STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS

Volume 74 (2018)

Supporting information for article:

Determination of the miscibility gap in the solid solutions series of methylammonium lead iodide/chloride

Alexandra Franz, Daniel M. Többens, Julia Steckhan and Susan Schorr

The terms MAPI and MAPCl will be used for any compound within the solid solution series, whose composition is on the respective side of the miscibility gap and which thus has essentially the crystal structure of the pure end member, but may exhibit a degree of anion substitution.

S1. Powder diffraction data with qualitative phase analysis

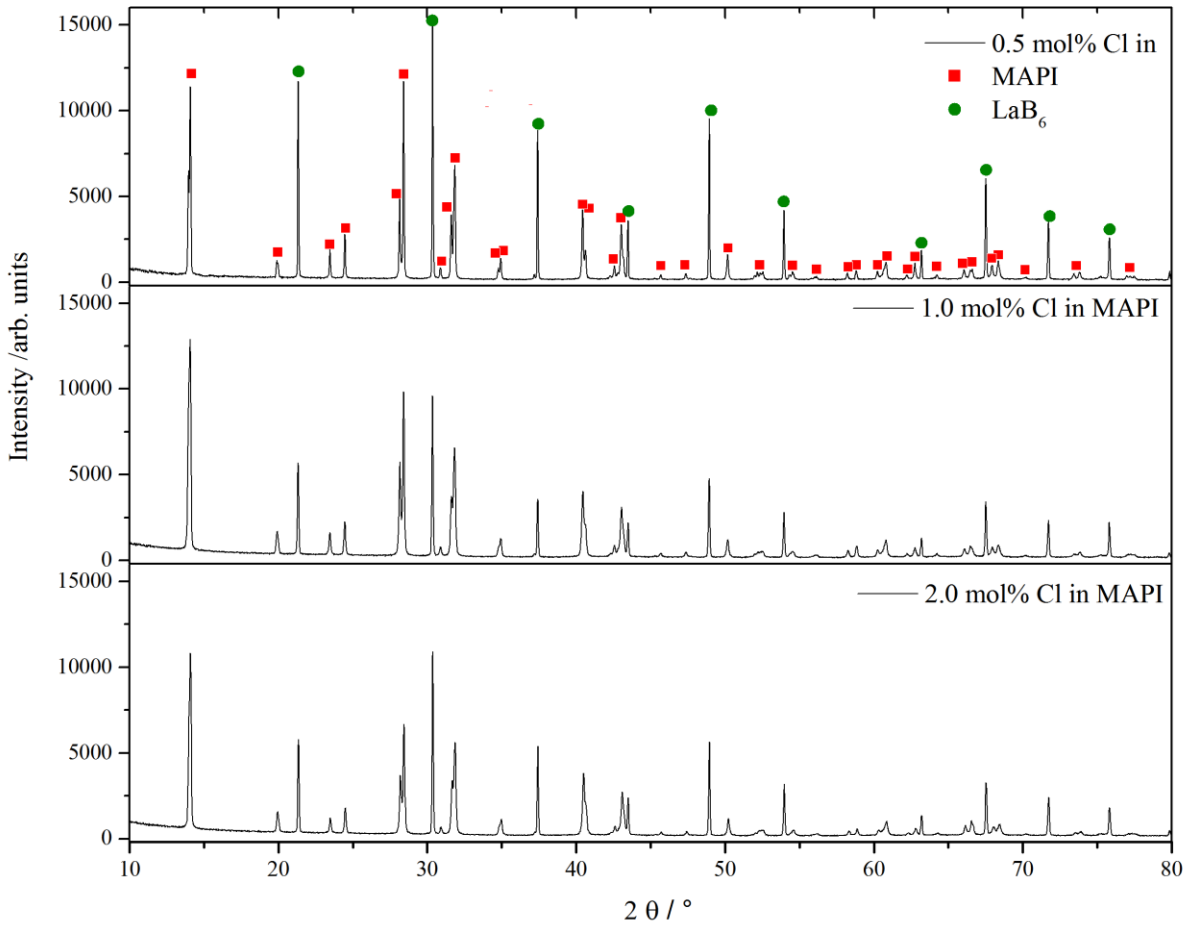

Figure S1 Diffractograms of the single phase samples of the iodine-rich side of the phase diagram. The red squares refer to the solid solution MAPI, green circles to LaB_6 which was used as an internal standard to increase the accuracy of lattice parameters.

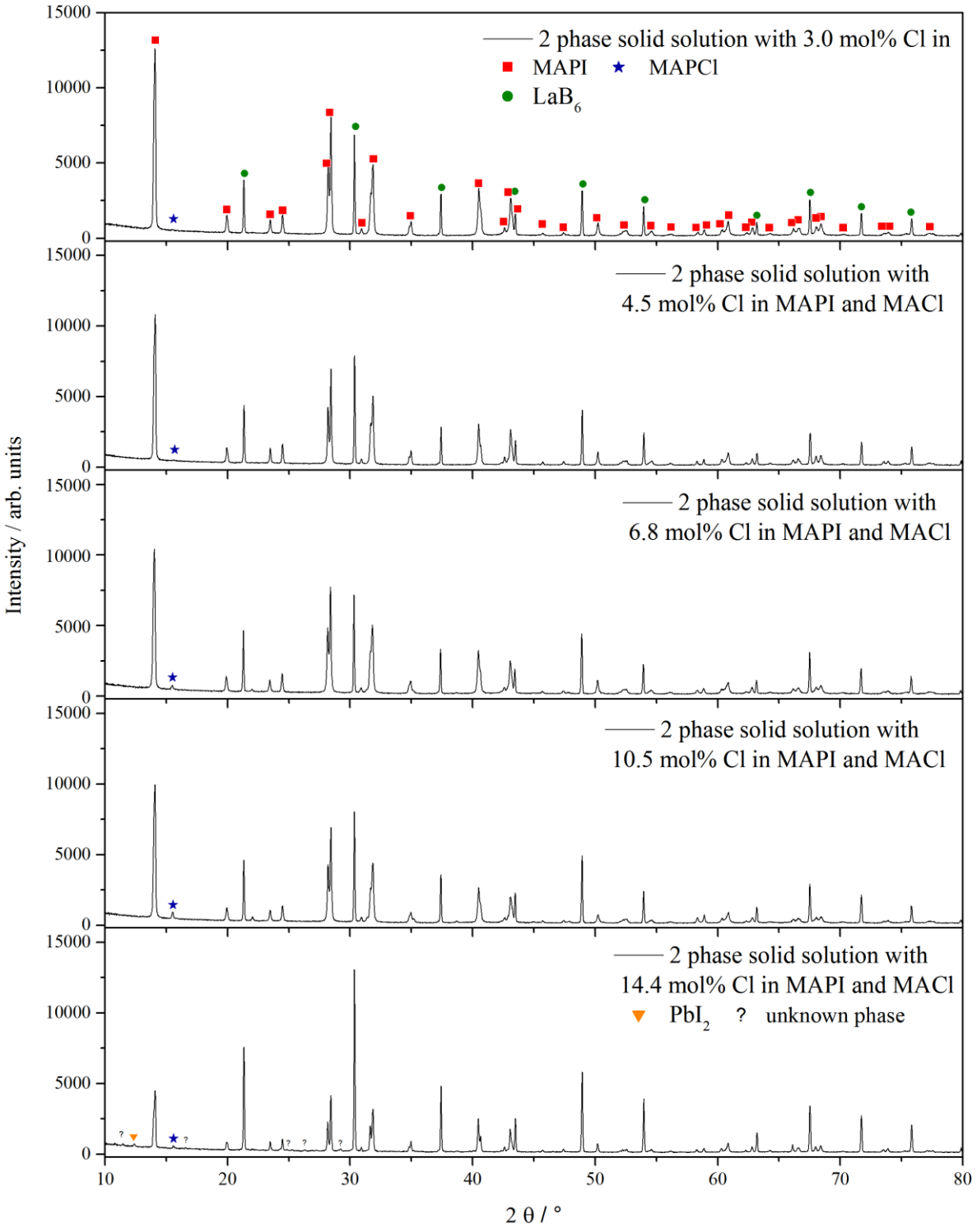

Figure S2 2 phase solid solutions with red squares referring to MAPI, blue stars referring to MACl, green circles to LaB_6. The bottommost graphic show small impurities of PbI_2. This shows the sensitivity of the synthesis method since exactly the same procedure was used for the sample with the same chemical composition show in Figure S3 (topmost graphic)

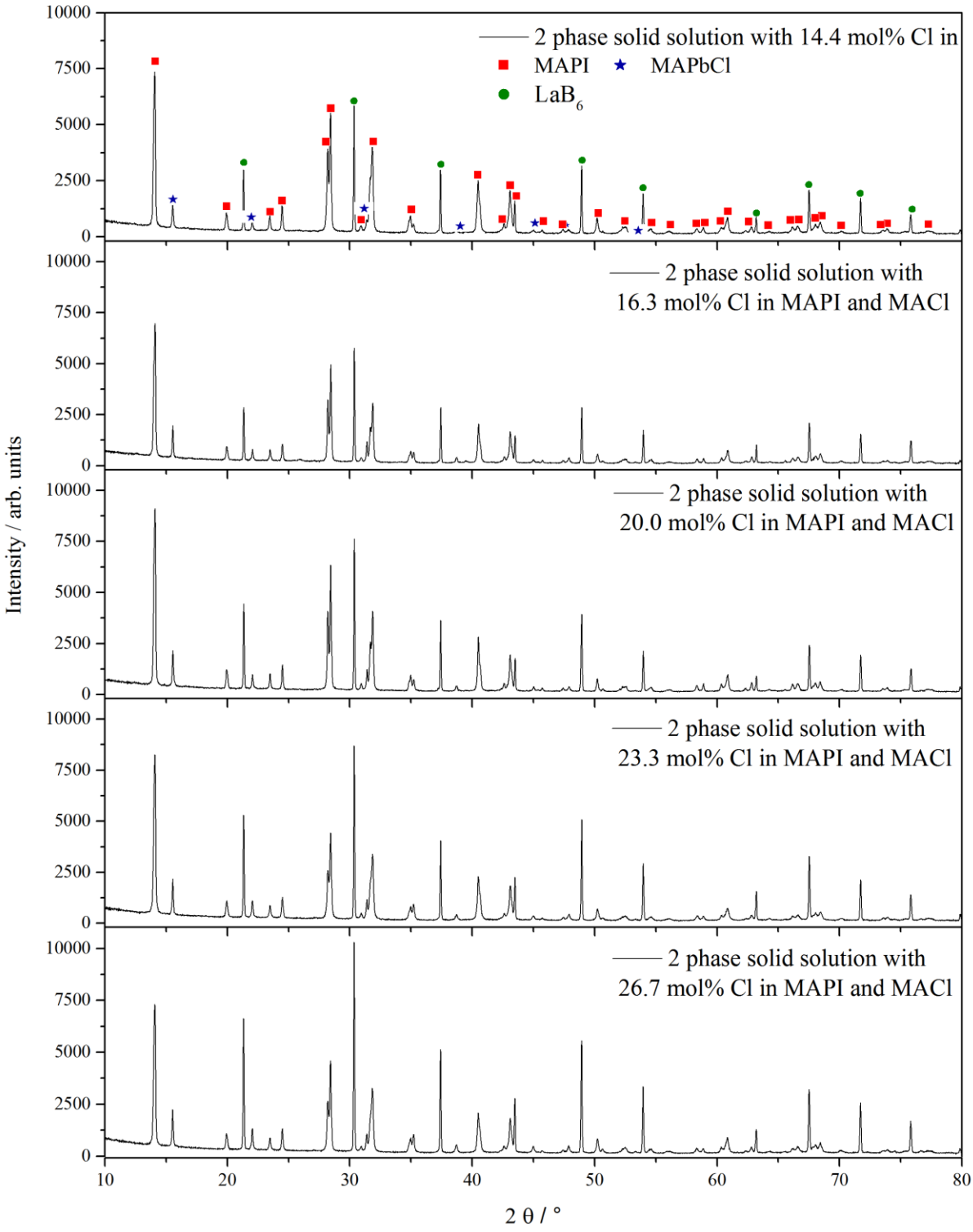

Figure S3 2 phase solid solutions with red squares referring to MAPI, blue stars referring to MACl, green circles to LaB_6.

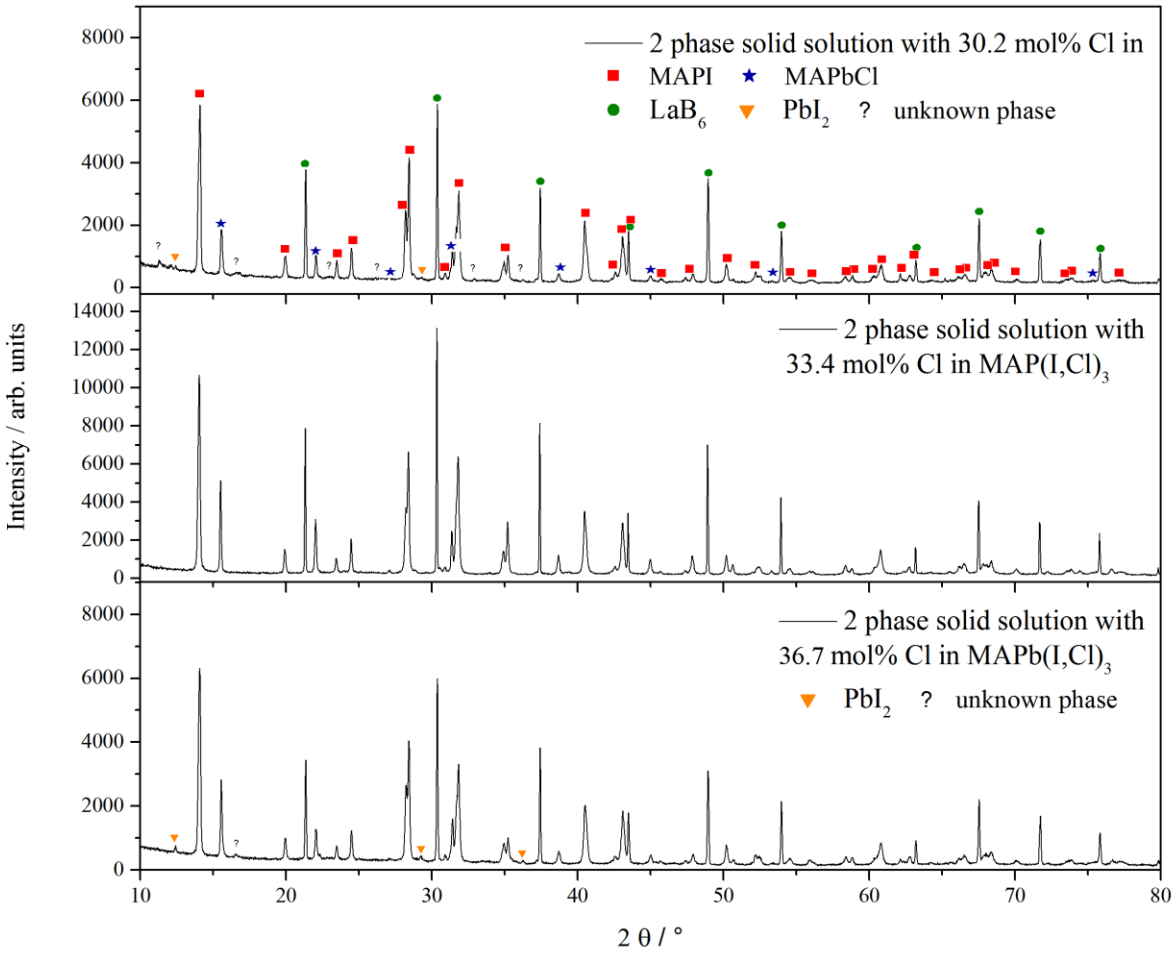

Figure S4 2 phase solid solutions with red squares referring to MAPI, blue stars referring to MACl, green circles to LaB_6, yellow triangles to small impurities of PbI_2.

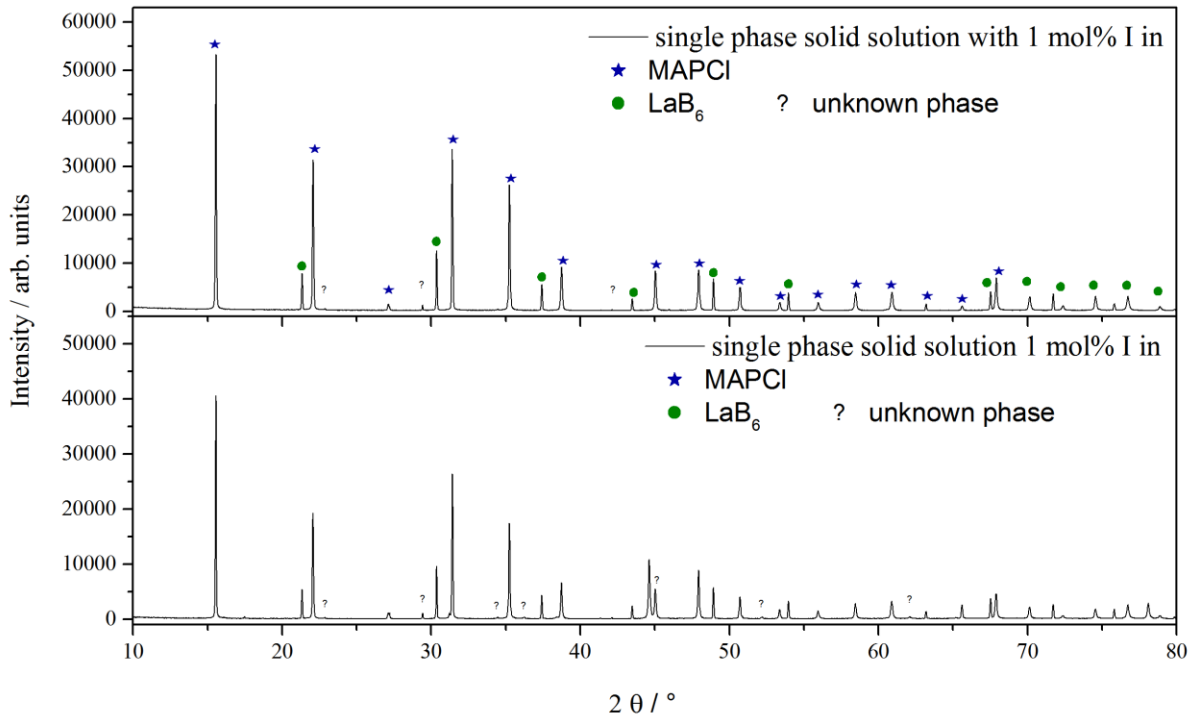

Figure S5 Single phase solid solution of MAPCl (blue stars) and LaB_6 (green circles)

S2. Lattice parameters of solid solution members

Table S1 Phase formation and lattice parameters as function of the chemical composition. The Cl content is given as molar fraction Cl / (Cl+I).

Cl content / mol%	MAPI			MAPbCl	MAPI	MAPCl	Comment
	a / Å	*c* / Å	pseudocubic <*a*> / Å	*a* / Å	Vegard estimation of Cl content / mol%		
0	8.873(1)	12.667(2)	6.294(1)	-	0.0	-	single phase
0.5	8.872(1)	12.661(2)	6.292(1)	-	0.2	-	single phase
1	8.870(1)	12.653(2)	6.290(1)	-	0.6	-	single phase
2	8.866(1)	12.639(2)	6.286(1)	-	1.3	-	single phase
2.3	8.868(1)	12.649(2)	6.289(1)	-	0.9	-	single phase
3	8.863(1)	12.631(2)	6.283(1)	5.666(12)	1.8	-	two phase, very small

							MAPCl fraction
4.5	8.864(1)	12.638(2)	6.285(1)	5.682(22)	1.5	-	two phase, very small MAPCl fraction
6.8	8.863(1)	12.632(2)	6.283(1)	5.689(3)	1.7	99.3	two phase
10.5	8.859(1)	12.629(2)	6.281(1)	5.689(2)	2.1	99.3	two phase
14.4	8.866(1)	12.649(2)	6.288(1)	5.698(16)	1.0	-	two phase, very small MAPCl fraction, impurities
14.4	8.866(1)	12.638(2)	6.286(1)	5.692(1)	1.3	98.8	two phase
16.3	8.862(1)	12.635(2)	6.283(1)	5.692(1)	1.7	98.8	two phase
20	8.864(1)	12.635(2)	6.284(1)	5.689(1)	1.6	99.3	two phase
23.3	8.862(1)	12.631(2)	6.283(1)	5.691(1)	1.8	99.0	two phase
26.7	8.863(1)	12.631(2)	6.283(1)	5.692(1)	1.8	98.8	two phase
30.2	8.868(1)	12.626(2)	6.285(1)	5.692(1)	1.5	98.8	two phase
30.2	8.868(1)	12.643(2)	6.288(1)	5.693(1)	1.0	98.7	two phase, impurities
33.4	8.871(1)	12.625(2)	6.286(1)	5.691(1)	1.3	99.0	two phase
36.7	8.871(1)	12.630(2)	6.287(1)	5.691(1)	1.2	99.0	two phase, impurities
99	-	-	-	5.685(1)	-	99.8	single phase,
99	-	-	-	5.686(1)	-	99.7	single phase,
100	-	-	-	5.687(1)	-	100.0	single phase,