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The purity of $SnCl_4$ as monitored by ^{35}Cl nuclear quadrupole resonance

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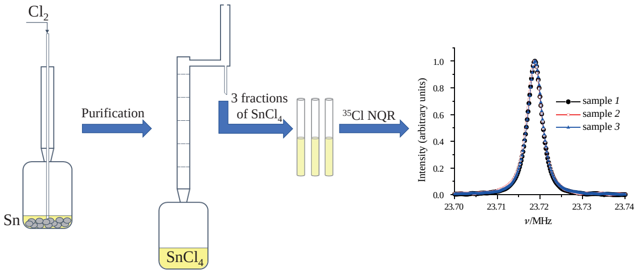
The nuclear quadrupole resonance (NQR) spectroscopy was used to control the comparative purity of three $SnCl_4$ samples subjected to successive stages of deep purification. The results showed that at 77 K the samples were identical in purity degree due to the 'freezing' of impurities into a separate fraction not affecting the perfection of the $SnCl_4$ crystal lattice. The results of relaxation measurements suggest that paramagnetic impurity atoms (Fe and Cr) contained in the samples in small amounts might be embedded into the crystal lattice causing extremely long spin–spin relaxation time.



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Tin tetrachloride is a precursor for the synthesis of organotin compounds[1–5] and a catalyst for organic synthesis.[6] The presence of impurities in tin(IV) halide compounds results in the changes in their physical properties which might differ considerably from the properties of the same compounds of high purity.[7–9] Organotin(IV) compounds are used as potential biological agents for the treatment of various diseases, so the purity of the raw $SnCl_4$ is of great importance.[7,8] The purity of $SnCl_4$ plays an important role in producing SnO_2 thin films as an *n*-type semiconductor.[10,11] Therefore, the technologies for obtaining such compounds as well as methods for monitoring their purity are relevant problems. The purity of $SnCl_4$ samples was earlier analyzed *via* IR and Raman spectroscopy.[12]

In this paper, we applied nuclear quadrupole resonance (NQR) spectroscopy to control the comparative purity of $SnCl_4$ samples.

Samples of $SnCl_4$[†] were synthesized and purified on a disk-type quartz distillation column. The impurity composition of the obtained $SnCl_4$ samples was determined by inductively coupled plasma mass spectrometry (ICP-MS).[12] The purity of the main fraction of $SnCl_4$ was 99.995 wt% (sample *1*), the head fraction purity was 99.95 wt% (sample *2*) and for the sample before purification it was 99.7 wt% (sample *3*). The relative purity of the samples was further compared using ^{35}Cl NQR spectroscopy.

In the NQR, the external factor with respect to the nucleus is the electric field gradient: EFG = $q_{ik} = -\partial E_i/\partial x_k = -\partial^2 U/\partial z_i \partial z_k$, where E_K is the strength and U is the potential of the field at the nuclear site, produced by the spatial distribution of charges (electron density) around the nucleus under study. In the system of principle axes, the EFG tensor is usually determined as $|q_{zz}| > |q_{xx}| > |q_{yy}|$. The EFG depends on the nucleus environment, thus, NQR spectra allow one to obtain the detailed information regarding crystal chemistry, electronic and geometric structure and crystal lattice characteristics of the substance.[13,14]

The measured spectroscopic parameters of the NQR include the quadrupole coupling constant (QCC), the EFG asymmetry parameter $\eta = |q_{xx} - q_{yy}|/q_{zz}$, the resonance line width ($\Delta\nu$) and spin–lattice (T_1) and spin–spin (T_2) relaxation times. The spin Hamiltonian of the quadrupole interaction is entirely defined by the interactions within the crystal field, therefore, NQR spectroscopy is direct, the most effective and accurate method of measuring these interactions. It allows the determination of the parameters of the nuclear quadrupole interaction for each atom, even if the latter occupies several crystallographically independent positions in the unit cell. Thus, the ^{35}Cl NQR spectrum of $SnCl_4$ measured at 77 K (as at room temperature the compound is in the liquid state) consists of a four lines at frequencies of 23.72, 24.14, 24.23 and 24.29 MHz.[15,16] The width of the resonance line is determined by the following factor:[13]

$$\Delta\nu = (T_2^*)^{-1} \sim (T_1)^{-1} + (T_2)^{-1} + \Delta A. \quad (1)$$

Here, the term ΔA is defined by the statistical distribution of the EFG components over the sample volume due to the inhomogeneity of the crystal and T_2^* is the effective free induction decay time. Molecular motions, such as torsion vibrations or reorientations, determine the spin–lattice relaxation

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[†] Tin metal (pure grade, Lanhit Ltd., Russia) and Cl_2 (pure grade, Lanhit Ltd., Russia) were used as initial components. Tin tetrachloride was prepared in a quartz apparatus consisted of a distilling column (reflux condenser), still, quartz hose and receiver for the sampling of prepared tin tetrachloride. Deep purification of tin tetrachloride was conducted in a perforated-plate rectification column (high-purity grade quartz) as described earlier.[12]

time T_1. The spin–spin relaxation time (spin–phase memory) T_2 is determined by magnetic dipole interactions. The NQR spectra of the vast majority of inorganic compounds show the line widths of 30–50 kHz owing to the presence of impurities, dislocations, vacancies and other defects in their lattice. They are defined by the term ΔA in the equation (1), whereas the contribution of the relaxation terms is much smaller.

The high sensitivity of the NQR spectra to the state of the crystal lattice has earlier been employed to study the behavior of impurities and the effect of various factors, such as particle size and density of the substance, on the quadrupole interaction parameters. It was noted that the NQR line width is a sensitive criterion of crystal quality.[17,18]

Preparation of the high purity samples yielding narrow NQR lines, inasmuch as ideally the line width is determined only by the relaxation terms in equation (1), was an important task of this work. The data on impurity content in the samples *1–3* obtained by inductively coupled plasma mass spectrometry[‡] (ICP-MS)[12] are given in Table 1.

Figure 1 depicts the recordings of the ^{35}Cl NQR spectra[§] in these samples. Spectroscopic parameters for each resonance line are given in Table 2. Extremely narrow lines are observed in the NQR spectra of all the samples which is very rare among the published spectra of inorganic compounds.[13] Moreover, recordings of the low-frequency resonance line in the NQR spectra of all the samples (see Figure 2) revealed their almost complete identity, thus indicating the same degree of purity of the samples studied. On tentative estimates, the resonance line widths in the spectra of the samples (Table 2) allows one to assume the negligible contribution of lattice defects or impurities into the perfection of their crystal lattice. In this instance, the NQR linewidth is determined, as it follows from equation (1), by the relaxation contribution $(T_2)^{-1}$ corresponding to the spin–spin relaxation time $T_2 \approx 250$–300 μs (see Table 2).

Table 1 Impurity content in the $SnCl_4$ samples *1–3* (10^{-4} wt%).

Impurity	Sample *1* Main fraction	Sample *2* Head fraction	Sample *3* Fraction after synthesis
Al	2	15	45
B	1	2	3
Ba	0.4	0.4	5
Bi	1	5	20
Ca	1	2	6
Cd	0.2	1	1
Co	0.4	1	1
Cr	0.5	1	5
Cu	0.5	2	30
Fe	1	10	60
Ge	0.5	18	20
K	0.5	0.5	1
Li	0.1	1	1
Mg	1	1	5
Mn	1	1	1
Na	0.5	0.5	0.5
Ni	0.5	3	10
Pb	2	20	120
Sb	1	10	20
Si	1.3	1.3	1.3
Sr	0.5	1	1
Ti	0.5	1	2
V	0.5	0.5	1
Zn	1	6	15

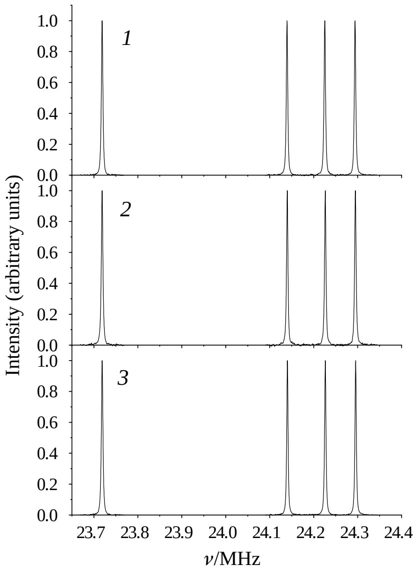

Figure 1 ^{35}Cl NQR spectra of $SnCl_4$ at 77 K for the samples *1*, *2* and *3*.

To confirm this statement, we measured the spin–spin relaxation time T_2 for the low-frequency lines (lines 1) in the NQR spectra of all the samples. Unexpectedly, extremely slow spin–spin relaxation was observed in all the samples, T_2 varied from 2550 to 3050 μs, which is an order of magnitude more than $1/\Delta\nu$ values (see Table 2). This evidenced that the relaxation contribution is still a small part of the line width in the spectra of all three samples. One cannot exclude herewith that the enhancement of the T_2 values occurs due to the magnetic impurities such as Fe and Cr (see Table 1) embedded in the crystal lattice of the samples. All other impurities were apparently ‘frozen’ at 77 K without affecting the ^{35}Cl NQR spectroscopic parameters (QCC and η) and the perfection of the $SnCl_4$ crystal lattice. A similar effect was earlier observed in BGO ($Bi_4Ge_3O_{12}$) crystals doped with minor amounts of paramagnetic atoms (0.015 mol% of Cr, 0.2 mol% of Gd, 0.2 mol% of Pr and 0.5 mol% of Nd).[19] These dopants did not affect the values of QCC and η in their ^{209}Bi NQR spectra but caused the elongation of the spin–spin relaxation time T_2 from 50 to 400 μs.

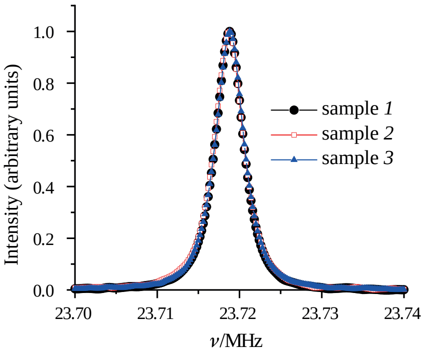

Figure 2 Recording of the ^{35}Cl low-frequency resonance line for three samples of $SnCl_4$ at 77 K.

[‡] Impurity composition was determined by inductively coupled plasma atomic emission spectroscopy using a Thermo iCAP 6300 Duo spectrometer.

[§] The ^{35}Cl NQR spectra were measured by the standard spin echo technique with a Hahn sequence of π/2 and π pulses separated by a time interval τ. A direct digital quadrature detection procedure at the carrier frequency was applied to the spin echo signal followed by summation over several scans to reduce the noise contribution. Since the spectra of all samples represented sets of narrow lines, further processing of the signal was carried out by the fast Fourier transform of the second half of the spin echo at the peak frequency of each line.[20] The real part of the Fourier transform was used as the spectrum. The spin–spin relaxation time T_2 was measured by the standard method of gradual increase in the interval τ between pulses followed by analysis of the dependence of the spin echo magnitude integral $I(\tau)$.

Table 2 Parameters of the ^{35}Cl NQR spectra at 77 K for the studied $SnCl_4$ samples.

Sample	Line	Frequency ν/MHz	Line width $\Delta\nu$/kHz	Inverse line width $1/\Delta\nu$ (μs)
Sample *1*	Line 1	23.718770(6)	3.692(19)	271(2)
	Line 2	24.139391(7)	3.420(20)	292(2)
	Line 3	24.225255(6)	3.600(19)	278(2)
	Line 4	24.294138(7)	3.547(25)	282(2)
Sample *2*	Line 1	23.718723(6)	3.862(19)	259(2)
	Line 2	24.139870(6)	3.315(18)	302(2)
	Line 3	24.226324(5)	3.397(16)	294(2)
	Line 4	24.294826(7)	3.593(24)	278(2)
Sample *3*	Line 1	23.718810(6)	3.771(19)	265(2)
	Line 2	24.140227(5)	3.179(16)	315(2)
	Line 3	24.226385(5)	3.364(16)	297(2)
	Line 4	24.295442(5)	3.321(19)	301(2)

In summary, the comparative purity of three $SnCl_4$ samples synthesized and purified on a disk-type quartz distillation column was determined *via* ICP-MS and estimated by the ^{35}Cl NQR. It was shown that the samples were identical in purity; this can be explained by the effect of 'freezing' the impurities at 77 K into a separate fraction, which does not affect the $SnCl_4$ crystal lattice perfection. The magnetic impurities such as Fe and Cr are evidently embedded in the crystal lattice of the samples significantly elongating the spin–spin relaxation time.

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