Supporting Information

Systematic and in situ EDXRD investigation on the formation of a new metal organogermanate - $Cu(OOCC_2H_4Ge)_2O_3$

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1) High-throughput synthesis

The bis-carboxyethylgermaniumsesquioxide (BCG) $(HOOCCH_2CH_2Ge)_2O_3$ was applied as a solid and the total amount kept constant at 6.8 mg (20 µmol). $Cu(NO_3)_2{\cdot}4H_2O$ was used as a aqueous solution (2 M). The filling level of the PTFE vessels amounted to 200 µL.

Table S 1. Molar ratios and exact amounts of the reactants for the high-throughput investigations of the system Ca^{2+} / $(HOOCCH_2CH_2Ge)_2O_3$ / H_2O / 2-propanol.

No.	BCG	$Cu(NO_3)_2{\cdot}4H_2O$	BCG [mg]	$Cu(NO_3)_2{\cdot}4H_2O$ [µl]	H_2O [µl]	2-propanol [µl]	product
	molar ratio		exact amounts				
1	1	1	6.8	10	10	180	$Cu(OOCC_2H_4Ge)_2O_3$
2	1	1	6.8	10	30	160	$Cu(OOCC_2H_4Ge)_2O_3$
3	1	1	6.8	10	50	140	$Cu(OOCC_2H_4Ge)_2O_3$
4	1	1	6.8	10	70	120	$Cu(OOCC_2H_4Ge)_2O_3$
5	1	1	6.8	10	90	100	$Cu(OOCC_2H_4Ge)_2O_3$
6	1	1	6.8	10	110	80	$Cu(OOCC_2H_4Ge)_2O_3$
7	1	1	6.8	10	130	60	$Cu(OOCC_2H_4Ge)_2O_3$
8	1	1	6.8	10	150	40	$Cu(OOCC_2H_4Ge)_2O_3$
9	1	1	6.8	10	170	20	no precipitate
10	1	2	6.8	20	15	165	$Cu(OOCC_2H_4Ge)_2O_3$
11	1	2	6.8	20	35	145	$Cu(OOCC_2H_4Ge)_2O_3$
12	1	2	6.8	20	55	125	$Cu(OOCC_2H_4Ge)_2O_3$
13	1	2	6.8	20	75	105	$Cu(OOCC_2H_4Ge)_2O_3$
14	1	2	6.8	20	95	85	$Cu(OOCC_2H_4Ge)_2O_3$
15	1	2	6.8	20	115	65	$Cu(OOCC_2H_4Ge)_2O_3$
16	1	2	6.8	20	120	60	$Cu(OOCC_2H_4Ge)_2O_3$
17	1	2	6.8	20	155	25	$Cu(OOCC_2H_4Ge)_2O_3$
18	1	2	6.8	20	170	10	no precipitate
19	1	3	6.8	30	15	155	$Cu(OOCC_2H_4Ge)_2O_3$
20	1	3	6.8	30	35	135	$Cu(OOCC_2H_4Ge)_2O_3$
21	1	3	6.8	30	55	115	$Cu(OOCC_2H_4Ge)_2O_3$
22	1	3	6.8	30	75	95	$Cu(OOCC_2H_4Ge)_2O_3$
23	1	3	6.8	30	95	75	$Cu(OOCC_2H_4Ge)_2O_3$
24	1	3	6.8	30	115	55	$Cu(OOCC_2H_4Ge)_2O_3$
25	1	3	6.8	30	135	35	$Cu(OOCC_2H_4Ge)_2O_3$
26	1	3	6.8	30	155	15	no precipitate
27	1	3	6.8	30	170	0	no precipitate
28	1	1.5	6.8	15	15	170	$Cu(OOCC_2H_4Ge)_2O_3$
29	1	1.5	6.8	15	35	150	$Cu(OOCC_2H_4Ge)_2O_3$
30	1	1.5	6.8	15	55	130	$Cu(OOCC_2H_4Ge)_2O_3$
31	1	1.5	6.8	15	75	110	$Cu(OOCC_2H_4Ge)_2O_3$
32	1	1.5	6.8	15	95	90	$Cu(OOCC_2H_4Ge)_2O_3$
33	1	1.5	6.8	15	115	70	$Cu(OOCC_2H_4Ge)_2O_3$
34	1	1.5	6.8	15	135	50	$Cu(OOCC_2H_4Ge)_2O_3$
35	1	1.5	6.8	15	150	35	$Cu(OOCC_2H_4Ge)_2O_3$
36	1	1.5	6.8	15	170	15	no precipitate
37	1	4.5	6.8	45	15	140	$Cu(OOCC_2H_4Ge)_2O_3$
38	1	4.5	6.8	45	35	120	$Cu(OOCC_2H_4Ge)_2O_3$
39	1	4.5	6.8	45	55	100	$Cu(OOCC_2H_4Ge)_2O_3$
40	1	4.5	6.8	45	75	80	$Cu(OOCC_2H_4Ge)_2O_3$
41	1	4.5	6.8	45	95	60	$Cu(OOCC_2H_4Ge)_2O_3$
42	1	4.5	6.8	45	115	40	$Cu(OOCC_2H_4Ge)_2O_3$
43	1	4.5	6.8	45	135	20	$Cu(OOCC_2H_4Ge)_2O_3$
44	1	4.5	6.8	45	155	0	$Cu(OOCC_2H_4Ge)_2O_3$
45	1	4.5	6.8	21.3 [mg]	170	30	no precipitate
46	1	0.68	6.8	6.8	15	178	$Cu(OOCC_2H_4Ge)_2O_3$
47	1	0.68	6.8	6.8	35	158	$Cu(OOCC_2H_4Ge)_2O_3$

48	1	0.68	6.8	6.8	55	138	**$Cu(OOCC_2H_4Ge)_2O_3$**
49	1	0.68	6.8	6.8	75	118	**$Cu(OOCC_2H_4Ge)_2O_3$**
50	1	0.68	6.8	6.8	95	98	**$Cu(OOCC_2H_4Ge)_2O_3$**
51	1	0.68	6.8	6.8	115	78	**$Cu(OOCC_2H_4Ge)_2O_3$**
52	1	0.68	6.8	6.8	135	58	**$Cu(OOCC_2H_4Ge)_2O_3$**
53	1	0.68	6.8	6.8	150	44	**$Cu(OOCC_2H_4Ge)_2O_3$**
54	1	0.68	6.8	6.8	170	23	**no precipitate**
55	1	0.4	6.8	4	16	180	**$Cu(OOCC_2H_4Ge)_2O_3$**
56	1	0.4	6.8	4	35	161	**$Cu(OOCC_2H_4Ge)_2O_3$**
57	1	0.4	6.8	4	55	141	**$Cu(OOCC_2H_4Ge)_2O_3$**
58	1	0.4	6.8	4	75	121	**$Cu(OOCC_2H_4Ge)_2O_3$**
59	1	0.4	6.8	4	95	101	**$Cu(OOCC_2H_4Ge)_2O_3$**
60	1	0.4	6.8	4	115	81	**$Cu(OOCC_2H_4Ge)_2O_3$**
61	1	0.4	6.8	4	135	61	**$Cu(OOCC_2H_4Ge)_2O_3$**
62	1	0.4	6.8	4	150	46	**$Cu(OOCC_2H_4Ge)_2O_3$**
63	1	0.4	6.8	4	170	26	**no precipitate**
64	1	0.2	6.8	2	18	180	**BCG**
65	1	0.2	6.8	2	38	160	**BCG**
66	1	0.2	6.8	2	58	140	**$Cu(OOCC_2H_4Ge)_2O_3$**
67	1	0.2	6.8	2	78	120	**$Cu(OOCC_2H_4Ge)_2O_3$**
68	1	0.2	6.8	2	98	100	**$Cu(OOCC_2H_4Ge)_2O_3$**
69	1	0.2	6.8	2	118	80	**$Cu(OOCC_2H_4Ge)_2O_3$**
70	1	0.2	6.8	2	138	60	**$Cu(OOCC_2H_4Ge)_2O_3$**
71	1	0.2	6.8	2	158	40	**$Cu(OOCC_2H_4Ge)_2O_3$**
72	1	0.2	6.8	2	170	28	**no precipitate**

2) Crystallographic data

Table S2. Summary of crystal data and refined structure parameters.

	$Cu(OOCC_2H_4Ge)_2O_3]_2$
formula	C6H8O7Ge2Cu
formula weight (g/mol)	400.85
crystal system	monoclinic
space group	$P2_1/n$ (No. 14)
a (pm)	1348.4(3)
b (pm)	509.6(1)
c (pm)	1599.2(3)
β (°)	114.44(3)
V (10^6 pm^3)	1000.4(3)
Z	4
ρ (g/cm3)	2.661
μ (mm-1)	8.903
absorption correction	numerical
total data collect.	26124
unique/obs. data ($I > 2\sigma(I)$)	2936, 2364
R_{int}	0.0478
R_1, wR_2 ($I > 2\sigma(I)$)	0.0279, 0.0536
R_1, wR_2 (all data)	0.0420, 0.0596
GOF	0.963
Δe min./max. (e/Å3)	-0.64, 0.65

3) IR spectroscopic investigation

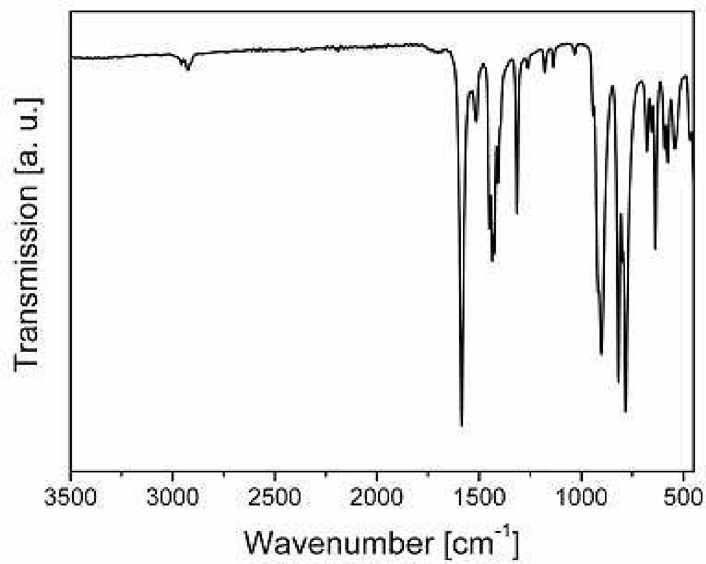

Figure S1. IR spectrum of $Cu(OOCC_2H_4Ge)_2O_3]_2$.

4) Thermal study

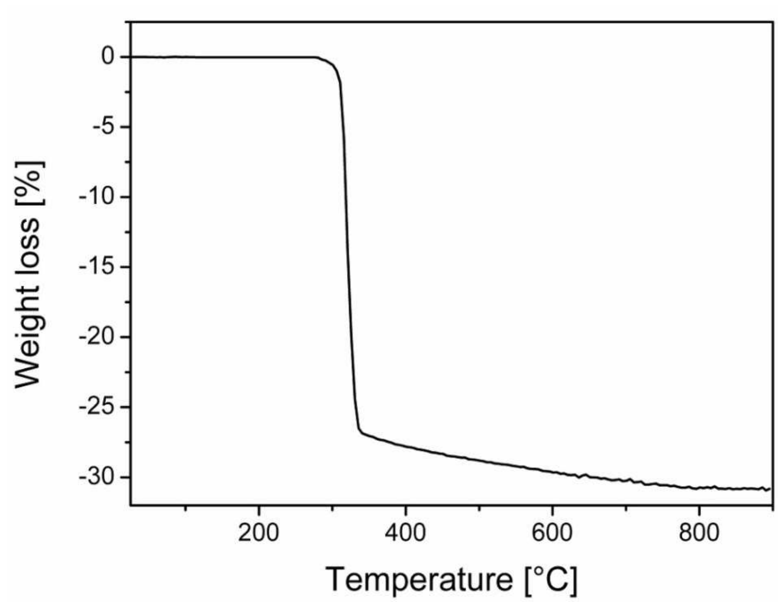

Figure S2. Thermogravimetric analysis of $Cu(OOCC_2H_4Ge)_2O_3$.

5) Selected bond lengths and angles

Table S3. Selected bond lengths [pm] and angles [°] of $Cu(OOCC_2H_4Ge)_2O_3$.

Atoms	Distance	Atoms	Angle
Cu-O1	202.0(2)	O1-Cu-O2	88.4(1)
Cu-O1	218.7(2)	O2-Cu-O3	169.8(1)
Cu-O2	198.8(2)	O2-Cu-O4	87.6(1)
Cu-O3	193.4(2)	O3-Cu-O4	91.5(1)
Cu-O4	195.2(2)	O1-Cu-O1	82.4(1)
Ge1-O5	174.4(2)	O5-Ge1-O6	110.6(1)
Ge1-O6	175.3(2)	O5-Ge1-O7	109.8(1)
Ge1-O7	175.8(2)	O6-Ge1-O7	104.6(1)
Ge1-C2	193.5(3)	O5-Ge1-C2	105.7(1)
C1-O1	126.5(4)	O6-Ge1-C2	117.8(1)
C1-O4	125.3(4)	O7-Ge1-C2	108.2(1)
Ge2-O5	175.3(2)	O5-Ge2-O6	108.2(1)
Ge2-O6	176.5(2)	O5-Ge2-O7	109.5(1)
Ge2-O7	175.1(2)	O6-Ge2-O7	104.2(1)
Ge2-C4	192.9(3)	O5-Ge2-C4	106.3(1)
C5-O2	125.1(4)	O6-Ge2-C4	1073(1)
C5-O3	126.2(4)	O7-Ge2-C4	120.9(1)

6) Sharp-Hancock plots and Arrhenius plot

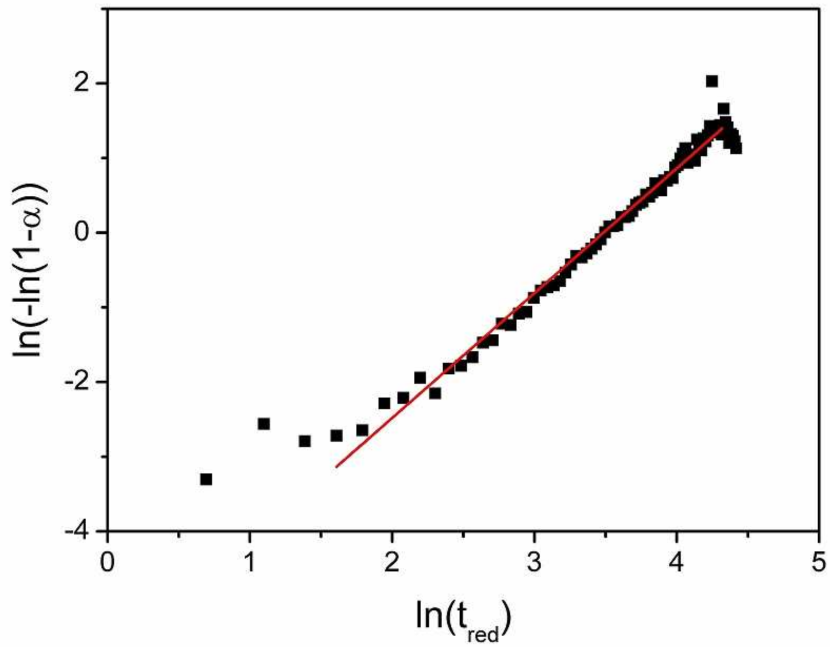

Figure S3. Sharp-Hancock plot of the formation of $Cu(OOCC_2H_4Ge)_2O_3$ at 120 °C. The first two data points are not included for the linear regression. A low intensity of the 022 reflection led to a lower quality in the fitting process and therefore in the integration of the signal intensity. Thus, these first two data points are out range.

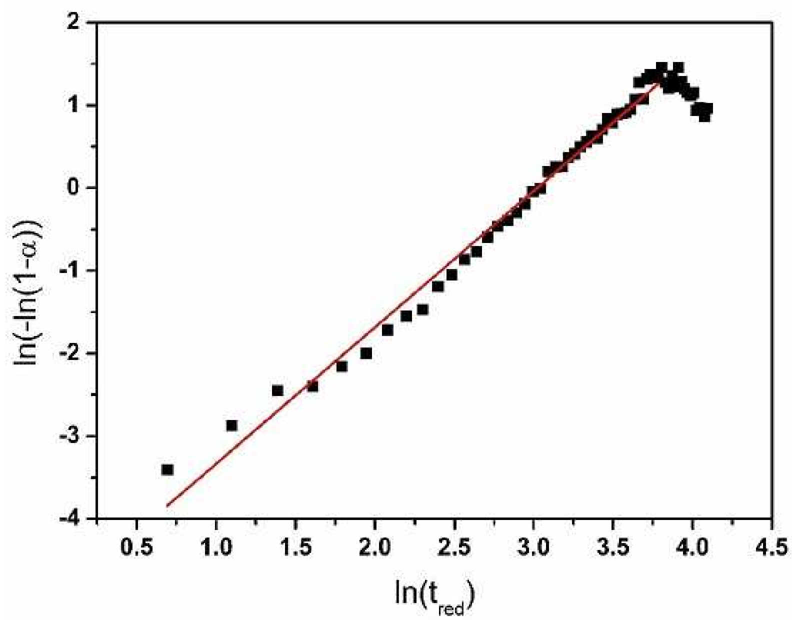

Figure S4. Sharp-Hancock plot of the formation of $Cu(OOCC_2H_4Ge)_2O_3$ at 125 °C.

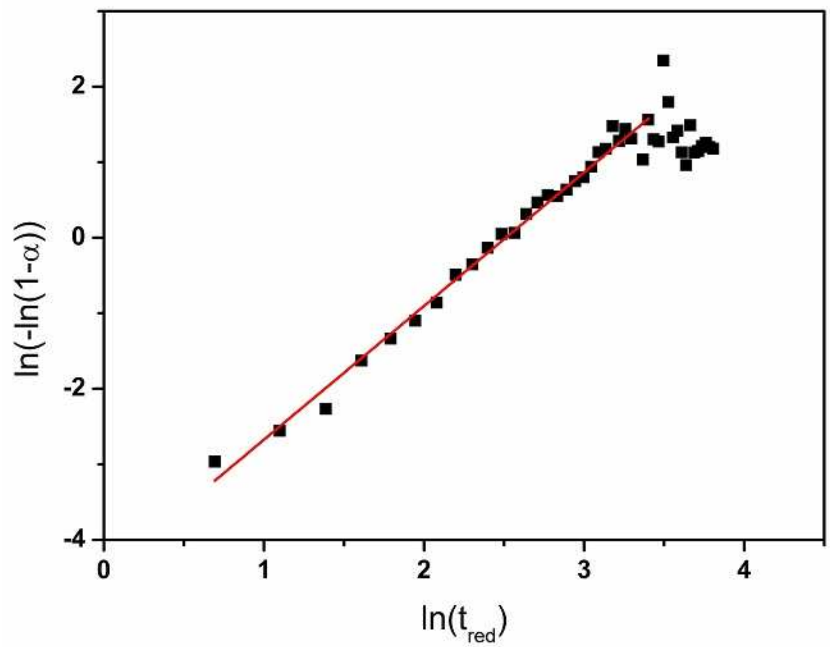

Figure S5. Sharp-Hancock plot of the formation of $Cu(OOCC_2H_4Ge)_2O_3$ at 130 °C.

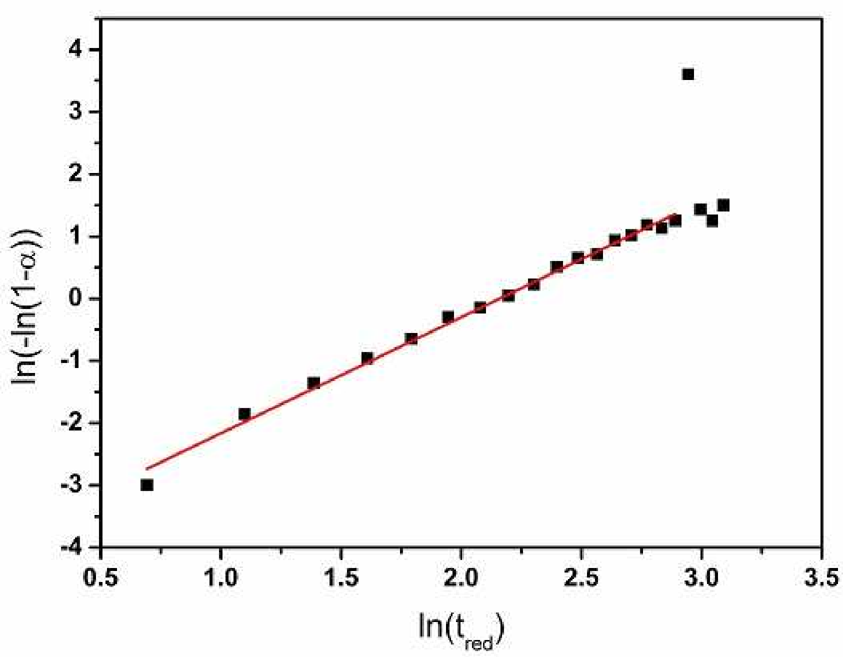

Figure S6. Sharp-Hancock plot of the formation of $Cu(OOCC_2H_4Ge)_2O_3$ at 135 °C.

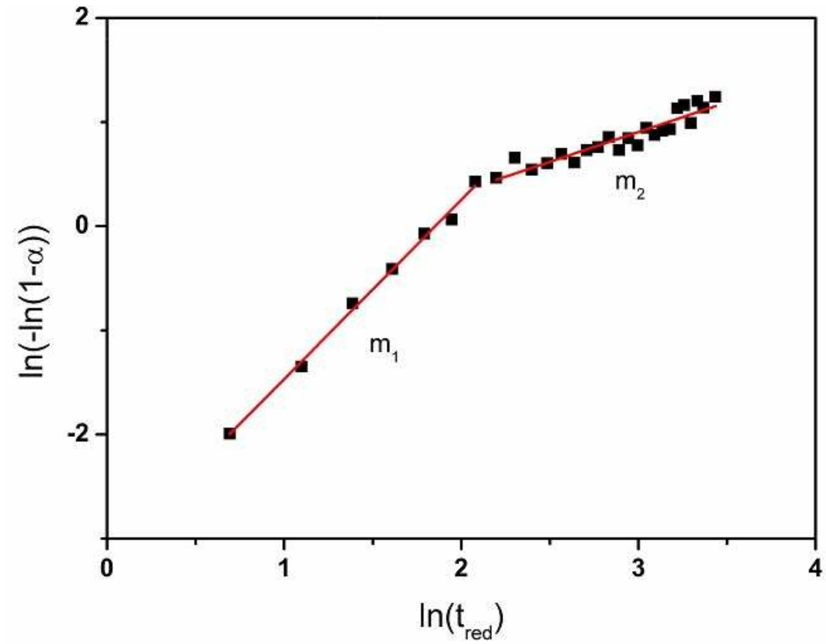

Figure S7. Sharp-Hancock plot of the formation of $Cu(OOCC_2H_4Ge)_2O_3$ at 140 °C.

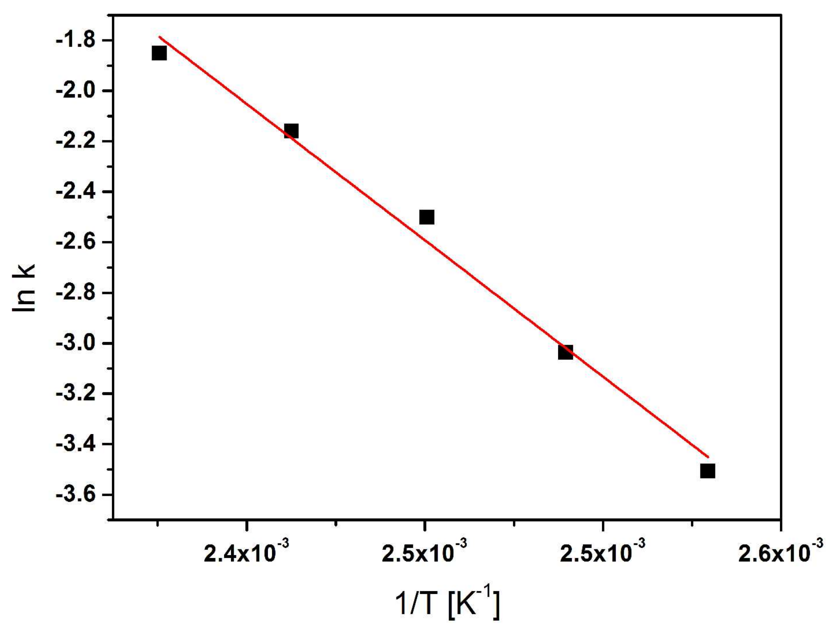

Figure S8. Arrhenius plot for the determination of the activation energy of $Cu(OOCC_2H_4Ge)_2O_3$.

Table S4. Theoretical models of reaction mechanisms of solid state reactions.

model of growth	$f(\alpha) = kt$	m
diffusion controlled		
$D_1(\alpha)$	$\alpha^2 = 0.25\ (t / t_{0.5})$	0.62
$D_2(\alpha)$	$(1 - \alpha) \ln (1 - \alpha) + \alpha = 0.1534\ (t / t_{0.5})$	0.57
$D_3(\alpha)$	$[1 - (1 - \alpha)^{1/3}]^2 = 0.0425\ (t / t_{0.5})$	0.54
$D_4(\alpha)$	$1 - 2\alpha/3 - (1 - \alpha)^{2/3} = 0.0367\ (t / t_{0.5})$	0.57
phase boundary controlled		
$R_2(\alpha)$	$1 - (1 - \alpha)^{1/2} = 0.2929\ (t / t_{0.5})$	1.11
$R_3(\alpha)$	$1 - (1 - \alpha)^{1/3} = 0.0367\ (t / t_{0.5})$	1.07
reaction first order		
$F_1(\alpha)$	$[-\ln (1 - \alpha)] = 0.6931\ (t / t_{0.5})$	1
nucleation controlled		
$A_2(\alpha)$	$[-\ln (1 -\alpha)]^{1/2} = 0.8326\ (t / t_{0.5})$	2
$A_3(\alpha)$	$[-\ln (1 -\alpha)]^{1/3} = 0.885\ (t / t_{0.5})$	3

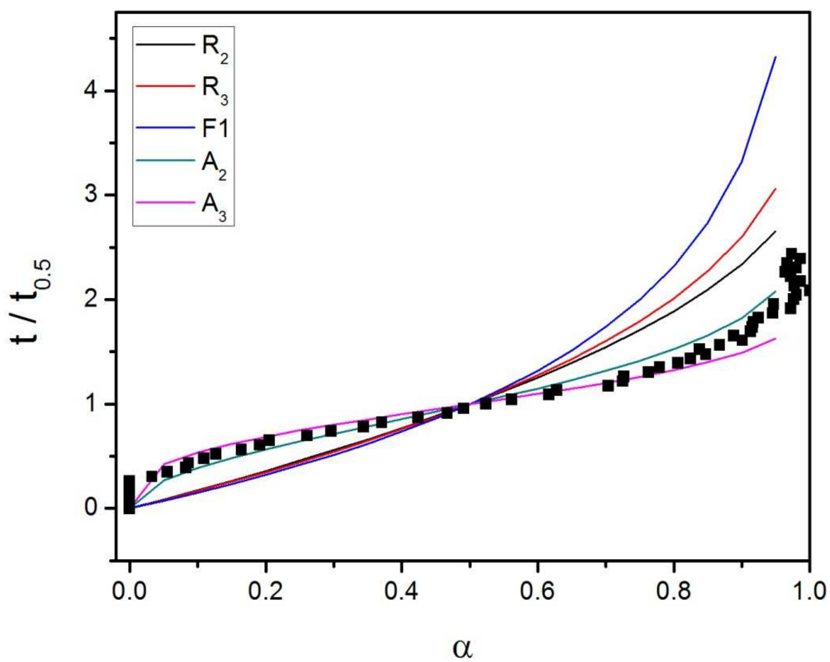

Figure S9. Comparison of the experimental reaction progress at 120 °C with theoretical curve progressions. The scattered curve demonstrates the experimental reaction progress.

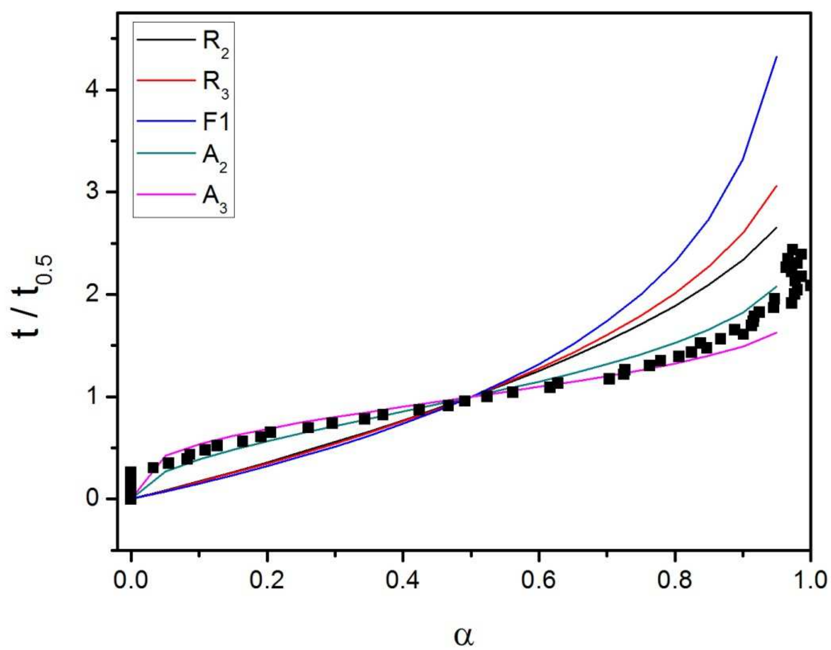

Figure S10. Comparison of the experimental reaction progress at 125 °C with theoretical curve progressions. The scattered curve demonstrates the experimental reaction progress.

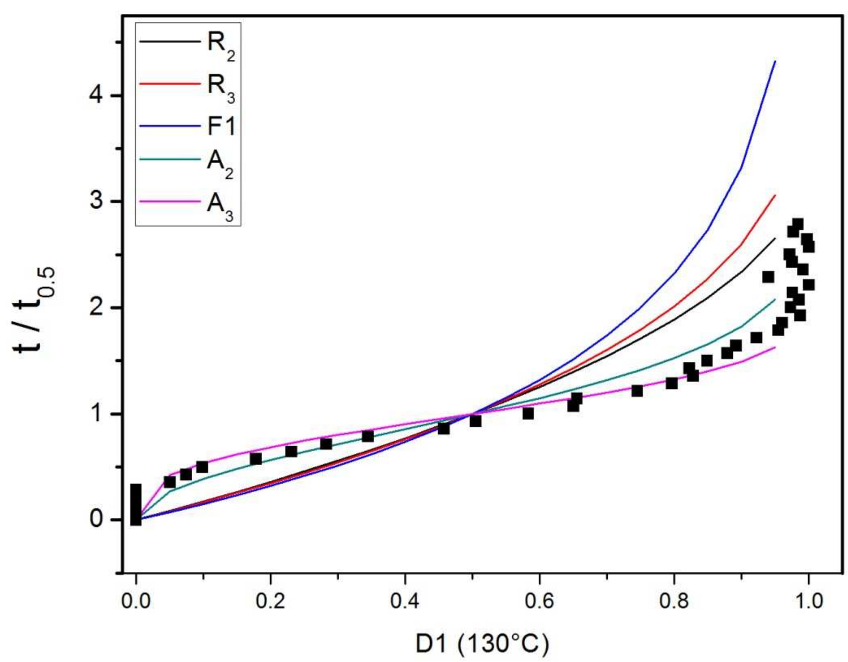

Figure S11. Comparison of the experimental reaction progress at 130 °C with theoretical curve progressions. The scattered curve demonstrates the experimental reaction progress.

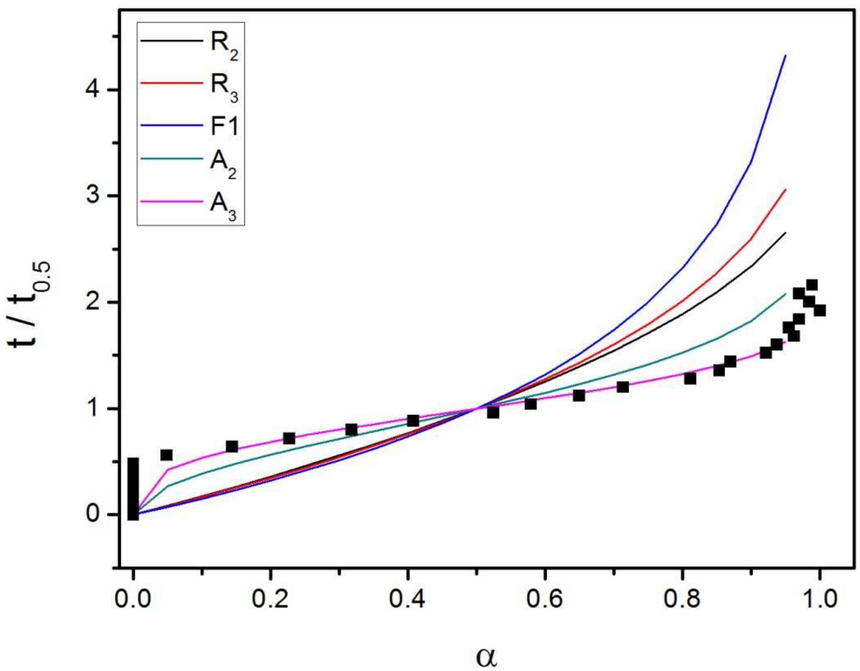

Figure S12. Comparison of the experimental reaction progress at 135 °C with theoretical curve progressions. The scattered curve demonstrates the experimental reaction progress.

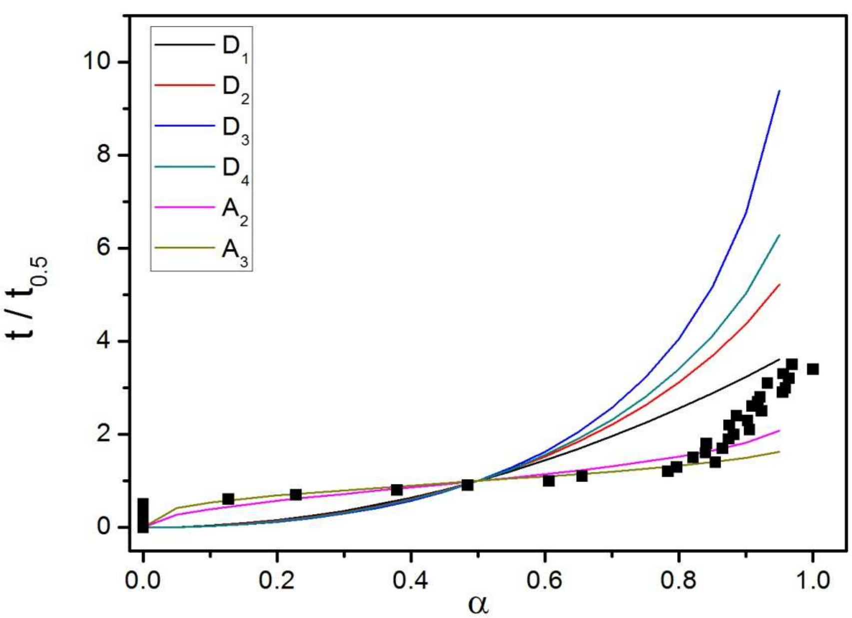

Figure S13. Comparison of the experimental reaction progress at 140 °C with theoretical curve progressions. The scattered curve demonstrates the experimental reaction progress.

Table S5. Activation energies of selected compounds.

	compound	activation energy [kJ/mol]
organogermanate	$Cu(OOCC_2H_4Ge)_2O_3$	113(7)
metal organic frameworks	HKUST-1[1]	73.3
	Fe-MIL-53[2]	66.4
	MOF-14[1]	82.2*
	$CAU\text{-}1\text{-}NH_2$[3]	136(6)
	$CAU\text{-}1\text{-}(OH)_2$**Error! Bookmark not defined.**	136(11)
thiometalates	$Mn_2Sb_2S_5(MDAP)$[4]	65(5)
	$[Co(C_6H_{18}N_4)][Sb_2S_4]$[5]	42
phosphate	SAPO-11[6]	93.3
phosphonoalkylsulfonate	$Sm(O_3PC_4H_8SO_3)$**Error! Bookmark not defined.**[7]	128(27)

*data evaluated by the method of Gualtieri[8]

1 Millange, F.; El Osta, R.; Medina, M. E.; Walton, R. I. *CrystEngComm*, **2011**, *13*, 103 – 108.

2 Haque, E.; Khan, N. A.; Park, J. H.; Jhung, S. H. *Chem. Eur. J*. **2010**, *16*, 1046 – 1052.

3 Ahnfeldt, T.; Stock, N. *CrystEngComm.*, submitted.

4 Engelke L. Dissertation, CAU Kiel, **2002**.

5 Kiebach, R.; Pienack, N. ; Ordolff, M.-E. ; Studt, F. ; Bensch, W. *Chem. Mater*. **2006**, *18* (5), 1196 – 1205.

6 Gharibeh, M.; Tompsett, G. A.; Conner, W. C.; Yngvesson, K. S. *Chem. Phys. Chem.* **2008**, *9*, 2580 – 2591

7 Feyand, M.; Näther, C.; Rothkirch, A.; Stock, N. *Inorg. Chem*. **2010**, *49*, 11158 – 11163

8 Gualtieri, A. F. *Phys. Chem. Miner*., **2001**, *28*, 719 – 728.