SYNTHESIS AND PHYSICAL PROPERTIES OF Co\textsuperscript{2+}Fe\textsuperscript{3+}(P\textsubscript{2}O\textsubscript{7})\textsubscript{2} and Mg\textsuperscript{2+}Fe\textsuperscript{3+}(P\textsubscript{2}O\textsubscript{7})\textsubscript{2}

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Received: 20 April 2001; revised version accepted 26 September 2001

Abstract

Investigations made by powder X-ray diffraction have shown that two new phosphates: Mg\textsuperscript{2+}Fe\textsuperscript{3+}(P\textsubscript{2}O\textsubscript{7})\textsubscript{2} and Co\textsuperscript{2+}Fe\textsuperscript{3+}(P\textsubscript{2}O\textsubscript{7})\textsubscript{2} are isostructural to Fe\textsuperscript{2+}Fe\textsuperscript{3+}(P\textsubscript{2}O\textsubscript{7})\textsubscript{2}. They crystallize in the orthorhombic Fe\textsuperscript{2+}Fe\textsuperscript{3+}(P\textsubscript{2}O\textsubscript{7})\textsubscript{2}-type structure (space group Pnma). The magnetic susceptibility measurement and Mössbauer effect have been reported.

An unusual feature of this presence of Fe\textsuperscript{3+}O\textsubscript{12}\textsuperscript{16-} trimers, where trigonal prismatic Fe\textsuperscript{2+} is linked to 2 opposite octahedral Fe\textsuperscript{3+} through shared faces; these isolated trimers are connected by P\textsubscript{2}O\textsubscript{7} groups. It clearly appears that Co\textsuperscript{2+} and Mg\textsuperscript{2+} occupy the trigonal prismatic Fe\textsuperscript{2+} site, whereas the octahedral site is occupied by Fe\textsuperscript{3+}. The room temperature Mössbauer spectrum is characteristic of the Fe\textsuperscript{3+} valence state.

Co\textsuperscript{2+}Fe\textsuperscript{3+}(P\textsubscript{2}O\textsubscript{7})\textsubscript{2} and Mg\textsuperscript{2+}Fe\textsuperscript{3+}(P\textsubscript{2}O\textsubscript{7})\textsubscript{2} exhibit an antiferromagnetic-paramagnetic transition respectively at $T_N = 8\pm 2$ K and $T_N = 14\pm 2$ K.

Keywords: Iron-cobalt phosphate; Iron magnesium phosphate; Magnetic properties.

1. Introduction

In previous works [1], we have investigated the Fe-P-O system at 900°C. In contrast with the Fe-Si-O system, there are many ternary compounds, often of the mixed-valence type, constituting a wide body of possibilities for studying the inductive effect of phosphorus on the Fe-O bond [2].

Studies of mixed valence pyrophosphates the type AB\textsubscript{2}(P\textsubscript{2}O\textsubscript{7})(A = Pb\textsuperscript{2+}, Sr\textsuperscript{2+}, Cu\textsuperscript{2+}, Ba\textsuperscript{2+}, B = Fe\textsuperscript{3+}...) have been studied by A. Boukhari et al [3,4]. In the course of establishing the phase relation, at 900°C, in the subsystem Fe\textsubscript{2}P\textsubscript{2}O\textsubscript{7}-FePO\textsubscript{4}-Fe\textsubscript{5}(P\textsubscript{2}O\textsubscript{7})\textsubscript{3}-Fe\textsubscript{2}P\textsubscript{4}O\textsubscript{12}, B. Malaman et al have obtained and studied a mixed-valence iron diphosphate Fe\textsubscript{2}(P\textsubscript{2}O\textsubscript{7})\textsubscript{2} [5,6]. The most prominent feature of its structure is the presence of isolated (Fe\textsubscript{3}O\textsubscript{12})\textsuperscript{16-} groups of 3 polyhedra which are made up with of a central (FeO\textsubscript{10})\textsuperscript{16-} trigonal prism, occupied by Fe\textsuperscript{2+}, and shares opposite faces with FeO\textsubscript{9} octahedra (Fig. 1). These (Fe\textsubscript{3}O\textsubscript{12})\textsuperscript{16-} groups are connected by (P\textsubscript{2}O\textsubscript{7})\textsuperscript{9-} diphosphate ions. We want to stress that any progress regarding Fe\textsubscript{2}(P\textsubscript{2}O\textsubscript{7})\textsubscript{2} structure is valuable because this compound is of substantial interest. It was desirable to undertake the possibility of the synthesis of a mixed phases $\text{Fe}^{2+}_{1-x}\text{M}^{2+}_x\text{Fe}^{3+}_x(P\textsubscript{2}O\textsubscript{7})_2$ (M = Mg, Co, Ni), and therefore to investigate cation distributions involving trigonal prismatic site.

This work reports the synthesis, and the X ray powder diffraction study of the 2 new phosphates Mg\textsuperscript{2+}Fe\textsuperscript{3+}(P\textsubscript{2}O\textsubscript{7})\textsubscript{2} and Co\textsuperscript{2+}Fe\textsuperscript{3+}(P\textsubscript{2}O\textsubscript{7})\textsubscript{2} which are isostructural to Fe\textsubscript{2}(P\textsubscript{2}O\textsubscript{7})\textsubscript{2}. The properties of these compounds have been investigated by the measurement of the magnetic susceptibility and the Mössbauer spectroscopy.
2. Experimental technique: Synthesis and characterisation

$\text{Co}^{3+}\text{Fe}^{3+}(\text{P}_2\text{O}_7)_2$ has been prepared by the ceramic method, from the starting mixture: $1/2\text{Fe}_6(\text{P}_2\text{O}_7)_3 + 1/2\text{Co}_2\text{P}_2\text{O}_7$, in which $\text{Fe}_6(\text{P}_2\text{O}_7)_3$ has been obtained by evaporation of solution of $\text{Fe(NO}_3)_3\cdot 9\text{H}_2\text{O}$ and $\text{H}_3\text{PO}_4$ and annealing at 400°C under nitrogen, then at 900°C under oxygen for 24h, whereas $\text{Co}_2\text{P}_2\text{O}_7$ is prepared from the mixture $\text{Co}_3\text{O}_4 + \text{NH}_4\text{H}_2\text{PO}_4$, annealed at 400°C and sintered at 900°C in the open air. The starting mixture, was grounded, and pressed into rectangular bricks and sintered at 900°C for 24h followed by 72h at 1000°C under oxygen.

$\text{Mg}^{2+}\text{Fe}^{3+}(\text{P}_2\text{O}_7)_2$ has been synthesized by mixing aqueous solutions of $\text{Mg(NO}_3)_2\cdot 6\text{H}_2\text{O} + 2\text{Fe(NO}_3)_3\cdot 9\text{H}_2\text{O} + 4\text{NH}_4\text{H}_2\text{PO}_4$. The solution has been evaporated to dryness and residue has been subsequently heated to 200°C. The obtained powder was annealed at 400°C under nitrogen for 24h, then ground and sintered at 900°C under oxygen for 2 weeks.

It is worth mentioning that the obtained products always contained a small amount of $\text{Fe}^{2+}$, detected by the Mössbauer effect, around 3% of the total iron, even if when pure oxygen is used. Then, in order to combine the components at a lower temperature, a more homogeneous starting mixture has been obtained from solution of the components, which has been progressively heated at 1000°C under oxygen, for (72h).

3. Results and discussion

3.1 X-ray powder data

X-Ray Powder diffraction patterns show that $\text{MgFe}_2(\text{P}_2\text{O}_7)_2$ and $\text{CoFe}_2(\text{P}_2\text{O}_7)_2$ crystallize in the orthorhombic $\text{Fe}_3(\text{P}_2\text{O}_7)_2$-type structure (Pnma). The close correspondence of the interplanar spacing and X-ray intensities indicate that the 3 compounds are isostructural. Accordingly the cell parameters have been refined from the observed spacing, leading to the set of parameters given in Table 1. X-ray diffraction analysis show also the presence of the main lines of $\text{Fe}_6(\text{P}_2\text{O}_7)_3$ phase.

3.2 Mössbauer data

The spectrum recorded at room temperature, is shown on Fig. 2 for $\text{CoFe}_2(\text{P}_2\text{O}_7)_2$. It has been fitted with three doublets (Table 2). The Mössbauer parameters, at 295K, of $\text{MgFe}_2(\text{P}_2\text{O}_7)_2$ are given in Table 3.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
Doublet & $\delta$ (mm/s) & $\Delta$ (mm/s) & $I/I^o$ & Site & Corresponding phase \\
\hline
1 & 0.41 & 0.27 & 96 & $\text{Fe}^{3+}$ & $\text{CoFe}_2(\text{P}_2\text{O}_7)_2$ \\
2 & 1.15 & 4.34 & 3 & $\text{Fe}^{2+}$ & \\
3 & 0.28 & 0.65 & 1 & $\text{Fe}^{3+}$ & $\text{Fe}_6(\text{P}_2\text{O}_7)_3$ \\
\hline
\end{tabular}
\caption{CoFe$_2$(P$_2$O$_7$)$_2$: Mössbauer parameters at 295K.}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
Doublet & $\delta$ (mm/s) & $\Delta$ (mm/s) & $I/I^o$ & Site & Corresponding phase \\
\hline
1 & 0.42 & 0.30 & 88 & $\text{Fe}^{3+}$ & $\text{MgFe}_2(\text{P}_2\text{O}_7)_2$ \\
2 & 1.18 & 4.32 & 2 & $\text{Fe}^{2+}$ & \\
3 & 0.36 & 0.77 & 10 & $\text{Fe}^{3+}$ & $\text{Fe}_6(\text{P}_2\text{O}_7)_3$ \\
\hline
\end{tabular}
\caption{MgFe$_2$(P$_2$O$_7$)$_2$: Mössbauer parameters at 295K.}
\end{table}
δ is the isomer shift related to iron at 295K, Δ the quadrupole splitting and I/I° the relative intensity.

The spectrum recorded at room temperature, is shown on Fig. 3 for MgFe₂(P₂O₇)₂.

The isomer shift for the first doublet is very characteristic of high-spin Fe³⁺ in pseudo-octahedral environment [7-9] in which the Fe³⁺ is bonded to oxygen ions that are also part of PO₄. Indeed, the observed room temperature isomer shift of 0.41 mm/s agrees well with the value of 0.44 mm/s, the average of the isomer shift for Fe³⁺ in seven compounds [10] in which Fe³⁺ is bonded to PO₄ group through an oxygen.

The parameters of a second doublet are very similar (particularly Δ = 4.34 mm/s) to those found for Fe₃(P₂O₇)₂ [5.6], this correspond to a Fe²⁺ in trigonal prismatic site. This result indicates that a small amount (3%) of Fe²⁺ subsists even if when pure oxygen is used.

The third doublet is assigned to a Fe³⁺ which corresponds to Fe₄(P₂O₇)₁, as have been shown by the X-ray diffraction analysis.

3.3 Susceptibility magnetic of CoFe₂(P₂O₇)₂ and MgFe₂(P₂O₇)₂

Variation of magnetic susceptibility as a function of temperature for the two compounds exhibit a magnetic transition at T_N = 8 ± 2 K for CoFe₂(P₂O₇)₂ (Fig. 4) and at T_N = 14 ± 2 K for MgFe₂(P₂O₇)₂ (Fig. 5) probably corresponding to
antiferromagnetic-paramagnetic transition. At 
\( T > T_N \) the \( \chi^{-1} = f(T) \) variation is linear, 
corresponding to the usual Curies-Weiss 
paramagnetism with 
\[ C_M = 9, \; \theta_p = -31 \text{K for MgFe}_2(P_2O_7)_2, \]
\[ C_M = 13, \; \theta_p = -34 \text{K for CoFe}_2(P_2O_7)_2. \]
The negative values of asymptotic Curie 
temperature indicate the presence of 
antiferromagnetic interactions, as we have been 
seen in the Fe\(_3\)(P\(_2\)O\(_7\))\(_2\) [5,6]. It is work noting that 
the measurement of the magnetization 4.2K does 
not detect any spontaneous magnetism.

![Figure 4: Magnetic susceptiblité versus temperature of CoFe\(_2\)(P\(_2\)O\(_7\))\(_2\).](image)

![Figure 5: Magnetic susceptiblité versus temperature of MgFe\(_2\)(P\(_2\)O\(_7\))\(_2\).](image)

4. Conclusion

The X-ray diffraction powder have shown that 
Mg\(^{2+}\)Fe\(^{3+}\)(P\(_2\)O\(_7\))\(_2\) and Co\(^{2+}\)Fe\(^{3+}\)(P\(_2\)O\(_7\))\(_2\) are 
isostructural to Fe\(^{2+}\)Fe\(^{3+}\)(P\(_2\)O\(_7\))\(_2\). According to 
Mössbauer spectroscopy study it appears that Co\(^{2+}\) 
and Mg\(^{2+}\) occupy the trigonal prismatic Fe\(^{3+}\) site, 
whereas the octahedral site is occupied by Fe\(^{3+}\). 
The room temperature Mössbauer spectrum is 
characteristic of the Fe\(^{3+}\) valence state.

The negative value of \( \theta_p \) suggests that the 
predominating interactions are antiferromagnetic. 
The application of the usual Goodenough’s [11] 
rules leads to the following conclusions :
- the cation-cation direct interaction is important 
since the cations separation is relatively small, 
through the common face (Fig. 1). In the case of 
CoFe\(_2\)(P\(_2\)O\(_7\))\(_2\) this interaction, occurring between 
half-filled overlapping orbitals are 
antiferromagnetic.
- The cation-anion-cation interactions are characterized by angles Fe-O-M near to 90° [6]; are moderately antiferromagnetic, thanks to delocalization superexchange and, partly, to correlation superexchange.

- The interactions between Fe₂MO₁₂: regarding the structure of Fe₄(P₂O₇)₂ there are many M-O-P-O-Fe paths connecting the groups, introducing a negative contribution to the exchange integral. Actually, the magnitude of the M-O-P-O-Fe interactions is an open question, as Néel temperature of 29 and 47K have been reported in NaFeP₂O₇ [12] and Na₃Fe₂(PO₄)₃ [13] respectively and only 4K in KBaFe₂(PO₄)₃ [14].

On the whole, it seems that the antiferromagnetic interactions should outweigh the ferromagnetic ones, this is consistent with the negative values of the Curie asymptotic temperature.

In order to verify these hypothesis, the neutron powder diffraction of CoFe₂(P₂O₇)₂ and MgFe₂(P₂O₇)₂ are in progress.

References