

Reconstructing Reliable Powder Patterns from Spikelets (Q)CPMG NMR Spectra: Simplification of UWNMR crystallography analysis

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Table S1. Details of NMR experimental parameters

Compound	Investigated nuclei	Spikelet separation (Hz)	WURST-sweep width (MHz)	Loops No.	sub-spectra No.	Step(s) (kHz).	D ₁ (s)
Ba(NO ₃) ₂	¹³⁷ Ba	2000	0.5	64	1	---	0.5
BaCO ₃	¹³⁷ Ba	5000	1	80	7	150	0.1
BaCl ₂ ·2H ₂ O	³⁵ Cl	1000	0.5	64	1	---	4
AlMe ₃	²⁷ Al	5000	1	64	5	100	2
AlMe ₃ ·THF	²⁷ Al	5000	1	64	5	100	2
Pb(HCOO) ₂	²⁰⁷ Pb	2500	0.5	75	1	178	7
Hg(CH ₃ COO) ₂	¹⁹⁹ Hg	5000	0.75	75	1	---	1450
Cs ₂ AgBiBr ₆	²⁰⁹ Bi	5000	2	12	1	---	4
Ga(NO ₃) ₃ ·9H ₂ O	⁷¹ Ga	1000	1	32	1	---	2
Ga ₁₃ (NO ₃) ₁₅ (OH) ₂₄ ·24H ₂ O	⁷¹ Ga	1000	1	32	1	---	2
In(NO ₃) ₃ ·5H ₂ O	¹¹⁵ In	5000	1	16	1	---	2
[Cl(Me)Ga(O ^t Bu)] ₂	⁷¹ Ga	5000	1	32	17	150	2

Table S2. Used external standards for NMR chemical shift referencing

Nuclei	External standard
¹³⁷ Ba	0.5 M solution of BaCl ₂ in D ₂ O (¹³⁷ Ba: 0.0 ppm)
³⁵ Cl	0.1 M solution of NaCl in D ₂ O (³⁵ Cl: 0.0 ppm)
²⁷ Al	1 M solution of Al(NO ₃) ₃ in D ₂ O (²⁷ Al: 0.0 ppm)
²⁰⁷ Pb	solid Pb(NO ₃) ₂ (²⁰⁷ Pb: -3473.6 ppm)
¹⁹⁹ Hg	The chemical shift referencing was calculated to the unified scale accordingly to IUPAC [1]
²⁰⁹ Bi	Saturated solution of Bi(NO ₃) ₃ ·5H ₂ O in concentrated HNO ₃ (²⁰⁹ Bi: 0.0 ppm)
⁷¹ Ga	1 M solution of Ga(NO ₃) ₃ in D ₂ O (⁷¹ Ga: 0.0 ppm)
¹¹⁵ In	0.1 M solution of In(NO ₃) ₃ in 0.5 M of HNO ₃ (¹¹⁵ In: 0.0 ppm)

Table S3. Crystallographic data of the investigated compounds

Compound	PDF or CSD code*	Space group	Reference
Ba(NO ₃) ₂	<i>01-070-9288</i>	Pa-3	[2]
BaCO ₃	<i>01-074-2663</i>	Pnam	[3]
BaCl ₂ ·2H ₂ O	<i>01-081-9342</i>	P21/n	[4]
AlMes ₃	TMEAL	C2/c	[5]
AlMes ₃ ·THF	YEVVAZ	P21/c	[6]
Pb(HCOO) ₂	BIYLAW01	P212121	[7]
Hg(CH ₃ COO) ₂	HGACET10	P21/a	[8]
Cs ₂ AgBiBr ₆	---	Fm-3m	[9]
Ga(NO ₃) ₃ ·9H ₂ O	<i>04-016-7745</i>	P21/c	[10]
Ga ₁₃ (NO ₃) ₁₅ (OH) ₂₄ ·24H ₂ O	<i>04-014-0474</i>	R-3	[11]
In(NO ₃) ₃ ·5H ₂ O	<i>04-017-7341</i>	C2/c	[12]

* PDF codes are denoted in italic font, CSD codes are denoted in bold font

One of the objectives specified the main text is to find positions and intensities of spikelets in a noisy spectrum so that the spectrum can then be smoothed. It should be realized that

- The noise cannot be filtered out, as its level can be higher than intensities of spikelets in some region(s) of the spectrum.
- An application of some “black box” peak-finding procedure (for example, the “findpeaks” function of Matlab®) is not practical, as it would return numerous local maxima of the noise in addition to the actual peaks.

The solution can be easily obtained, however, since the spectrum is densely and uniformly sampled. Thus, two peaks are picked to define a bin, and maxima are located in all bins of a spectrum. Subsequently the investigated spectrum is smoothed out by an interpolation. This procedure was implemented in Matlab® independently from the software described in the main text. The block diagram follows.

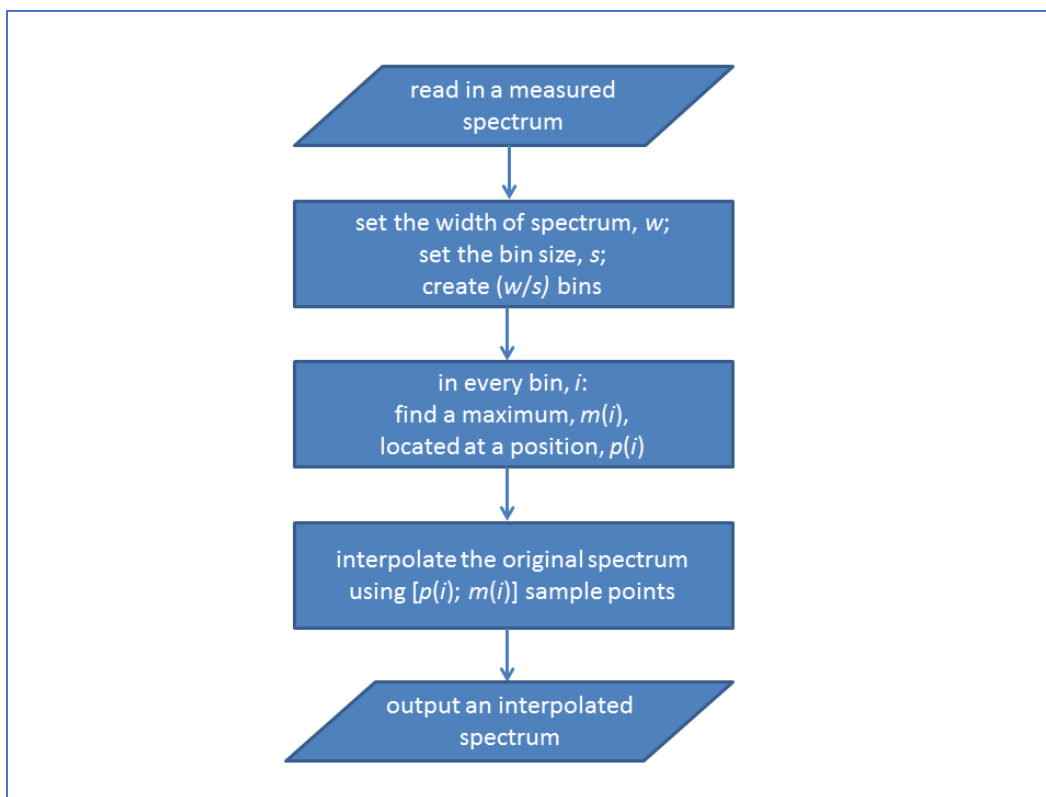


Chart S1. Description of a procedure for verifying the spectral shape.

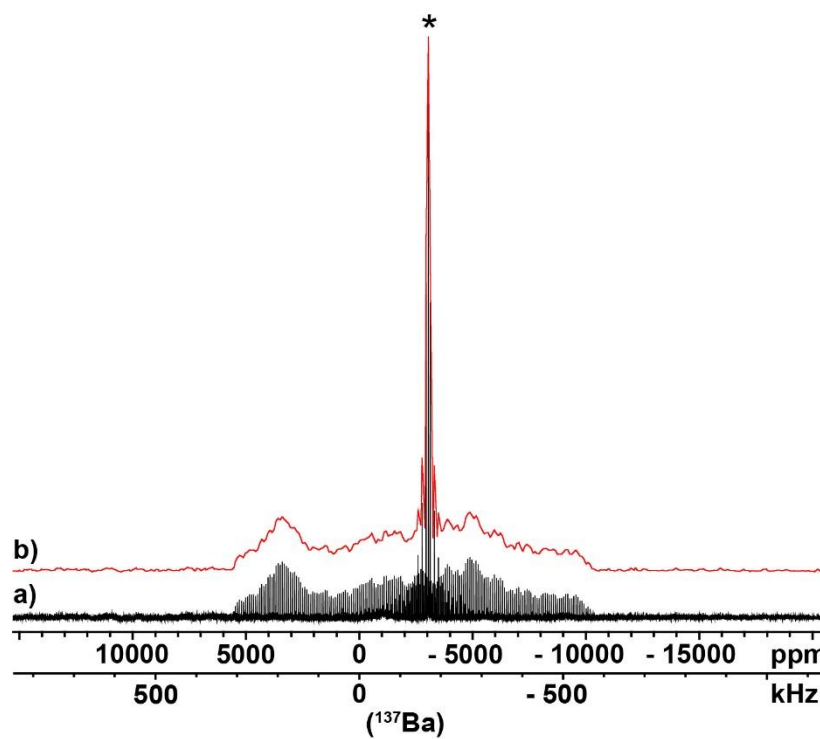


Figure S1. Full experimental ^{137}Ba WURST-QCPMG NMR spectrum of BaCO_3 (a) and the spectral profile (b) obtained by the UWNMR SpectralShape software. Impurity is denoted by an asterisk (*).

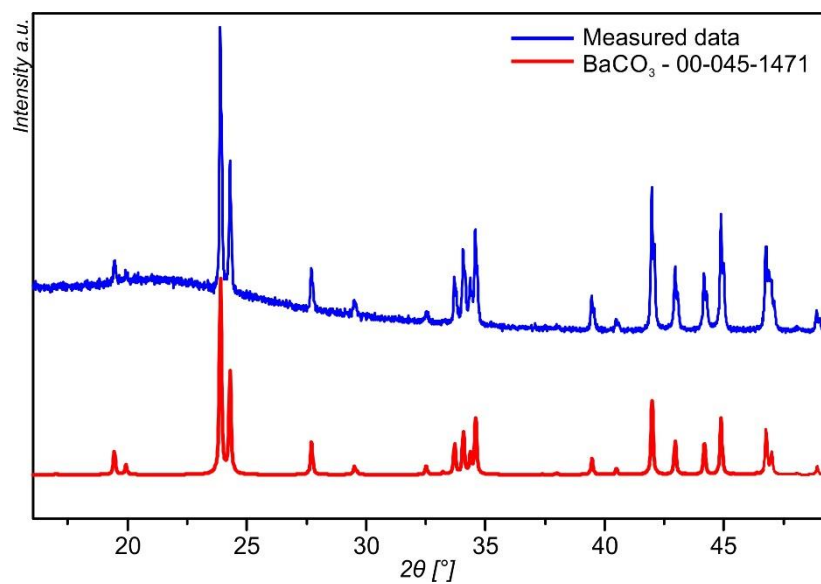


Figure S2. Phase analysis of the measured powder diffraction pattern (blue) of the BaCO₃ sample confirming the presence of one phase - BaCO₃ (calculated pattern (red), PDF card no. 00-045-1471).

Table S4. Comparison of NMR parameters obtained by fitting spectral envelopes provided by different approaches for chosen model compounds

Compound	Investigated nuclei	δ_{iso} , ppm	C_Q , MHz	η_Q	Ω , ppm	κ	α , deg	β , deg	γ , deg	Fitting
Ba(NO ₃) ₂	¹³⁷ Ba	-49(5)	6.9(0.10)	0.02(0.01)	26(15)	0.80(0.20)	43(15)	11(20)	---	1
		-47(5)	6.9(0.10)	0.02(0.01)	24(15)	0.70(0.20)	53(20)	32(20)	---	2
		-49(5)	6.9(0.10)	0.02(0.01)	25(15)	0.82(0.20)	60(20)	5(20)	---	3
BaCl ₂ ·2H ₂ O	³⁵ Cl (site A)	167(10)	2.27(0.12)	0	39(25)	-0.60(0.20)	89(20)	47(15)	49(20)	1
		164(10)	2.20(0.12)	0	43(25)	-0.60(0.20)	100(25)	30(15)	66(20)	2
		163(10)	2.28(0.12)	0	31(25)	-0.71(0.20)	93(25)	45(15)	59(20)	3
	³⁵ Cl (site B)	154(10)	3.48(0.15)	0.30(0.10)	52(25)	0.20(0.20)	22(15)	12(10)	0(25)	1
		158(10)	3.49(0.15)	0.30(0.10)	47(25)	0.10(0.20)	15(15)	15(10)	5(25)	2
		149(10)	3.50(0.15)	0.29(0.10)	55(25)	0.14(0.20)	17(15)	12(10)	0(25)	3
AlMe ₃	²⁷ Al (1)	242(15)	49.2(0.50)	0.01(0.01)	126(10)	-0.99(0.20)	170(15)	0(10)	110(10)	1
		226(15)	48.8(0.50)	0.01(0.01)	118(10)	-0.99(0.20)	180(15)	0(10)	100(10)	2
		242(15)	49.3(0.50)	0.01(0.01)	134(10)	-0.99(0.20)	168(15)	0(10)	102(10)	3
AlMe ₃ ·THF	²⁷ Al (2)	130(10)	27.0(0.30)	0.17(0.08)	47(5)	0.05(0.08)	195(10)	83(5)	210(10)	1
		133(10)	26.8(0.30)	0.17(0.08)	51(5)	0.07(0.08)	200(10)	80(5)	215(15)	2
		133(10)	26.5(0.30)	0.16(0.08)	55(5)	0.05(0.08)	210(10)	87(5)	230(15)	3
Hg(CH ₃ COO) ₂	¹⁹⁹ Hg	-2485(40)	---	---	1814(65)	0.82(0.07)	---	---	---	1
		-2488(40)	---	---	1811(60)	0.82(0.07)	---	---	---	2
		-2475(40)	---	---	1800(60)	0.78(0.07)	---	---	---	3

$\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$, $C_Q = eQV_{33}/h$, $\eta_Q = (V_{11} - V_{22})/V_{33}$, $\Omega = \delta_{11} - \delta_{33}$, $\kappa = 3(\delta_{22} - \delta_{iso})/\Omega$; Euler angles are defined in [13]. ¹ NMR parameters obtained by fitting spectral envelope (created by USS software) using Bruker TopSpin software; ² NMR parameters obtained by fitting spectral envelop (created by USS software) using Dmfit software; ³ NMR parameters obtained by fitting (using TopSpin software) spectral profile yielded by co-addition of spin echo followed by Fourier transformation.

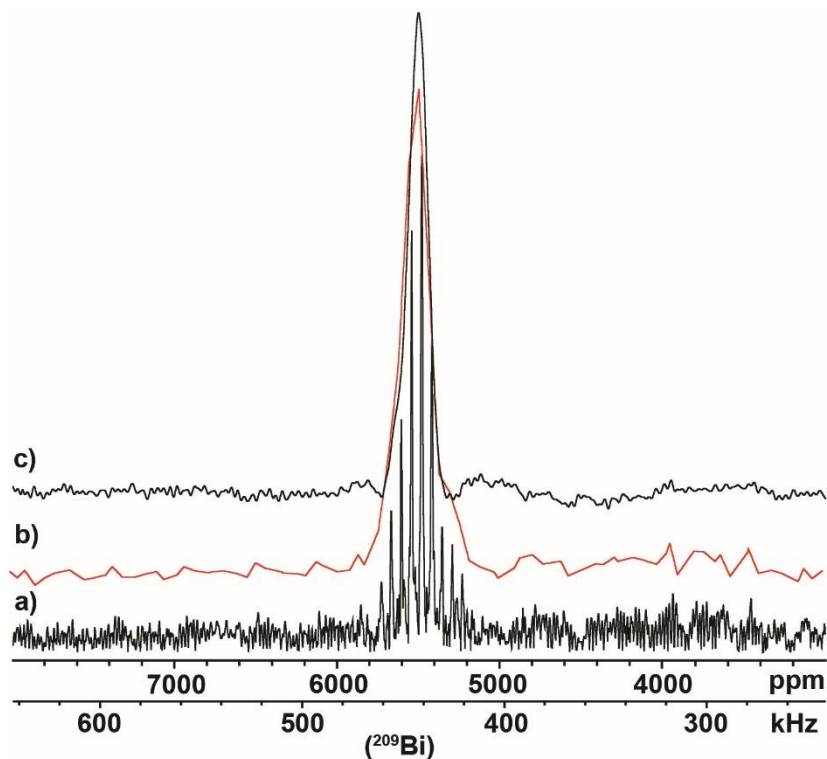


Figure S3. Experimental ^{209}Bi WURST-QCPMG NMR spectrum (a) of $\text{Cs}_2\text{AgBiBr}_6$, the spectrum profile (b) obtained by the UWNMR SpectralShape software, and experimental ^{209}Bi Hahn-echo ($\pi/2-t_1-\pi-aq.$, $t_1 = 6.5 \mu\text{s}$) spectrum (c).

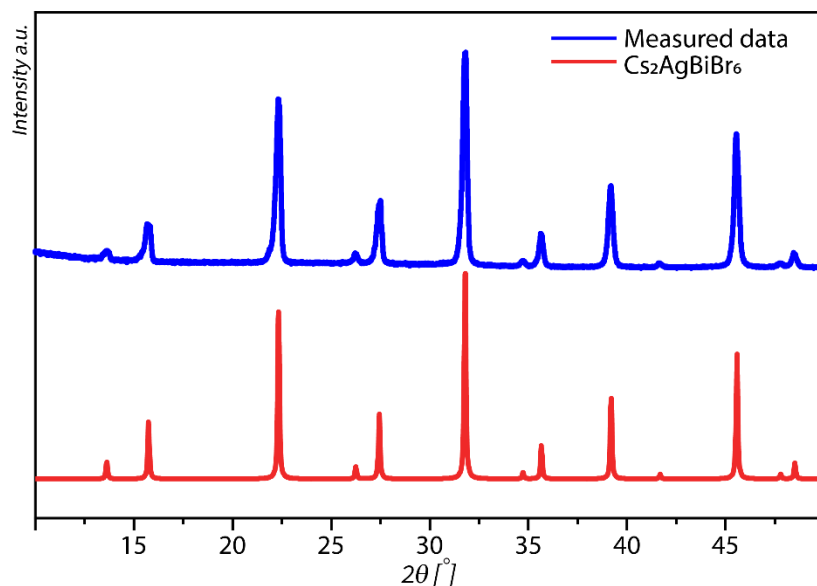


Figure S4. Phase analysis of the measured powder diffraction pattern (blue) confirming the presence of $\text{Cs}_2\text{AgBiBr}_6$ phase (calculated pattern (red))

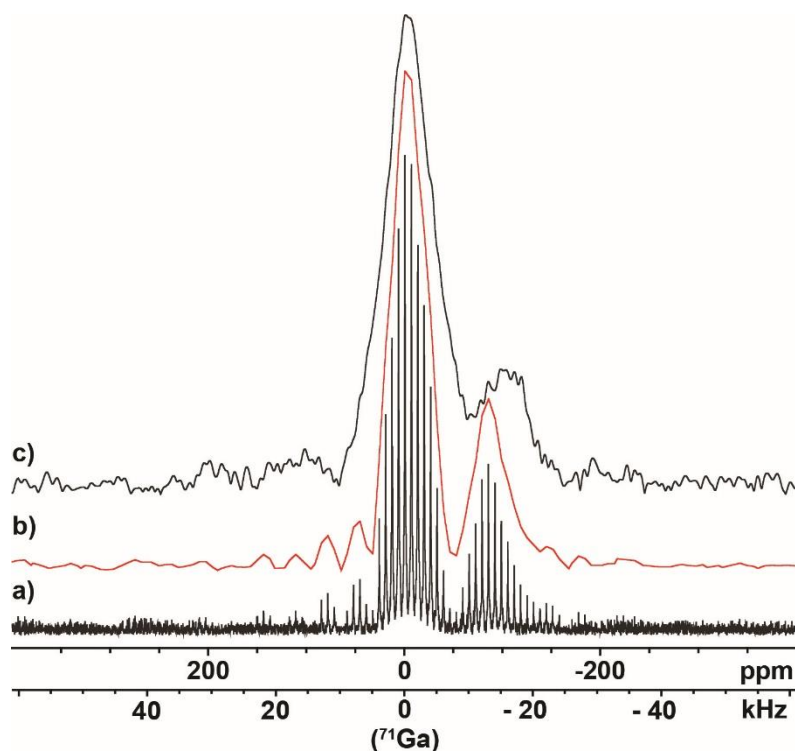


Figure S5. Experimental ^{71}Ga WURST-QCPMG NMR spectrum (a) of $\text{Ga}(\text{NO}_3)_3$, the spectrum profile (b) obtained by the UWNMRSpectralShape software, and experimental ^{71}Ga Hahn-echo ($\pi/2$ - t_1 - π - $aq.$, $t_1 = 150 \mu\text{s}$) spectrum (c).

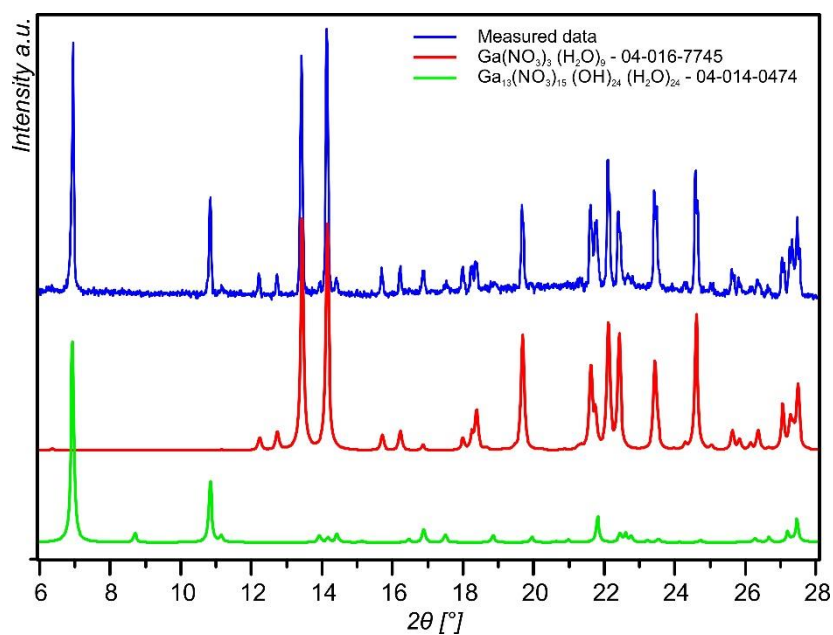


Figure S6. Phase analysis of the measured powder diffraction pattern (blue) confirming the presence of $\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ga}_{13}(\text{NO}_3)_{15}(\text{OH})_{24} \cdot 24\text{H}_2\text{O}$ phases (calculated patterns (red), PDF card 04-016-7745 and (green) PDF card 04-014-0474 respectively).

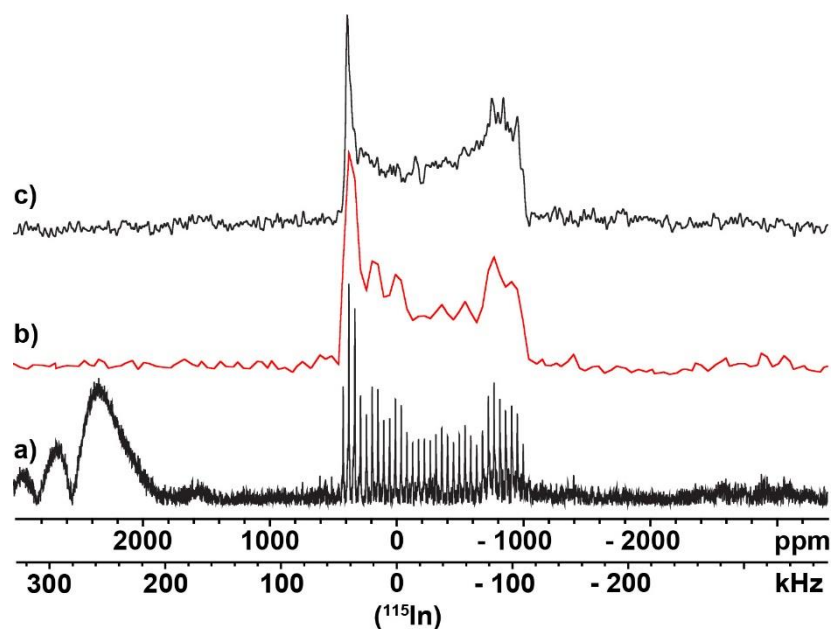


Figure S7. Experimental ^{115}In WURST-QCPMG NMR spectrum (a) of $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, the spectrum profile (with corrected background) (b) obtained by the UWNMR SpectralShape software, and experimental ^{115}In Hahn-echo ($\pi/2$ - t_1 - π - $aq.$, $t_1 = 160 \mu\text{s}$) spectrum (c).

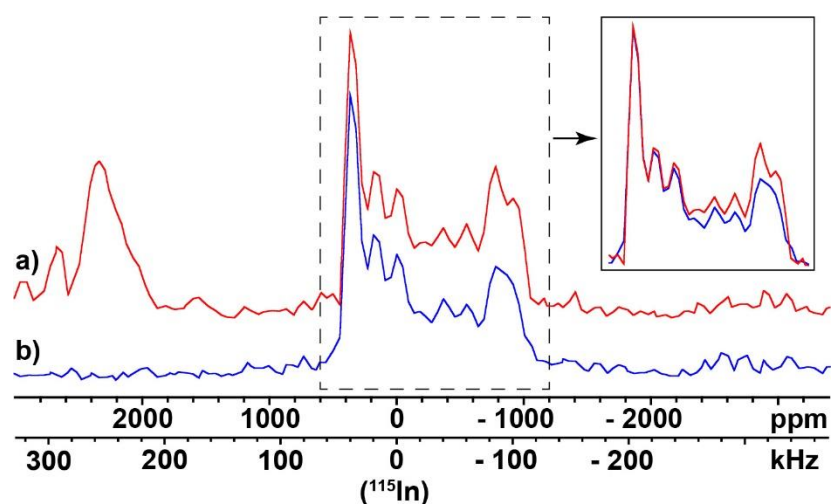


Figure S8. Profiles obtained by the UWNMR SpectralShape software of the ^{115}In WURST-QCPMG NMR spectrum of $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ processed with full (a) and cut (b) FID.

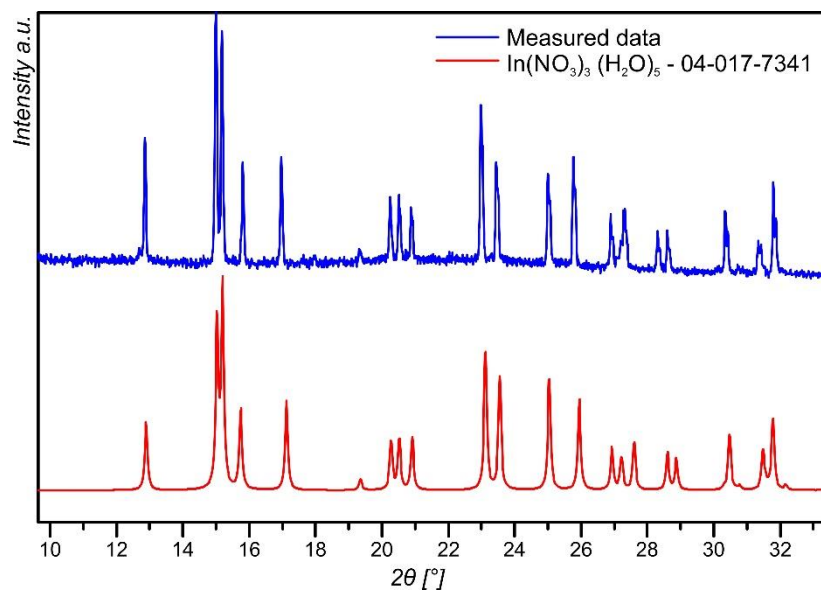


Figure S9. Phase analysis of the measured powder diffraction pattern (blue) confirming the presence of $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ phase (calculated pattern (red), PDF card no. 04-017-7341)

References

- [1] R.K. Harris, E.D. Becker, S.M. Cabral de Menezes, P. Granger, R.E. Hoffman, K.W. Zilm, Further conventions for NMR shielding and chemical shifts, *Pure Appl. Chem.* 80 (2008) 59–84. <https://doi.org/10.1351/pac200880010059>.
- [2] V.A. Trounov, E.A. Tserkovnaya, V.N. Gurin, M.M. Korsukova, L.I. Derkachenko, S.P. Nikanorov, Effect of centrifugation on the crystal structure of barium nitrate, *Tech. Phys. Lett.* 28 (2002) 351–353. <https://doi.org/10.1134/1.1477015>.
- [3] C.M. Holl, J.R. Smyth, H.M.S. Laustsen, S.D. Jacobsen, R.T. Downs, Compression of witherite to 8 GPa and the crystal structure of BaCO₃II, *Phys. Chem. Miner.* 27 (2000) 467–473. <https://doi.org/10.1007/s002690000087>.
- [4] V.P. Ting, P.F. Henry, M. Schmidtman, C.C. Wilson, M.T. Weller, Probing hydrogen positions in hydrous compounds: information from parametric neutron powder diffraction studies, *Phys. Chem. Chem. Phys.* 14 (2012) 6914–6921. <https://doi.org/10.1039/C2CP40366H>.
- [5] R.G. Vranka, E.L. Amma, Crystal structure of trimethylaluminum, *J. Am. Chem. Soc.* 89 (1967) 3121–3126. <https://doi.org/10.1021/ja00989a008>.
- [6] L. Brieger, A. Hermann, C. Unkelbach, C. Strohmman, Crystal structure and quantum-chemical calculations of a trimethylaluminium-THF adduct, *Acta Crystallogr. Sect. E Crystallogr. Commun.* 74 (2018) 267–270. <https://doi.org/10.1107/S2056989018001275>.
- [7] A. Lanza, A. Gambirasi, M. Favaro, L. Peruzzo, M. Chiurato, F. Nestola, Re-investigation of lead(II) formate, *Acta Crystallogr. Sect. C Cryst. Struct. Commun.* 69 (2013) 41–43. <https://doi.org/10.1107/S010827011204913X>.
- [8] R. Allmann, No Title, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* 138 (1973) 366–373.
- [9] A.H. Slavney, T. Hu, A.M. Lindenberg, H.I. Karunadasa, A Bismuth-Halide Double Perovskite with Long Carrier Recombination Lifetime for Photovoltaic Applications, *J. Am. Chem. Soc.* 138 (2016) 2138–2141. <https://doi.org/10.1021/jacs.5b13294>.
- [10] A.D. Hendsbee, C.C. Pye, J.D. Masuda, Hexaaquagallium(III) trinitrate trihydrate, *Acta Crystallogr. Sect. E.* 65 (2009) i65. <https://doi.org/10.1107/S1600536809028086>.
- [11] E. Rather, J.T. Gatlin, P.G. Nixon, T. Tsukamoto, V. Kravtsov, D.W. Johnson, A Simple Organic Reaction Mediates the Crystallization of the Inorganic Nanocluster [Ga₁₃(μ₃-OH)₆(μ₂-OH)₁₈(H₂O)₂₄](NO₃)₁₅, *J. Am. Chem. Soc.* 127 (2005) 3242–3243. <https://doi.org/10.1021/ja043520t>.
- [12] M.A. Malyarik, S.P. Petrosyants, A.B. Ilyukhin, Y.A. Buslaev, Polyfunctionality of the nitrate group, coordination numbers of trivalent indium in nitrate complexes, and crystal structures of (In(NO₃)(H₂O)₅)(NO₃)₂ and HK₆(In(NO₃)₄(H₂O)₂)₃(NO₃)₄, *Russ. J. Inorg. Chem. (Engl. Transl.)* 28 (1993) 1849–1854.
- [13] W.P. Power, R.E. Wasylishen, S. Mooibroek, B.A. Pettitt, W. Danchura, Simulation of NMR powder line shapes of quadrupolar nuclei with half-integer spin at low-symmetry sites, *J. Phys. Chem.* 94 (1990) 591–598. <https://doi.org/10.1021/j100365a019>.