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THE ^{27}Al MAS NMR STUDY OF THE $Y_3Al_5O_{12}$ AND $Y_3Al_5O_{12}$:Cr GARNETS

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I. Introduction

Due to its unique optical, mechanical and thermal properties, yttrium-aluminium garnet (YAG, chemical formula – $Y_3Al_5O_{12}$) and solid solutions based on YAG are widely used in the laser and acousto-optic technology [1,2]. The YAG single crystals were intensively investigated for last several decades by different methods, including optical spectroscopy as well as acoustic and heat pulse techniques [1-3]. The YAG crystals were investigated by nuclear magnetic resonance (NMR) technique also [4-9].

The crystal structure of $Y_3Al_5O_{12}$ garnet can be represented as a set of oxygen octahedrons and tetrahedrons containing the Al atoms. Previous solid-state ^{27}Al NMR investigations of the YAG confirm that in the $Y_3Al_5O_{12}$ crystals there are two different Al sites (octahedral and tetrahedral), whose difference in the ^{27}Al chemical-shift values, enables the separation of the two contribution which differ in the quadrupolar coupling constant $C_Q = e^2qQ/h$ [4-9]. According to NMR spectroscopy data the Al^{3+} ions in the $Y_3Al_5O_{12}$ crystal lattice occupy oxygen-coordinated octahedral and tetrahedral sites in the ratio: three tetrahedral sites $N(Al_{IV})$ to two octahedral sites ($N(Al_{IV}) : N(Al_{VI}) = 3 : 2$).

An $Y_3Al_5O_{12}$ crystal allows various isomorphic substitutions and properties of these crystals substantially depend on the chemical composition and structural order (or disorder) in the distribution of admixture atoms over the sites of the crystal lattice. In particular, the optical and luminescence properties of the Cr-doped $Y_3Al_5O_{12}$ crystal ($Y_3Al_5O_{12}$:Cr or YAG:Cr) can be essentially modified by substitutional occupation of the octahedral and tetrahedral sites by Cr ions in different valence states, generally Cr^{3+} and Cr^{4+} [10-13].

This work reports a ^{27}Al magic angle spinning (MAS) NMR investigations of the nominally-pure YAG and YAG:Cr crystals.

II. Experimental

The nominally-pure un-doped and Cr-doped $Y_3Al_5O_{12}$:Cr single crystals of high optical quality and chemical purity were grown by standard Czochralski method along the [111] crystallographic direction in the (N_2 + 3% O_2) atmosphere with growth rate of 2 mm per hour [12]. The Cr impurity was added to the melt composition of as Cr_2O_3 oxide in amounts 1 – 5 at. %.

The ^{27}Al MAS NMR spectra were registered at frequency 104.26652 MHz and induction of magnetic field B = 9.4T using a Bruker Avance-400 NMR spectrometer. A 4 mm diameter rotor was filled with a powdered (polycrystalline) sample and spinning under magic angle with the frequency 14 kHz. The ^{27}Al nucleus (natural abundance – 100 %) has spin $I = 5/2$ and for the selective excitation of the central transition ($+1/2 \leftrightarrow -1/2$), the optimal pulse duration will be equal to the duration of a non-selective $\pi/2$ pulse divided by $(I + 1/2) = 3$ [14]. A free induction decay signals were recorded after application of a single radiofrequency pulse. A total of 100 acquisitions were sufficient to resolve the characteristic Al spectral features for the polycrystalline samples.

It should be noted that large differences in the quadrupolar coupling constants between tetragonal AlO_4 groups ($C_Q = e^2qQ/h$ typically about 6 MHz) and octahedral AlO_6 groups (typically $C_Q < 0.6$ MHz) lead to large differences in the linewidth and lineshape of the MAS NMR signals [6,15]. Due to large second-order quadrupolar broadening, the ^{27}Al too a greater extent, the NMR line-shapes are very broad and require special acquisition conditions to obtain understandable spectra. When the quadrupolar coupling constant $C_Q > 10$ MHz it become impossible to acquire the whole spectrum at once in the acquisition linewidth [15].

III. Results and discussion

The ^{27}Al MAS NMR spectra of crystalline YAG powder obtained for different radio-frequency pulse length are presented in Fig. 1. We can see that lineshape of different MAS NMR signals depends on the pulse duration. From our analysis of the observed spectra it was concluded that only from ^{27}Al MAS NMR spectrum obtained with pulse duration 0.7 μs it follows the relation 2 : 3 for the population of octahedrally, $N(Al_{VI})$ and tetrahedrally, $N(Al_{IV})$ coordinated Al sites. The ^{27}Al MAS NMR spectra of yttrium-aluminium garnet with a touch of Cr^{3+} ions were obtained by single-pulse experiments with pulse duration of 0.7 μs.

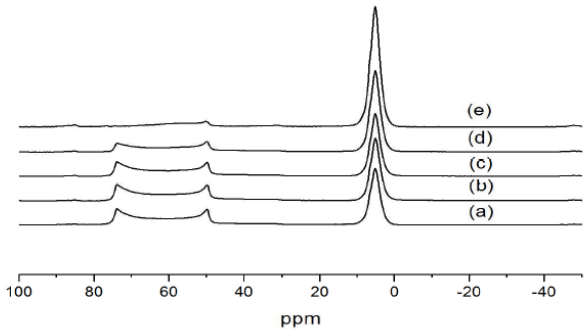

Fig. 1. The ^{27}Al MAS NMR spectra of the YAG polycrystalline powder, obtained for different pulse duration. (a) – 0.3 μs; (b) – 0.7 μs; (c) – 1 μs; (d) – 2 μs; (e) – 3 μs.

In 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 observed the ^{27}Al MAS NMR spectra contain two peaks corresponding to the tetragonal (AlO_4) and octahedral (AlO_6) structural atomic groups. The lineshape of ^{27}Al MAS NMR signal is determined by the second-order quadrupolar shift only, because the dipolar interactions between magnetic moments of the ^{27}Al nuclei are completely averaged as a consequence of sample rotation [15].

The yttrium-aluminium garnet ($Y_3Al_5O_{12}$) crystal has a body-centred cubic structure [16]. There are two structurally non-equivalent positions of aluminium atoms in the YAG crystals: the Al occupies 16 octahedral positions and 24 tetrahedral positions and this is in a good agreement with our NMR data – $N(Al_{VI}) : N(Al_{IV}) \cong 2 : 3$ (Fig. 2, spectrum a). In the YAG crystal the point symmetry of tetrahedral (AlO_4) structural groups are S_4 [16]. The presence of an electric quadrupole moment means that the ^{27}Al nucleus will interact strongly with the local electric field surrounding of the nucleus. This interaction has a significant effect on the observed NMR spectrum. The strength of local electric field gradient (EFG) is described by a second rank tensor with principal axis elements V_{ii} (i = x, y, z) [15]. The symmetry of the EFG manifests predictable and large effects in the spectral line shape of the ^{27}Al species in the solid state and is quantified by the asymmetry parameter, η ($\eta = (V_{xx} - V_{yy})/V_{zz}$)). In the case of radial and axial symmetry of the EFG tensor around the quadrupolar nucleus ($V_{xx} = V_{yy}$) and $\eta = 0$ [15].The ^{27}Al MAS NMR spectra, which are presented in Fig. 2, reveal the characteristic two-peak MAS quadrupolar powder pattern for a tetrahedral aluminium site in the $Y_3Al_5O_{12}$ crystal with a radially-symmetric EFG tensor [15]. This single site is adequately

fit with η equals to 0, a quadrupolar coupling parameter, C_Q, set to 6 MHz. The value of a quadrupolar coupling parameter gives the important information about different types of the aluminium coordination in a crystal lattice. The four-coordinated aluminium possesses a quadrupolar coupling constant C_Q equals about 6 MHz.

In the YAG lattice the point symmetry of octahedral AlO_6 groups is C_{3i} [16] and so the environment of Al atom has a very symmetric but slightly distorted octahedron [14,16]. Due to the axial symmetry of the slightly distorted octahedral aluminium position in the YAG lattice the EFG tensor is characterized by only one (V_{zz}) component and $C_Q < 1$ MHz. So, the asymmetry parameter $\eta = 0$ for AlO_6 groups in the garnet lattice. This result is confirmed experimentally (Fig. 2). A symmetric peak at about 5 ppm in the ^{27}Al MAS NMR spectrum is attributed to the AlO_6 groups and an asymmetric broad peak is assigned to the AlO_4 groups. The different frequency positions of the MAS NMR signals of the aluminium-oxygen bonding groups are connected with different ^{27}Al isotropic chemical shifts of the AlO_4 and AlO_6 groups [6].

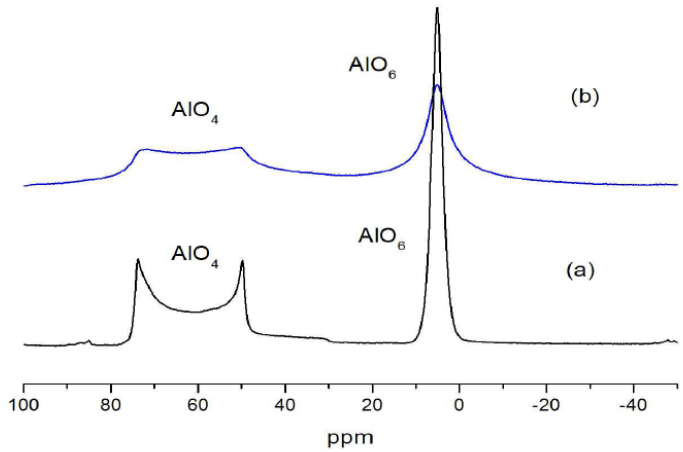

Fig. 2. The ^{27}Al MAS NMR spectra of the YAG (a) and YAG:Cr (b) polycrystalline powders. (a) $N(Al_{VI}) : N(Al_{IV}) \cong 2 : 3 \cong 0.67$; (b) $N(Al_{VI}) / N(Al_{IV}) \cong 4.6 : 5.4 \cong 0.85$.

From Fig. 2 (spectrum b) we can see that in the yttrium-aluminimum garnet with a touch of Cr^{3+} ions, there is a distortion (broadening) of the ^{27}Al MAS NMR lineshape for both AlO_4 and AlO_6 groups. These deformations of NMR lineshapes of the ^{27}Al nuclei can be connected with the change of local electric field gradient at the sites of Al nuclei and as result of interaction of the Cr^{3+} paramagnetic ions with magnetic moment of the ^{27}Al nuclei.
The simulation of the experimental ^{27}Al MAS NMR spectrum of the $Y_3Al_5O_{12}$:Cr (Fig. 2b) gives the fractions of the AlO_6 and AlO_4 groups: $N(Al_{VI}) / N(Al_{IV}) \cong 0.85$. 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.

IV. Conclusions

The ^{27}Al MAS NMR spectroscopy of the un-doped YAG crystals clearly shows the relation 2 : 3 for occupation of the octahedrally and tetrahedraly coordinated Al sites. This result coincides with corresponding structural reference data for YAG crystals. The ^{27}Al MAS NMR spectroscopy also shows that the doping of YAG crystals by Cr leads to variation of the occupation by Al atoms both octahedral and tetrahedral cationic sites of the garnet lattice. Finally, it should be noted that the MAS NMR spectroscopy is a very sensitive and powerful method for investigation the local structure of main structural units in ordered and disordered solids and redistribution of atoms between different sites caused by doping impurities.

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