Supporting information:
Alumosilicate relatives: the Chalcogenoalumogermanates $Rb_3(AlQ_2)_3(GeQ_2)_7$ (Q = S, Se)

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Table 1S. Details of the X-Ray Data Collection and Refinement for $Rb_3(AlS_2)_3(GeS_2)_7$ (**1**).

formula	$Al_3Ge_7Rb_3S_{20}$
formula weight	1486.68
T/K	190(2)
crystal system	monoclinic
space group	$P2_1/c$
a/Å	6.7537(3)
b/Å	37.7825(19)
c/Å	6.7515(3)
α/deg	90.00
β/deg	90.655(4)
γ/deg	90.00
Z	2
V/Å^3	1722.68(14)
ρ/gcm^{-3}	2.866
μ/mm^{-1}	11.527
F(000)	1388
reflections collected	9210
unique data	2701
R_{int}	0.0236
parameters	151
R_1[a] [I>2σ(I)]	0.0242
wR_2[b]	0.0543

[a]$R_1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, [b]$wR_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and calc $w=1/[\sigma^2(Fo^2)+(0.0303P)^2+1.2164P]$ where $P=(Fo^2+2Fc^2)/3$

Table 2S. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for $Rb_3(AlS_2)_3(GeS_2)_7$ (**1**).

Label	x	y	z	Occupancy	U_{eq}*
Rb(1)	0.02694(9)	0.834942(13)	0.23810(7)	1	0.04905(16)
Rb(2)	0.5000	0.0000	0.5000	1	0.0656(3)
S(1)	0.02727(16)	0.49915(2)	0.25220(14)	1	0.0228(2)
S(2)	0.08375(14)	0.66326(2)	0.23620(14)	1	0.0194(2)
S(3)	0.10013(16)	0.58404(2)	0.52444(14)	1	0.0225(2)
S(4)	0.16283(15)	0.08765(3)	0.46081(14)	1	0.0215(2)
S(5)	0.17555(15)	0.25313(3)	0.30016(14)	1	0.0213(2)
S(6)	0.34807(14)	0.58821(3)	0.03464(14)	1	0.0211(2)
S(7)	0.40444(15)	0.04675(3)	0.03650(16)	1	0.0261(2)
S(8)	0.42500(15)	0.14112(2)	0.05236(14)	1	0.0212(2)
S(9)	0.47334(16)	0.31575(2)	0.04279(14)	1	0.0214(2)
S(10)	0.65594(15)	0.22756(2)	0.07032(15)	1	0.0211(2)
Ge(1)	0.08478(7)	0.035677(11)	0.01286(7)	0.75	0.01665(12)
Ge(2)	0.09531(7)	0.604557(12)	0.21689(7)	0.80	0.01768(12)
Ge(3)	0.38022(7)	0.259078(12)	0.05004(7)	0.70	0.01704(12)
Ge(4)	0.40764(9)	0.092970(15)	0.24352(9)	0.50	0.01826(14)
Ge(5)	0.59662(7)	0.178619(11)	0.24022(7)	0.75	0.01665(12)
Al(1)	0.08478(7)	0.035677(11)	0.01286(7)	0.25	0.01665(12)
Al(2)	0.09531(7)	0.604557(12)	0.21689(7)	0.20	0.01768(12)
Al(3)	0.38022(7)	0.259078(12)	0.05004(7)	0.30	0.01704(12)
Al(4)	0.40764(9)	0.092970(15)	0.24352(9)	0.50	0.01826(14)
Al(5)	0.59662(7)	0.178619(11)	0.24022(7)	0.25	0.01665(12)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3S. Details of the X-Ray Data Collection and Refinement for $Rb_3(AlSe_2)_3(GeSe_2)_7$ (**2**).

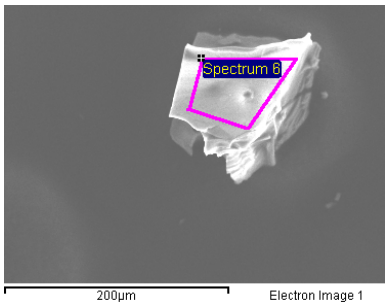
formula	$Al_3Ge_7Rb_3Se_{20}$
formula weight	2424.68
T/K	293(2)
crystal system	monoclinic
space group	$P2_1/c$
a/Å	7.0580(5)
b/Å	39.419(2)
c/Å	7.0412(4)
α/deg	90.00
β/deg	90.360(5)
γ/deg	90.00
Z	2
V/Å^3	1958.9(2)
ρ/gcm^{-3}	4.111
μ/mm^{-1}	27.652
F(000)	2108
reflections collected	12638
unique data	3671
R_{int}	0.0503
parameters	166
R_1[a] [I>2σ(I)]	0.0380
wR_2[b]	0.0855

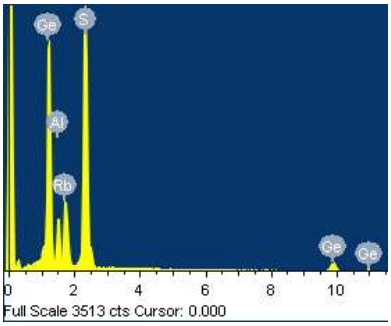
[a]$R_1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, [b]$wR_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and calc $w=1/[\sigma^2(Fo^2)+(0.0459P)^2+0.0000P]$ where $P=(Fo^2+2Fc^2)/3$

Table 4S. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for $Rb_3(AlSe_2)_3(GeSe_2)_7$ (**2**).

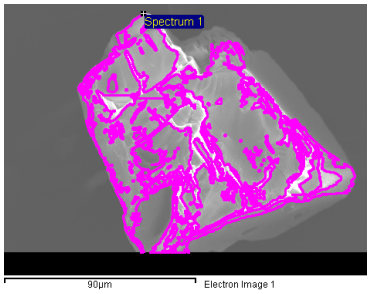
Label	x	y	z	Occupancy	U_{eq}*
Se(1)	0.02684(11)	0.49826(2)	0.24529(11)	1	0.03483(19)
Se(2)	0.07507(10)	0.664190(19)	0.22319(11)	1	0.03008(18)
Se(3)	0.10812(11)	0.58398(2)	0.52003(12)	1	0.03489(19)
Se(4)	0.16255(10)	0.08574(2)	0.47416(12)	1	0.03349(19)
Se(5)	0.16520(10)	0.25344(2)	0.31973(11)	1	0.03445(19)
Se(6)	0.35009(10)	0.58855(2)	0.01532(11)	1	0.03254(18)
Se(7)	0.41193(11)	0.04643(2)	0.03483(14)	1	0.0407(2)
Se(8)	0.42822(11)	0.14137(2)	0.05470(12)	1	0.03311(18)
Se(9)	0.46731(11)	0.317507(19)	0.06199(12)	1	0.03375(19)
Se(10)	0.66141(10)	0.228863(19)	0.08710(12)	1	0.03262(19)
Rb(1)	0.0382(2)	0.83511(3)	0.22695(16)	1	0.0810(4)
Rb(2)	0.5000	0.0000	0.5000	1	0.0918(7)
Al(1)	0.068(9)	0.0346(18)	0.036(9)	0.20	0.0272(5)
Al(2)	0.123(6)	0.6041(17)	0.202(10)	0.18	0.0249(4)
Al(3)	0.384(6)	0.2599(12)	0.042(4)	0.30	0.0245(5)
Al(4)	0.408(5)	0.0952(8)	0.269(4)	0.57	0.0226(12)
Al(5)	0.610(13)	0.178(3)	0.241(13)	0.25	0.0250(7)
Ge(1)	0.0879(6)	0.03570(14)	0.0149(6)	0.80	0.0272(5)
Ge(2)	0.0931(3)	0.60441(11)	0.2063(7)	0.82	0.0249(4)
Ge(3)	0.3761(9)	0.25963(16)	0.0713(5)	0.70	0.0245(5)
Ge(4)	0.409(2)	0.0916(4)	0.2438(18)	0.43	0.0226(12)
Ge(5)	0.5963(14)	0.1786(3)	0.2559(14)	0.75	0.0250(7)

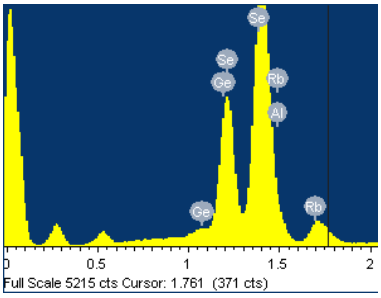
*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.



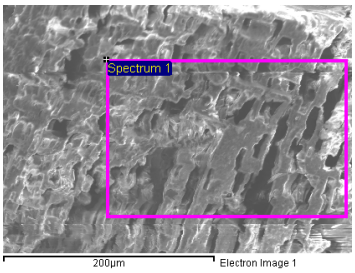


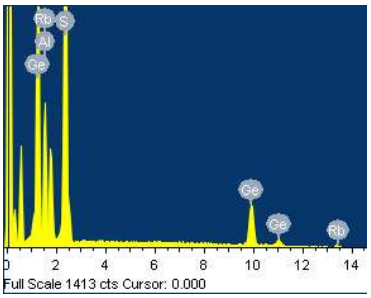
1. Al 10.8, Ge 21.8, S 58.0, Rb 9.51 at. %



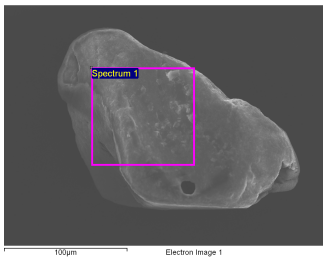


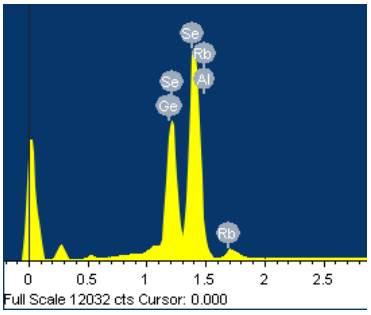
2. Al 11.9, Ge 20.7, Se 57.4, Rb 9.9 at. %





3. Al 19.7, Ge 18.4, S 53.9, Rb 8.0 at. %





4. Al 3.7, Ge 26.1, Se 64.1, Rb 6.1 at. %

Figure 5S. SEM/EDX of 1. $Rb_3(AlS_2)_3(GeS_2)_7$ (**1**), 2. $Rb_3(AlSe_2)_3(GeSe_2)_7$ (**2**), 3. $Rb_3(AlS_2)_3(GeS_2)_7$ (**1**) after hydrolysis and 4. black byproduct of **2**.

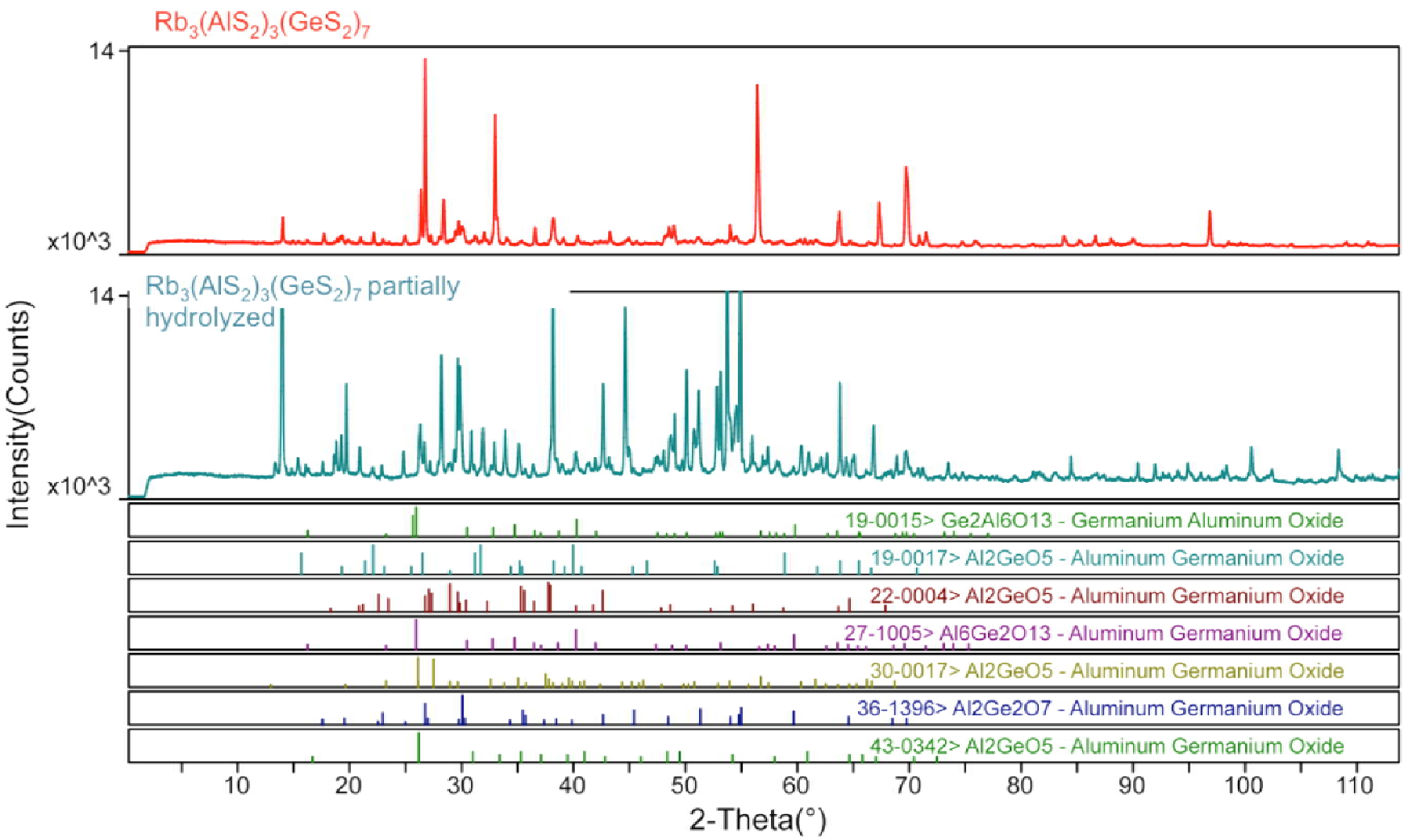


Figure 6S. Measured powder diffraction patterns of $Rb_3(AlS_2)_3(GeS_2)_7$ (**1**) and of **1** after hydrolysis. Simulated powder patterns of several oxides that are likely to be present in hydrolyzed **1** are listed below and indicate the complex composition of hydrolyzed **1**. $Rb_3(AlS_2)_3(GeS_2)_7$ (**1**) is still present after it has been suspended in water for 2 days. This was also confirmed by heating hydrolysed **1** at 10^{-4} bar at ca. 700 ºC. From the residue crystals of $Rb_3(AlS_2)_3(GeS_2)_7$ (**1**) were revovered. The unit cell corresponds to the cell found for **1**.

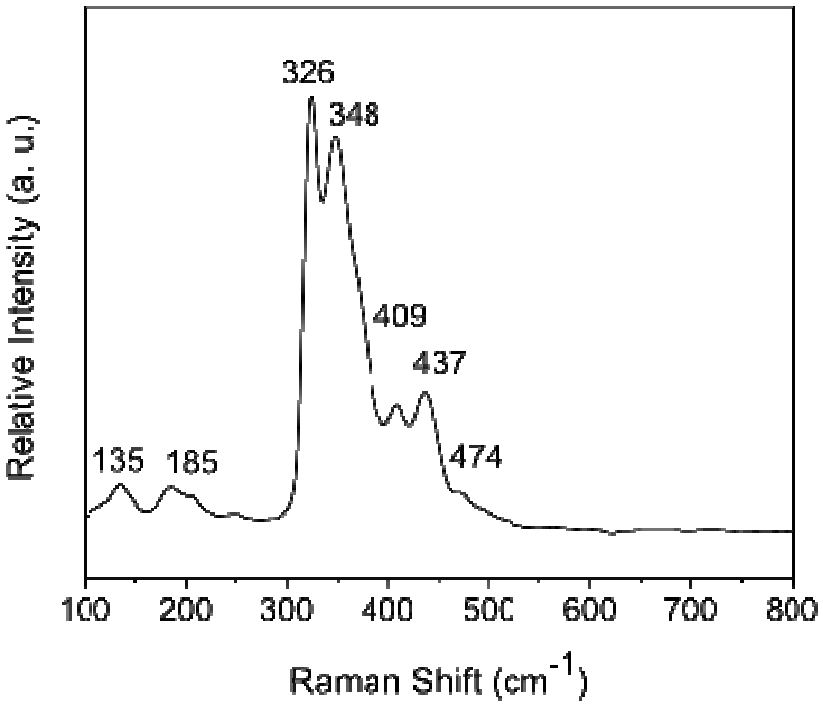


Figure 7S. Raman spectrum of $Rb_3(AlS_2)_3(GeS_2)_7$ (**1**). Raman bands observed in Rb_2S-GeS_2-glasses are ν(Ge-S-Ge) = 340 cm^{-1} and ν(Ge-S^-) = 476 cm^{-1}. See Nelson, C. R.; Poling, S. A.; Martin, S. W. *J. Non-Cryst. Solids* **2004**, *337*, 78 for literature and data on Ge-S Raman spectra.

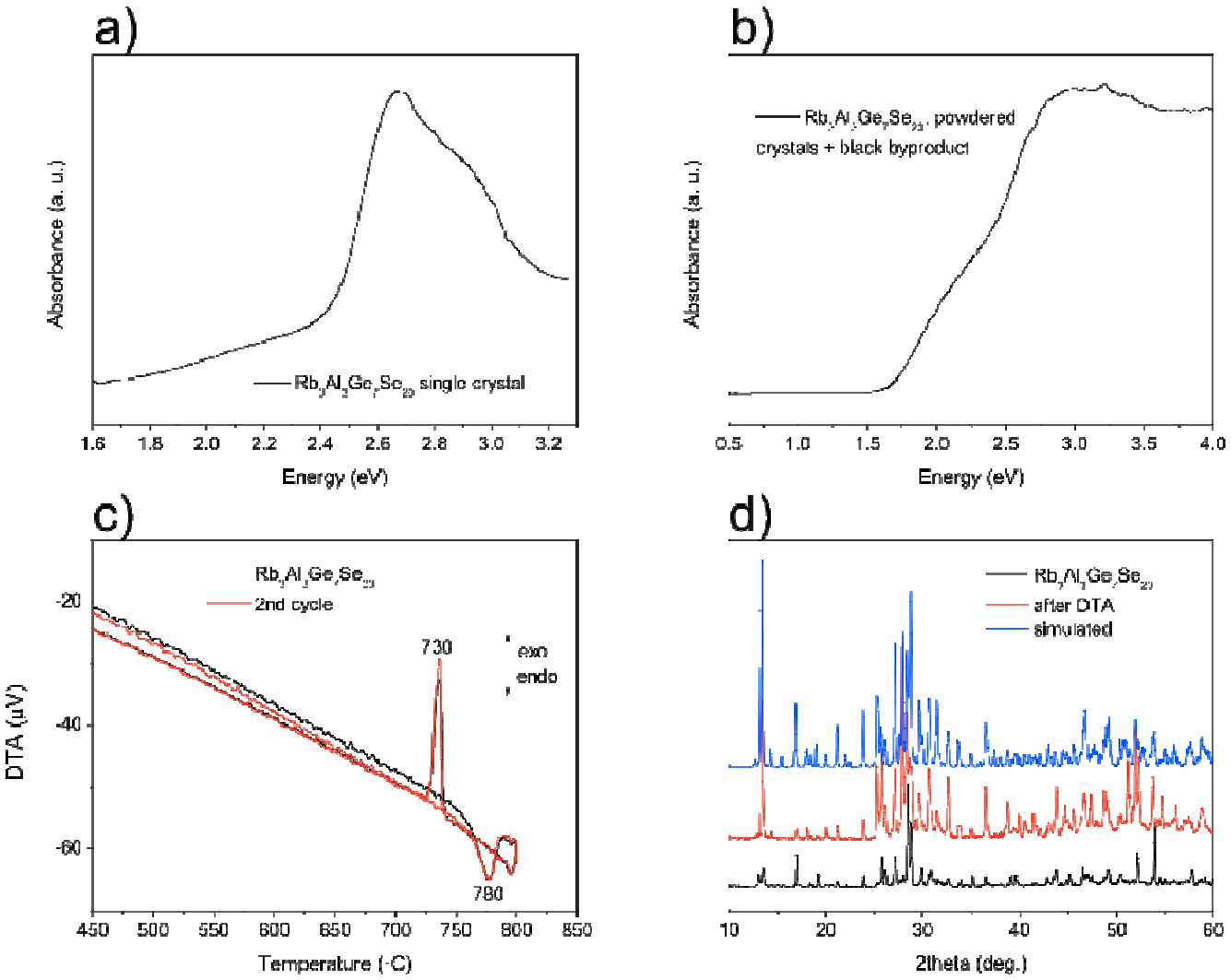


Figure 8S. $Rb_3(AlSe_2)_3(GeSe_2)_7$ (**2**). a) UV/Vis absorption spectrum of a single crystal. b) UV/Vis absorption spectrum of powdered samples that contain a black byproduct. c) Differential thermal analysis (recorded in sealed quartz ampules, (N_2 flow, heating rate 5ºC/min), d) Powder X-ray diffraction pattern.