Topological polymorphism and temperature-driven topotactical transitions of metal-organic coordination polymers

Vadim A. Dubskikh,[a] Anna A. Lysova,*[a,b] Denis G. Samsonenko,[a,b]
Danil N. Dybtsev,*[a,b], Vladimir P. Fedin[a,b]

[a]Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 3 Acad. Lavrentiev Ave., 630090, Novosibirsk, Russia

[b]Novosibirsk State University, 2 Pirogov Str., 630090, Novosibirsk, Russia

*Corresponding authors: lysova@niic.nsc.ru; dan@niic.nsc.ru

Table S1. Crystal data and structure refinement for **1**–**2**.

Compound/parameter	**1**	**2**
Empirical formula	$C_{45}H_{47}Mg_3N_5O_{17}S_6$	$C_{42}H_{40}Mg_3N_4O_{16}S_6$
M, g/mol	1195.16	1122.07
Crystal system	*Triclinic*	*Monoclinic*
Space group	$P\bar{1}$	$C2/c$
a, Å	9.7723(6)	18.7842(6)
b, Å	12.8960(9)	14.8469(4)
c, Å	13.7128(10)	19.2101(5)
α, deg.	104.309(6)	90
β, deg.	109.946(6)	104.519(3)
γ, deg.	96.773(5)	90
V, Å^3	1534.78(19)	5186.4(3)
Z	1	4
D(calc.), g/cm^3	1.293	1.437
μ, mm^{-1}	0.318	0.370
F(000)	620	2320
Crystal size, mm	0.24 × 0.20 × 0.19	0.27 × 0.12 × 0.09
θ range for data collection, deg.	2.27–25.68	2.19–25.68
Index ranges	$-11 \le h \le 11$, $-15 \le k \le 15$, $-16 \le l \le 16$	$-22 \le h \le 19$, $-18 \le k \le 14$, $-23 \le l \le 19$
Reflections collected / independent	22815 / 5815	11286 / 4921
R_{int}	0.0317	0.0167
Reflections with $I > 2\sigma(I)$	5032	4408
Goodness-of-fit on F^2	1.088	1.040
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0602$, $wR_2 = 0.1816$	$R_1 = 0.0495$, $wR_2 = 0.1383$

R indices (all data)	$R_1 = 0.0683$, $wR_2 = 0.1868$	$R_1 = 0.0546$, $wR_2 = 0.1415$
Largest diff. peak / hole, *e*/Å^3	1.114 / −0.532	1.028 / −1.169

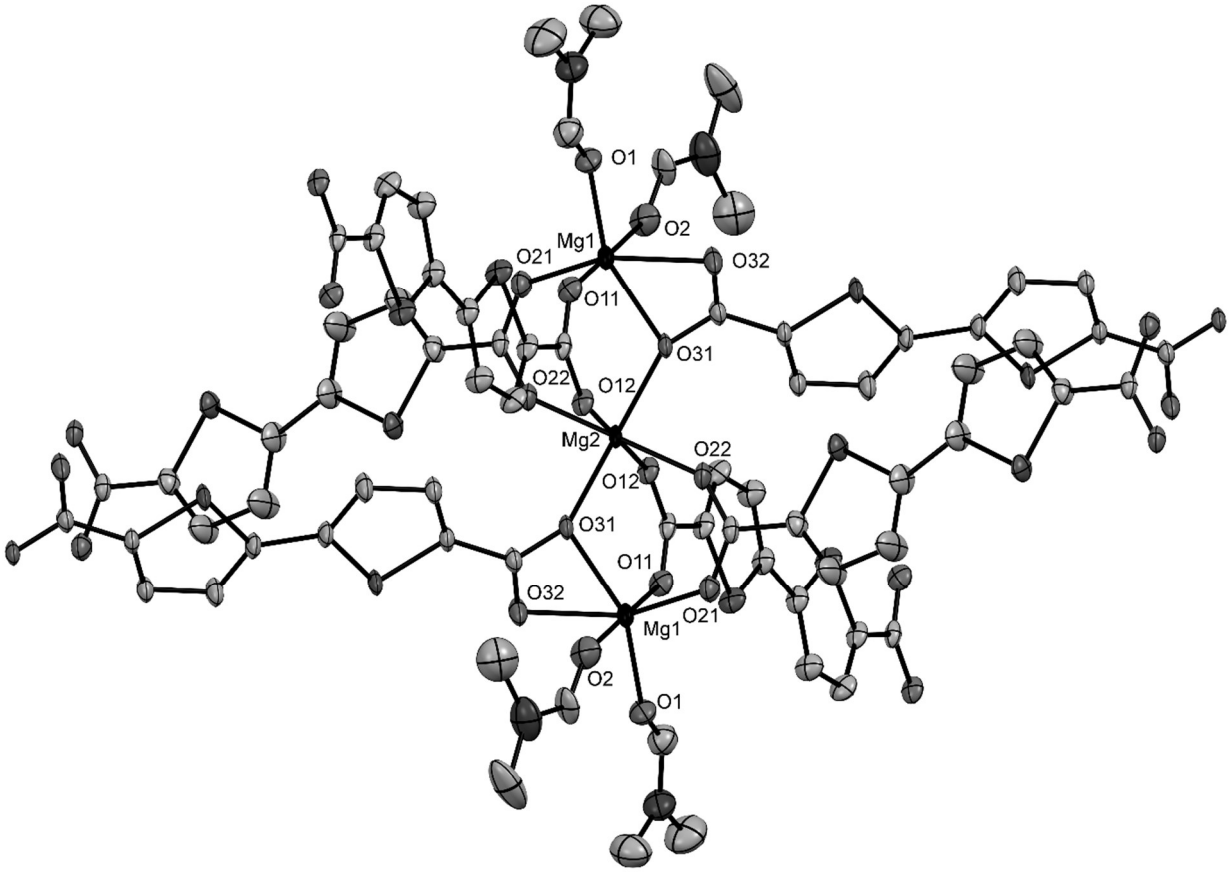


Fig. S1. Coordination environment of Mg(II) cations in **1**. Ellipsoids of 50% probability. Only one of possible orientation of coordinated DMF molecules is shown. Hydrogen atoms are not shown.

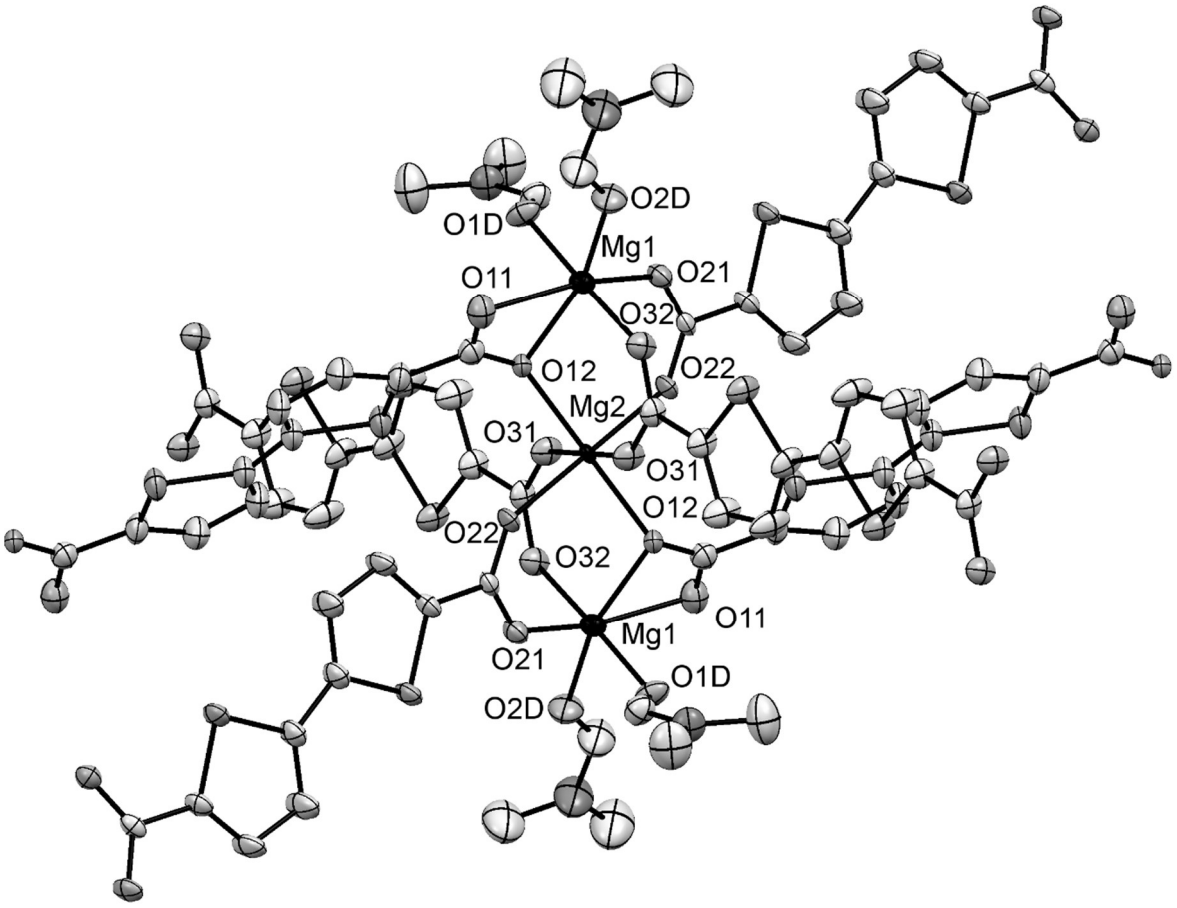


Fig. S2. Coordination environment of Mg(II) cations in **2**. Ellipsoids of 50% probability. Only one of possible orientation of coordinated DMF molecules is shown. Hydrogen atoms are not shown.

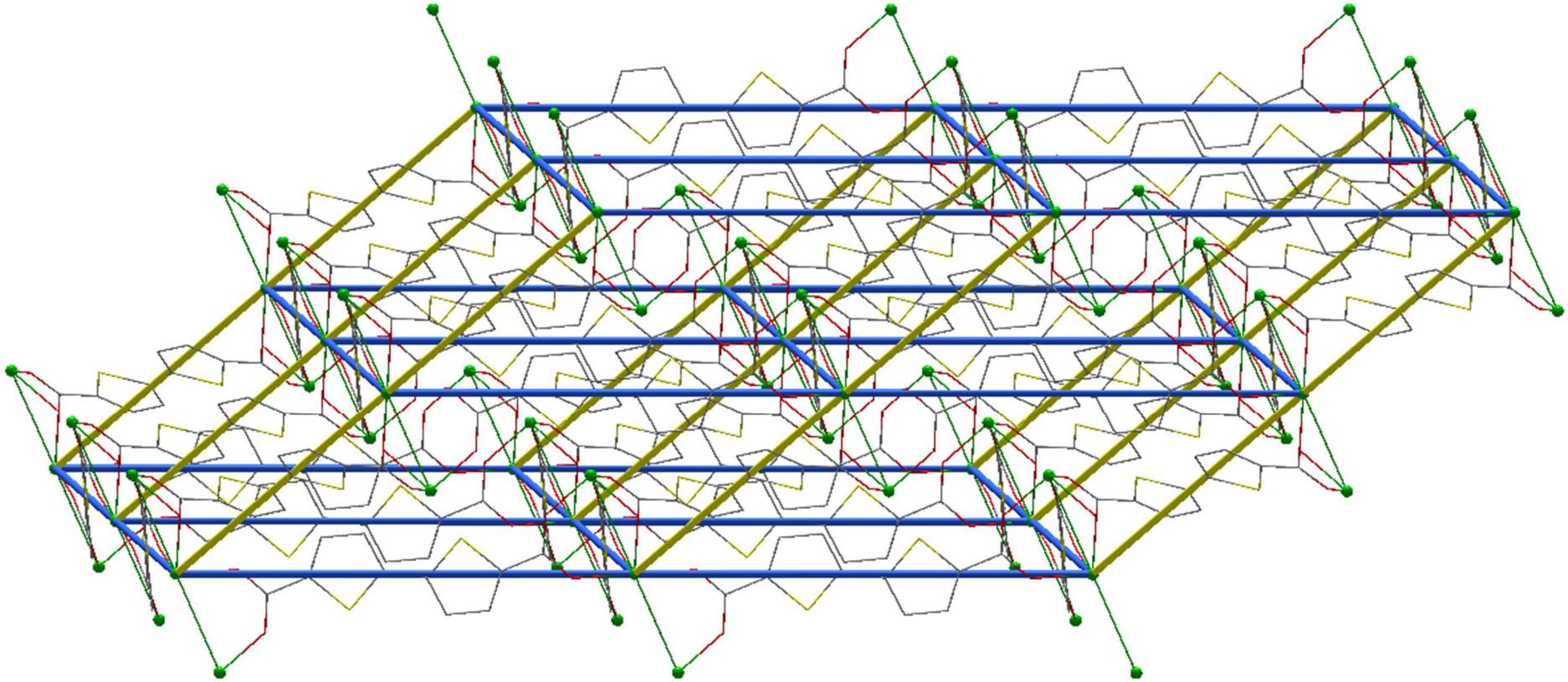


Fig. S3. Crystal structure **1**. Blue and yellow lines highlight **pcu** topology of the framework. The Mg atoms are connected to emphasize the $\{Mg_3(RCOO)_6\}$ building units. Solvent molecules and hydrogen atoms are omitted.

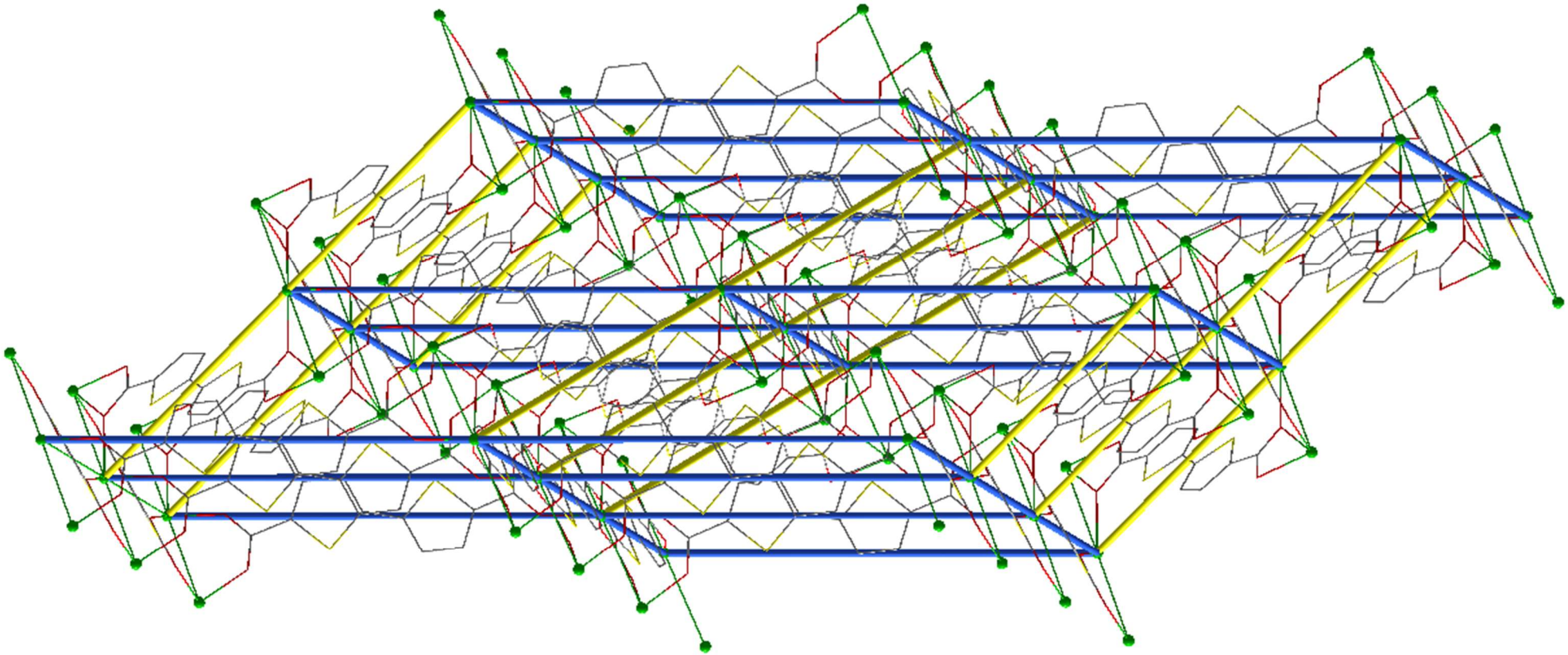
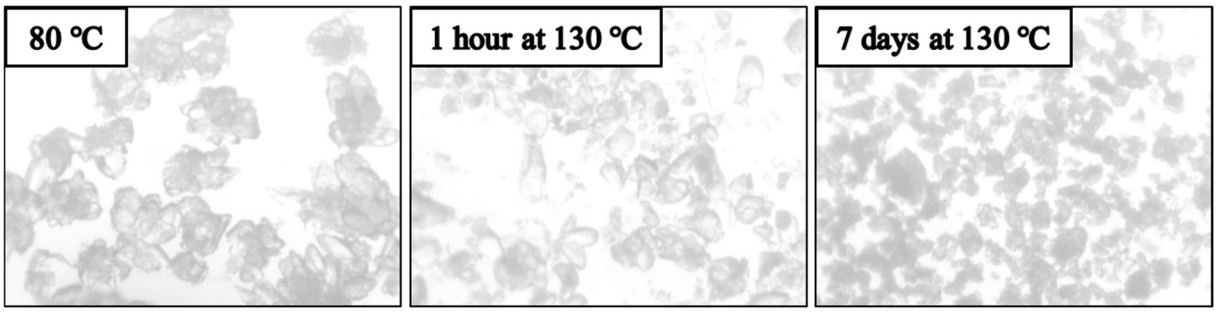


Fig. S4. Crystal structure **2**. Blue and yellow lines highlight **sxb** topology of the framework. The Mg atoms are connected to emphasize the $\{Mg_3(RCOO)_6\}$ building units. Solvent molecules and hydrogen atoms are omitted.



(a) **(b)** **(c)**

Fig. S5. Photographs of the product crystals of **1** formed at 80 °C (a), kept in mother liquor at 130 °C during 1 hour (b), and 7 days (c), indicating of the formation of the HT phase **2**.

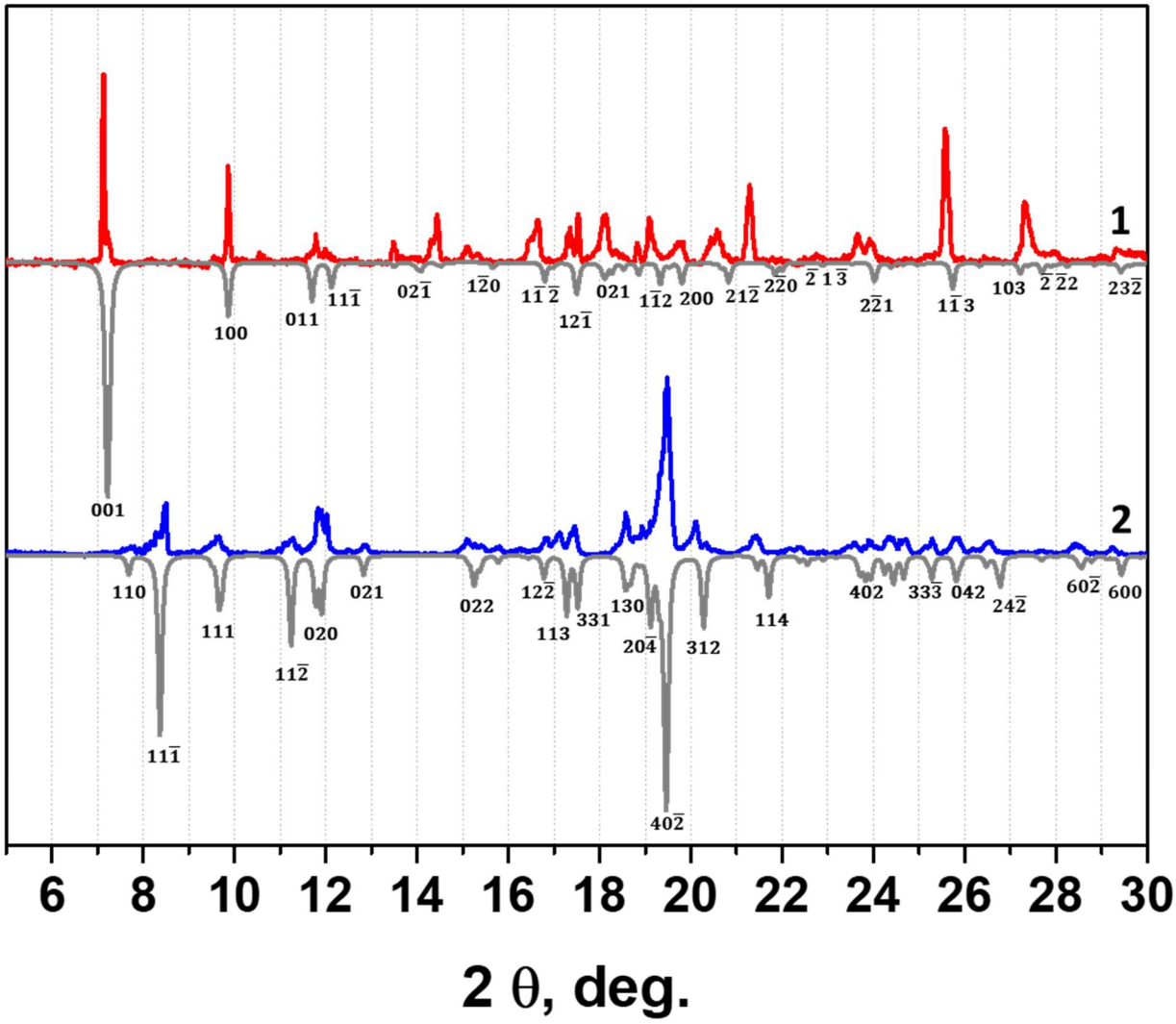


Fig. S6. Powder X-ray diffraction patterns for compounds **1** and **2** (practical – in color, theoretical – in grey) with indexes of the reflexes of both phases **1** and **2**.