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A new Orthophosphate $[Ni_3\square]P_2O_8$ with Olivine-related Structure: Synthesis and Infrared Study

M.-Th. PAQUES-LEDENT

Département de Chimie Générale et de Chimie Physique, B6, Université de Liège, 4000 Sart Tilman par Liège I, Belgique

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So far, two lacunary orthophosphates $[Co_3\square]P_2O_8$, $[Mg_3\square]P_2O_8$ with olivine related structure were known [1]. In this paper, we describe a new isostructural orthophosphate $[Ni_3\square]P_2O_8$ and we compare the infrared spectra of the three compounds.

Synthesis

The Ni compound is obtained after heating of a stoichiometric mixture of $NiCO_3$ and $(NH_4)_2HPO_4$ in Pt crucible. The coaking is madc at 900 °C during three days with intermediate mixings and grindings. The yellow powdered sample corresponds to a stable phase. Vainly, we have tried to obtain this phosphate by solid state exchange reaction between $LiNiPO_4$ (belonging to a true olivine structure) and $NiSO_4$, as described before by Berthet *et al.* [1]. According to this latter scheme, we have prepared the Co and Mg lacunary orthophosphates: these are metastable phases which are transformed into high temperature phases with a change of coordination for a part of the bivalent cations [2, 3].

Structure

The identification of the new phase is made after comparison of the X-ray powder diagrams of the Ni compound and of the Co and Mg lacunary olivines. The X-ray diagram has been indexed on the basis of a monoclinic unit cell; the dimensions are listed in Table I. The space group is $P2_1/b$ and $Z = 2$.

These dimensions are hardly smaller than the cell parameters obtained for the $[Mg_3\square]P_2O_8$ compound [1], what is in better accordance with the compared cell dimensions for the $LiNiPO_4$ and $LiMgPO_4$ olivines, than with the infrared values of ionic radii for Mg^{2+} and Ni^{2+} cations in sixfold coordination: $r.Mg^{2+} = 0.66$ Å; $r.Ni^{2+} = 0.69$ Å [4]. According to Berthet [1], the Ni cations with octahedral coordination are located on two different sites: 2 Ni are in "2b" sites with C_i symmetry, 4 Ni are in "4 e" sites (C_1 symmetry) while the vacancies correspond to "2 a" sites (C_i symmetry). In $LiNiPO_4$ (space group D_{2h}^{16}, $Z = 4$) all Li atoms are on C_i sites, all Ni atoms on C_s sites.

The substitution of atoms by vacancies in the olivine structure has an effect upon the fourth bonding of three oxygen atoms of every PO_4 tetrahedron.

Infrared Spectra

Firstly we observe a strong analogy between the IR spectra of $[Mg_3\square]P_2O_8$, $[Co_3\square]P_2O_8$ and $[Ni_3\square]P_2O_8$ in the range 450–1200 cm^{-1}, what confirms the isostructural relationship between the three phosphates. Such an observation is added to our study of phosphates and arsenates $A^{I}B^{II}X^{V}O_4$ with an olivine structure [5]: in these compounds we have observed that for each chemical family, the IR pattern of the range ~450–1200 cm^{-1} is typical of vibrations of the XO_4 isolated groups, engaged in an orthorhombic olivine structure.

The theoretical treatment for $[Ni_3\square]P_2O_8$ crystals leads to $23\ A_u + 22\ B_u$ infrared-active normal modes of vibration, but we observe again a limited number of bands.

From the experimental spectra, we discuss two points, the spectral range with a common pattern and the range below 400 cm^{-1}.

The Frequency Range from 850 to 1200 cm^{-1}

A series of four bands are clearly related to complex stretching vibrations (symmetric and antisymmetric) of the PO_4 groups. However, one band with the lowest frequency appears at a very little value as compared with the stretching frequencies of PO_4 in $LiMgPO_4$ and $LiNiPO_4$ (Table II): the lack of cation in one next C_i position has an effect upon the vibra-

TABLE I. Unit Cell Dimensions of Orthorhombic and Lacunary Olivines.

	$LiNiPO_4$ [6]	$[Ni_3\square]P_2O_8$	$LiMgPO_4$ [6]	$[Mg_3\square]P_2O_8$
$a =$	5.85_5 Å	5.82 Å	5.89 Å	5.91 Å
$b =$	10.02 Å	10.15 Å	10.12 Å	10.21 Å
$c =$	4.67 Å	4.70 Å	4.68 Å	4.73 Å
$\gamma =$		90°.58		90°.60

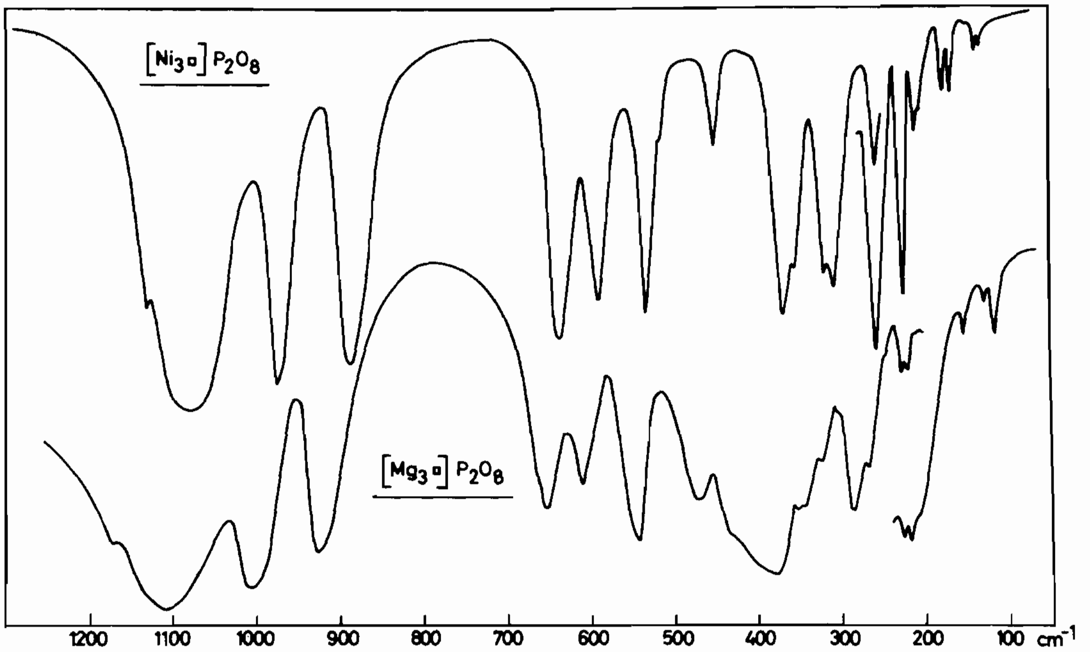

Figure. Infrared spectra of $[Ni_3\square]P_2O_8$ and $[Mg_3\square]P_2O_8$.

TABLE II. Infrared Frequencies (cm^{-1}).

$LiMgPO_4$ [5]	$[Mg_3\square]P_2O_8$	$LiNiPO_4$ [5]	$[Ni_3\square]P_2O_8$	$LiCoPO_4$ [5]	$[Co_3\square]P_2O_8$
1157	1173	1148	1138	1148	1130
1113	1106	1102	1085	1104	1090
1070		1058		1057	
1000	1006	972	980	967	978
958	928	944	893		890
	654		640		631
	612		593		593
	542		536		536
	472		454		438
	~380		370		
	350 sh		356		334
	323 sh				
			318		286
			307		
	285		257		247
	266		224		218
	224		211		
	217		177		147
	151		169		
	125		139		
	114		133		

tional stretching mode of PO_4 corresponding to this frequency – effect which is different for the three other stretching modes. A similar behaviour has been observed and discussed for $LiB^{II}PO_4$, $LiB^{II}AsO_4$ compounds with true olivine structure. As a consequence we observe a very large splitting of the stretching frequencies. As shown before [5] for true olivines, the splitting of the antisymmetric stretching modes of PO_4 in this structure is related to an unequal distribution of the bonding forces within the tetrahedral group. In lacunary olivine compounds, we observe a strongly increasing splitting of the stretching frequencies, the increase of this splitting must be essentially related to an increasing disparity between the four P–O bonding forces in PO_4, disparity resulting from ordered vacancies in the olivine structure (see above). Between 700 and 500 cm^{-1}, we observe also strong similarities for the internal frequencies of PO_4, related essentially to antisymmetric bending modes.

The Frequency Range below 400 cm^{-1}

For Ni and Co lacunary olivines, this range essentially corresponds to "external" modes; the IR pattern is changing with the increase of the atomic mass of the bivalent cation (comparison of Mg and Ni compounds) and also with the increase of the interatomic dimensions *viz.* ionic radii (comparison of IR frequencies of Ni and Co compounds). These observed modifications and the proposed assignment are in accordance with the earlier results for the $LiB^{II}PO_4$ olivine compounds [5].

Experimental

IR Spectra

The spectra have been recorded by a conventional pressed disc technique with a Beckman IR 12 spectrometer (200–1200 cm^{-1}) and a Polytec FIR 30 interferometer (40–350 cm^{-1}).

X-Ray Diagram

The X-ray powder diagrams were obtained with a C.G.R. diffractometer using CoK_α radiation.

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