

Electronic Supplementary Information

For

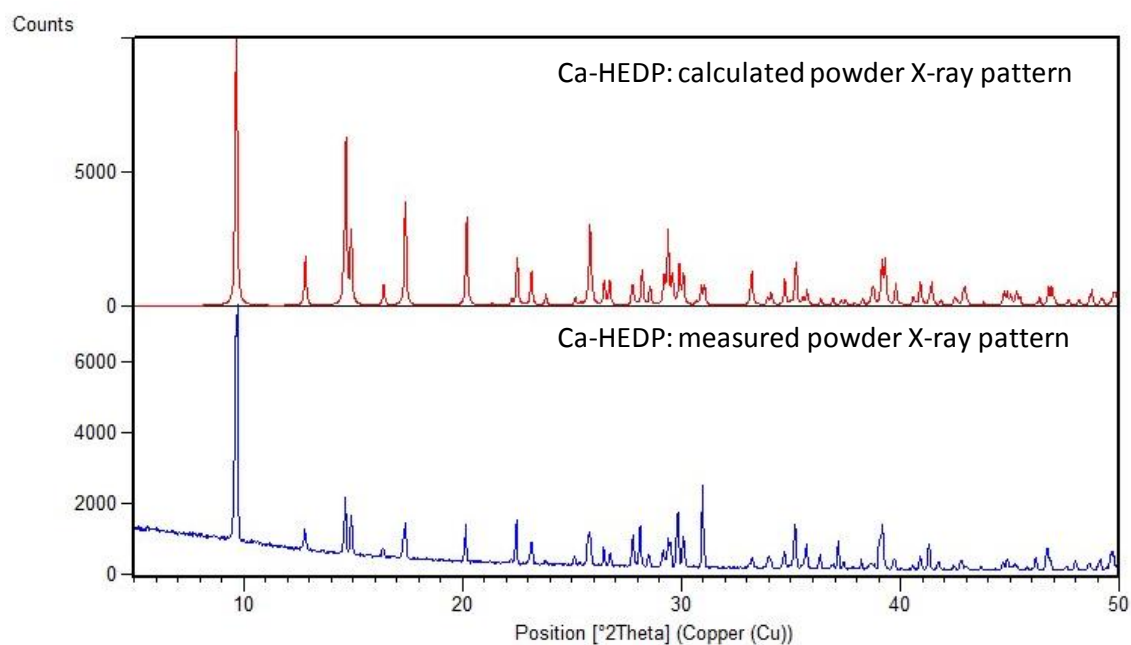
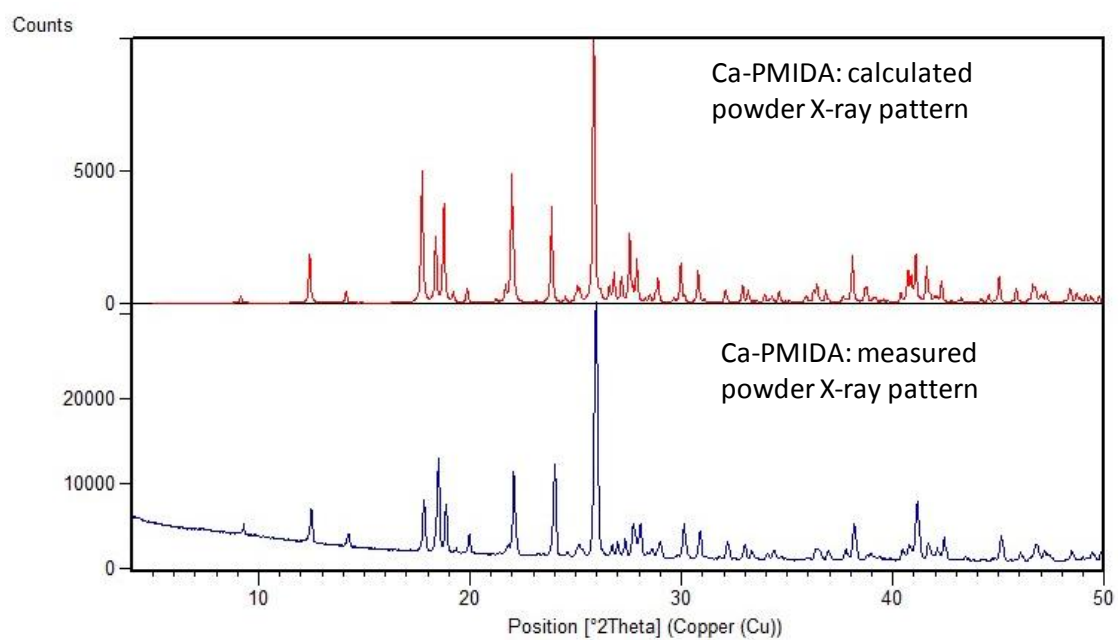
“Crystal Engineering in Confined Spaces. A Novel Method to Grow Crystalline Metal Phosphonates in Alginate Gel Systems”

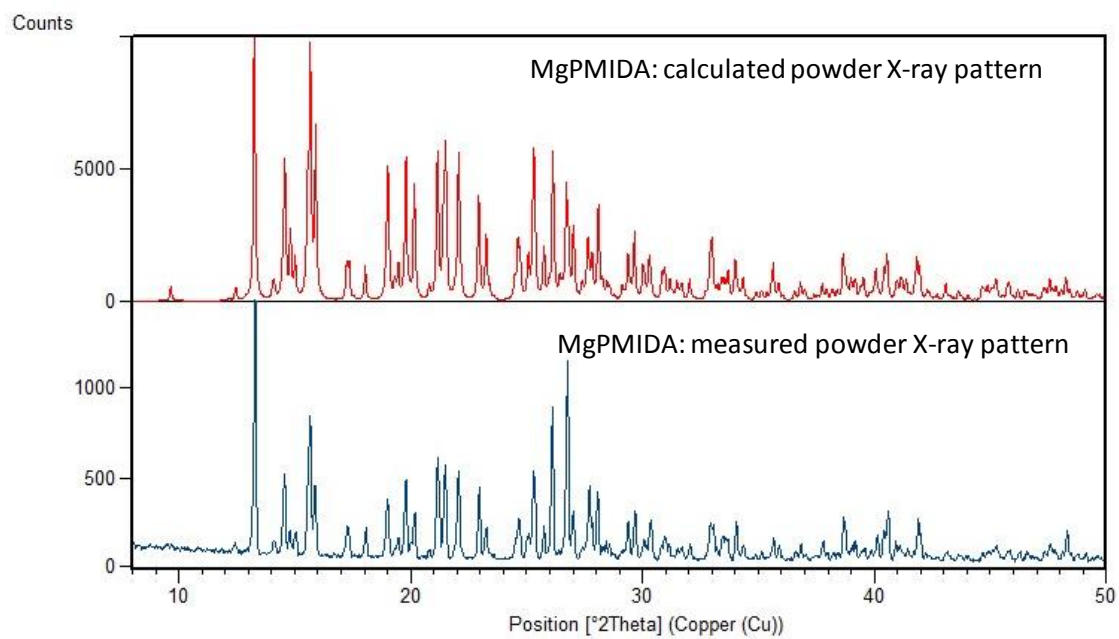
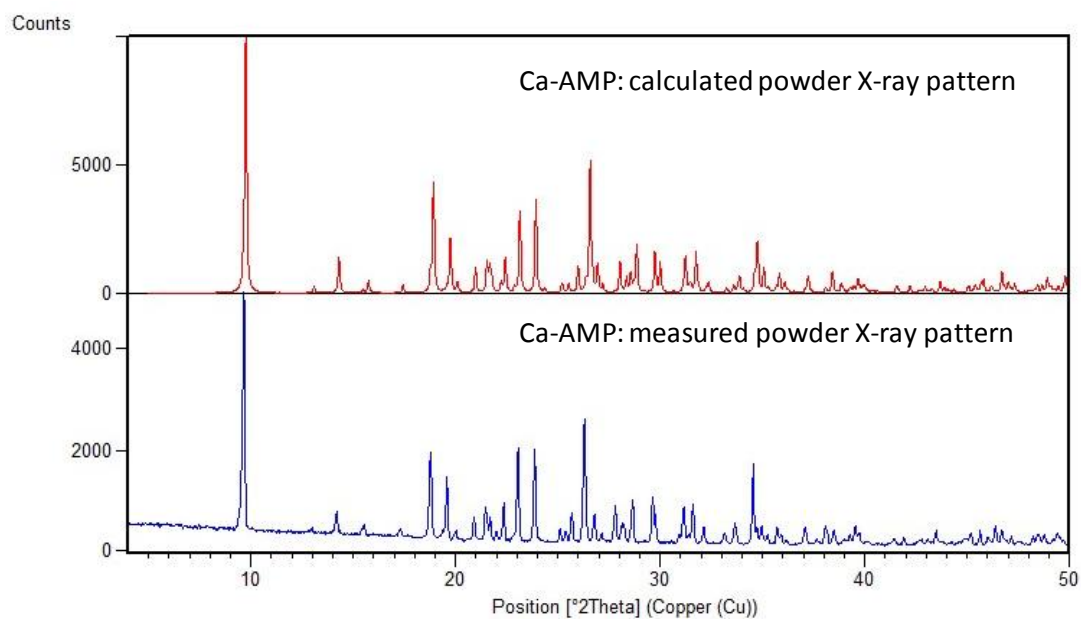
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Powder XRD patterns for bulk samples and corresponding calculated patterns





Experimental Set-up

		Metal Ion		Ligand	
		Ce		AMP	
pH value	Experiment Date	Collection Date	Comments on gel appearance	Sample Number	Comments on isolated solids
No pH control	19 June 2010	24 June 2010	white amorphous-looking solid	1	-
1.00	19 June 2010	24 June 2010	white amorphous-looking solid	2	-
2.00	19 June 2010	24 June 2010	white amorphous-looking solid	3	-
3.00	19 June 2010	24 June 2010	white amorphous-looking solid	4	-
4.08	19 June 2010	24 June 2010	white small sphere-like solid	5	-
5.00	19 June 2010	24 June 2010	destroyed gel-amorphous white solid inside	6	-
		Ce		HEDP	
pH value	Experiment Date	Collection Date	Comments on gel appearance	Sample Number	Comments on isolated solids
No pH control	19 June 2010	24 June 2010	white small sphere-like solid	7	-
1.00	19 June 2010	24 June 2010	yellow emulsion-few small spherical particles at the bottom	8	-
2.03	19 June 2010	24 June 2010	white amorphous solid in sunsension	9	-
3.06	19 June 2010	24 June 2010	white amorphous solid within the gel, clear excess liquid	10	-
4.01	19 June 2010	24 June 2010	white amorphous solid within the gel, clear excess liquid	11	-
5.09	19 June 2010	24 June 2010	white amorphous solid within the gel, clear excess liquid	12	-

		Ce		BHTPMP	
pH value	Experiment Date	Collection Date	Comments on gel appearance	Sample Number	Comments on isolated solids
No pH control	20 June 2010	24 June 2010	dark yellowish gel-sediment at the bottom-probably Ligand	13	yellow glue+soft gel
1.03	20 June 2010	24 June 2010	dark yellowish gel-sediment at the bottom-probably Ligand + few white particles in the gel	14	yellow glue+soft gel
2.09	20 June 2010	24 June 2010	white amorphous material in the gel-yellow amorphous material within the gel and yellow amorphous material in suspension	15	Looks like dehydrated gel
3.02	20 June 2010	24 June 2010	white amorphous material in the gel-yellow amorphous material within the gel and yellow amorphous material in suspension	16	Looks like dehydrated gel
4.02	20 June 2010	24 June 2010	white amorphous material within the gel-amorphous yellow material within the gel and yellow amorphous material in suspension	17	Looks like dehydrated gel
5.01	20 June 2010	24 June 2010	destroyed gel, white amorphous material on top of the gel	18	many dried-up gel pieces
		Ce		EDTMP	
pH value	Experiment Date	Collection Date	Comments on gel appearance	Sample Number	Comments on isolated solids

No pH control	21 June 2010			27	
1.03	21 June 2010	24 June 2010	white powder within the gel and in the excess liquid	28	nothing inside the gel
2.02	21 June 2010	24 June 2010	white powder within the gel and in the excess liquid	29	completely deformed/ dehydrated/shrunk gel
3.02	21 June 2010	24 June 2010	white powder within the gel and in the excess liquid	30	-
3.92	21 June 2010	24 June 2010	white powder within the gel and in the excess liquid	31	no
5.05	21 June 2010	24 June 2010	white powder within the gel and in the excess liquid	32	no
		Ce		HDTMP	
pH value	Experiment Date	Collection Date	Comments on gel appearance	Sample Number	Comments on isolated solids
No pH control	21 June 2010	24 June 2010	few white particles on the gel, few yellow particles in the excess liquid	33	-
1.01	21 June 2010	24 June 2010	white powder in the gel, colorless gel "balls" at the bottom	34	colorless "glue"
2.00	21 June 2010	24 June 2010	white powder within the gel, powdery suspension in the excess liquid	35	shrunk "dehydrated" gel
3.00	21 June 2010	24 June 2010	white powder within the gel, powdery suspension in the excess liquid	36	shrunk "dehydrated" gel
4.12	21 June 2010	24 June 2010	white powder within the gel, powdery suspension in the excess liquid	37	shrunk "dehydrated" gel
5.1	21 June 2010	24 June 2010	destroyed gel, white	38	shrunk "dehydrated" gel

			powder,yellow gel pieces		
		Ce		DTPMP	
pH value	Experiment Date	Collection Date	Comments on gel appearance	Sample Number	Comments on isolated solids
No pH control	21 June 2010			39	-
1.04	21 June 2010	24 June 2010	white powder within the gel, a lot of precipitate in the excess liquid	40	-
2.02	21 June 2010	24 June 2010	white powder within the gel, a lot of precipitate in the excess liquid	41	-
3.09	21 June 2010	24 June 2010	white powder within the gel, a lot of precipitate in the excess liquid	42	-
4.01	21 June 2010	24 June 2010	white powder within the gel, a lot of precipitate in the excess liquid	43	-
5.01	21 June 2010	24 June 2010	white powder within the gel, a lot of precipitate in the excess liquid	44	-
		Ce		HPAA	
pH value	Experiment Date	Collection Date	Comments on gel appearance	Sample Number	Comments on isolated solids
No pH control	21 June 2010	24 June 2010	Well-formed small white spherical particles on the gel and at the bottom	45	yellow gel-white spheres made up from thin needles
1.06	21 June 2010	24 June 2010	Well-formed small white spherical particles on the gel and at the bottom	46	yellow gel-white spheres made up from thin needles
2.09	21 June 2010	24 June 2010	Well-formed large white spherical particles on the gel and at the bottom	47	yellow gel-white spheres made up from thin needles
3.17	21 June 2010	24 June 2010	small white spherical particles	48	yellow gel-white spheres made up

			on the gel and at the bottom		from thin needles
4.12	21 June 2010	24 June 2010	small white spherical particles on the gel and at the bottom	49	completely deformed gel
5.34	21 June 2010	24 June 2010	small white spherical particles on the gel and at the bottom	50	-
		Ce		PMIDA	
pH value	Experiment Date	Collection Date	Comments on gel appearance	Sample Number	Comments on isolated solids
No pH control	22 June 2010	24 June 2010	white powder within the gel-few white particles at the bottom	51	-
3.50	22 June 2010	24 June 2010	white powder within the gel-few white particles at the bottom	52	-
4.04	22 June 2010	24 June 2010	white precipitate only on the gel	53	-
4.52	22 June 2010	24 June 2010	white precipitate only on the gel	54	-
5.04	22 June 2010	24 June 2010	destroyed gel, white precipitate on the gel pieces	55	shrunk gel
5.50	22 June 2010	24 June 2010	No product obtained		-
		Ca		AMP	
pH value	Experiment Date	Collection Date	Comments on gel appearance	Sample Number	Comments on isolated solids
No pH control	19 June 2010	25 June 2010	White crystals in the excess liquid and on the gel	63	Crystals formed also inside the gel
	19 June 2010			64	
2.04	19 June 2010	25 June 2010	White crystals in the excess liquid and on the gel	65	Crystals formed also inside the gel
2.99	19 June 2010	25 June 2010	White microcrystalline precipitate in the excess liquid and	66	Crystals formed also inside the gel

			on the gel		
	19 June 2010			67	
	19 June 2010			68	
		Ca		HEDP	
pH value	Experiment Date	Collection Date	Comments on gel appearance	Sample Number	Comments on isolated solids
No pH control	19 June 2010	25 June 2010		69	
1.05	19 June 2010	25 June 2010	Large pieces of white particles on the gel surface and in the excess liquid	70	nothing inside the gel
2.02	19 June 2010	25 June 2010	white precipitate outside of and inside the gel and in the excess liquid	71	Shrunk gel
3.02	19 June 2010	25 June 2010	a lot of well-formed white microcrystalline balls on the gel surface and in the excess liquid	72	Crystals formed also inside the gel
4.14	19 June 2010	25 June 2010	destroyed gel, looks like gelatinous liquid + incorporated pieces of precipitate all over the gel	73	powder, gel traces
5.12	19 June 2010	25 June 2010	destroyed gel, looks like gelatinous liquid + incorporated pieces of precipitate all over the gel	74	powder, gel traces
		Ca		PBTC	
pH value	Experiment Date	Collection Date	Comments on gel appearance	Sample Number	Comments on isolated solids
No pH control	-	-	-	81	-
	-	-	-	82	-

2.06	20 June 2010	28 June 2010	"mushrooms" inside- Thrown out	83	Thrown out
2.99	20 June 2010	28 June 2010	"mushrooms" inside- Thrown out	84	Thrown out
	-	-	-	85	-
5.00	20 June 2010	28 June 2010	"mushrooms" inside- Thrown out	86	Thrown out
		Ca		HDTMP	
pH value	Experiment Date	Collection Date	Comments on gel appearance	Sample Number	Comments on isolated solids
No pH control	22 June 2010	-		93	
1.09	22 June 2010	25 June 2010	white powder, film and small spherical particles	94	Crystals formed also inside the gel
2.00	22 June 2010	25 June 2010	Aggregated crystals within the gel and in surrounding liquid	95	"tree"-like aggregates
3.08	22 June 2010	25 June 2010	Aggregated spherical crystals within the gel and in surrounding liquid	96	"balls" and "films"
4.08	22 June 2010	25 June 2010	Aggregated spherical crystals within the gel and in surrounding liquid	97	"balls" and "films"
		Ca		HPAA	
pH value	Experiment Date	Collection Date	Comments on gel appearance	Sample Number	Comments on isolated solids
2.07	22 June 2010	25 June 2010	white big spherical aggregates within the gel and the excess liquid	107	"balls" look very compact
3.03	22 June 2010	25 June 2010	white big spherical aggregates within the gel and the excess liquid	108	"balls" look very compact
4.05	22 June 2010	25 June 2010	destroyed gel, "balls" everywhere, looks like two products present	109A	crystals stuck strongly at the bottom of the vial. 1st product = the powder on the gel
			the material from	109B	2nd product = the

			the bottom of experiment 109B		crystals
5.01	22 June 2010	25 June 2010	Powdery aggregates, look like leaves	110	destroyed gel
		Ba		HEDP	
pH value	Experiment Date	Collection Date	Comments on gel appearance	Sample Number	Comments on isolated solids
No pH control	23 June 2010	02 July 2010	clear	129	through away
2.07	23 June 2010	02 July 2010	white powdery microparticles	130	-
3.00	23 June 2010	02 July 2010	white powdery microparticles	131	-
4.01	23 June 2010	02 July 2010	white powdery microparticles-malformed gel-few white amorphous sphere-like particles in the gel	132	destroyed gel
5.03	23 June 2010	02 July 2010	white powdery microparticles-malformed gel-few white amorphous sphere-like particles in the gel	133	destroyed gel
5.99	23 June 2010	02 July 2010	a lot of small sphere-like particles in the gel, some of them well-formed	134	-
		Ba		PBTC	
pH value	Experiment Date	Collection Date	Comments on gel appearance	Sample Number	Comments on isolated solids
No pH control	23 June 2010	02 July 2010	clear	141	through away
1.03	23 June 2010	02 July 2010	clear	142	through away
2.01	23 June 2010	02 July 2010	white precipitate on and inside the gel	143	-
3.04	23 June 2010	02 July 2010	white precipitate on and inside the gel	144	-
4.01	23 June	02 July	white powdery	145	destroyed gel

	2010	2010	microparticles		
5.00	23 June 2010	02 July 2010	white powdery microparticles in the excess liquid, no solid on, or inside the gel	146	-
		Ba		EDTMP	
pH value	Experiment Date	Collection Date	Comments on gel appearance	Sample Number	Comments on isolated solids
No pH control	23 June 2010	12 July 2010	clear	147	thrown away
1.01	23 June 2010	12 July 2010	clear	148	thrown away
2.01	23 June 2010	12 July 2010	clear	149	thrown away
2.99	23 June 2010	12 July 2010	clear	150	thrown away
4.02	23 June 2010	12 July 2010	white powder at the bottom of the vial	151	-
5.01	23 June 2010	12 July 2010	clear	152	thrown away
		Ba		HDTMP	
pH value	Experiment Date	Collection Date	Comments on gel appearance	Sample Number	Comments on isolated solids
No pH control	21 June 2010	12 July 2010	gel like product	153	-
1.03	21 June 2010	12 July 2010	clear	154	thrown away
2.03	21 June 2010	12 July 2010	clear	155	thrown away
2.86	21 June 2010	12 July 2010	clear	156	thrown away
4.04	21 June 2010	12 July 2010	clear	157	thrown away
5.04	21 June 2010	12 July 2010	clear	158	thrown away
		Ba		HPAA	
pH value	Experiment Date	Collection Date	Comments on gel appearance	Sample Number	Comments on isolated solids
No pH control	21 June 2010	12 July 2010	black grains on the gel and excess liquid	165	thrown away
1.04	21 June 2010	12 July 2010	black grains on the gel and excess	166	thrown away

			liquid		
2.2	21 June 2010	12 July 2010	black grains on the gel and excess liquid	167	thrown away
3.01	21 June 2010	02 July 2010	SINGLE CRYSTALS	168	isolated
4.01	21 June 2010	02 July 2010	SINGLE CRYSTALS	169	isolated
5.00	21 June 2010	02 July 2010	white powder inside and on the gel, some at the bottom of the vial	170	-
		Ba		PMIDA	
pH value	Experiment Date	Collection Date	Comments on gel appearance	Sample Number	Comments on isolated solids
No pH control	22 June 2010	12 July 2010	clear	171	thrown away
3.53	22 June 2010	12 July 2010	clear	172	thrown away
4.11	22 June 2010	12 July 2010	clear	173	thrown away
4.5	22 June 2010	12 July 2010	pieces of destroyed gel	174	thrown away
5.02	22 June 2010	12 July 2010	clear	175	thrown away
5.5	22 June 2010	12 July 2010	small crystals inside and on the gel and the bottom of the vial	176	-
		Ca		PMIDA	
pH value	Experiment Date	Collection Date	Comments on gel appearance	Sample Number	Comments on isolated solids
2.85	22 June 2010	12 July 2010	small crystals inside and on the gel and the bottom of the vial	177	isolated
		Mg		PMIDA	
pH value	Experiment Date	Collection Date	Comments on gel appearance	Sample Number	Comments on isolated solids
4.50	22 June 2010	12 July 2010	small crystals inside and on the gel and the bottom of the vial	178	isolated
5.00	22 June 2010	12 July 2010	powdery product	179	-

5.50	22 June 2010	12 July 2010	powdery product	180	-
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