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Magnetic properties of the $M(PO_3)_3$ (M = Ti, V) metaphosphates

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Two metaphosphates with the formula $M(PO_3)_3$ (M = Ti and V) have been synthesized and characterized. Their crystal structures consist of isolated MO_6 octahedra linked through infinite $[PO_3]_\infty$ chains of PO_4 tetrahedra. The IR and UV–VIS results for these compounds are consistent with chain structures in which the Ti^{III} and V^{III} cations exhibit octahedral symmetry. The EPR spectrum of the titanium metaphosphate at 4.2 K shows a nearly Lorentzian signal centred at $g = 1.77$, which disappears at 100 K. EPR results obtained for the doped $Sc(PO_3)_3$: 0.1% Ti^{III} metaphosphate are discussed on the basis of an effective trigonal symmetry. For the vanadium metaphosphate, the EPR spectrum exhibits a weak signal attributed to V^{3+} ions, with a zero-field splitting parameter D estimated at between 2 and 8 cm^{-1}. Magnetic measurements show ferromagnetic and antiferromagnetic interactions for the titanium and vanadium metaphosphates, respectively. A value of $J/k = -0.92(2)$ K has been obtained by fitting the experimental magnetic curve for $V(PO_3)_3$ to an analytical expression deduced for a three-dimensional Heisenberg model.

Introduction

The solid state chemistry of metaphosphates in which the transition metal exhibits a trivalent oxidation state is traditionally considered as unusual.[1] The great ability of the phosphate frameworks to stabilize reduced oxidation states is produced for the relatively high charge in PO_4^{3-} tetrahedra that favours the formation of anionic frameworks with a high degree of mechanical, chemical and thermal stability.[2,3] These compounds exhibit interesting properties (magnetic, heterogeneous catalysis, ion exchange, optical, *etc.*) with potential applications. In this way, titanium-doped sapphire has been in recent years the major innovation in the field of solid state tunable laser materials.[4,5]

Different synthetic methods to prepare transition metal phosphates in reduced oxidation states have been described,[1] but although good crystals for X-ray structure determination were obtained, pure phases have not been prepared. This fact has precluded carring out any study on the physical properties of these materials. Recently, a method based on the control of the M/P ratio in the reaction medium has led to the attainment of pure phases with different oxidation states.[6–8]

The crystal structures of the titanium and vanadium metaphosphates have been determined from single-crystal X-ray diffraction data.[9,10] Both compounds are isostructural, their structures can be described as being formed from isolated MO_6 octahedra linked through infinite $[PO_3]_\infty$ chains of PO_4 tetrahedra (Fig. 1). Each MO_6 group is bridged to six neighbouring MO_6 octahedra by phosphate groups and each octahedron shares its six apices with six different PO_4 tetrahedra. These groups are also placed in adjacent layers and lead to a three-dimensional network, in which the metallic cations occupy three different crystallographic positions.

The present work reports the spectroscopic and magnetic properties of the titanium and vanadium metaphosphate compounds. In the case of the titanium compound, phases of $Sc(PO_3)_3$ doped with 0.1% Ti^{III} have also been prepared and used to study the EPR behaviour of Ti^{III} in order to better understand their magnetic properties.

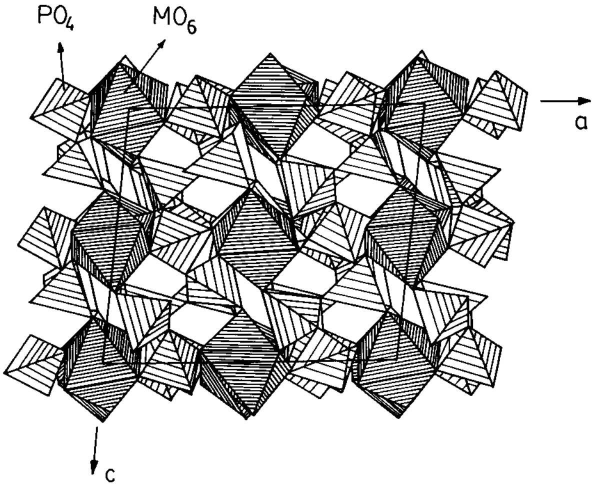

Fig. 1 Crystal structure of the $M(PO_3)_3$ (M = Ti, V) metaphosphates

Experimental

Synthesis of the compounds

The $V(PO_3)_3$ compound was synthesized starting with a mixture of V_2O_5 and $(NH_4)_2HPO_4$, with a molar ratio of 1M : 10P. The mixture was placed in an alumina crucible, heated at 300 °C for 4 h, then heated up to 800 °C followed by rapid cooling to room temperature. Attempts to prepare the $Ti(PO_3)_3$ phase by reduction of the TiO_2 oxide with an excess of $(NH_4)_2HPO_4$ were unsuccessful. This fact can be attributed to the instability of the Ti^{III} ion in air. Therefore, we modified the experimental method using as starting materials metallic titanium and an excess of $(NH_4)_2HPO_4$. A flux of nitrogen was maintained during the reaction time to avoid the oxidation to Ti^{IV}. Blue and green powders for titanium and vanadium compounds were obtained, respectively. These phases were washed with water and dried over P_2O_5 for 24 h. The metal ion and phosphorus contents were confirmed by ICP-AES analysis. Found: Ti, 16.5; P, 32.4. $Ti(PO_3)_3$ requires: Ti, 16.8; P, 32.6. Found: V, 17.3; P, 32.0. $V(PO_3)_3$ requires: V, 17.7, P, 32.3.

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X-Ray crystallography

A STOE automatic powder diffraction system, operating at 40 kV, 20 mA, with monochromatic Cu-Kα_1 radiation (1.5406 Å), was used to record the X-ray powder diffraction patterns of the $Ti(PO_3)_3$ and $V(PO_3)_3$ compounds. A ω–2θ scan was performed, with steps of 0.05° in 2θ and a fixed counting time of 6 s. The X-ray powder diffraction patterns were indexed using the LSUCRE program[11] in a monoclinic unit cell with the *Ic* space group, previously determined, from X-ray single crystal data, by Harrison *et al.*[9] and Middlemiss *et al.*[10] for the titanium and vanadium metaphosphates, respectively. The refined unit-cell parameters are: $a=9.551(6)$, $b=19.38(1)$, $c=10.810(7)$ Å, $\beta=97.76(4)°$ for $Ti(PO_3)_3$ and $a=10.599(1)$, $b=19.076(1)$, $c=9.417(1)$ Å, $\beta=97.94(1)°$ for $V(PO_3)_3$. The parameters reported in refs. 9 and 10 are: $a=9.551(2)$, $b=19.355(3)$, $c=10.730(2)$ Å, $\beta=97.874(3)°$ for $Ti(PO_3)_3$ and $a=10.615(2)$, $b=19.095(4)$, $c=9.432(1)$ Å, $\beta=97.94(1)°$ for $V(PO_3)_3$.

Physicochemical characterization techniques

IR spectra (KBr pellets) were obtained with a Nicolet FT-IR 740 spectrophotometer. Diffuse reflectance spectra were registered at room temperature on a Cary 2415 spectrometer in the range 5000–50 000 cm^{-1}. A Bruker ESP 300 spectrometer, operating at X band, was used to record the EPR polycrystalline spectra between 4.2 and 300 K. The temperature was stabilized by an Oxford Instrument (ITC 4) regulator. The magnetic field was measured with a Bruker BNM 200 gaussmeter and the frequency inside the cavity was determined using a Hewlett-Packard 5352B microwave frequency counter. Magnetic measurements were performed on polycrystalline samples between 1.8 and 300 K, using a Quantum Design SQUID magnetometer (MPMS-7) with a magnetic field of 0.1 T, a value in the range of linear dependence of the magnetization *vs.* magnetic field even at 1.8 K.

Results and Discussion

IR and UV–VIS spectroscopies

The most important bands observed in the IR spectra of the $Ti(PO_3)_3$ and $V(PO_3)_3$ phases are shown in Table 1, together with those for other isostructural metaphosphates for comparison. The compounds exhibit a strong band above 1240 cm^{-1} which is assigned to the $\nu_{as}(P{-}O_{ext})$ stretching antisymmetric vibration of the metaphosphate groups. The high value observed for this band in the $Ti(PO_3)_3$ compound (see Table 1) is attributed to the shorter P—O bond distances present in this metaphosphate in comparison with those obtained for the other $M(PO_3)_3$ (M = V, Cr, Mo) phases.[10] Additional bands in the 1010–1240 cm^{-1} region can also be observed due to the simultaneous existence of PO_2 and PO_3 groups in the phosphate anions. The band observed at approximately 970 cm^{-1} in these compounds is attributed to the antisymmetric stretch $\nu_{as}(P{-}O_{int})$ of the P—O—P bridge bonds. Likewise, there are at least three or four signals of medium intensity in the range 675–780 cm^{-1}, corresponding to the symmetric stretch $\nu_s(P{-}O_{int})$ of P—O—P bridge bonds, which are characteristic of metaphosphates with a chain structure, in good agreement with the structural data.

Finally, the IR spectra of the compounds exhibit bands with poor resolution in the range 470–610 cm^{-1}. These bands can be assigned to the antisymmetric stretching modes in the MO_6 octahedra, probably coupled with the antisymmetric bending modes of the chain groups, [$\delta_{as}(O{-}P{-}O)$].[12–14]

Table 1 Selected IR bands (cm^{-1}) and empirical assignments for several $M(PO_3)_3$ (M = Sc, V, Ti, Cr, Mo) metaphosphates, between 400 and 1500 cm^{-1}[a]

Assignment	Sc[b]	Ti	V	Cr[b]	Mo[b]
$\nu_{as}(P{-}O_{ext})\lvert PO_2\rvert$	1265 vs	1385 vs	1240 vs	1240 vs	1250 vs
	1200 s	1240 s			
	1180 s	1115 s	1150 s	1160 s	
	1125 s			1130 s	1125 s
$\nu_s(P{-}O_{ext})\lvert PO_2\rvert$		1090 s	1095 s	1095 vs	1085 s
$\nu(P{-}O_{ext})\lvert PO_3\rvert$	1045 s	1040 s		1050 s	
			1020 s	1020 s	1025 s
					1010 s
$\nu_{as}(P{-}O_{int})\lvert P{-}O{-}P\rvert$	970 s	960 s	975 s	975 s	955 s
	770 m	770 m	770 m	775 m	775 m
	755 m	750 m	765 m	760 w	
$\nu_s(P{-}O_{int})\lvert P{-}O{-}P\rvert$	715 m	715 m	715 m		745 m
				725 m	
					705 m
	680 m	690 w	685 m	685 w	675 m
$\nu_{as}(M{-}O)$	610 m				610 w
				570 m	
		560 m	560 m	560 m	
$\delta_{as}(O{-}P{-}O)$	540 m				545 m
				520 m	
	510 m		510 m		500 s
				490 m	
	440 m	470 m	480 m		470 m

[a] vs, very strong; s, strong; m, medium; w, weak. [b] Taken from ref. 7.

The reflectance diffuse spectrum of $Ti(PO_3)_3$ shows a strong band centred at 17 300 cm^{-1} which corresponds to the spin allowed transition $^2E_g \rightarrow {}^2T_{2g}$ in an octahedral symmetry. A shoulder can also be observed at 14 800 cm^{-1} which is attributed to the Jahn–Teller splitting of the excited ^2E_g state. The reflectance diffuse spectrum of $V(PO_3)_3$ shows two strong absorptions centred at 14 400 and 22 500 cm^{-1}, together with a weak signal at about 10 200 cm^{-1}. This spectrum has already been described in a previous work,[8] where the *Dq* and Racah parameters were calculated.

EPR and magnetic properties of $Ti(PO_3)_3$

EPR spectra at 9.4 GHz were obtained in powder samples of $Ti(PO_3)_3$ and in samples of $Sc(PO_3)_3$ doped with 0.1% Ti^{3+} at temperatures between 4.2 and 100 K (see Fig. 2). The Ti^{III}

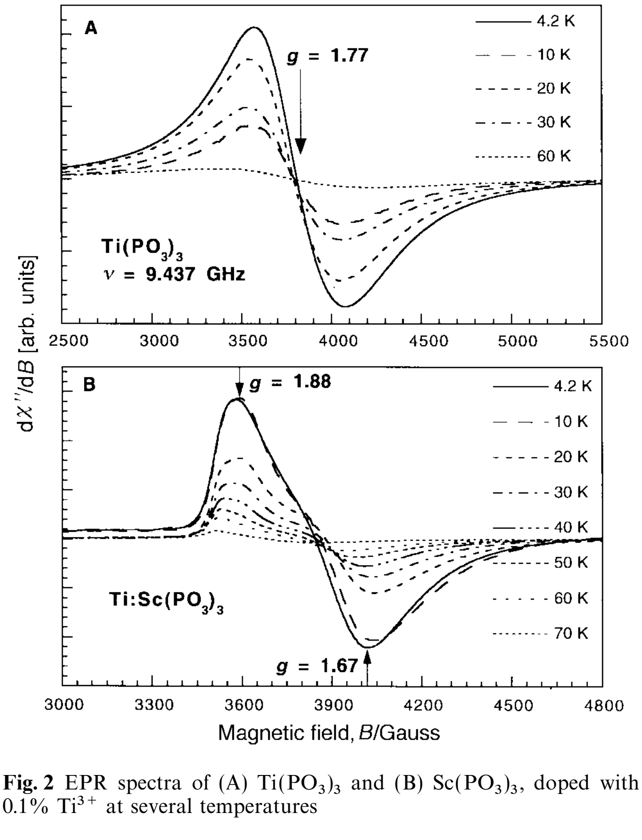

Fig. 2 EPR spectra of (A) $Ti(PO_3)_3$ and (B) $Sc(PO_3)_3$, doped with 0.1% Ti^{3+} at several temperatures

compound shows a nearly Lorentzian resonance centred at $g=1.77$, with a linewidth of about 500 G at 4.2 K. This resonance broadens with increasing temperature above 50 K. It loses intensity and disappears at 100 K. The Ti^{III} doped sample has a linewidth of about 400 G at 4 K, which reduces with increasing temperature. The lineshape reflects the powder character of the sample and changes with temperature. The g-factor values corresponding to the peaks of the signal at 4 K are $g=1.67$ and 1.88 [see Fig. 2(b)]. This signal rapidly loses intensity above 50 K.

A detailed analysis of the EPR results is hampered by the presence of three Ti^{III} sites and by the powder character of the samples. However, some conclusions may be obtained from the data. Since the structures of the Sc and Ti metaphosphates are very similar, most differences between results for the pure Ti^{III} and the Ti^{III} doped samples should be attributed to the exchange interactions between Ti^{III} ions in the pure compound. The resonance shown in Fig. 2(a) is the result of the collapse due to the exchange of those expected for the three different Ti^{III} ions.

The EPR results in the Sc^{III} compound doped with Ti^{III} may be qualitatively understood considering the theory described by Abragam and Bleaney.[15] The D ground state orbital of Ti^{III} is broken by the cubic field of the octahedron of oxygen ligands in a ground state triplet (Γ_5) and an excited state doublet (Γ_3), the splitting being $\Delta=10\,Dq\approx17\,300\ \mathrm{cm}^{-1}$, according to our spectroscopic data. A distortion of the octahedron having trigonal symmetry breaks the orbital degeneracy of the Γ_5 triplet into a singlet and a doublet with an energy splitting δ. The spin–orbit interaction $\lambda\boldsymbol{L.S}$ ($\lambda=145\ \mathrm{cm}^{-1}$ for the free Ti^{III} ion) mixes these states and gives rise to g-values depending on the crystalline field splittings Δ and δ, and on λ. The range of the observed g-values indicates that the singlet orbital state is lowest in energy. Otherwise, one of the g-values would be much smaller. Neglecting mixing of the ground state spin doublet with excited states at $\Delta\approx17\,300\ \mathrm{cm}^{-1}$ due to the spin–orbit interactions, its g-factor becomes:[15]

$$g_{\parallel}=-1+3\cos(2\gamma) \tag{1a}$$

$$g_{\perp}=|1+\cos(2\gamma)-2^{1/2}\sin(2\gamma)| \tag{1b}$$

In eqn. (1a) and (1b) $\tan(2\gamma)=\surd2[\lambda/(\delta+\lambda/2)]$. The orbital reduction factor[15] k due to covalence is not considered. The presence of three Ti^{III} sites introduces a large uncertainty in the g-factors calculated from the data. However, using the free ion spin–orbit parameter λ for Ti^{III}, the observed g-values indicate $\delta\approx1000\ \mathrm{cm}^{-1}$ for the average trigonal splitting. In the Ti^{III}-doped sample, the resonance narrows and move to lower fields with increasing temperature [Fig. 2(b)]. This fact results as a consequence of a dynamical Jahn–Teller averaging of the signal which occurs above 50 K. The same process would be responsible for the fast relaxation mechanism which vanishes at $T>100$ K. These results are similar to those observed in single crystal samples of chrysoberyl[16] and $LaMgAl_{11}O_{19}$,[17] two materials investigated for their potential applications for tunable lasers, in which the Ti^{III} ions occupy similar octahedral sites with oxygen as ligands.

Variable-temperature magnetic susceptibility measurements, performed on a powder sample of $Ti(PO_3)_3$ from 1.8 to 100 K, are shown in Fig. 3. The χ_m^{-1} *vs* T line follows a Curie–Weiss law in practically all the temperature range studied. The Curie constant value is $C_m=0.17(1)\ \mathrm{cm}^3\ \mathrm{K\ mol}^{-1}$, which is notably lower than that expected from the g-values obtained from the EPR spectra. The calculated value of the Curie–Weiss constant is $\theta=+0.3(1)$ K. The χ_mT product at room temperature is 1.17 μ_B and remains unchanged until 20 K. At lower temperatures than 20 K a slight increase of the χ_mT product can be observed. This result suggests the existence of ferromagnetic interactions in the $Ti(PO_3)_3$ compound.

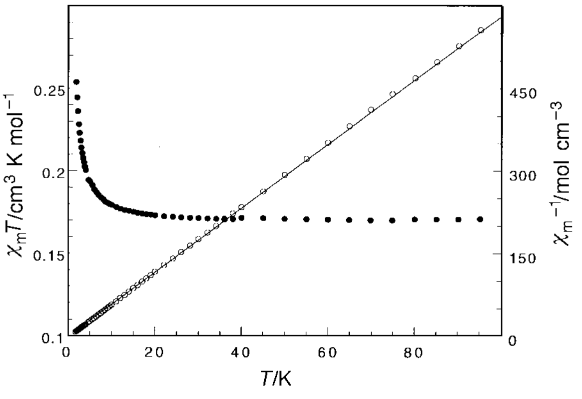

Fig. 3 Thermal evolution of the χ_m^{-1} and χ_mT product of $Ti(PO_3)_3$

EPR and magnetic properties of $V(PO_3)_3$

The X-band EPR powder spectrum of $V(PO_3)_3$ recorded at 4.2 K shows only a weak signal belonging to the V^{3+} ions at a magnetic field of about 1580 G. This observed 'half-field' signal corresponds to the forbidden $\Delta M_s=\pm2$ transition.[8] The zero-field splitting parameter D was estimated as between 2 and 8 cm^{-1}, which is in the range usually observed for V^{III} compounds.[8,18]

The thermal evolution of the molar magnetic susceptibility for the $V(PO_3)_3$ compound is shown in Fig. 4. The susceptibility follows a Curie–Weiss law between 1.8 and 300 K, with $C_m=0.86(1)\ \mathrm{cm}^3$ K mol and $\theta=-7.2(1)$ K. The negative temperature intercept together with the observed decrease in the effective magnetic moment with decreasing temperature (Fig. 4) suggest the presence of antiferromagnetic interactions in this compound. However, it is necessary to take into account that similar behaviour could be also originated by a contribution such as a positive zero-field splitting, which was observed from the EPR data. Both contributions are qualitatively similar and to consider them simultaneously presents great difficulties. For this reason, we have tried to fit the experimental data under each of these hypotheses separately. Using the van Vleck equation an analytical expression for the magnetic susceptibility as a function of the temperature and the D parameter was calculated.[19] However, considering the D value obtained from the Weiss temperature ($\theta=2/3\ D$), the calculated curve deviates drastically from the experimental ones (dotted line in Fig. 4). Satisfactory fits can be obtained only by using D values higher than 40 K. However, these results are completely unrealistic considering the EPR measurements.

An expression for the magnetic susceptibility was derived from the high temperature expansion series for an antiferromagnetic Heisenberg simple cubic lattice calculated by

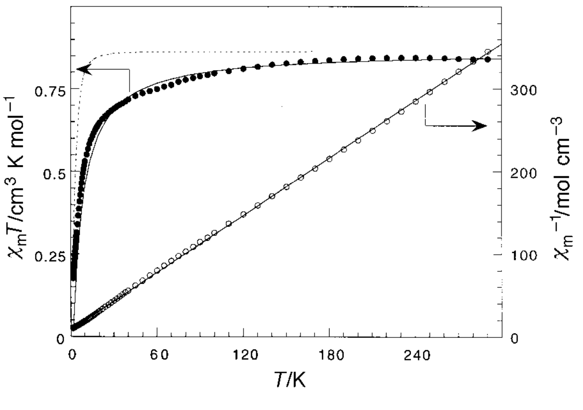

Fig. 4 Thermal evolution of the χ_m^{-1} and χ_mT product of $V(PO_3)_3$. Dotted and continuous lines represent the best fit considering only the effect of the zero-field splitting and the J exchange parameters, respectively (see text).

Rushbrooke and Wood.[20] The best fit corresponds to the continuous line in Fig. 4 and was obtained with a J/k value of $-0.92(2)$ K. The calculated curve agrees rather well with the experimental one at high temperatures, but deviates appreciably at low temperatures where the effect of the zero-field splitting is more important. So, we can conclude that both the antiferromagnetic interactions and the zero-field splitting determine the magnetic behaviour observed for $V(PO_3)_3$.

Considering the structural features of both $Ti(PO_3)_3$ and $V(PO_3)_3$ compounds, it can be concluded that the magnetic interactions are propagated by a superexchange mechanism *via* PO_4 groups as observed for other transition metal phosphates.[21] Owing to the three-dimensional character of the crystal structure of these compounds it is very difficult to establish exactly their magnetic exchange pathways.

Concluding remarks

The $M(PO_3)_3$ (M = Ti and V) metaphosphates exhibit a chain structure in which the metallic cations occupy three different crystallographic positions with approximately octahedral symmetry. The EPR spectrum at 4.2 K of the titanium metaphosphate presents a nearly Lorentzian signal. For the scandium(III) metaphosphate powder samples doped with 0.1% Ti^{III}, the EPR study indicates that the singlet orbital state is lowest in energy and allows us to estimate an average value of the trigonal splitting parameter $\delta \approx 1000\ \mathrm{cm}^{-1}$. The magnetic study of the $Ti(PO_3)_3$ phase shows the presence of ferromagnetic interactions. For the $V(PO_3)_3$ compound, the magnetic behaviour is determined by both the antiferromagnetic interactions and the zero-field splitting. Magnetic interactions in these compounds are propagated by different exchange pathways *via* PO_4 tetrahedra.

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