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Vacancies ordering in new metastable orthophosphates $[Co_3\square]P_2O_8$ and $[Mg_3\square]P_2O_8$ with olivin-related structure

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Abstract

A new vacancies containing allotropic form of cobalt and magnesium orthophosphates has been prepared by solid-state exchange reaction, according to the model:

$$2CoLiPO_4 + Li_2SO_4 \rightarrow [Co_3\square](PO_4)_2 + CoSO_4$$
$$2MgLiPO_4 + Li_2SO_4 \rightarrow [Mg_3\square](PO_4)_2 + MgSO_4\,.$$

The structure of the new form was investigated and is shown to be very closely related with that one of the olivin starting materials: vacancies and bivalent cations are ordered on octahedral sites. The new phases are metastable and undergo irreversible transformation at rather low-temperature into the well known high-temperature phase.

Résumé

Une nouvelle variété allotropique des orthophosphates de cobalt et de magnésium a été préparée par réaction d'échange à l'état solide; le schéma de la réaction est le suivant:

$$2CoLiPO_4 + Li_2SO_4 \rightarrow [Co_3\square](PO_4)_2 + CoSO_4$$
$$2MgLiPO_4 + Li_2SO_4 \rightarrow [Mg_3\square](PO_4)_2 + MgSO_4\,.$$

La structure cristallographique a été déterminée. Elle possède une analogie étroite avec celle des composés olivines de départ: une répartition ordonnée des lacunes et des cations bivalents existe sur les sites octaédriques du composé de départ. Les nouvelles phases sont métastables et se transforment irreversiblement par chauffage en la variété stable bien connue.

In several recent papers, we described a method[1–3] which allowed us to prepare numerous new metastable spinel compounds with ordered vacancies; starting with lithium containing compounds, the nonstoichiometric phases were obtained by solid-state exchange reaction, according to the scheme below:

$$2\,Li^+ \rightarrow M^{2+} + \square$$

where M^{2+} is a bivalent cation and the sign $\square$ stands for a vacancy.

In this exchange-reaction process, the basic structure of the starting oxide remains unchanged; however in most cases an order appears, between the vacancies and the exchanged bivalent cations on the lithium sites.

While the new vacancies containing compounds are quite stable at room temperature, they generally collapse when the temperature is raised at a few hundred degrees C.

In this paper, we describe two new metastable phases prepared by this method: $[Co_3\square]P_2O_8$ and $[Mg_3\square]P_2O_8$.

1. Experimental

The solid state exchange process can be described by the reaction:

$$[Li_2Mg_2]P_2O_8 + \underset{\text{in excess}}{MgSO_4} \xrightarrow{660^\circ C} [Mg_3\square]P_2O_8 + Li_2SO_4$$

$$[Li_2Co_2]P_2O_8 + \underset{\text{in excess}}{CoSO_4} \xrightarrow{680^\circ C} [Co_3\square]P_2O_8 + Li_2SO_4\,.$$

2. Starting materials

The lithium containing materials $[Mg_2Li_2]P_2O_8$ and $[Co_2Li_2]P_2O_8$ belong to the olivin group (Newnham *et al.*[4]). The orthorhombic space group is *Pmnb*. The cell parameters determined on a Guinier Camera

Table 1. *Cells parameters of olivine orthophosphates and corresponding metastable exchanged compounds*

	$[Mg_2Li_2]P_2O_8$	$[Mg_3\square]P_2O_8$	$[Co_2Li_2]P_2O_8$	$[Co_3\square]P_2O_8$
a	5.87 ± 0.02 Å	5.911 ± 0.02 Å	5.92 ± 0.02 Å	5.920 ± 0.02 Å
b	10.15 ± 0.03	10.214 ± 0.03	10.20 ± 0.03	10.334 ± 0.03
c	4.68 ± 0.02	4.734 ± 0.02	4.70 ± 0.02	4.75 ± 0.02
γ		90° 60′		91° 04′

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[1] J. C. Joubert and A. Durif, Préparation de spinelles lacunaires par réaction d'échange a l'état solide. C.R. Acad. Sc. [Paris] **256** (1963) 4403—4405.

[2] J. C. Joubert and A. Durif, Préparation de quelques spinelles lacunaires. Bull. Soc. franç. Miner. Crist. **87** (1964) 517—519.

[3] J. C. Joubert, Etude des surstructures dans les oxydes mixtes du type spinelle. Thèse Grenoble (1965).

[4] R. Newnham and M. J. Redman, Crystallographic data for $LiMgPO_4$, $LiCoPO_4$, $LiNiPO_4$ with $LiMnPO_4$. J. Amer. Ceram. Soc. **48** (1965) 547.

($CoK\alpha_1$) are given in Table 1. The oxygen packing is hexagonal compact; there are two kinds of octahedral sites in the structure respectively occupied by Li^+ and $Mg^{2+}(Co^{2+})$.

3. Investigation of the structure of these defect exchanged phases

By analogy with the unit cells of the starting materials, it was easy to determine those of the new compounds; the values are listed in Table 1 along with those corresponding to the lithium compounds. Figures 1 and 2 show the analogy between the x-ray diffractograms of the starting and the exchanged materials. Of course, due to the structural differencies, no direct analogy exists between the diffractograms corresponding to the two allotropic forms of the same compounds.

The structure is very close to that of the starting material: half of the lithium sites are occupied by new bivalent cations. Several back reflections are splitted, indicating the symmetry cannot be orthorhombic anymore, however the monoclinic distortion is very weak. Writing the full group symbol of the starting material $P\frac{2_1}{m}\frac{2_1}{n}\frac{2_1}{b}$. The monoclinic space group of the defect compound could be $P2_1/m$, $P2_1/n$ or $P2_1/b$, with three different vacancies orderings. (These are subgroups of the former one.)

Systematic x-ray extinctions show the space group to be $P2_1/b$, so that in the elementary cell, the vacancies are located on the symmetry centers.

Figure 3 represents the projection of the structure on the (001) plane, in the defect form of cobalt orthophosphate. Starting with the

Table 2

Position parameters of the ions in $[Mg_3\square]P_2O_8$ *and* $[Co_3\square]P_2O_8$ *structures*

Position in group $P2_1/b$	$[Mg_3\square]P_2O_8$			$[Co_3\square]P_2O_8$		
	x	y	z	x	y	z
	Standard deviation: ± 0.008			Standard deviation: ± 0.008		
2□ in 2*a*						
$2M^{2+}$(II) in 2*b*						
$4M^{2+}$(I) in 4*e*	0.236	0.277	−0.023	0.227	0.278	−0.017
4P in 4*e*	0.242	0.103	0.426	0.277	0.100	0.430
4O(I) in 4*e*	0.266	0.079	0.306	0.279	0.081	−0.258
4O(II) in 4*e*	0.259	0.453	0.202	0.246	0.462	0.193
4O(III) in 4*e*	0.059	0.190	0.350	0.096	0.168	0.298
4O(IV) in 4*e*	0.439	0.145	0.272	0.493	0.139	0.258

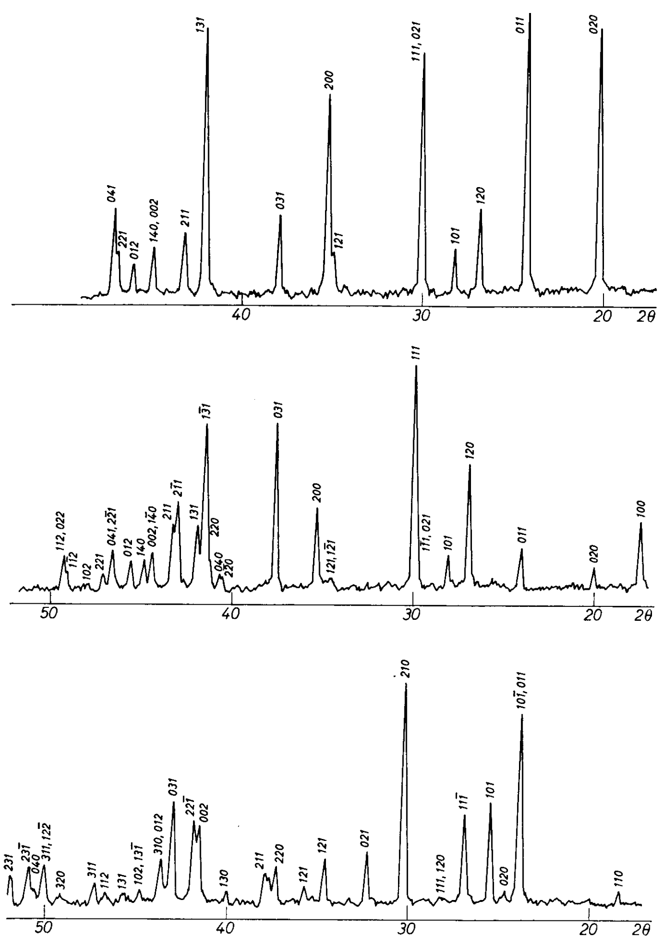

Fig. 1. Comparison between the x-ray diffractometer diagrams [$\lambda(CoK\alpha)$] of the compounds $[LiCo]PO_4$, $[Co_3\square]P_2O_8$, $Co_3P_2O_8$

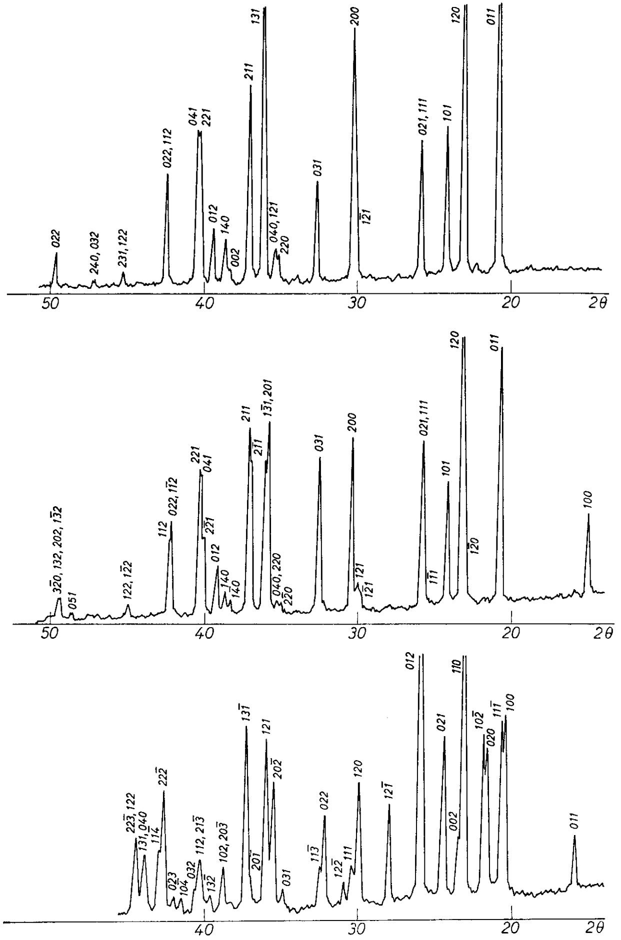

Fig. 2. Comparison between the x-ray diffractometer diagrams [λ(Cu$K\alpha$)] of the compounds [LiMg]PO$_4$, [Mg$_3$□]P$_2$O$_8$, Mg$_3$P$_2$O$_8$

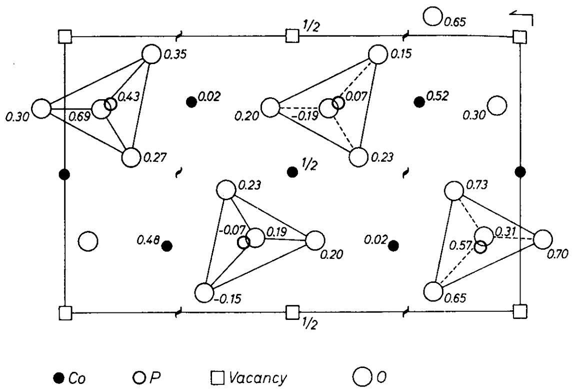

Fig. 3. Projection of the cations on (001) plane in [Co$_3$□]P$_2$O$_8$

available values for the position parameters in the olivine MnLiPO$_4$ [5], which is isomorphous with MgLiPO$_4$ and CoLiPO$_4$, and assuming the positions of the ions do not move much during the exchange process, we refined the position parameters corresponding to the new lacunary compounds. The results are listed in Table 2. Tables 3 and 4 reproduce

Table 3. *Recording of* [Mg$_3$□](PO$_4$)$_2$ I_{obs} *against* I_{calc}

h k l	d_{obs}	d_{calc}	I_o	I_c	h k l	d_{obs}	d_{calc}	I_o	I_c	h k l	d_{obs}	d_{calc}	I_o	I_c
1 0 0	5.896	5.911	12	32	0 0 2		2.367	4	2	0 5 1	1.8730	1.8755	28	15
0 2 0		5.107	0	3	1 $\bar{4}$ 0	2.352	2.353	14	24	1 $\bar{3}$ 2	1.8478	1.8494	36	60
0 1 1	4.293	4.295	84	47	1 4 0	2.332	2.335	16	8	2 0 2		1.8475		
1 $\bar{2}$ 0	3.881	3.884	151	137	0 1 2	2.306	2.306	61	56	3 $\bar{2}$ 0		1.8445		
1 2 0	3.838	3.845			2 $\bar{2}$ 1	2.258	2.258	268	238	1 3 2		1.8430		
1 0 1	3.691	3.695	32	12	0 4 1	2.2476	2.247			3 2 0		1.8319	0	11
1 $\bar{1}$ 1	3.487	3.482	75	82	2 2 1	2.2410	2.2427			2 $\bar{1}$ 2		1.8200	0	5
0 2 1		3.472			1 0 2		2.1974			3 0 1		1.8190	0	15
1 1 1		3.467			1 $\bar{1}$ 2	2.1486	2.1500	142	136	2 1 2		1.8159	0	14
1 $\bar{2}$ 1	3.004	3.003	141	105	0 2 2		2.1475			2 $\bar{4}$ 1	1.794	1.7967	135	210
1 2 1	2.983	2.985			1 1 2		2.1465			3 $\bar{1}$ 1		1.7937		
2 0 0	2.950	2.955			1 $\bar{4}$ 1		2.1069	0	4	1 $\bar{5}$ 1		1.7926		
0 3 1	2.761	2.764	112	129	1 4 1		2.0943	0	0	3 1 1	1.7822	1.7879		
2 $\bar{2}$ 0	2.566	2.569	57	45	2 $\bar{3}$ 1	2.022	2.0271	32	19	1 5 1		1.7829		
0 4 0		2.553			1 $\bar{2}$ 2		2.0212			2 4 1		1.7811		
2 2 0	2.548	2.546			1 2 2		2.0156			2 $\bar{2}$ 2	1.7417	1.7409	432	376
1 $\bar{3}$ 1		2.512	301	295	2 3 1		2.0103	0	0	0 4 2	1.7328	1.7359		
2 0 1		2.507			3 0 0			0	5	0 2 2		1.7337		
1 3 1	2.490	2.496			0 3 2		1.9434	0	0	3 $\bar{2}$ 1		1.7187	21	7
2 $\bar{1}$ 1	2.439	2.439	280	266	2 $\bar{4}$ 0		1.9420	0	1	3 2 1	1.7070	1.7084	87	76
2 1 1	2.427	2.430			2 4 0		1.9224	0	5	0 6 0		1.7022		

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[5] S. Geller and J. L. Durand, Refinement of the structure of LiMnPO$_4$. Acta Crystallogr. **13** (1960) 325–331.

Table 4. *Rekording of* $[\mathrm{Co_3}\square](\mathrm{PO_4})_2$ I_{obs} *against* I_{calc}

h k l	d_{obs}	d_{calc}	I_o	I_c
1 0 0	5.947	5.92	50	43
0 2 0	5.177	5.17	18	5
0 1 1	4.32	4.32	58	44
$1\,\bar{2}\,0$		3.93	traces	20
1 2 0	3.86	3.86	266	289
1 0 1	3.710	3.70	38	38
$1\,\bar{1}\,1$		3.50	504	542
0 2 1		3.50		
1 1 1	3.476	3.47		
$1\,\bar{2}\,1$	3.028	3.027	4	24
1 2 1	2.991	2.994		4
2 0 0	2.958	2.960	227	222
0 3 1	2.790	2.788	547	555
$2\,\bar{2}\,0$	2.587	2.588	97	96
0 4 0	2.581	2.583		
2 2 0	2.548	2.548	1172	1187
$1\,\bar{3}\,1$	2.536	2.537		
2 0 2		2.512		
1 3 1	2.507	2.508	790	787
$2\,\bar{1}\,1$	2.448	2.449		
2 1 1	2.430	2.432		
$1\,\bar{4}\,0$	2.382	2.383		
0 0 2	2.372	2.374		
1 4 0	2.352	2.352		
0 1 2	2.313	2.314	160	152
$2\,\bar{2}\,1$	2.273	2.273	374	378
0 4 1	2.270	2.269		
2 2 1	2.243	2.245		
1 0 2	2.203	2.204	27	9
$1\,\bar{1}\,2$	2.157	2.158	227	164
0 2 2		2.157		
1 2 2	2.151	2.152		
$1\,\bar{4}\,1$		2.130	traces	
1 4 1		2.107	traces	
$2\,\bar{3}\,1$		2.044	traces	∼0
$1\,\bar{2}\,2$	2.030	2.032	171	186
1 2 2		2.022		
2 3 1		2.014	0	9
3 0 0	1.972	1.973	45	63
$2\,\bar{4}\,0$		1.964		
0 3 2		1.955		17
2 4 0		1.929	traces	0
0 5 1		1.895	89	5
$1\,\bar{3}\,2$		1.862		0
$3\,\bar{2}\,0$	1.8508	1.854	167	105
2 0 2		1.852		
1 3 2		1.851		
3 2 0		1.832	traces	
$2\,\bar{1}\,2$	1.821	1.827	137	42
3 0 1		1.822		
2 1 2		1.819		
$2\,\bar{4}\,1$		1.815	traces	0
$1\,\bar{5}\,1$		1.813		0
$3\,\bar{1}\,1$	1.798	1.799	898	910
1 5 1	1.794	1.796		
3 1 1		1.789		
2 4 1		1.787		
$2\,\bar{2}\,2$		1.750	1662	1625

the recording of the new lacunary olivine compounds. For the 70 first reflections, the agreement factor R was 10% for $[\mathrm{Co_3}\square]\mathrm{P_2O_8}$ and 12% for $[\mathrm{Mg_3}\square]\mathrm{P_2O_8}$; no temperature correction was attempted. This rather high value can be due to the difficulty of measuring the intensities in monoclinic compounds using powder patterns. In an other way, it is possible the exchange process was not taken into completion. Still the remaining lithium is probably less than 5%.

4. Thermal stability of the two lacunary olivine phases

The metastable compounds transform into the stable vacancy-free forms, according to the two weakly exothermic reactions:

$$[\mathrm{Mg_3}\square]\mathrm{P_2O_8} \xrightarrow{820^\circ\mathrm{C}} \mathrm{Mg_3P_2O_8}$$

$$[\mathrm{Co_3}\square]\mathrm{P_2O_8} \xrightarrow{870^\circ\mathrm{C}} \mathrm{Co_3P_2O_8}\,.$$

The temperatures of the rapid transformation were determined by differential thermal analysis (heating speed 300°/h).

The reaction seems to be irreversible. In both cases, the transformation produces an increase of the cell volume of about 10%. Thus in spite of the presence of vacancies, the defect forms have a higher density than the stable high-temperature forms, in which the oxygen packing is no more compact. This can be understood easily from the structure of $\mathrm{Co_3P_2O_8}$ and $\mathrm{Mg_3P_2O_8}$, which was investigated by CALVO[6].

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[6] C. CALVO, The crystal structures of some divalent metal ion phosphates. Bull. Soc. Chim. de France, n° spécial (1968), 1744—1747.

The elementary cell contains two formula units with the parameters:

$\mathrm{Co_3P_2O_8}$: $a = 7.557$; $b = 8.365$; $c = 5.067$; $\beta = 94^\circ\,05'$

$\mathrm{Mg_3P_2O_8}$: $a = 7.01$; $b = 8.21$; $c = 5.03$; $\beta = 90^\circ\,25'$.

Among the six $\mathrm{Co^{2+}}$($\mathrm{Mg^{2+}}$) distributed over the unit cell, four have a tetrahedral and two an octahedral oxygen environment. The $\mathrm{PO_4}$ tetrahedra do not share corners. The oxygen packing is thus rather loose.

Remark

It has to be noted that in these two examples, the oxygen network is not affected by the exchange process, and that the structure of the lacunary phase remains still very close to that one of original lithium compound.