NMR TOP SIGNALS OF THE $^{27}$Al IN SOLID SOLUTIONS BASED ON THE YAG CRYSTAL

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The Two-dimensional One Pulse (TOP) experiment is the simplest 2D – experiment [1-4]. In this experiment 2D signal $s(t_1,t_2)$ of the sample, which rotates with frequency $\omega_R$ is obtained from identical 1D signals - free induction decays (FID), separated by $t_R = 2\pi/\omega_R$ in both $t_1$ and $t_2$ dimensions. The main strength of TOP method lies in its rapid interpretation of MAS signals of half-integer quadrupolar nuclei [3]. In [1-3] affirms that TOP spectroscopy leads to a better resolution of information disguised in conventional 1D MAS spectra and it is an ideal method for study of satellite transition of quadrupolar nuclei. In this communication we represent the application of TOP method to study of $^{27}$Al 2D – spectra of nominally pure and Cr-doped yttrium-aluminium garnet YAG ($Y_3Al_5O_{12}$ and $Y_3Al_5O_{12}$:Cr) crystals.

In Fig. 1 and Fig. 2 are presented the $^{27}$Al MAS NMR spectra obtained for powdered crystalline samples $Y_3Al_5O_{12}$ and $Y_3Al_5O_{12}$:Cr. All $^{27}$Al MAS NMR spectra, which are observed in YAG, contain two peaks corresponding to the tetragonal ($AlO_4$) and octahedral ($AlO_6$) structural atomic groups. The simulation of the experimental $^{27}$Al MAS NMR spectra of the $Y_3Al_5O_{12}$ and $Y_3Al_5O_{12}$:Cr give the fractions of the $AlO_6$ and $AlO_4$ groups: $N(AlVI) / N(AlIV) \approx 0.67$ for YAG and $N(AlVI) / N(AlIV) \approx 0.85$ for YAG:Cr. So the doping by Cr of the $Y_3Al_5O_{12}$ crystals leads to variation of the occupation by Al atoms both octahedrally- and tetrahedrally-coordinated sites of the garnet lattice.

![Fig. 1. The theoretical (a) and experimental (b) curves for $^{27}$Al MAS NMR spectrum of the nominally-pure polycrystalline $Y_3Al_5O_{12}$ sample.](image1)

![Fig. 2. The theoretical (a) and experimental (b) curves for $^{27}$Al MAS NMR spectrum of the nominally-pure Cr-doped polycrystalline $Y_3Al_5O_{12}$:Cr sample.](image2)

The isotropic chemical shifts ($\delta_{iso}$), quadrupolar coupling constants ($C_Q$) of the $^{27}$Al nuclei in the $AlO_4$ and $AlO_6$ structural groups obtained by Dmfit program [5] are presented in Table 1.
Table 1. Quadrupole coupling constants ($C_Q$), isotropic chemical shifts ($\delta_{iso}$), and the broadening parameters ($\Delta \nu_L$) of the Lorentzian function, for Al_{VI} and Al_{IV} in the un-doped and Cr-doped YAG crystals. The asymmetry parameter $\eta = 0$.

<table>
<thead>
<tr>
<th>The Al sites in YAG crystal</th>
<th>Un-doped YAG</th>
<th>Cr-doped YAG</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_Q$(MHz)</td>
<td>$\delta_{iso}$(ppm)</td>
</tr>
<tr>
<td>Tetrahedral</td>
<td>6.1</td>
<td>82</td>
</tr>
<tr>
<td>Octahedral</td>
<td>0.6</td>
<td>5.38</td>
</tr>
</tbody>
</table>

In Fig. 3 and Fig. 4 are presented the $^{27}$Al TOP NMR spectra obtained for powdered crystalline samples Y$_3$Al$_5$O$_{12}$ and Y$_3$Al$_5$O$_{12}$:Cr.

![Fig. 3](image1.png)
![Fig. 4](image2.png)

**Fig. 3.** The $^{27}$Al TOP spectrum of YAG with different projections of 2D-spectrum.

**Fig. 4.** The $^{27}$Al TOP spectrum of YAG:Cr with different projections of 2D-spectrum.

From comparison of Fig. 3 and Fig. 4 we conclude that the TOP MAS NMR spectroscopy is a sensitive and powerful method for investigating the local structure of main structural units in ordered and disordered solids and the redistribution of atoms between different sites caused by doping impurities.


