.1x10^{-4}</td>
</tr>
<tr>
<td>MgO 2Al₂O₃</td>
<td>1.25x10^{-4}</td>
<td>0.17x10^{-4}</td>
<td>4x10^{-4}</td>
</tr>
<tr>
<td>MgO 2.8Al₂O₃</td>
<td>0.99x10^{-4}</td>
<td>0.2x10^{-4}</td>
<td>----</td>
</tr>
<tr>
<td>MgO·Al₂O₃ (MA 1:1 Mn 0.1)</td>
<td>4.3x10^{-4}</td>
<td>0.015</td>
<td>1.2x10^{-4}</td>
</tr>
<tr>
<td>MgO 2.5Al₂O₃·Mn0.1</td>
<td>≤1x10^{-4}</td>
<td>0.03</td>
<td>1.4x10^{-2}</td>
</tr>
</tbody>
</table>

Crystals labelled as ‘Mn' have been doped with manganese.
MgO Absorption spectra

Optical absorption spectra of MgO crystal:
1 - before irradiation,
2 - after fast neutron irradiation $\Phi = 10^{14}$ cm$^{-2}$,
3 - $\Phi = 10^{15}$ cm$^{-2}$,
4 - $\Phi = 10^{16}$ cm$^{-2}$,
5 - $\Phi = 10^{18}$ cm$^{-2}$.

Radiation defects in MgO:
- 250 nm – F, F$^+$ centres
- 357, 975 nm – F$^2$ center
- 570 nm – F$^3$ center or more complicated centers

Two absorption bands at 280 and 217 nm have been reported earlier and associated with Fe$^{3+}$.
MgO Absorption spectra

Additional absorption spectra of different MgO with various impurities concentration: 
1. MgO(4) irradiated by fast neutron fluence $\Phi=10^{14}$ cm$^{-2}$
2. MgO(5) $\gamma$-irradiated $D=10^4$Gy,
3. MgO(6) $\gamma$-irradiated $D=10^4$Gy.

Optical absorption spectra of MgO crystal irradiated by fast neutron fluence $\Phi=10^{18}$ cm$^{-2}$ and annealed at $T=773$ K
Photoluminescence spectra of MgO (4) crystal after irradiation by fast neutrons with fluence $\Phi = 10^{18} \text{ cm}^{-2}$ at different excitation wavelengths.
MgO Photoluminescence spectra

Photoluminescence spectra of MgO:Cr\textsuperscript{3+}:
1 – at room temperature;
2 - at 80 K.

Representation of MgO (100) plane containing Cr\textsuperscript{3+} impurity centers:

a) octahedral center;
b) tetragonal center Cr\textsuperscript{3+} - V\textsubscript{Mg}\textsuperscript{'} [100] direction,
c) tetragonal center Cr\textsuperscript{3+} - V\textsubscript{Mg} - Cr\textsuperscript{3+}, [100] direction,
d) rhombic center Cr\textsuperscript{3+} - V\textsubscript{Mg}\textsuperscript{'} [110] direction.

On the right luminescence characteristics are shown.
MgO Photoluminescence spectra

- Photoluminescence spectra of MgO crystal irradiated by fast neutrons with fluence $\Phi=10^{18}$ cm$^{-2}$ (1)
- and annealed at 900 K (2-4)
- excitation wavelengths:
  - (1,2) - 565 nm,
  - (3) - 545 nm,
  - (4) - 515 nm
- The Mn$^{2+}$ ions have a 3d$^5$ electron configuration. All electron transitions for this configuration are forbidden.
- “Me$^{2+}$-F+ (or F)”

$T=80$ K
MgO·Al₂O₃ Absorption spectra

Absorption spectra of MgO·Al₂O₃ single crystals: 1. before irradiation,
2. after fast neutron \( \Phi=10^{16}\text{cm}^{-2} \),
3. \( \Phi=10^{20}\text{cm}^{-2} \).

244 nm F-center (anion vacancies captured two electrons)
261 nm F⁺-center (anion vacancies captured one electron)
295 nm electron centers formed at positively charged anti-site defects
365 nm hole trapped at tetrahedral and octahedral cation vacancies
MgO·2.8Al₂O₃ Absorption spectra

Absorption spectra of α-Al₂O₃:Cr:
1. before irradiation,
2. after fast neutron irradiation $\Phi=10^{16}\text{cm}^{-2}$
3. additional absorption spectrum
4. MgO·2.8Al₂O₃ single crystals before irradiation
5. after fast neutron $\Phi=10^{16}\text{cm}^{-2}$
Spinel photoluminescence excitation spectra

- Photoluminescence excitation spectra of MgO·Al₂O₃·Mn₀.₁ crystal:
  1 - $\lambda_{\text{lum}} = 520$ nm,
  2 - $\lambda_{\text{lum}} = 700$ nm.

The Mn²⁺ ions have a 3d⁵ electron configuration. All electron transitions for this configuration are forbidden.

The restrictions caused by the selection rule are removed owing to the exchange interaction.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Bands position, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^6A_{1g}(S) \rightarrow ^4T_{1g}(F)$</td>
<td>254</td>
</tr>
<tr>
<td>$^6A_{1g}(S) \rightarrow ^4A_{2g}(F)$</td>
<td>268</td>
</tr>
<tr>
<td>$^6A_{1g}(S) \rightarrow ^4T_{1g}(P)$</td>
<td>288</td>
</tr>
<tr>
<td>$^6A_{1g}(S) \rightarrow ^4E_{g}(D)$</td>
<td>367</td>
</tr>
<tr>
<td>$^6A_{1g}(S) \rightarrow ^4T_{2g}(D)$</td>
<td>390</td>
</tr>
<tr>
<td>$^6A_{1g}(S) \rightarrow ^4E_{g}(G), ^4A_{1g}(G)$</td>
<td>433</td>
</tr>
<tr>
<td>$^6A_{1g}(S) \rightarrow ^4T_{2g}(G)$</td>
<td>455</td>
</tr>
<tr>
<td>$^6A_{1g}(S) \rightarrow ^4T_{1g} (G)$</td>
<td>520</td>
</tr>
</tbody>
</table>
SPINEL photoluminescence spectra

Photoluminescence spectra of magnesium aluminium spinel.
Solid line – natural spinel,
dashed line – synthetic crystal MgO Al₂O₃,
dotted line - synthetic crystal MgO 2.8Al₂O₃.

In natural spinel spectra some zero-phonon lines were observed in the region of the Cr³⁺ ions electron transition ²E₉ → ⁴A₂g:

R-lines predetermined by Cr³⁺ ions, which replace Al³⁺ ions in the octahedral sites of the spinel lattice;
N-lines related to the Cr³⁺ ions the local symmetry, which differs from symmetry of sites occupied by Al³⁺ in normal spinel.
SPINEL photoluminescence spectra

Photoluminescence spectra of magnesium aluminium spinel \( \text{MgO \text{Al}_2\text{O}_3} \) in the zero – phonon line region.

Solid line – before irradiation,

dashed line – after fast neutron irradiation fluence \( 10^{16} \text{ cm}^{-2} \),

dotted line - after irradiation by fast neutron fluence \( 10^{20} \text{ cm}^{-2} \).

\[
\begin{align*}
\text{luminescence intensity} & \\
T = 80 \text{ K} & \\
N – \text{lines} & \\
R_1 & \\
R_2 & \\
\text{luminescence intensity} & \\
\text{692} & \\
\text{688} & \\
\lambda, \text{nm} & 684
\end{align*}
\]
SPINEL photoluminescence spectra

**Photoluminescence spectra of synthetic (1) and natural pink (2) spinel with manganese**

- \(\text{Mn}^{2+}_{\text{tet}}\) - 520 nm
- \(\text{Mn}^{2+}_{\text{oct}}\) - 625 nm

**Photoluminescence spectra of:**

- (a) \(\text{MgO} \cdot \text{Al}_2\text{O}_3 : \text{Mn}0.1\) crystal irradiated by fast neutrons \(\Phi=10^{16}\text{cm}^{-2}\)
- (b) \(\text{MgO} \cdot 2.8\text{Al}_2\text{O}_3\) 1- before irradiation, 2 – after irradiation.

\(T = 80\text{ K}\)
CONCLUSIONS

- The photoluminescence (PL), its excitation (PLE) and optical absorption spectra of MgO and stoichiometric and nonstoichiometric MgO•nAl₂O₃ crystals containing chromium and manganese ions and defects produced with fast neutron irradiation have been investigated.

- Extension of R- and N-lines is observed in synthetic stoichiometric spinel. Broadening of the R- and N-lines is observed also after the irradiation of spinel crystals with fast neutrons. Furthermore the great deviation from stoichiometry leads to the local structure of α-Al₂O₃ formation around Cr³⁺ ions.

- The orange emission is attributed to Mn²⁺ in octahedral coordination, the band at 570 nm belongs to a complex centre “Mn²⁺-F⁺ (or F centre)”.
Conclusion

- It is shown that the irradiation leads to the formation of two types of complex centres: 1) “Me$^{2+}$-F$^+$ (or F) centre” and 2) complex centres, which consist of cation vacancy and impurity (iron, manganese) ions.

- The increase of fast neutron flux leads to the release of holes and their capture by Me$^{2+}$, producing Me$^{3+}$ or Me$^{4+}$ luminescence. Luminescence of chromium, iron and manganese ions of different symmetry is observed.

- The INAA results about MgO and MgO•nAl$_2$O$_3$ micro and macro components allowed to explain the observed changes in the optical absorption, photoluminescence and photoluminescence excitation spectra of analyzed materials.
Thank you for your attention
The spinel belongs to double oxides of the $X^{2+}(Y^{3+})_2O_4$ type, where $X$ is Mg$^{2+}$, Fe$^{2+}$, Mn$^{2+}$ or other bivalent ions, and $Y$ is Al$^{3+}$, Fe$^{3+}$, Cr$^{3+}$, Mn$^{3+}$ or other trivalent ions. Magnesium aluminium spinel MgO $n$Al$_2$O$_3$ (if stoichiometric, $n=1$) is a cubic-type face centred crystal. The elementary cell consists of 8 formula units $XY_2O_4$. Oxygen ions create a close-packed arrangement with 64 tetrahedral and 32 octahedral interstices per cell. If eight bivalent ions occupy 8 tetrahedral (A) sites, and 16 trivalent ions – 16 octahedral (B) sites, the spinel is described by the space symmetry group $O_{7h}$ and is called “normal”. For the “inverse” spinel, a half of the trivalent (Y) ions is located in the tetrahedral position; the other part of $Y$ and $X$ ions is usually statistically distributed between the octahedral positions. If we use an inversion parameter $i$, the chemical formula of magnesium aluminium spinel may be expressed by $^{IV}$(Mg$_{1-i}$Al$_i$)$^{VI}$[Mg$_i$Al$_{2-i}$]O$_4$, where $^{IV}$ ( ) and $^{VI}$[ ] represents the tetrahedral (A sites; 8a) and the octahedral sites (B site; 16d). Assuming $i = 1$, we obtain a formula Al[MgAl]O$_4$ for the inverse spinel.
Fragment of MgO lattice containing defects

- **F⁺-center luminescence band - 390 nm (blue)**
- **F⁻-center luminescence band - 540 nm (green)**

- \( \text{Mg}^{2+} \)
- \( \text{O}^{2-} \)
- \( \text{Me}^{2+} \)
- \( \text{Me}^{3+} \)
- \( \text{F}^+ \) or \( \text{F}^- \) center
- Cation vacancy
- Interstitial cation
- Interstitial anion