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γ-irradiated $[(CH_3)_4N]_2SiF_6$ single crystal investigation by electron paramagnetic resonance technique

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Abstract

In this study, γ-irradiation damage centers in $[(CH_3)_4N]_2SiF_6$ single crystal has been investigated by electron paramagnetic resonance spectroscopy (EPR) at room temperature. It has been found that γ-irradiation produces the $(CH_3)_3\dot{N}^+$ radicals in this compound. The *g* factor and the hyperfine constant for H atoms, measured as 28.7 G, were found to be isotropic. The hyperfine coupling constant of the N nucleus, observed $(CH_3)_3\dot{N}^+$ hole radical in $[(CH_3)_4N]_2SiF_6$ was found to be anisotropic with $A_{//} = 15$ and $A_\perp = 23$ G, respectively. This means that each methyl groups rotate around the C_{3v}-axis and they also rotate around the C_{3v}-axis of $(CH_3)_3\dot{N}^+$ radical. These results were compared with the earlier studies in $(CH_3)_3\dot{N}^+$ radical and discussed.

Keywords: EPR; γ-irradiation; Single crystal; $(CH_3)_3\dot{N}^+$ radical

1. Introduction

It is well known that free radicals can be produced in crystals via γ-, x-, or uv-irradiation and these free radicals can be studied by the electron paramagnetic resonance (EPR) technique. The electron paramagnetic resonance (EPR) investigations provide the most complete information about the structure and the motional behaviour of radicals. In literature, several authors have studied the $(CH_3)_3\dot{N}^+$ radical produced in various substances [1–4]. As a result of these studies, it can be concluded that the crystal field effects are not much effective on the structure of the $(CH_3)_3\dot{N}^+$, but the motional behaviour of this radical was found to be different in $(CH_3)_4NCl$, $(CH_3)_4NBF_4$, and $(CH_3)_4NPF_6$ from those of which are trapped in betaine, betaine hydrochloride, betaine monohydrate and in $[(CH_3)_3NH]_2SnCl_6$. In the former compounds in addition to methyl group reorientations around the N–C bonds and the reorientation of the $(CH_3)_3\dot{N}^+$ around its C_{3v}-axis, in the latter compounds the rotation or jumping reorientation of the C_{3v}-axis of the $(CH_3)_3\dot{N}^+$ radical has been observed [4]. This radical species could be produced by γ-irradiation, through the breakage of the N–H bond of the $[(CH_3)_4N]^+$ ions or the breakage of an N–C bond of the $[(CH_3)_4N]^+$ ions [3]. As a continuation of this kind of studies, we report in this paper the EPR spectra of γ-irradiation products in $[(CH_3)_4N]_2SiF_6$ and to our knowledge this compound was not previously investigated in single crystal form at room temperature. In this study, the motional behaviour of $(CH_3)_3\dot{N}^+$ radical was investigated in single crystal form at room temperature.

2. Experimental

$[(CH_3)_4N]_2SiF_6$ single crystals were prepared by slow evaporation at ambient temperature from an aqueous solution containing stoichiometric amounts of H_2SiF_6 and $(CH_3)_4NOH$ (1:1 proportion). The X-ray study of the $[(CH_3)_4N]_2SiF_6$ single crystal at ambient temperature shows that this compound is face centred cubic. The space group

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F_m3_m, of antifluorite type, has $a = 11.172$ Å parameter [5]. The unit cell contains four molecules ($Z = 4$). Suitably sized crystals were irradiated with ^{60}Co γ-ray source at ambient temperature to a dose of about 158 kGy. The dimensions of single crystal are about $1 \times 2 \times 3$ mm^3. The EPR spectra were recorded with a Varian E-109C model, X-band EPR spectrometer using 63 mW microwave power and the modulation frequency of the magnetic field was 100 kHz. The modulation amplitude was around 16 G. The single crystals were rotated on a Lucit pillar about three mutually perpendicular planes (*ab*, *ac* and *bc*) and the spectra were recorded at 10° steps. The *g* values were obtained by comparison with a diphenylpicrylhydrazyl(dpph) sample of $g = 2.0036$.

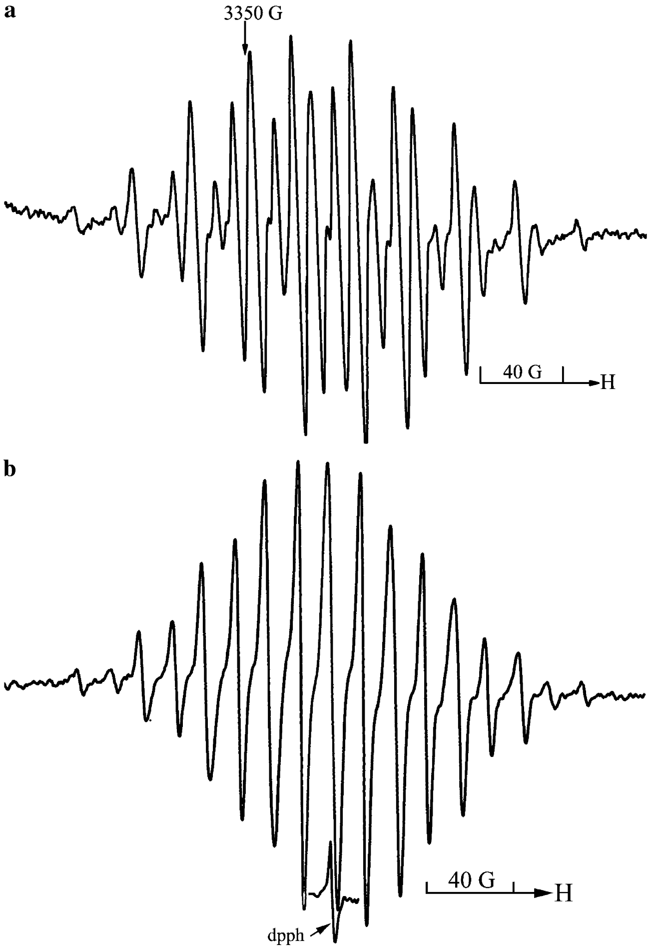

Fig. 1. (a) The EPR spectrum of γ-irradiated $[(CH_3)_4N]_2SiF_6$ single crystal (a) when the magnetic field is in the (*bc*) plane and 140° away from the *b*-axis. (b) The EPR spectrum of γ-irradiated $[(CH_3)_4N]_2SiF_6$ single crystal at room temperature. The magnetic field is along the *c*-axis.

3. Results and discussion

Fig. 1a and b show the recorded EPR spectra of γ-irradiated $[(CH_3)_4N]_2SiF_6$ single crystals at room temperature, when the magnetic field is in the (*bc*)-plane and 140° away from the *b*-axis and along the *c*-axis, respectively. The recorded EPR spectra at all orientations of the magnetic field show many lines at room temperature, which are attributed to $(CH_3)_3\dot{N}^+$ radicals. The spectrum in Fig. 1a exhibits an intensity distribution as 1:1:9:1:9:36:9:36:84:36:84:126:84:126:126:126:126:84:126:84:126:84:36:-84:36:9:1:9:1:1 when the magnetic field is along the *b*-axis. This spectrum belongs to the $(CH_3)_3\dot{N}^+$ radical since the hyperfine interactions of the free electron with nine equivalent methyl protons and ^{14}N nucleus of nuclear spin $I = 1$ with the hole $(CH_3)_3\dot{N}^+$ radical. At this orientation the hyperfine value of protons of the methyl groups is almost isotropic and $a_{CH_3} = 29$ G. In Fig. 1b, this spectrum was recorded when the magnetic field was along the *c*-axis. At this orientation the hyperfine value of the protons is $a_{CH_3} = 29$ G and $A_N = 14.5$ G. The hyperfine coupling constant of protons is isotropic and methyl groups are equivalent. The hyperfine coupling constant of the N nucleus with the hole in $(CH_3)_3\dot{N}^+$ in $[(CH_3)_4N]_2SiF_6$ was found to be axially symmetric. The principal values and their direction cosines of EPR parameters are given in Table 1. The principal values and the averages of A_N for $(CH_3)_3\dot{N}^+$ radical are given in Table 2 in various substances with the results of the present work. Each methyl groups rotates around their C_{3v}-axes and they also rotate around the C_{3v}-axis of $(CH_3)_3\dot{N}^+$ radical. In addition to these motions, the C_{3v}-axis of $(CH_3)_3\dot{N}^+$ radical seem to rotate with an angle around the *c*-axis of the crystal, since $A_z < A_x = A_y$ is in Table 2 and the signal is isotropic in the (*ab*) plane. The isotropic *g* value of the radical in $[(CH_3)_4N]_2SiF_6$ is $g = 2.004$ and is in agreement with the previously obtained values for this radical. The powder spectrum

Table 1
The principal values and direction cosines with respect to *a*, *b* and *c* axes of *g* and the A_N hyperfine tensors of the $(CH_3)_3\dot{N}^+$ radical observed in γ-irradiated $[(CH_3)_4N]_2SiF_6$ single crystal at room temperature

g_N	Direction cosines			Hyperfine A_N (G)	Direction cosines		
	c	*a*	*b*		*c*	*a*	*b*
$g_z = 2.0041$	0.805	0.291	0.518	$A_z = 15$	0.997	−0.025	−0.063
$g_x = 2.0036$	−0.046	0.900	−0.433	$A_x = 23$	−0.003	0.914	−0.406
$g_y = 2.0032$	−0.592	0.325	0.738	$A_y = 23$	0.068	0.405	0.912

A_N are in G. $\Delta g = \pm 0.0005$ and $\Delta A = \pm 0.5$G.

Table 2
The principal values and the averages of the ^{14}N nucleus hyperfine coupling constants (in G) of $(CH_3)_3\dot{N}^+$ radicals in various substances at room temperature

Substance	g_{izo}	a_{CH_3}	A_x	A_y	A_z	A_N	Reference
$[(CH_3)_4N]_2SiF_6$	2.0043	28.7	23	23	15	20.3	Present work
$[(CH_3)_4N]_2ZnCl_4$	2.0044	28.7	14.5	19	28.7	20.7	[1]
$(CH_3)_3NHBF_4$	2.0024	28.5	4.3	10	46.2	20.2	[1]
$(CH_3)_4NPF_6$	2.0046	28.8	22.8	22.8	16.2	20.6	[6]
$[(CH_3)_4N]_2CdCl_4$	2.0032	29	–	–	–	20	[2]
$[(CH_3)_4N]InCl_4$	2.003	28.6	14	16.2	29.2	19.8	[2]
$[(CH_3)_4N]CdCl_3$	2.0036	29.2	12.8	12.8	33.1	19.8	[3]
$[(CH_3)_3NH]_2SnCl_6$	2.002	29.4	7.2	7.2	46.4	20.3	[3]
$(CH_3)_4NCl$	2.0044	26.7	20.4	20.4	13.2	18	[4]
$(CH_3)_4NCl$	–	28.9	24.6	25	13.6	21.1	[7]
Betaine	–	28.2	7.9	5.3	50.8	21.3	[7]
$(CH_3)_4NBF_4$	2.0051	28.8	22.5	22.5	16.2	20.3	[6]

$\Delta g = \pm 0.0005$ and $\Delta A = \pm 0.5$ G.

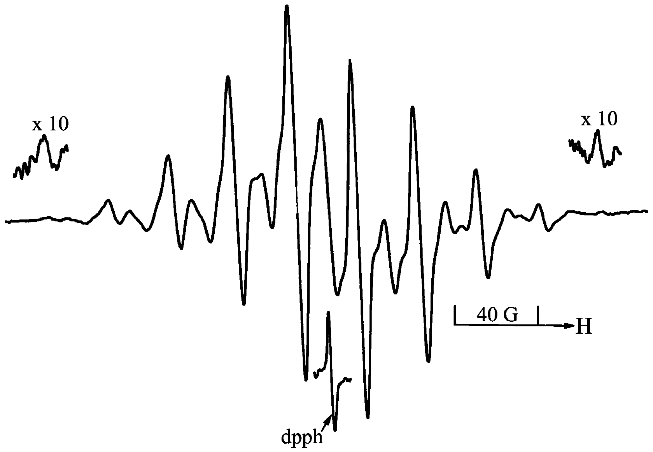

Fig. 2. The EPR spectrum of γ-irradiated $[(CH_3)_4N]_2SiF_6$ powder crystals at room temperature.

is shown in Fig. 2, with its g value is $g = 2.0043$. The hyperfine coupling constant of protons is $a_{CH_3} = 28.7$ G and the hyperfine coupling constant of nitrogen nucleus is not measured exactly.

4. Conclusions

The EPR results presented in this study indicate the radicals induced by γ-irradiation in $[(CH_3)_4N]_2SiF_6$ is $(CH_3)_3\dot{N}^+$. The EPR parameters of the radicals are found to be consistent with the previous results in the literature. In this single crystal, radical was found to be in various motions. As a result of this work, it can be concluded that the C_{3v}-axis of the $(CH_3)_3\dot{N}^+$ radical seem to rotate around the c-axis of the crystal since the EPR spectra did not changed in the (ab) plane.

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