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^{27}Al nuclear magnetic resonance studies of the $\text{Y}_{3-x}\text{Lu}_x\text{Al}_5\text{O}_{12}$ mixed garnets

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Abstract

The character of the substitutional order, the chemical shift, and the nuclear quadrupole coupling in the mixed yttrium–lutetium aluminium garnets $\text{Y}_{3-x}\text{Lu}_x\text{Al}_5\text{O}_{12}$ ($0 \leq x \leq 3$) were studied for the first time using ^{27}Al magic angle spinning (MAS) and multiple quantum (MQ) MAS nuclear magnetic resonance (NMR). The relatively narrow distribution of the isotropic NMR line shifts, revealed by MQ MAS NMR, in crystals with compositions $x = 0.75$ and $x = 1$ compared to mixed garnets of other compositions showed that these crystals are partially ordered solid solutions. The aluminium quadrupole coupling constants and isotropic chemical shifts were evaluated for all garnets under study.

1. Introduction

The yttrium and lutetium aluminium garnets ($\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{Lu}_3\text{Al}_5\text{O}_{12}$) are important laser crystals [1]. They are also used in some other technical applications. Because of their wide abundance, the $\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{Lu}_3\text{Al}_5\text{O}_{12}$ crystals have been studied with different experimental methods. The mixed yttrium–lutetium aluminium garnets $\text{Y}_{3-x}\text{Lu}_x\text{Al}_5\text{O}_{12}$ ($0 < x < 3$) have been studied much less, although they—like many other crystalline solid solutions—are very promising materials for further applications due to the possibility of altering their technical parameters by varying their composition.

One of the most complex problems in the physics of solid solutions is the character of substitution at lattice sites with ions of miscible components [2, 3]. When the ionic radii are rather similar, the ions may substitute for each other randomly, forming a highly disordered

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solid solution with an ion distribution predicted by statistical probability. Generally, however, it can be energetically favourable for ions of a certain kind to be surrounded by ions of the same kind or by ones of another kind. In that case, the substitution is characterized by a short-range order. In the limit of strong correlations upon mixing, some long-range order can occur, as, for example, in a superlattice at certain compositions. Substitutional ordering in mixed crystals influences strongly many of their physical properties, leading, in particular, to anomalies in the composition dependences of the electrical resistance in alloys [2, 4], of bond lengths and energy gaps (see [5] and references therein), and of the heat conductivity and ultrasound attenuation in insulator and semiconductor solid solutions [6].

There have been no direct studies of the substitutional order in mixed yttrium–lutetium aluminium garnets. Nevertheless, it was found in [7, 8] that the relaxation time of thermal phonons and the coefficient of ultrasound attenuation for $Y_{3-x}Lu_xAl_5O_{12}$ had some unusual composition dependences with a rather narrow maximum at $x = 0.75$ against a background of the ordinary bell-like decrease of these parameters in mixed crystals compared to the pure yttrium and lutetium garnets. Those results were treated in [7] as evidence of some partial substitutional order near that particular composition, while no long-range ordering was found by means of x-ray powder diffraction.

Since nuclear magnetic resonance (NMR) characteristics such as chemical shift, line shape, and relaxation times are very sensitive to the local structure in crystals, NMR investigation should be quite fruitful for revealing the substitutional order in mixed crystals, especially in the case of weak ordering. In fact, NMR has been used to study the partial substitutional order in the $Y_{3-x}Yb_xAl_5O_{12}$ mixed garnets [9], in mixed yttrium–erbium aluminates [10], and in binary and ternary semiconductor solid solutions (see [5, 11, 12] and references therein). In [9, 10], the ^{27}Al absorption line shape was analysed; various numbers of paramagnetic Yb and Er ions in the Al surroundings were detected due to large shifts induced by interaction with electron moments. In the $Hg_{1-x}Cd_xTe$, $Cd_{1-x}Zn_xTe$, and $Cd_{1-x}Zn_xGeP_2$ semiconductor alloys [5, 11, 12], various local surroundings of Te and P were distinguished due to their different chemical shifts using magic angle spinning (MAS) NMR. Studying the local environment of the Al ions in the $Y_{3-x}Lu_xAl_5O_{12}$ garnets is a more complicated problem because the ^{27}Al nuclei have a quadrupole moment ($I = 5/2$) in contrast to the dipolar ^{205}Te and ^{31}P nuclei, and the aluminium resonance lines are anisotropically broadened even under the condition of magic angle spinning. In addition, the Y and Lu ions are not in the nearest neighbourhood of aluminium and their distribution affects the Al chemical shift more weakly. It should be noted that continuous NMR was applied in [7] for studying the $Y_{3-x}Lu_xAl_5O_{12}$ single crystals also. Noticeable narrowing of the central ^{27}Al NMR line corresponding to the tetrahedral oxygen environment was observed at $x = 0.75$ compared to broadened NMR lines for other intermediate compositions. However, the NMR technique employed in [7] did not allow the authors either to reveal reasons for such narrowing and to investigate the substitutional order in the mixed yttrium–lutetium garnets or to observe distinctly NMR lines corresponding to aluminium in the octahedral oxygen surroundings.

In this paper we present results of studies of the mixed $Y_{3-x}Lu_xAl_5O_{12}$ ($0 \leq x \leq 3$) garnets by means of ^{27}Al MAS NMR and multiple quantum (MQ) MAS NMR. MAS allowed us to find chemical shifts and parameters of the nuclear quadrupole coupling for both tetrahedral and octahedral aluminium sites, and to evidence the composition dependence of the character of the substitutional disorder. The newly developed MQ MAS method [13, 14] made it possible to separate isotropic shifts of NMR lines against a background of the anisotropic quadrupole coupling and then to reveal the physical nature of the NMR line narrowing and broadening in the mixed garnets. The results obtained give an example of successful application of MQ MAS NMR for detecting the order in ion substitution in mixed crystals.

2. Experimental procedure

Single crystals of the Y_{3-x}Lu_xAl₅O₁₂ mixed garnets were grown by the Czochralski method. The lutetium concentration x was equal to 0, 0.6, 0.75, 1, 2, and 3. According to the x-ray diffraction, the mixed garnets keep the crystalline structure of the pure Y₃Al₅O₁₂ garnet with cubic symmetry, space group $Ia\bar{3}d$ (O_h^{10}). The unit-cell parameter a varies from 12.008 Å for the Y₃Al₅O₁₂ garnet to 11.914 Å for the Lu₃Al₅O₁₂ garnet (see table 1), following well the Vegard law. Before the NMR measurements, the specimens were powdered.

Table 1. The unit-cell parameter a for the Y_{3-x}Lu_xAl₅O₁₂ garnets.

x	0	0.6	0.75	1	2	3
a (Å)	12.008	11.989	11.984	11.976	11.945	11.914

In the pure Y₃Al₅O₁₂ garnet, there are two different aluminium crystallographic sites in the octahedral and tetrahedral oxygen environments [15]. The oxygen octahedra and tetrahedra are distorted in such a way that the axial crystalline field at the Al ions is directed along the cubic axis (tetrahedral sites) and along the diagonals of the unit cell (octahedral sites). In accordance with the garnet structure, the MAS spectrum of ²⁷Al consists of two sets of lines whose positions and shapes are defined by the chemical shifts and quadrupole coupling with the asymmetry parameter η_Q equal to 0 [16, 17].

The ²⁷Al MAS and MQ MAS experiments for the samples under study were performed on a Bruker Avance400 NMR pulse spectrometer using a commercial 4 mm MAS probehead at room temperature. The spectra were acquired at a Larmor frequency of 104.3 MHz. The spinning rate was 12 kHz. A $\pi/12$ single pulse was used to obtain MAS spectra. The spectral width was 33 kHz for observing the central transitions for both octahedral and tetrahedral aluminium sites and 1000 kHz for observing all spinning sidebands corresponding to the octahedral site. The backward linear prediction was used to facilitate the phase correction for sidebands. A three-pulse sequence was applied to get the two-dimensional 3Q MAS spectra. NMR line shifts were referenced to the 1 M Al(NO₃)₃ aqueous solution.

3. Results and discussion

The ²⁷Al MAS spectra obtained for the pure yttrium aluminium garnet were similar to those published earlier [16, 17]. For the octahedral site, one can see the central line and all sidebands corresponding to satellite transitions ($\pm 1/2 \leftrightarrow \pm 3/2$ and $\pm 3/2 \leftrightarrow \pm 5/2$), while for the tetrahedral site only the central line and several near sidebands are observable because of the stronger quadrupole coupling for this site (figure 1). The spectra can be well fitted with the parameters listed in table 2 when the asymmetry parameter is assumed equal to 0. The nuclear quadrupole coupling constants, e^2qQ/h (e is the electron charge, eq is the zz component of the electric field gradient tensor, Q is the nuclear quadrupole moment, and h is the Planck constant), were the same within the experimental accuracy as in [7, 16–19] for both tetrahedral and octahedral sites. The chemical shifts were similar to those measured in [16, 17].

For another pure garnet under study, Lu₃Al₅O₁₂, the MAS spectra can also be well fitted with $\eta_Q = 0$ and other parameters listed in table 2. As far as we know, the quadrupole constants for the Lu₃Al₅O₁₂ garnet were measured only in [7] by means of continuous NMR for a single-crystal sample. For the octahedral site, the result obtained in the present work coincides with that found in [7], but for the tetrahedral site the value 6.24 MHz from table 2 is slightly smaller than that given in [7]. The chemical shifts are reported here for the first time.

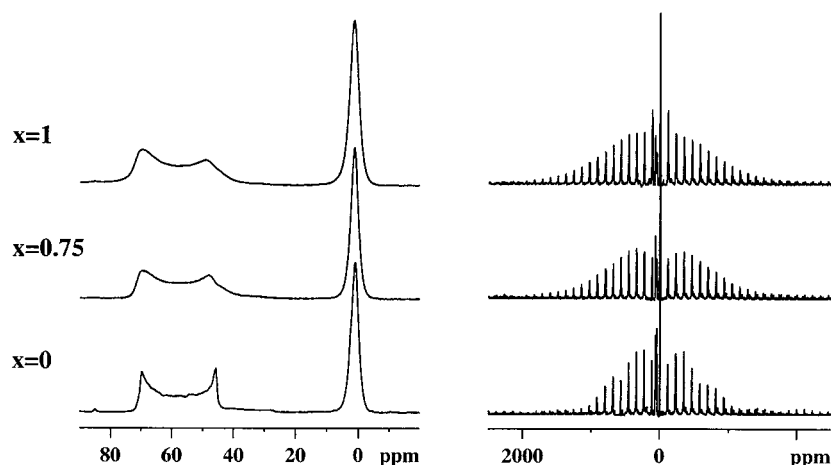


Figure 1. ^{27}Al MAS spectra for the $\text{Y}_{3-x}\text{Lu}_x\text{Al}_5\text{O}_{12}$ garnets of composition $x = 0, 0.75,$ and $1.$ Left: central lines corresponding to the tetrahedral and octahedral aluminium sites; right: sidebands for the octahedral site.

Table 2. The quadrupole coupling constant e^2qQ/h and the isotropic chemical shift δ_{ch} for the octahedral and tetrahedral aluminium sites and the width Δ at half-intensity of the central MAS line for the octahedral site.

x	Octahedral site			Tetrahedral site	
	e^2qQ/h (MHz)	δ_{ch} (ppm)	Δ (ppm)	e^2qQ/h (MHz)	δ_{ch} (ppm)
0	0.65 ± 0.01	1.32 ± 0.05	2.7 ± 0.1	6.05 ± 0.01	77.0 ± 0.5
0.6	0.91 ± 0.03	1.7 ± 0.1	3.3 ± 0.1	6.09 ± 0.03	78 ± 1
0.75	0.92 ± 0.02	1.8 ± 0.1	2.7 ± 0.1	5.98 ± 0.03	77.5 ± 0.5
1	1.04 ± 0.03	2.0 ± 0.1	3.4 ± 0.1	6.07 ± 0.04	79 ± 1
2	1.16 ± 0.03	2.3 ± 0.1	4.1 ± 0.2	6.17 ± 0.05	79 ± 1
3	1.20 ± 0.02	2.8 ± 0.1	3.0 ± 0.1	6.24 ± 0.02	79.0 ± 0.05

For the mixed crystals under study, the MAS spectra were rather similar to those for the pure garnets. Examples for $x = 0.75$ and 1 are shown in figure 1 together with the spectrum for the pure yttrium garnet. However, the central lines for the octahedral site are noticeably broadened compared to those for the pure garnets as is seen in figure 1 and table 2 except for the case of $x = 0.75$. At that particular composition, the central line is as narrow as for $\text{Y}_3\text{Al}_5\text{O}_{12}$. In addition, the MAS spectra for both octahedral and tetrahedral sites in mixed garnets are visibly distorted. Nevertheless, one can evaluate from the MAS spectra the chemical shifts and quadrupole constants for the tetrahedral and octahedral sites; the values obtained are listed in table 2. The quadrupole constants for the tetrahedral site are in rather good agreement with the results obtained in [7] for the relevant single crystals. The quadrupole constants for the octahedral sites as well as the chemical shifts for both aluminium sites are measured in the present work for the first time.

The distortion of MAS spectra in the mixed garnets can be explained by alterations in local symmetry and fields on the Al nuclei as a result of distortion of the unit cells due to substitution for Y with Lu. In the pure yttrium garnet lattice, aluminium ions in both octahedral and tetrahedral oxygen surroundings have six neighbour Y located at the dodecahedral sites [15]. In the mixed yttrium–lutetium solid solutions, Y and Lu are distributed over those sites.

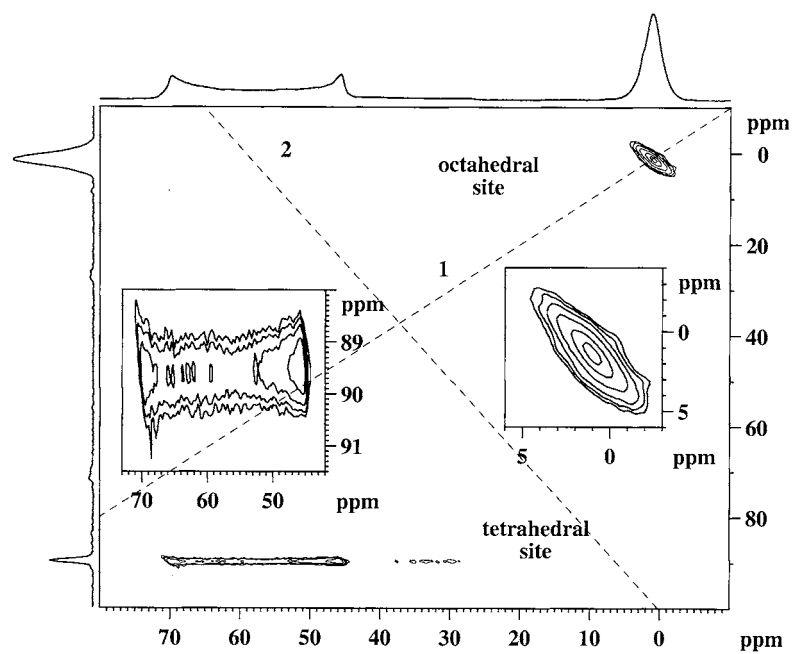
For disordered mixed crystals with composition specified by x , the probability $P(n, x)$ of Al having n Y and $6 - n$ Lu in its environment is given by

$$P(n, x) = \left\{ \frac{6!}{n!(6-n)!} \right\} \left(\frac{x}{3} \right)^n \left(1 - \frac{x}{3} \right)^{6-n}. \quad (1)$$

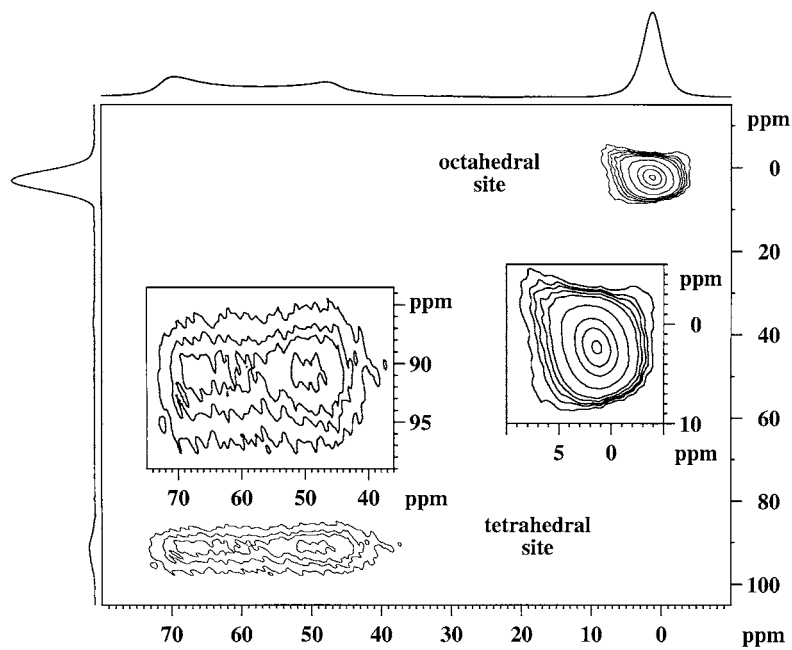
In partially ordered solid solutions, the ion distribution changes, leading to higher probabilities for some selected n -values. Every distinct environment of aluminium is expected to have distinct isotropic shifts (chemically as well as quadrupole induced in nature) of the NMR lines. Thus, the distribution of various environments should be related to the distribution of isotropic shifts in mixed crystals. Therefore, the relative narrowing of the octahedral central line for $x = 0.75$ can be considered as a hint of partial ordering near that composition. However, Al MAS lines in the mixed aluminium garnets are anisotropically broadened because of the second-order quadrupole coupling. The anisotropic broadening disguises the distribution of the isotropic shifts especially for the tetrahedral aluminium site, while for the octahedral site, the quadrupole constant is rather small (table 2) and one can expect the central MAS line broadening for this site to be somewhat driven by isotropic couplings. To study the distribution of the isotropic shifts we used $3Q$ MAS NMR [13, 14].

Examples of the 2D spectra obtained by $3Q$ MAS after shearing Fourier transformation are shown in figure 2 for $x = 0, 0.6$, and 0.75 . In these spectra, the anisotropy axis is directed horizontally. This means that a projection of the 2D spectrum onto the vertical axis displays only isotropic shifts while the second-order quadrupole-broadened ridges appear parallel to the horizontal axis. The top 1D spectra are single-pulse MAS spectra. The left 1D patterns are traces in the isotropic dimension. Two aluminium sites, octahedral and tetrahedral, are clearly seen in figure 2. The ridges corresponding to the tetrahedral site are spread along the anisotropy axis showing strong nonhomogeneous broadening. In mixed garnets they are somewhat distorted. While the vertical projections for the tetrahedral and octahedral sites remain unsplit in mixed garnets, the corresponding lines are notably broadened. This can be seen in figure 3 where the isotropic linewidth at half-intensity versus composition for both aluminium sites is depicted for all samples under study together with the composition dependence of the octahedral central MAS linewidth. Taking into account the relatively weak quadrupole coupling for aluminium in the octahedral environment, one can suggest that the octahedral isotropic lines are broadened mainly because of variations in the chemical shift, whereas variations in the quadrupole-induced isotropic shift can make noticeable contributions to the tetrahedral linewidth. The isotropic line broadening is very considerable for mixed crystals with $x = 0.6$ and 2 , which is direct evidence of a wide distribution of isotropic shifts in them. However, as can be seen from figures 2 and 3, the isotropic lines for both aluminium sites are notably narrowed for $x = 0.75$ and somewhat narrowed for $x = 1$ compared to other mixed garnets although, in agreement with relation (1), the linewidth should increase with increasing x until about $x = 1.5$ for random solid solutions. Thus, the isotropic shift distribution is quite narrow for these particular compositions, which evidences the presence of some substitutional order in these mixed garnets; the ordering is stronger for the composition $x = 0.75$. One can speculate that the substitutional order at $x = 0.75$ may affect the electric field gradients on aluminium and therefore lead to a slight decrease in the quadrupole coupling constant corresponding to the tetrahedral site for this composition (see table 2). The accuracy of measurements was not sufficient for observing a possible similar trend in the chemical shift, which can also be seen in table 2.

From the MQ MAS spectra one can also find directly the isotropic chemical shift δ_{ch} . Two additional axes which are necessary for the calculations are shown in figure 2(a). The chemical shift axis has a slope equal to 1; the quadrupole-induced shift axis has a slope equal



(a)



(b)

Figure 2. ^{27}Al MQ MAS spectra for $\text{Y}_{3-x}\text{Lu}_x\text{Al}_5\text{O}_{12}$ garnets of composition $x = 0$ (a), 0.6 (b), and 0.75 (c). Insets show enlarged patterns for the octahedral and tetrahedral sites. In (a), 1 is the chemical shift axis and 2 is the quadrupole-induced shift axis. The top 1D spectra are single-pulse MAS spectra. The 1D spectra on the left are projections of 2D MQ MAS patterns onto the isotropic axis.

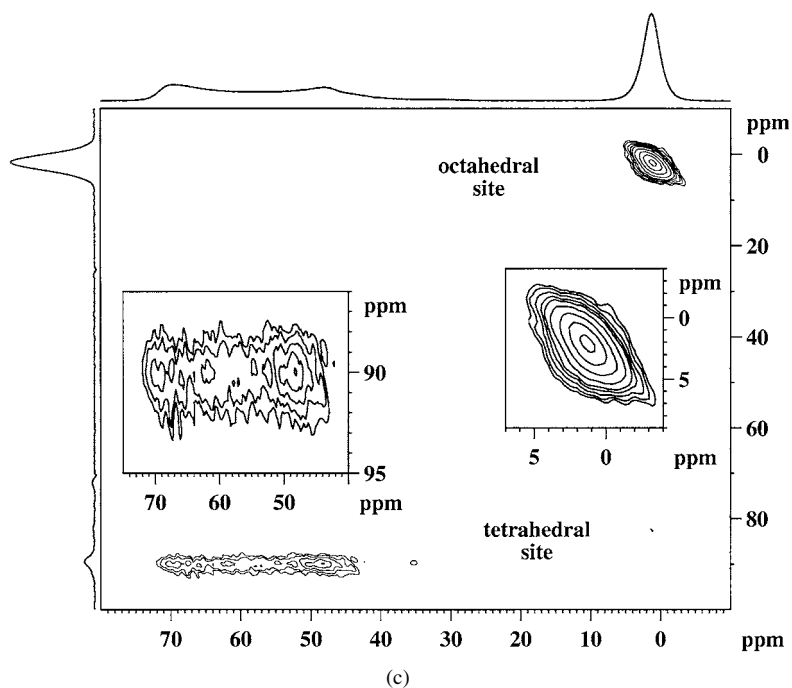


Figure 2. (Continued)

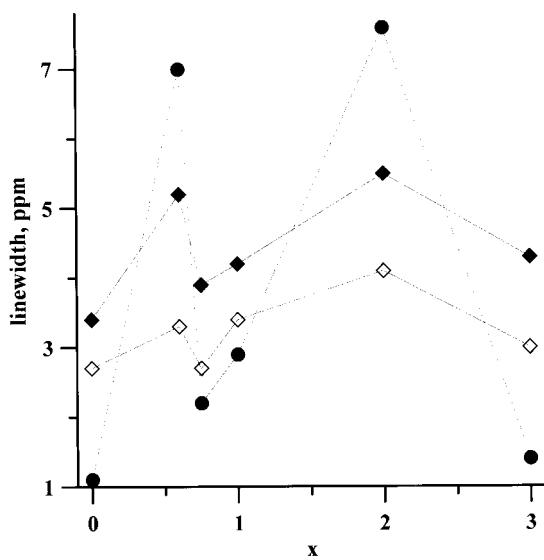


Figure 3. Composition dependence of the width at half-intensity of ^{27}Al MQ MAS isotropic lines for the octahedral (closed diamonds) and tetrahedral (closed circles) sites and of the central ^{27}Al MAS line for the octahedral site (open diamonds).

to $-17/10$. The projection of the centre of gravity of the lines along the latter axis onto the chemical shift axis gives δ_{ch} . The results of such direct calculations agree with those obtained by simulations of the MAS spectra.

4. Conclusions

^{27}Al MAS and MQ MAS NMR studies of the mixed yttrium–lutetium aluminium garnets $\text{Y}_{3-x}\text{Lu}_x\text{Al}_5\text{O}_{12}$ ($0 \leq x \leq 3$) were made to obtain the chemical shifts and the quadrupole coupling constants for the octahedral and tetrahedral aluminium sites and to reveal the character of the substitution for Y with Lu for different compositions. It was suggested that the distribution of the Y and Lu ions over the lattice sites is related to the distribution of the isotropic shifts of NMR lines. The latter was revealed using the $3Q$ MAS technique. It was shown that mixed garnets of composition $x = 0.75$ and $x = 1$ are partially ordered solid solutions. The results obtained give an example of successful application of MQ MAS NMR for detecting the substitutional order in mixed crystals.

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