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Chemical Shift, Chemical Shift Anisotropy, and Spin-Lattice Relaxation Time in ^{89}Y-MAS and -Static NMR of Yttrium Compounds

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The chemical shift, the range of chemical shift anisotropy, and the spin-lattice relaxation times (T_1) in Y_2O_3, $Y_3Al_5O_{12}$, and Y_2O_2S have been measured by solid state ^{89}Y (nuclear spin 1/2)-MAS and -static NMR. The static NMR data and T_1 are reported for the first time. The range of chemical shift anisotropy was 1500—2400 Hz. This range was influenced more by the nature of the atom bound to Y than by the coordination number or the crystallographic symmetry of Y. Very long T_1 values were obtained for Y_2O_2S (6.61 h) and Y_2O_3 (3.92 h at 24d site and 3.81 h at 8b site). On the other hand, the T_1 value (1.10 h) of $Y_3Al_5O_{12}$ is much shorter compared with those of Y_2O_2S and Y_2O_3. The next-nearest neighboring atom of Y in $Y_3Al_5O_{12}$ is identified as Al, which has the nuclear spin 5/2 of 100% natural abundance. The most likely origin of significantly shorter T_1 of $Y_3Al_5O_{12}$ is a dipole–dipole interaction between ^{89}Y and ^{27}Al.

Despite the fact that ^{89}Y has 100% natural abundance with nuclear spin 1/2, only a limited amount of information[1—8] is available on ^{89}Y solid state NMR because of its low resonance frequency (14.706 MHz at 7.05 T), low sensitivity (1.08×10^{-4} times to ^{1}H), and long spin-lattice relaxation time (several hours). Oldfield et al.[1,2] reported the ^{89}Y-MAS NMR spectra of several yttrium compounds such as Y_2O_3 and $YCl_3\cdot6H_2O$. Further, Dupree and Smith[3] investigated the structural influences on the MAS NMR chemical shifts and resonance linewidths of ^{89}Y in Y_2O_3, yttrium aluminates and yttrium silicates. The spin-lattice relaxation time (T_1) and the spin–spin relaxation time (T_2) of ^{89}Y were measured in single crystal $Y_3Fe_5O_{12}$ at 4.2 K by Shemyakov and Savosta[4] and T_2 was measured in $YBa_2Cu_3O_7$ by Balakrishnan et al.[5] and Han et al.[6] In these two Y compounds, paramagnetic atoms, Fe and Cu, shortened the T_1 to several ms. Grey et al.[7] studied rare-earth-doped yttrium stannates and titanates ($Y_2Sn_2O_7$ and $Y_2Ti_2O_7$) using ^{89}Y-MAS NMR, in which rare-earth atoms doping affected both the chemical shift and linewidths. ^{89}Y-MAS NMR spectra of Si_3N_4 sintered with the 15% Y_2O_3 and 3 wt% Yb_2O_3 were reported by MacKenzie and Meinhold.[8] In all studies, no information on a chemical shift anisotropy and the spin-lattice relaxation times in paramagnetic-free ^{89}Y compounds has been presented.

Yttrium compounds have become indispensable materials for superconductors, the matrices of phosphors, and other uses. For example, $Y_3Al_5O_{12}$ is generally used as the matrix of Tb-doped green phosphor, and both Y_2O_2S and Y_2O_3 are used as the matrices of Eu-doped red phosphors. The ability of such superconductors and phosphors strongly depends on the physical and chemical properties of the materials. Therefore, we have to establish a method to assess them precisely and easily. In a series of our investigations, ^{89}Y solid state NMR was used for the purpose, although ^{89}Y NMR is rather difficult technically, as mentioned above. Generally, the chemical shift anisotropy in a static NMR tells us the symmetry of the crystalline field around Y atoms and T_1 and T_2 become a probe for the distribution of other nuclei and/or paramagnetic atoms surrounding the observed Y atom. Before we investigate and evaluate rather complex rare-earth element doped materials, it is important to know ^{89}Y NMR properties such as isotropic chemical shift, chemical shift anisotropy and T_1 and T_2 of pure Y compounds, $Y_3Al_5O_{12}$, Y_2O_2S, and Y_2O_3, which are used as the mother compounds of other materials. In the present paper, we assign anisotropic chemical shifts in their static ^{89}Y NMR spectra, in comparison with isotropic chemical shifts calculated from the static NMR spectra and those measured in MAS-NMR spectra. And the spin-lattice relaxation times were measured for the first time. The results obtained in this work show that ^{89}Y-solid state NMR becomes a highly useful probe for elucidating the crystal structure and physical and chemical properties of Y compounds.

Experimental

Materials: The samples employed in this investigation were prepared by the method described in the handbook of phosphors.[9] The preparation procedures are as follows. $Y_3Al_5O_{12}$: BaF_2 was added to raw materials, Y_2O_3 and Al_2O_3, as the flux in an alumina crucible; the mixture was fired at 1470 °C for several hours.

Y_2O_2S: Na_2CO_3, K_3PO_4, S, and C were added to a raw material, Y_2O_3, as the flux in an alumina crucible; the mixture was fired at 1200 °C for several hours.

Y_2O_3: $BaCl_2\cdot2H_2O$, H_3BO_3, and LiCl were added to a raw material, Y_2O_3, as the flux in an alumina crucible; the mixture was fired at 1450 °C for several hours.

Y_2O_3, $Y_3Al_5O_{12}$, and Y_2O_2S prepared by the above methods were washed with pure water for several times and dried. The raw material, Y_2O_3, was prepared by Mitsubishi Chemical Co., Ltd., and the raw material, Al_2O_3, and other materials used for the flux were purchased from Wako Co., Ltd., Junsei Co., Ltd., and Kanto Chemical Co., Ltd. All materials purchased were reagent grade.

Apparatus and Measurements: The crystal structure of the employed samples was identified in powder by X-ray diffractometer with monochromated Cu $K\alpha$ (Philips PW1700 diffractometer). The amount of impurity was determined by Seiko-SPS-1200A ICP and Rigaku 3370 fluorescence X-ray spectrometer. The amounts of impurities of all samples were less than 1 ppm. The measurements of ^{89}Y NMR spectra were carried out at 14.706 MHz on a Bruker MSL-300 spectrometer. The MAS spectra and the static spectra were measured with a low frequency CP MAS probe (dia. 7 mm) at a spinning rate of 5 kHz, and with a static probe (dia. 10 mm). A 90° pulse widths were 11 μs (MAS) and 15 μs (static). An aqueous solution of 1.5 M $Y(NO_3)_3$ aqueous solution ($1\ M = 1\ mol\,dm^{-3}$) was used as 0 ppm external reference. A single pulse was used for MAS and static measurements. All measurements were performed at room temperature.

Results and Discussion

The crystal structures of $Y_3Al_5O_{12}$, Y_2O_2S, and Y_2O_3 identified by X-ray diffraction are shown in Figs. 1-(a), -(b), and -(c),[10,11] respectively. The coordination schemes of Y are schematically depicted in Fig. 2 according to the individual crystallographic symmetries. The crystallographic characteristics, i.e., coordination number of Y atom and crystallographic symmetry, are given in columns (1) and (2) in Table 1.

The ^{89}Y-MAS and -static spectra of $Y_3Al_5O_{12}$, Y_2O_2S, and Y_2O_3 are shown in Figs. 3, 4, and 5, respectively. The chemical shifts of MAS signals, σ_{iso} (MAS), are given in column (3) of Table 1.

Assignment of ^{89}Y-Static and -MAS Signals: As $Y_3Al_5O_{12}$ has one type of yttrium atom with the symmetry of C_{8v} (axial symmetry), only one peak appeared at 239 ppm in the ^{89}Y-MAS NMR spectrum, as shown in Fig. 3-(a). The ^{89}Y-static signal showed a typical powder pattern of the axial symmetry[12] as indicated in Fig. 3-(b). If we assume $\sigma_{22} = \sigma_{33} = \sigma_{\perp}$, $\sigma_{11} = \sigma_{\parallel}$, where σ represents the chemical shift tensor, $\sigma_{\parallel}$ and $\sigma_{\perp}$ in the static spectra of $Y_3Al_5O_{12}$ are assigned to $\sigma_{\parallel} = 306$ ppm and $\sigma_{\perp} = 203$ ppm, as shown in Fig. 3-(b). These values were tabulated in column (4) of Table 1. Further, the isotropic chemical shift, σ_{iso} (static), calculated from $(\sigma_{\parallel} + 2\sigma_{\perp})/3$ was 237 ppm, which is shown in column (5) in Table 1. The calculated σ_{iso} (static) is in good agreement with the σ_{iso} (MAS) of $Y_3Al_5O_{12}$ within the experimental error.

^{89}Y-MAS and -static NMR spectra of Y_2O_2S are shown in Figs. 4-(a) and -(b), respectively. As the symmetry of Y atom in Y_2O_2S is C_{3v} (axial symmetry), only one peak was observed in the MAS spectrum and the powder pattern of axial symmetry appeared in the static spectrum similar to $Y_3Al_3O_{12}$. The σ_{iso} (static), 287 ppm, is in good agreement with the σ_{iso} (MAS), 293 ppm. In these two cases of $Y_3Al_5O_{12}$ and Y_2O_2S, the static NMR signals sensitively reflected the coordination symmetry around Y.

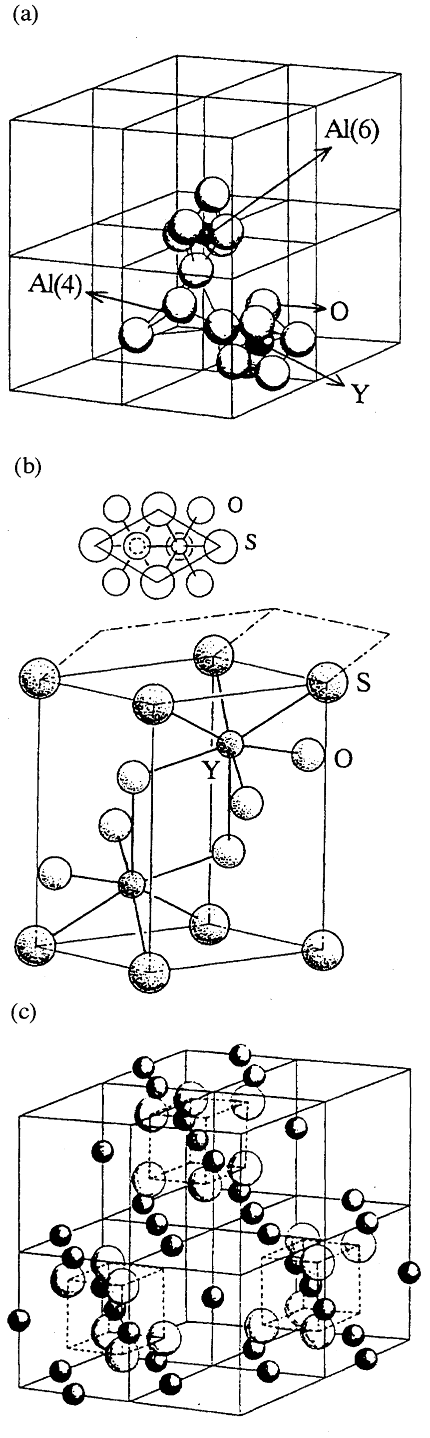

Fig. 1. Crystal structures of $Y_3Al_5O_{12}$ (a), Y_2O_2S (b), and Y_2O_3 (c).

Two peaks with the ratio of signal intensities of 3 : 1 appeared in the ^{89}Y-MAS spectrum of Y_2O_3 as shown in Fig. 5-(a). According to the Y_2O_3 crystal scheme[10] shown in Fig. 1-(c), the larger peak at 330 ppm in the ^{89}Y-MAS spectrum is assigned to Y in 24d site and the smaller peak at 289 ppm is assigned to Y in 8b site.

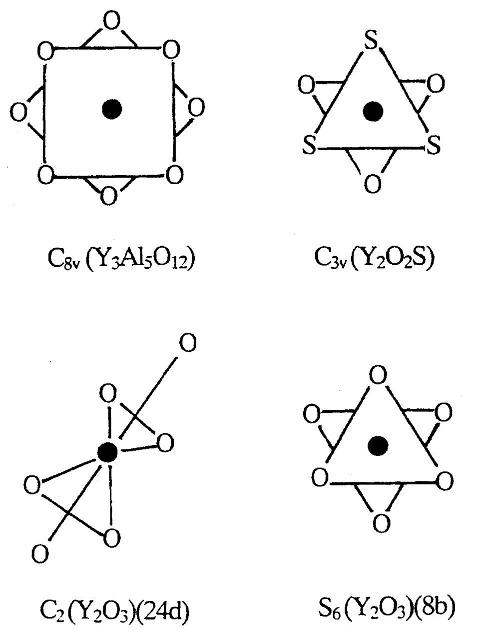

Fig. 2. Coordination schemes of yttrium compounds. ●: Y atom.

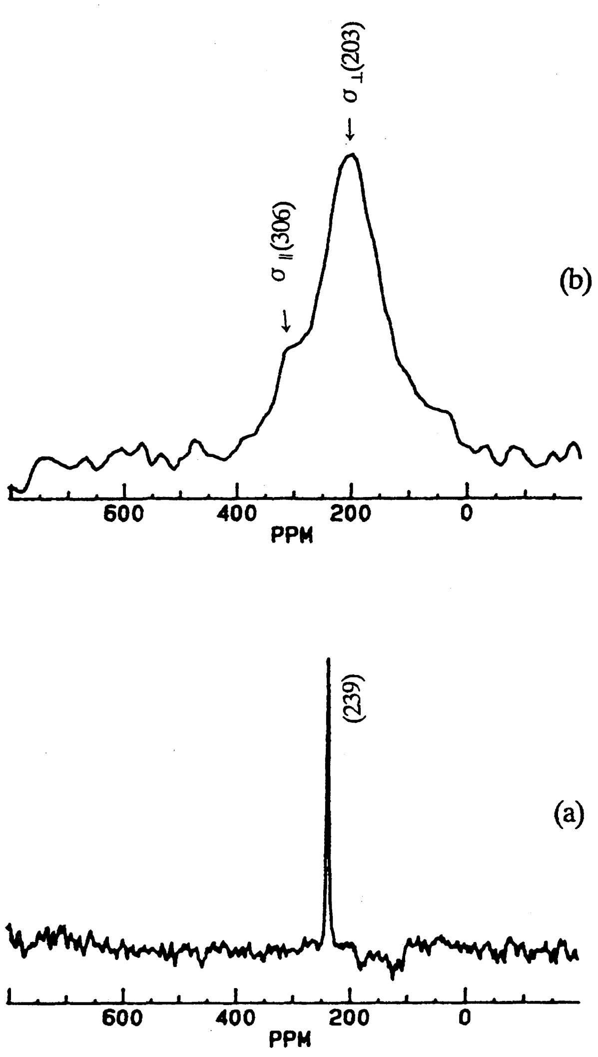

Fig. 3. Solid state NMR spectra of $Y_3Al_5O_{12}$. (a): MAS; spectral width: 15000 Hz, data point: 4 K, pulse width: 11 μs, aquisition number: 23 times, recycle time: 1000 s, spinning rate: 5000 rps. (b): Static; spectral width: 50000 Hz, data point: 4 K, pulse width: 7 μs, aquisition number: 159 times, recycle time: 1000 s.

The Y atom at 24d site is in C_2 (rhombohedral) symmetry, and would show the typical anisotropic powder pattern in the static spectrum. On the other hand, Y at 8b site is in S_6 (axial) symmetry. Considering these facts and that σ_{iso} (static)$\fallingdotseq\sigma_{iso}$ (MAS), signals in the static spectrum are uniquely assigned for the first time as shown in Fig. 5-(b), i.e. $\sigma_{11} = 399$ ppm, $\sigma_{22} = 299$ ppm, and $\sigma_{33} = 282$ ppm for Y(24d), and $\sigma_{\parallel} = 352$ ppm and $\sigma_{\perp} = 250$ ppm for Y(8b). The σ_{iso} (static), $\{= (\sigma_{11} + \sigma_{22} + \sigma_{33})/3\}$ and σ_{iso} (MAS) are 327 ppm and 330 ppm for 24d site, and 284 ppm and 289 ppm for 8b site, respectively, as tabulated in Table 1.

As mentioned above, ^{89}Y solid state NMR has been scarcely reported because of its technical difficulty. The static NMR data for these three typical Y compounds, which are presented in this paper for the first time, could become useful as a standard because these three Y compounds are indispensible basic compounds in the phosphors.

Effect of the Coordination State to the Isotropic Chemical Shift: Dupree and Smith[3] made the following comment on the ^{89}Y isotropic chemical shifts of compounds containing Y–O–Y, Y–O–Al, or Y–O–Si bonds: The isotropic chemical

Table 1. Crystallographic and ^{89}Y NMR Characteristics for Yttrium Compounds

Column		$Y_3Al_5O_{12}$	Y_2O_2S	Y_2O_3 (24d)	Y_2O_3 (8b)
(1)	Coordination number	8	7	6	6
	Bind of coordinating atoms	(O8)	(O4, S3)	(O6)	(O6)
(2)	Crystallographic symmetry	C_{8v}(a,s)[a]	C_{3v}(a,s)	C_2(r,s)[b]	S_6(a,s)
(3)	Chemical shift of MAS, σ_{iso} (MAS), in ppm	239	293	330	289
(4)	Chemical shift of static in ppm	$\sigma_{\parallel}$=306	$\sigma_{\parallel}$=394	σ_{11}=399	$\sigma_{\parallel}$=352
		$\sigma_{\perp}$=203	$\sigma_{\perp}$=234	σ_{22}=299	$\sigma_{\perp}$=250
				σ_{33}=282	
(5)	Isotropic chemical shift of static, σ_{iso} (static), in ppm	237	287	327	284
(6)	Chemical shift anisotropy in Hz, ( ) in ppm	1510 (103)	2360 (161)	1600 (109)	1500 (102)
(7)	Half-width of signal under MAS in Hz	69.4	75.5	74.1	74.1
(8)	Spin-lattice relaxation time (T_1) in s, ( ) in h	3950 (1.10)	23800 (6.61)	14100 (3.92)	13700 (3.81)

a) (a,s): axial symmetry. b) (r,s): rhombohedral symmetry.

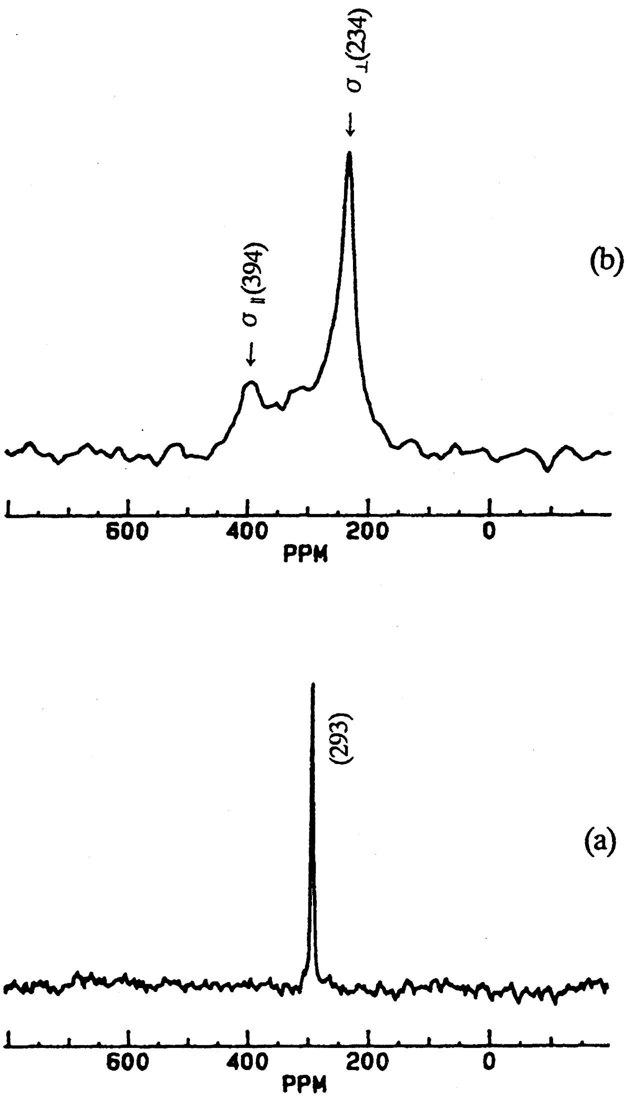

Fig. 4. Solid state NMR spectra of Y_2O_2S. (a): MAS; spectral width: 15000 Hz, data point: 4 K, pulse width: 11 μs, the signal was aquisited after 150000 s (41.7 h) after dummy one pulse, spinning rate: 5000 rps. (b): Static; spectral width: 50000 Hz, data point: 4 K, pulse width: 7 μs, aquisition number: 87 times, recycle time: 1000 s.

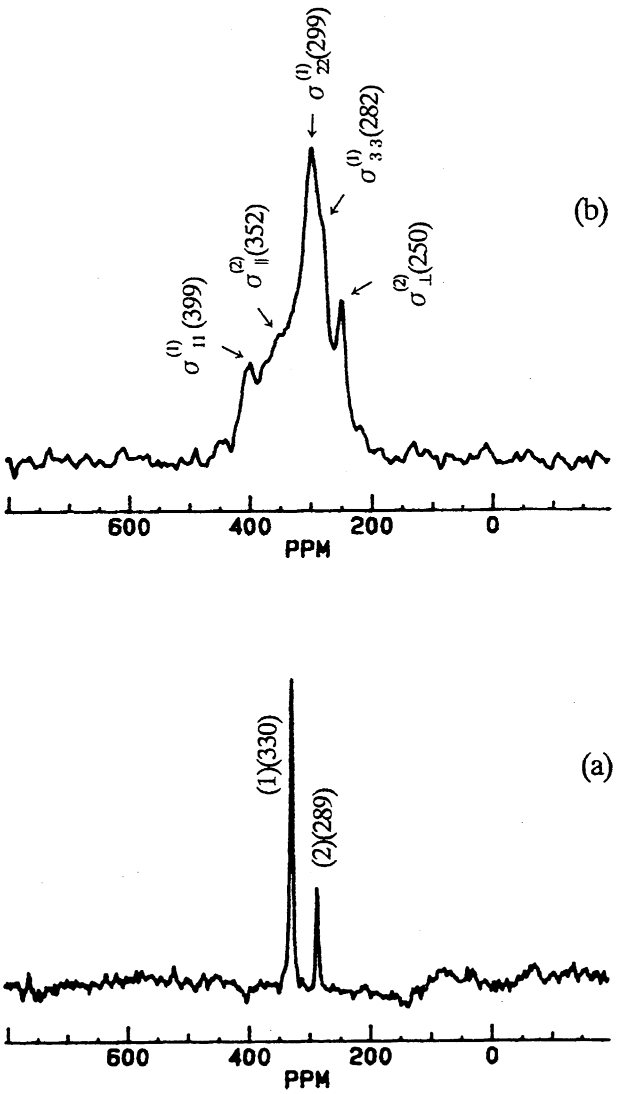

Fig. 5. Solid state NMR spectra of Y_2O_3. (a): MAS; spectral width: 15000 Hz, data point: 4 K, pulse width: 7 μs, aquisition number: 60 times, recycle time: 1000 s, spinning rate: 5000 rps. (b): Static; spectral width: 50000 Hz, data point: 4 K, pulse width: 7 μs, aquisition number: 63 times, recycle time: 1000 s.

shift is sensitive to the local coordination number and to the nature of the next-nearest neighboring atoms. In the case of compounds with the same kind of next-nearest neighboring atoms, the central Y ion becomes more ionic with increasing in the coordination number, and hence the isotropic Y signal shifts to the higher field. On the other hand, in the case of compounds with the different kind of the next-nearest atoms, electron-negativities (EN) of the next-neighboring atom become more effective and the isotropic Y signal shifts to the higher field with increasing in EN (for example in the order of Y–O–Y (EN(OY)≈3.69), Y–O–Al (EN(OAl)≈3.73), and Y–O–Si (EN(OSi)≈4.0)).[3,13)] The observed isotropic chemical shift of $Y_3Al_5O_{12}$ showed the smallest value (i.e. shift to the highest field) on comparison to others. This is reasonable because O–Al is more electronegative than O–Y and the coordination number is 8.

Concerning the ^{89}Y NMR of Y_2O_2S, no data are available. Y in Y_2O_2S has the axial symmetry and is coordinated by 4 oxygen and 3 sulfur atoms. The chemical shift of the axially 7O-coordinated ^{89}Y in Y–O–Y, if it exists, will be expected to appear at higher field than the σ_{iso} (MAS) = 289 ppm of the 6O-coordinated ^{89}Y in Y_2O_3 (axially symmetric 8b site). The σ_{iso} (MAS) of the ^{89}Y in Y_2O_2S, however, was 293 ppm and the signal appeared in the lower field than that of 289 ppm. This result is reasonably explained by the difference of electronegativity of the neighbor atoms, that is, the fact that the EN(S) = 2.5 is smaller than EN(O) = 3.5.[14)] A similar large low-field shift by the coordinated S atom was observed in S-coordinated Al and O-coordinated Al (129 ppm for $Al-S_4$ and 40 ppm for $Al-O_4$).[15)]

Chemical Shift Anisotropy and Half-Width of Signal:

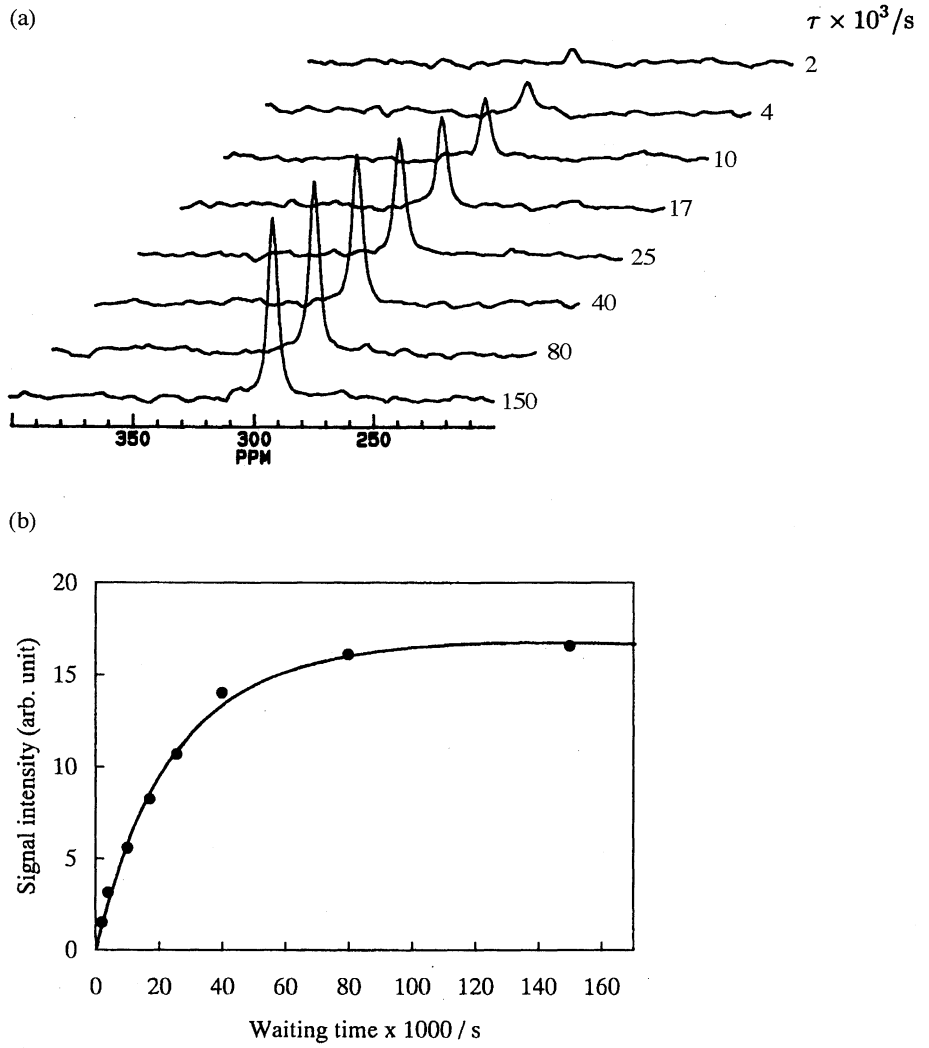

Fig. 6. (a): ^{89}Y-MAS NMR spectra of Y_2O_2S for the spin-lattice relaxation time measurement by the saturation recovery method. Spectral width: 15000 Hz, data point: 2 K, 90° pulse width: 11 μs, aquisition number: 1 time, spinning rate: 5000 rps. (b): Plot of the peak intensity (I) vs. waiting time (τ). The curve was fitted by the function of $I = I_0\{1 - \exp(-\tau/T_1)\}$, where I_0 is constant, by employing the non-linear least square method. RSS = 0.086.

The chemical shift anisotropies calculated from $(\sigma_{\parallel} - \sigma_{\perp})$ or $\{\sigma_{11} - (\sigma_{22} + \sigma_{33})/2\}$ of static signals and the half-widths of the signals under MAS are tabulated in columns (6) and (7) in Table 1, respectively. Both in Y_2O_3 containing Y–O–Y bonds in 6O-axial or rhombohedral symmetries, and in $Y_3Al_5O_{12}$ containing Y–O–Al bonds in 8O-coordinated state, the chemical shift anisotropies of the ^{89}Y are in the range of 1500—1600 Hz (100—110 ppm). This indicates that the next-nearest atom X in the Y–O–X bond and the coordination symmetry do not strongly affect the chemical shift anisotropy in Y–O_n systems. On the other hand, in Y_2O_2S in the 4O- and 3S-axially coordinated state, the chemical shift anisotropy was 2360 Hz (161 ppm) and is significantly larger than that in others (Y–O system). The chemical shift anisotropy might be influenced much more by the type of atom directly bonded to Y than the coordination number and the crystallographic symmetry.

Spin-Lattice Relaxation Time: A typical example of the ^{89}Y-MAS spectra for determination of T_1 by the saturation recovery method and of the plot of the signal intensity vs. waiting time (τ) is shown for Y_2O_2S in Figs. 6-(a) and -(b), respectively. The curve was fitted by employing the non-linear least square method to the function of $I = I_0\{1 - \exp(-\tau/T_1)\}$, where I_0 is constant. The obtained T_1 values of three compounds are given in column (8) in Table 1.

The T_1 value of Y_2O_2S was extremely long, 6.61 h, and the T_1 values of Y_2O_3 were 3.92 h and 3.81 h for the ^{89}Y at 24d and 8b sites, respectively. The chemical shift anisotropy can affect the spin-lattice relaxation time in such a way that T_1 is reversibly proportional to the square of the anisotropy. Although the chemical shift anisotropy, as mentioned above, is about 1.5 times larger in Y_2O_2S than in Y_2O_3, the T_1 value of Y in Y_2O_2S is not smaller by a factor of 1/2.25, but is rather larger than that in Y_2O_3. Therefore, the chemical shift anisotropy should not be an origin of the spin-lattice relaxation mechanism. The reason why Y_2O_2S has a such long T_1 is not clear in this study. One possibility may be the rigidity of the crystal of Y_2O_2S.

On the other hand, T_1 of $Y_3Al_5O_{12}$ is 1.10 h and it is much shorter compared with those of Y_2O_2S and Y_2O_3. If we consider about the same chemical shift anisotropy between $Y_3Al_5O_{12}$ and Y_2O_3 (24d and 8b), it is easily concluded that the anisotropy is not the main origin of differences of the spin-lattice relaxation time in these case.

The neighbor atom of Y–O– in Y_2O_2S and Y_2O_3 is Y, which has the nuclear spin $I^{Y} = 1/2$ and the gyromagnetic ratio $\gamma^{Y} = -1.3108\times10^7$ rad·Tesla^{-1}·sec^{-1}, whereas that in $Y_3Al_5O_{12}$ is ^{27}Al, which has the nuclear spin $I^{Al} = 5/2$ and $\gamma^{Al} = 6.9704\times10^7$ rad·Tesla^{-1}·sec^{-1}. Therefore, the most likely origin of the much shorter T_1 of $Y_3Al_5O_{12}$ is thought to be the dipole–dipole interaction between ^{89}Y and ^{27}Al.[16]

Conclusions

Tb-doped $Y_3Al_5O_{12}$ and Eu-doped Y_2O_2S or Y_2O_3 are green and red phosphors, respectively. Therefore, it is very important to evaluate the chemical and physical properties of the phosphors precisely at the atomic level for better development of the phosphors. Recently, ^{89}Y solid state NMR spectroscopy is highlighted to this purpose, despite the technical difficulty. Before proceeding the investigation in rather complex materials, i.e., rare-earth ion-doped Y compounds, we have to confirm the NMR property of mother Y compounds of phosphors. In the present paper, the anisotropic chemical shift in the static NMR, observed and calculated isotropic chemical shifts, and the spin-lattice relaxation time of ^{89}Y in the three mother compounds, $Y_3Al_5O_{12}$, Y_2O_2S, and Y_2O_3, were presented, some of which are the first data investigated so far. These data will be useful for coming studies of the phosphor.

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