

Electronic Supplementary Information (ESI)

Rapid mechanochemical synthesis and properties in Pb-Bi-S system

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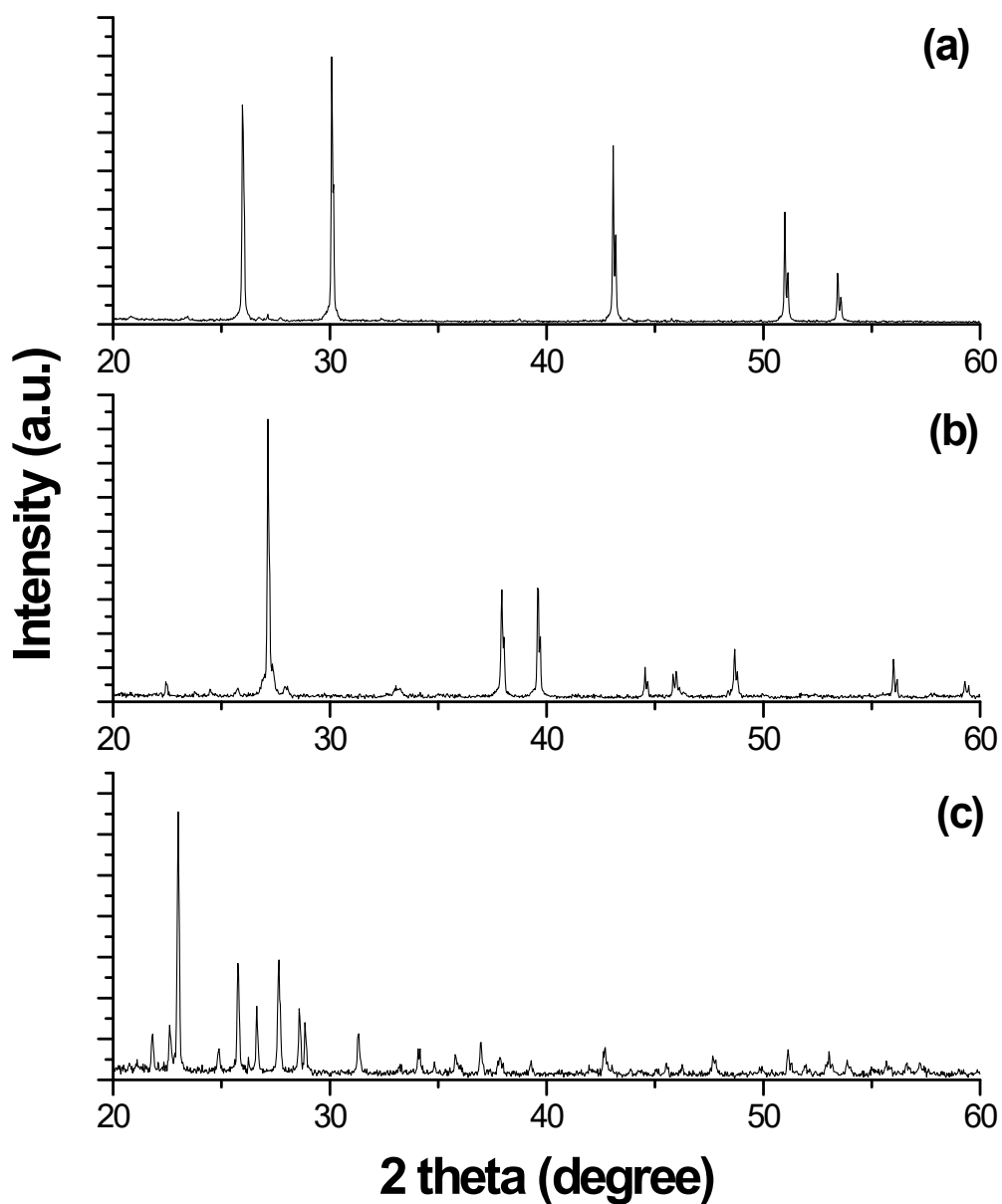


Fig. S1. XRD patterns of starting materials: (a) galena PbS (ICDD PDF 00-005-0592), (b) bismuth Bi (ICDD PDF 01-085-1329) and (c) sulfur S (ICDD PDF 00-024-0733). In the XRD pattern (a), all the other diffraction peaks except five most intensive ones belong to anglesite, PbSO_4 (ICDD PDF 00-036-14612).

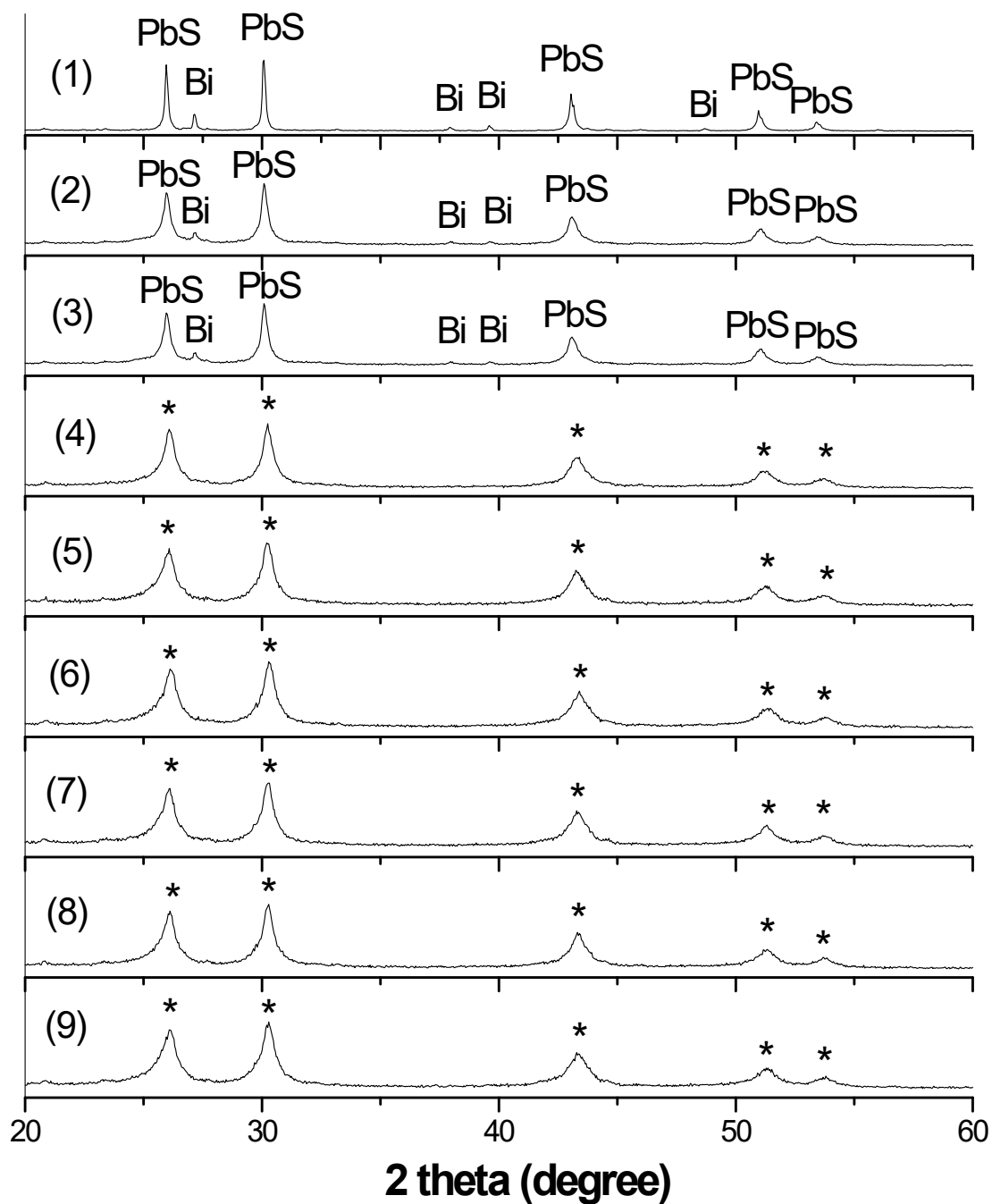


Fig. S2. XRD patterns of mechanochemically synthesized samples in Pb-Bi-S system: (1) – 0.5 min, (2) – 1 min, (3) – 3 min, (4) – 5 min, (5) – 10 min, (6) – 15 min, (7) – 30 min, (8) – 60 min, (9) – 120 min (stars correspond to enriched PbS with Bi in a new Pb-Bi-S system). All the other diffraction peaks except five most intensive ones belong to anglesite, PbSO_4 (ICDD PDF 00-036-14612).

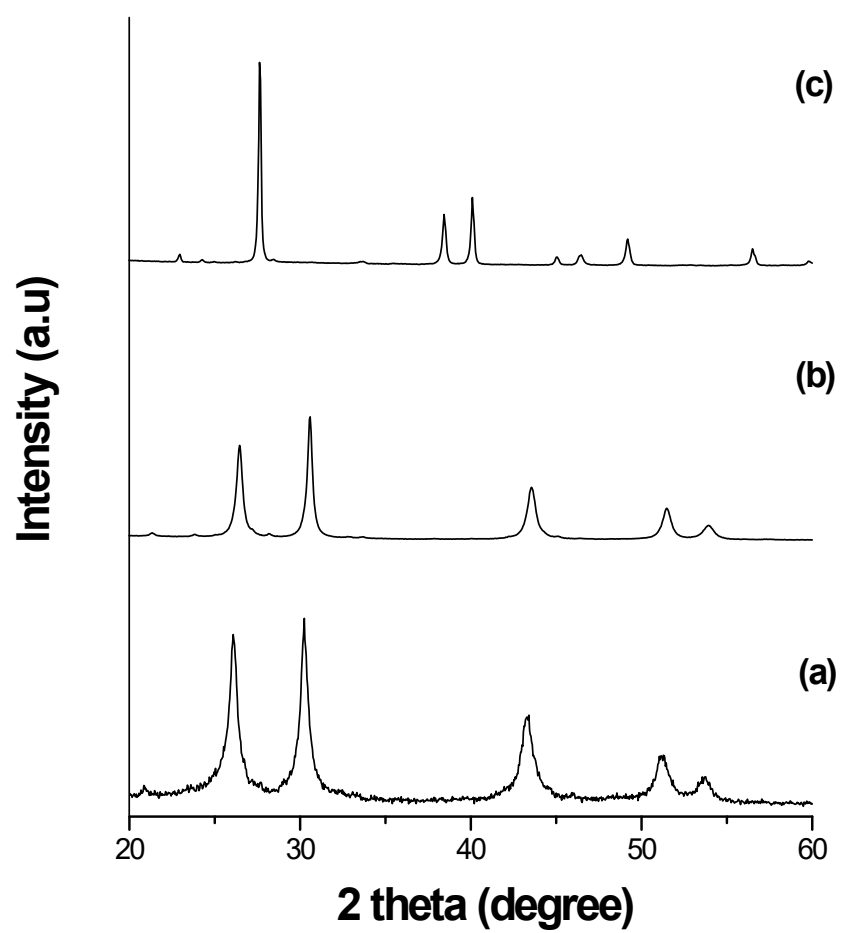


Fig. S3 XRD patterns of samples milled for 5 min: (a) Pb-Bi-S system, (b) PbS, and (c) Bi

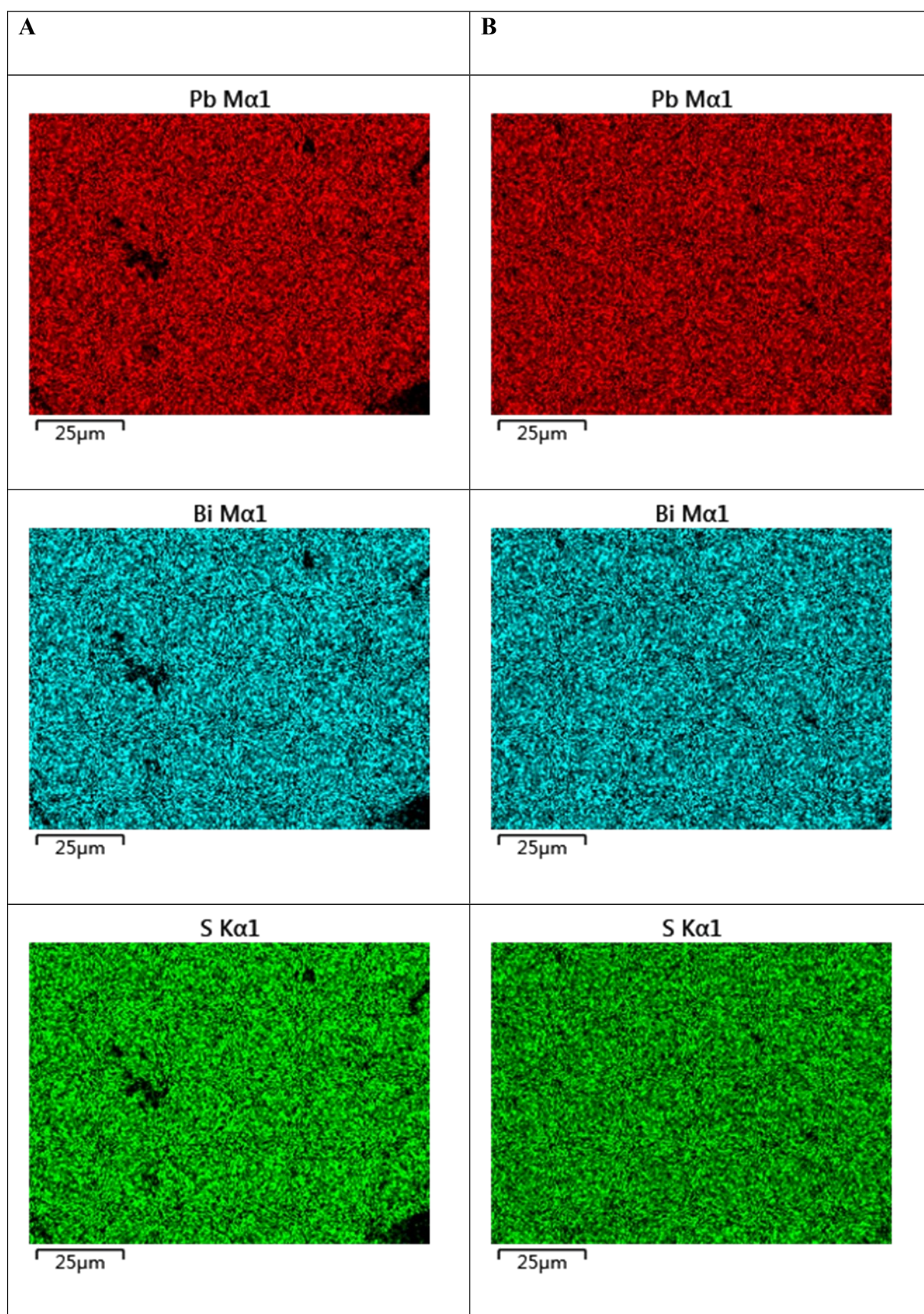


Fig. S4 Energy dispersive X-ray spectroscopy (EDX) mappings for samples milled for 5 min (A) and 120 min (B), respectively.

Table S1 Rietveld analysis for samples milled for 5 min and 120 min, respectively.

Sample		Cell parameter (Å)	Crystallite size (nm)	Microstrain (%)	Rwp (%)
Milling time (min)	SPS				
5	-	5.920	15	0.56	12.79
5	+	5.916	5	-	11.70
120	-	5.902	10	0.82	11.09
120	+	5.918	5	-	12.88

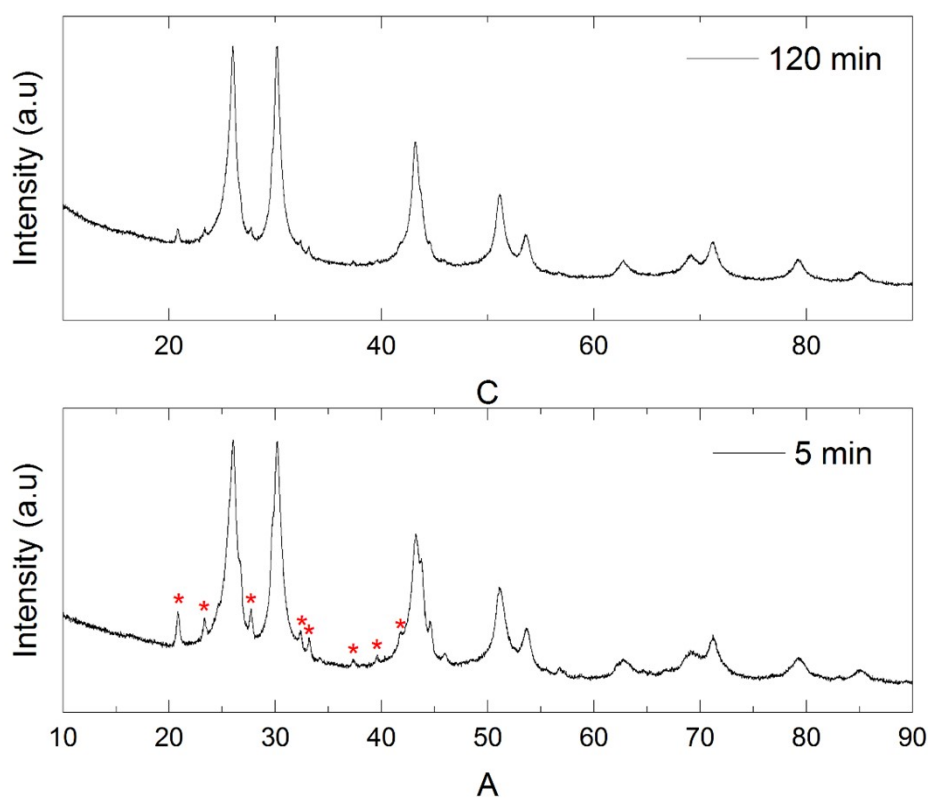


Fig. S5. XRD patterns of Pb-Bi-S samples milled for 5 and 120 min after SPS treatment (red stars mark diffraction peaks corresponding to anglesite PbSO₄).

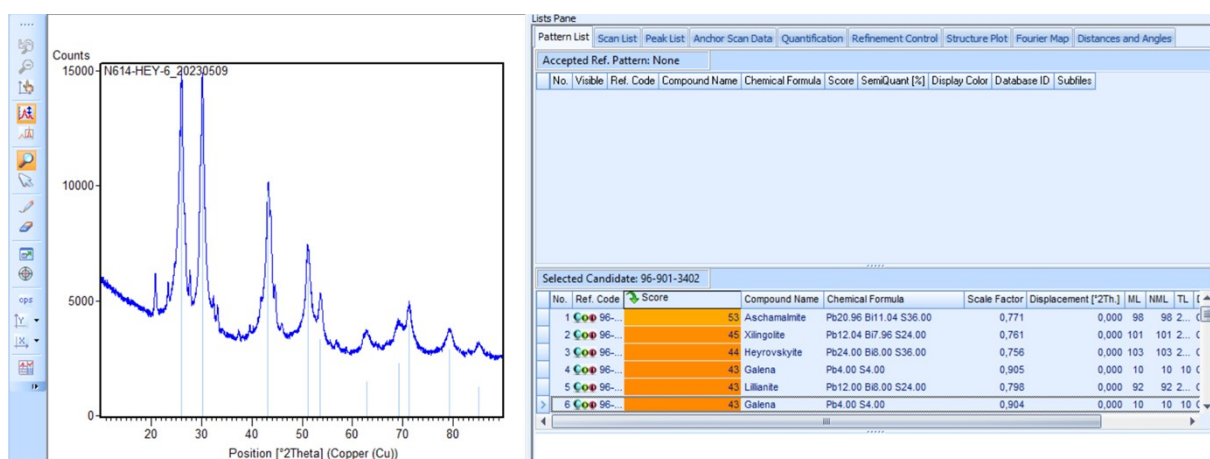


Fig. S6. A screenshot from the XRD analysis program showing the highest match of aschamalmite phase for the sample milled for 120 min and treated by SPS.

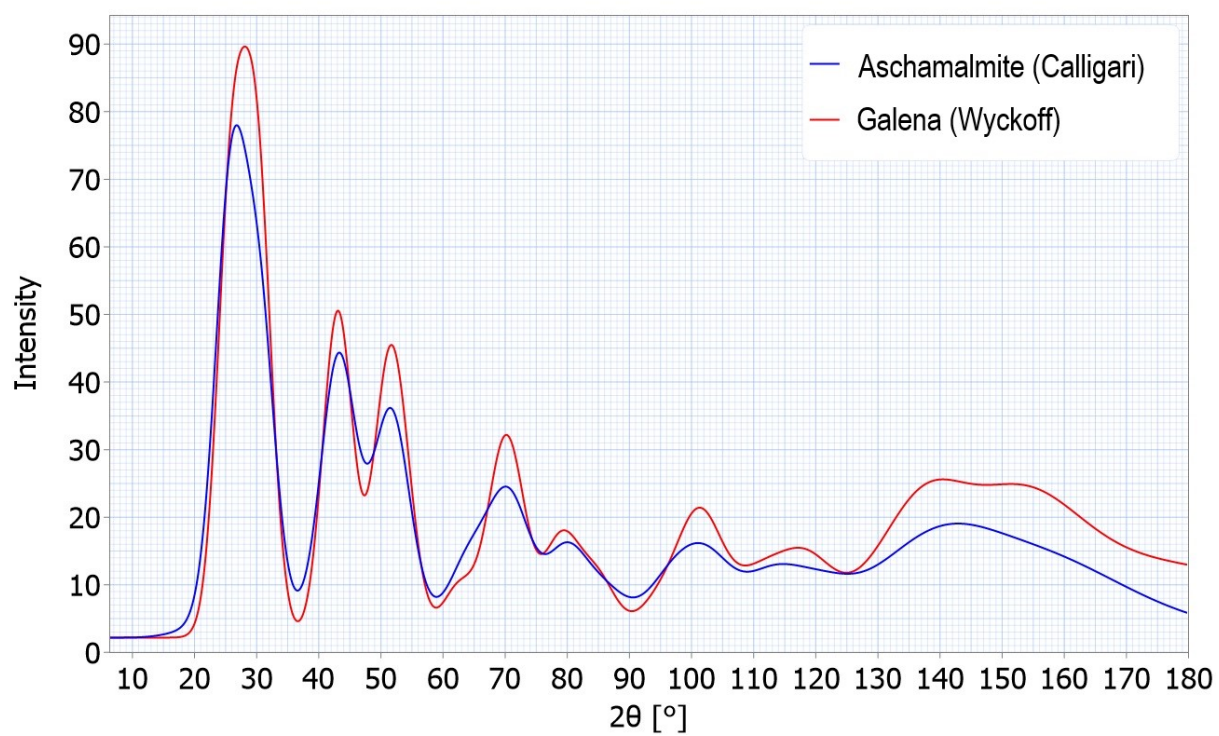


Fig. S7 Simulation in Crystal Maker program for sample with crystalline size 15 nm.

Experimental empirical equation for parametrization of values S_{BET} and c_{Bi}

For description of specific surface area, S_{BET} and bismuth dissolution, c_{Bi} in dependence on milling time, t_M the following exponential empirical equations were applied:

$$c_{Bi}(t_M) = c_{Bi}^{max} (1 + e^{-k_{Bi} t_M}) = 7.00 (1 + e^{-0.270 t_M}) \quad (1)$$

$$c_{S_{BET}}(t_M) = c_{S_{BET}}^{max} (1 + e^{-k_{S_{BET}} t_M}) = 0.77 (1 + e^{-0.307 t_M}) \quad (2)$$

In equations (1) and (2) c_{Bi}^{max} and $c_{S_{BET}}^{max}$ represent maximum decrease of parameters c_{Bi} and $c_{S_{BET}}$ at $t_M=120$ min. Calculated coefficients of determination R^2 were 95.7% for c_{Bi} and 97.6% for $c_{S_{BET}}$, respectively.