

Crystal Structure and Luminescence Properties of Silver in $\text{AgM}(\text{PO}_3)_3$ ($M = \text{Mg}, \text{Zn}, \text{Ba}$) Polyphosphates

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Received November 9, 1998; in revised form February 10, 1999; accepted February 11, 1999

The relationships between the crystal structures and the luminescent properties of the $\text{AgM}(\text{PO}_3)_3$ ($M = \text{Mg}, \text{Zn}, \text{Ba}$) polyphosphates are reported in comparison with those of AgPO_3 . The structure of the magnesium and zinc phosphates is characterized by long polyphosphates chains connected to infinite chains of $[\text{AgO}_6]$ and $[\text{MO}_6]$ polyhedra sharing faces. The basic structural phosphate unit in $\text{AgBa}(\text{PO}_3)_3$ is a P_3O_9 ring. Silver atoms are located in distorted octahedral sites. Two types of luminescent centers have been observed. The UV emission observed in all these materials is typical of isolated Ag^+ ions. The visible emission observed only in the zinc phosphate is probably the result of a silver–zinc association. © 1999 Academic Press

Key Words: crystallized polyphosphates; Rietveld; luminescence; silver; pairs.

INTRODUCTION

Basically the mechanism of fluorescence of Ag^+ involves $4d^95s \leftrightarrow 4d^{10}$ transitions strictly forbidden for the free ion but partially allowed in crystals or glasses by coupling with lattice vibrations of odd parity. The silver luminescence in crystals was extensively reported for the alkali or alkali-earth fluorides (1, 2). Various centers were observed reflecting the locations of Ag^+ in different sites associated with substitutional, interstitial positions and also with the formation of small silver clusters consistent with the rock salt and the fluorite-type structures.

In a parallel way silver luminescence of oxide glasses was investigated in relation to the preparation of materials used as γ -radiation and X-ray dosimeters and to explore the possibility of white light generation (3–5). In rich silver glasses two types of emitting centers were tentatively attributed to isolated Ag^+ and Ag^+-Ag^+ pairs (5, 6). To confirm unambiguously these previous assignments a clear correlation between luminescent properties and the crystal chemistry of silver oxides was needed. In the selected

crystals, a silver–oxygen distances must be characteristic of the Ag–O ionic bond, i.e., they must involve minimum Ag–O separation of about 230–240 pm (7).

Phosphate crystals can be considered as model systems since the strong covalent P–O bond induces systematically an ionic character of the opposite silver–oxygen bonds. In this context the present investigation is focussed on the relationships between the structure and the luminescent properties of $\text{AgM}(\text{PO}_3)_3$ ($M = \text{Mg}, \text{Zn}, \text{Ba}$) and AgPO_3 . The magnesium and zinc polyphosphates are representative of isolated silver introduced in a covalent framework whereas in the barium polyphosphate the silver site is surrounded by strongly ionic barium–oxygen bonds. The pairing effect is illustrated by the properties of AgPO_3 and in some degree by the behavior of the zinc polyphosphate.

EXPERIMENTAL

1. Material Elaboration

Polycrystalline samples of AgPO_3 and $\text{AgZn}(\text{PO}_3)_3$ were prepared according the published procedures (5, 8). $\text{AgMg}(\text{PO}_3)_3$ and AgBaP_3O_9 were synthesized by heating stoichiometric quantities of AgNO_3 , MgO or BaCO_3 , and $\text{NH}_4\text{H}_2\text{PO}_4$. The reagents are carefully mixed and progressively heated up to 350°C to allow both ammonia and nitrogen oxide vapors to evaporate. After a final grinding, the powder is heated at 550°C ($M = \text{Mg}$) and at 450°C ($M = \text{Ba}$) for 24 h. Both phosphates are white. No impurity was detected in the X-ray powder diagram.

2. Structural Investigation

The structures of AgPO_3 and $\text{AgZn}(\text{PO}_3)_3$ have been already reported (8, 9). The structures of $\text{AgMg}(\text{PO}_3)_3$ and AgBaP_3O_9 were determined using the Rietveld profile analysis to the X-ray diffraction diagram of the polycrystalline samples. Calculation was realized from the FULL PROF program (10). The details of the data collection and of the

TABLE 1
Condition Used for the Data Collection of the X-Ray Diffraction
of AgMg(PO₃)₃ and AgBaP₃O₉

Wavelength (Å)	$\lambda_{K_{\alpha 1}}=1.54060$; $\lambda_{K_{\alpha 2}}=1.54443$	
Step scan increment ($^{\circ}2\theta$)	0.02	
2θ range ($^{\circ}$)	5–120	
Program	FULLPROF (10)	
Profile parameters	AgMg(PO ₃) ₃	AgBaP ₃ O ₉
Zeropoint ($^{\circ}2\theta$)	0.026(5)	– 0.0181(1)
Pseudo-Voigt function		
(PV = $\eta L + (1 - \eta)G$)	$\eta = 0.52(3)$	0.57(7)
Caglioti law parameters	0.0021(7)	0.245(4)
U =		
V =	– 0.0022(9)	0.061(1)
W =	0.0148(2)	0.0092(1)
Asymmetry parameter (up to $40(^{\circ}2\theta)$)	0.0031(2)	0.012(2)
Parameters		
Space groups	<i>P cca</i> (Z=8)	<i>P2₁2₁2₁</i> (Z=4)
Crystalline parameters (pm)		
a =	1388.8(1)	1106.84(1)
b =	1073.02(1)	1231.27(1)
c =	997.301(5)	591.09
Density (g/cm ³) d =	3.28(2)	3.94(2)
No. of reflections	2216	1449
No. of refined parameters	71	72
Global profile discrepancy factors		
R _F	0.042	0.048
R _B	0.056	0.060
R _P	0.078	0.093
R _{wP}	0.094	0.106
cR _P	0.105	0.120
cR _{wP}	0.119	0.134
χ^2	1.49	2.39

Rietveld refinements are given in Table 1. The initial atomic coordinates were those of AgZn(PO₃)₃ for the magnesium polyphosphate and of NaBaP₃O₉ (11) for the barium polyphosphate. In Fig. 1, the comparison between the experimental and final calculated diffraction data is presented. The resulting atomic coordinates and their e.s.d.'s are listed in Table 2. Tables 3a and 3b give selected bond distances and angles.

3. Optical Measurements

Excitation and emission spectra have been recorded at 300 K using a SPEX FL212 fluorimeter. The diffuse reflectance spectra properties were studied with a UV-visible-NIR spectrometer VARIAN CARY 2415.

THE STRUCTURE OF AgM(PO₃)₃ (M = Mg, Ba)

1. Structure of AgM(PO₃)₃

AgMg(PO₃)₃ is made up of infinite phosphate chains containing [PO₄] tetrahedra sharing two common corners. The phosphorus-oxygen distances and the P–O–P angles are typical of long chain polyphosphates (12). Two groups of

P–O distances are observed: the largest distances ($d = 159$ pm) are related to the P–O–P linkage within the chain and the shortest distances ($d = 149$ pm) characterize P–O bonds involving terminal oxygens.

The magnesium and silver atoms are located, respectively, in a slightly distorted octahedron and in an antiprism sharing faces to give rise to infinite chains in parallel alternately to the (210) plane ($z = 0.5$) and to the (-210) plane ($z = 0$) with a 1:1 silver–magnesium ordering along these chains (Fig. 2). The Mg–Ag distances are alternately 317.8 and 327.1 pm. The Mg–O distances range between 202 and 215 pm which can be compared to the Mg–O distances in MgO (210 pm) (13) and in the diphosphate β -Mg₂P₂O₇ ($205 < d_{\text{Mg-O}} < 215$ pm) (14). The silver ion is located in an off-center position of the oxygenated antiprism and the silver–oxygen distances are found in rather wide limits between 235 and 272 pm. The shortest silver–silver distance is 564 pm. Within these metallic chains long silver–oxygen distances face short magnesium–oxygen distances and vice versa.

AgZn(PO₃)₃ and AgMg(PO₃)₃ belong to the same structural type, i.e., identical cation distribution and close interatomic distances. In the zinc polyphosphate the shortest silver–silver distance is 565 pm and within the silver–zinc chains the Zn–Ag distance are, respectively, 318 and 328 pm (8).

2. Structure of AgBaP₃O₉

This phosphate which belongs to the NaBaP₃O₉ structure type (11) is actually a cyclotriphosphate: the basic phosphorus oxygen structure unit is a P₃O₉ ring anion consisting of [PO₄] tetrahedra which share two corners with the two others. In this configuration the P–O distance within the ring (161 pm) is longer than those involving the terminal oxygens (150 pm). Silver atoms are located in distorted octahedra with a large dispersion of the silver–oxygen distances which are included between 231 and 265 pm. The two shortest Ag–O bonds (Ag–O₁₁ and Ag–O₁₂) are in almost linear configuration (Fig. 3). In this phosphate the shortest Ag–Ag distance is 591 pm.

The barium atoms are surrounded by eight oxygens by considering the Ba–O distances lower than 309 pm. Each silver oxygenated site shares a common edge with four barium sites and the shortest silver–barium distances are distributed in a narrow range between 394 and 412 pm. In this structural arrangement all silver oxygen bonds face strongly ionic barium oxygen bonds (Fig. 3). AgBaP₃O₉ and NaBaP₃O₉ have the same structure.

3. Structure of AgPO₃

The structure of AgPO₃ was described previously by Jost (9). In long polyphosphate chains the [PO₄] tetrahedra

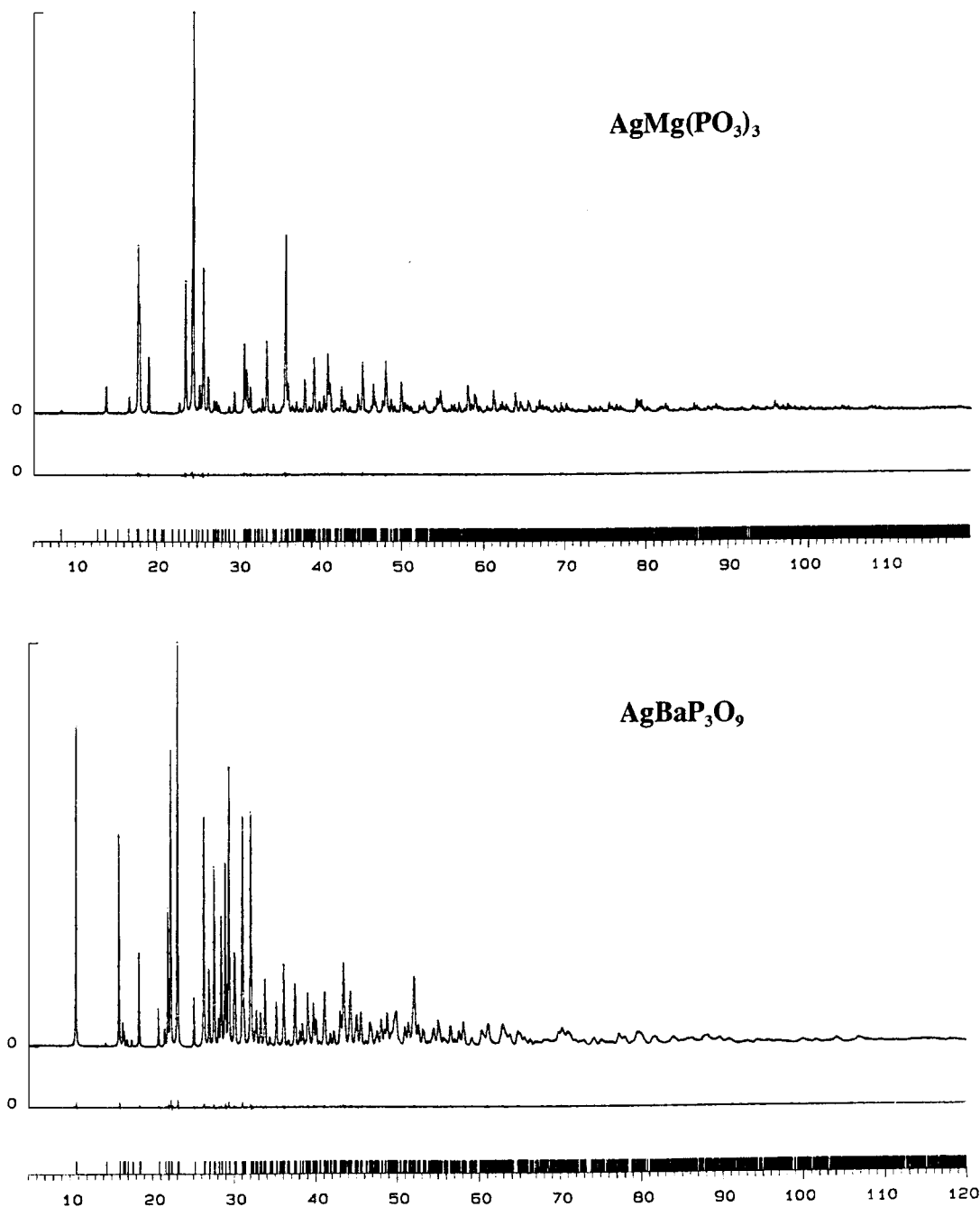


FIG. 1. X-ray diffraction patterns of AgBaP_3O_9 and $\text{AgMg}(\text{PO}_3)_3$ showing comparisons between experimental (···) and calculated (—) data.

share two corners giving rise to helical chains with four tetrahedra per turn. The two crystallographic silver ions are located in polyhedra with five oxygen neighbors sharing one corner (Fig. 4). The shortest silver-silver distance (315 pm) is slightly larger than the interatomic distance in silver metal (289 pm).

LUMINESCENT PROPERTIES OF THE $\text{AgM}(\text{PO}_3)_3$ ($M = \text{Mg, Zn, Ba}$) POLYPHOSPHATES

Diffuse reflectance spectra of $\text{AgMg}(\text{PO}_3)_3$ and $\text{AgZn}(\text{PO}_3)_3$ are compared in Fig. 5. For both phosphates a single absorption band slightly broader

TABLE 2

Final Atomic Coordinates and Isotropic Temperature Factors (with Standard Deviations in Brackets) for $\text{AgMg}(\text{PO}_3)_3$ and AgBaP_3O_9

Atoms	x	y	z	B_{iso} (\AA^2)
$\text{AgMg}(\text{PO}_3)_3$				
Ag	0.3770(1)	0.2488(2)	0.0244(6)	2.24(2)
Mg1	0.25	0.5	0.4670(5)	0.8(1)
Mg2	0	0	0	0.6(1)
P1	0.1489(2)	0.0458(3)	0.2385(3)	0.64(7)
P2	0.1260(3)	0.2504(6)	0.0486(2)	0.56(5)
P3	0.1007(7)	0.4693(7)	0.2158(7)	0.6(1)
O _{B1}	0.25	0	0.2934(1)	1.1(2)
O _{B2}	0.1808(4)	0.1700(6)	0.1583(7)	0.8(2)
O _{B3}	0.0648(5)	0.3482(6)	0.1355(7)	1.1(1)
O _{B4}	0.5	0.4686(4)	0.25	0.9(1)
O _{NB1}	0.0921(4)	0.0831(8)	0.3581(7)	1.1(2)
O _{NB2}	0.3932(5)	0.0439(8)	0.1422(7)	1.3(2)
O _{NB3}	0.2973(6)	0.3178(7)	0.4724(7)	1.0(2)
O _{NB4}	0.0570(6)	0.1737(7)	0.9738(7)	0.8(2)
O _{NB5}	0.3503(5)	0.4453(8)	0.1210(7)	0.9(2)
O _{NB6}	0.1510(5)	0.4311(8)	0.3391(7)	1.2(2)
AgBaP_3O_9				
Ag	0.4764(1)	0.1359(6)	0.1014(2)	2.10(2)
Ba	0.1079(6)	0.0828(6)	0.0984(1)	1.11(1)
P1	0.4132(3)	0.3707(2)	0.3852(7)	0.88(7)
P2	0.2993(3)	0.1859(2)	0.5915(8)	1.00(7)
P3	0.1523(3)	0.3578(2)	0.3964(8)	1.07(7)
O1	0.2793(7)	0.4207(6)	0.3892(4)	1.3(1)
O2	0.1806(6)	0.2621(6)	0.5769(7)	1.4(1)
O3	0.4039(7)	0.2763(5)	0.5871(6)	0.9(1)
O11	0.4991(7)	0.4525(5)	0.4784(1)	1.5(1)
O12	0.4412(6)	0.3190(5)	0.1568(5)	1.2(2)
O21	0.3021(5)	0.1156(7)	0.3825(5)	1.5(1)
O22	0.3065(6)	0.1311(6)	0.8197(4)	1.4(2)
O31	0.1302(6)	0.3065(5)	0.1635(4)	1.3(1)
O32	0.0616(6)	0.4315(6)	0.5070(1)	1.5(2)

for the zinc compound and peaking around 235 nm is observed.

The excitation spectra recorded at 315 nm emission wavelength and the emission spectra under a 230 nm excitation wavelength of the magnesium and zinc polyphosphates are compared in Fig. 6. The excitation in the UV band gives rise to a single emission band peaking at 315 nm with an identical Stokes shift (11700 cm^{-1}). Similar excitation and emission spectra are observed for AgBaP_3O_9 with a red shift of the emission and excitation maxima occurring, respectively, at 365 and 250 nm which corresponds to an increase of the Stokes shift (12600 cm^{-1}). Additional emission ($\lambda_{\text{exc}} = 350 \text{ nm}$) and excitation ($\lambda_{\text{em}} = 600 \text{ nm}$) bands are observed for $\text{AgZn}(\text{PO}_3)_3$ which are the signature of a second luminescent center (Fig. 7). AgPO_3 exhibits at room temperature a unique emission band peaking around 550 nm and a corresponding unique excitation band with a maximum at 380 nm (Fig. 7). The emission intensities of

all the investigated samples are relatively weak. This property which can be due to the site symmetry of the luminescent centers in addition to probable thermal quenching processes will be explained by a further detailed study of the thermal dependence of the emission decay time.

RELATIONSHIPS BETWEEN THE CRYSTAL STRUCTURES AND THE LUMINESCENT PROPERTIES

1. Color of the Phosphates

The interpretation of the color change of the silver salts with bond length has been previously explained by assuming that the top of the valence band is composed of non-bonding core orbitals— $4d$ or hybridized $4d5s$ orbitals—of the Ag^+ ion (7). Therefore, the shorter the silver oxygen distance, the stronger the $4s5d$ hybridization and the smaller the energy gap of the material, i.e., the energy difference between $4d$ (mixed with $5s$) and $5s$ (mixed with $4d$) levels. This model can account for the white color of the investigated polyphosphates in which the silver oxygen minimum distance is 231 pm ($M = \text{Mg}, \text{Zn}, \text{Ba}$), 237 pm in AgPO_3 and the mean Ag–O distances are, respectively, 254 pm (Mg, Zn) and 283 pm (Ba). These distances are larger than the Ag–O bond length in black Ag_2O which is only 205 pm (15). In these conditions the silver–oxygen bonds which face strongly covalent P–O bonds can be considered as primarily ionic.

2. Luminescence Spectra

As mentioned above the smaller silver–silver distances in the $\text{AgM}(\text{PO}_3)_3$ ($M = \text{Mg}, \text{Zn}, \text{Ba}$) polyphosphates are large

TABLE 3a

Details of Interatomic Distances (pm) and Selected Angles in the $(\text{PO}_3)_\infty$ Chains of $\text{AgMg}(\text{PO}_3)_3$ (a) and in the (P_3O_9) rings of AgBaP_3O_9 (b)

(a) $\text{AgMg}(\text{PO}_3)_3$			
P1–O _{B1} :	158.6(5)	P2–O _{B2} :	158.7(8)
–O _{B2} :	161.7(7)	–O _{B3} :	160.5(8)
–O _{NB1} :	148.6(8)	–O _{NB3} :	149.6(9)
–O _{NB2} :	147.9(9)	–O _{NB4} :	146.8(9)
P3–O _{B3} :	160.6(1)	P1–O _{B1} –P1:	139.5(4)
–O _{B4} :	158.7(8)	P1–O _{B2} –P2:	131.0(7)
–O _{NB5} :	148.4(1)	P2–O _{B3} –P3:	129.3(6)
–O _{NB6} :	147.2(1)	P3–O _{B4} –P3:	130.2(7)
(b) AgBaP_3O_9			
P1–O1:	160.5(8)	P2–O2:	161.8(8)
–O3:	166.9(9)	–O3:	160.7(8)
–O11:	149.0(8)	–O21:	151(1)
–O12:	152.6(9)	–O22:	151.1(9)
P3–O1:	160.7(8)	P1–O3–P2:	122.6(5)
–O2:	162.0(9)	P1–O1–P3:	128.5(1)
–O31:	153.5(9)	P2–O2–P3:	127.8(2)
–O32:	150.3(8)		

TABLE 3b
Interatomic Distances in the $[\text{AgO}_6]$ and $[\text{MO}_n]$ ($M = \text{Mg}$ ($n = 6$); Ba ($n = 8$)) Polyhedra of $\text{AgMg}(\text{PO}_3)_3$ (a) and AgBaP_3O_9 (b)

(a) $\text{AgMg}(\text{PO}_3)_3$						
Atoms	O_{NB1}	O_{NB2}	O_{NB3}	O_{NB4}	O_{NB5}	O_{NB6}
Ag	246.9(8)	250.3(8)	258.4(8)	262.6(9)	234.8(9)	272.0(8)
Mg1	—	—	$2 \times 206.4(4)$	—	$2 \times 215.5(8)$	$2 \times 201.7(8)$
Mg2	$2 \times 210.5(7)$	$2 \times 210.6(7)$	—	$2 \times 204.0(8)$	—	—
(b) AgBaP_3O_9						
Atoms	O11	O12	O21	O22	O31	O32
Ag	232.4(7)	231.0(7)	255.9(8)	251.3(8)	241.9(8)	263.5(8)
Ba	281.1(6)	267.2(8)	275.7(9)	281.1(8)	279.1(7)	271.7(7)
			293.1(8)	3.09.0(7)		

which excludes the formation of silver pairing. Therefore the UV luminescence can be unambiguously attributed to isolated Ag^+ . By comparison with the results of the Ag^+ luminescence in alkali halides, the excitation and emission bands involve $4d^{10} \leftrightarrow 4d^9 5s$ transitions. The Russell-Saunders states are split by the effect of the crystal field which give rise to several excited states originating from the 1D and 3D levels of the $4d^9 5s$ state. The excitation bands correspond to transitions from the ground state to the triplet state whereas the emission is due to the spin forbidden transition between the lowest triplet state to the singlet ground state (1, 2).

Such luminescences result basically from the location of silver atoms in off-center position in their oxygenated sites. This conclusion is related to the fact that no luminescence was detected at room temperature in the white Nasicon type phosphate $\text{AgZr}_2(\text{PO}_4)_3$. In this monophosphate the silver atoms are located at the center of an oxygenated antiprism in which the metal oxygen distance is 256 pm and the closest silver-silver distance is 636 pm (16). The Stokes shifts in magnesium and zinc polyphosphates are identical (11700 cm^{-1}) and smaller than that observed in barium polyphosphate (13000 cm^{-1}). This is the consequence of the host lattice stiffness due to the rigid silver-magnesium (zinc) oxygenated chains. In contrast the more spacious silver site

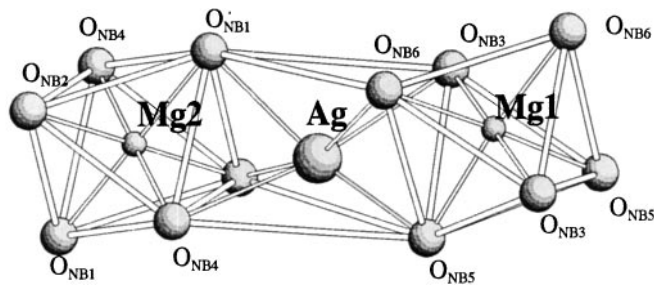


FIG. 2. Schematic representation of silver-magnesium ordering polyhedra along a chain in $\text{AgMg}(\text{PO}_3)_3$.

of the barium polyphosphate is surrounded by four barium oxygenated polyhedra. Such a loose structure permits a larger increase of the silver-oxygen distance in the excited states.

Finally the origin of the visible emission typical $\text{AgZn}(\text{PO}_3)_3$ must be discussed. This polyphosphate has the same structure as the magnesium phase with approximately the same interatomic distances. On the other hand, the spectral distributions of the emission and excitation bands are identical to the room temperature spectra of AgPO_3 with a slight blue shift of the excitation energy maximum (5). This silver polyphosphate was not detected as an impurity in the X-ray powder diagram of the zinc phosphate. But at low temperature the luminescent properties of these phases

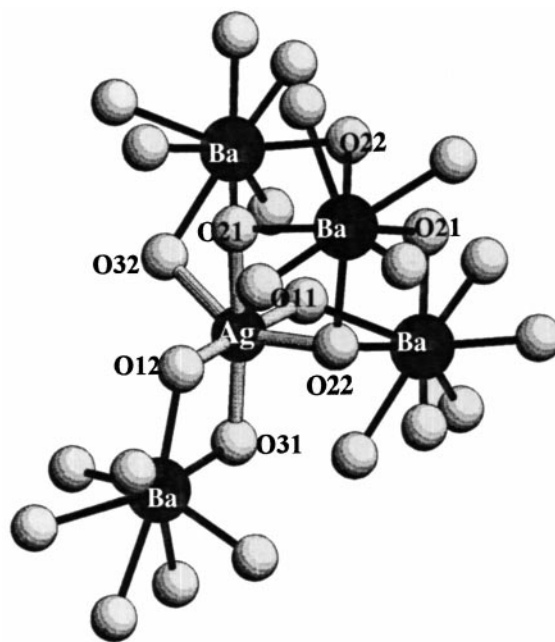


FIG. 3. Connection between the $[\text{AgO}_6]$ and $[\text{BaO}_8]$ polyhedra in AgBaP_3O_9 .

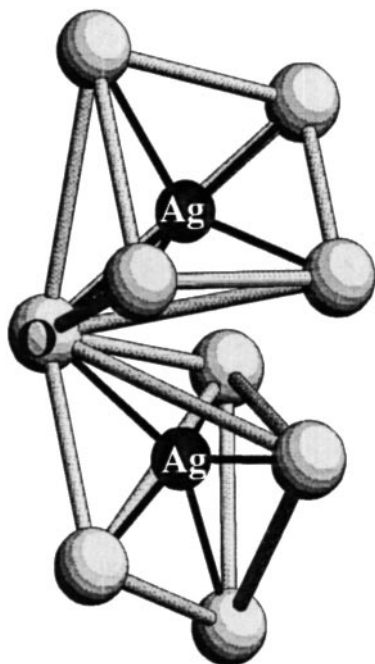


FIG. 4. Oxygenated sites for silver in AgPO_3 (9).

are clearly distinct. This result is illustrated by Fig. 8 which compares the excitation and the emission spectra of AgPO_3 and the (C) center of $\text{AgZn}(\text{PO}_3)_3$ recorded at 4 K. In AgPO_3 the visible emission was assigned to the $\text{Ag}^+ - \text{Ag}^+$ pairing effect, since all the silver atoms belong to such pairs in which the silver-silver distance is 315 pm (9). Silver pairs cannot exist in the structure of $\text{AgZn}(\text{PO}_3)_3$ where the closest silver-silver distance is 645 pm but short silver-zinc

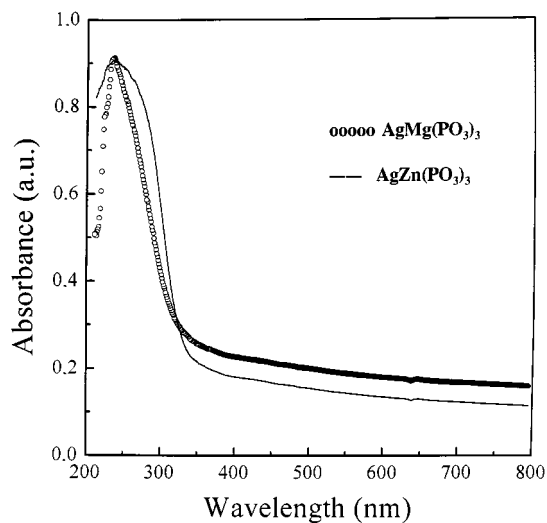


FIG. 5. Diffuse reflectance spectra of $\text{AgMg}(\text{PO}_3)_3$ and AgBaP_3O_9 , recorded at room temperature.

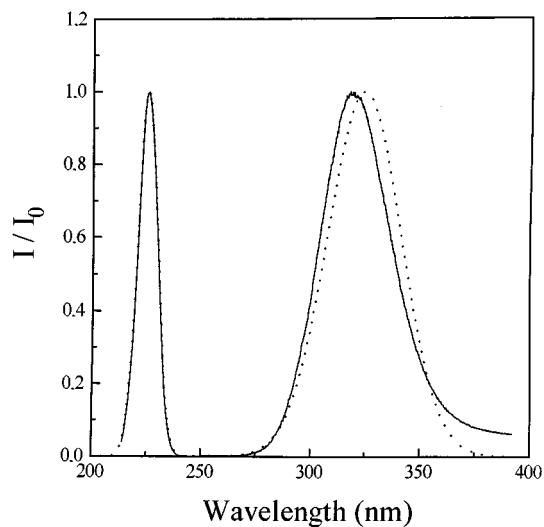


FIG. 6. Excitation ($\lambda_{\text{em}} = 320 \text{ nm}$) and emission ($\lambda_{\text{exc}} = 230 \text{ nm}$) spectra of $\text{AgZn}(\text{PO}_3)_3$ (dotted line) and $\text{AgMg}(\text{PO}_3)_3$ (solid line) at room temperature.

distances (318.5 pm) are found within the $(\text{Zn}, \text{AgO}_6)_n$ chains. From these arguments the existence of a new $d^{10} - d^{10}$ luminescent center can be inferred as the result of a $\text{Ag}^+ - \text{Zn}^{2+}$ association. Some theoretical calculations are presently in progress to estimate the pertinence of this assumption.

CONCLUSION

The white color of the silver polyphosphates $\text{AgM}(\text{PO}_3)_3$ ($M = \text{Mg}, \text{Zn}, \text{Ba}$) permits a detailed examination of their

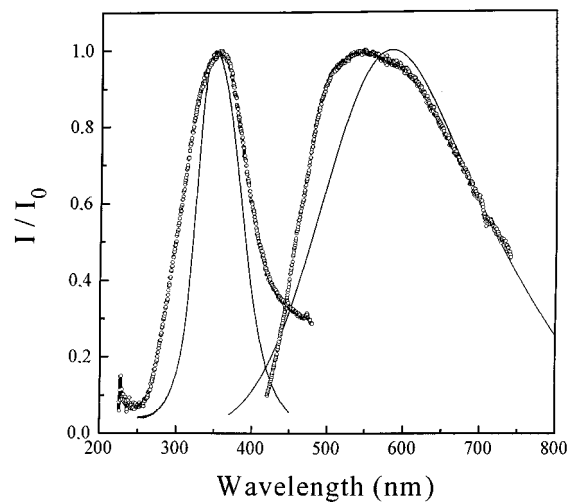


FIG. 7. Excitation ($\lambda_{\text{em}} = 600 \text{ nm}$) and emission ($\lambda_{\text{exc}} = 350 \text{ nm}$) of $\text{AgZn}(\text{PO}_3)_2$ (—) and AgPO_3 (○○○○) recorded at room temperature.

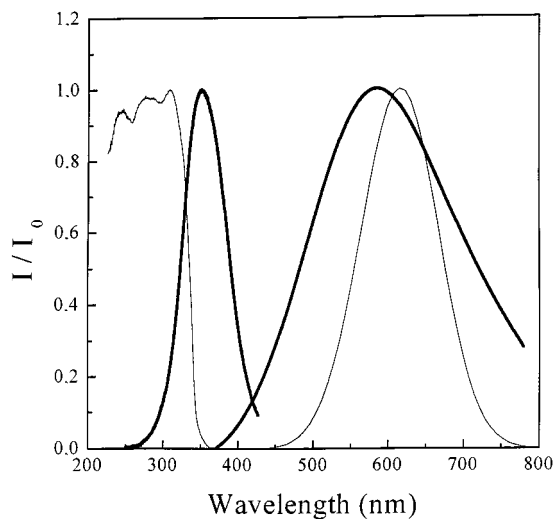


FIG. 8. Emission and excitation spectra of AgPO_3 and of the (C) center of $\text{AgZn}(\text{PO}_3)_3$ recorded at $T = 4$ K. (—) AgPO_3 ($\lambda_{\text{em}} = 600$ nm, $\lambda_{\text{exc}} = 300$ nm); (—) $\text{AgZn}(\text{PO}_3)_3$ ($\lambda_{\text{em}} = 600$ nm, $\lambda_{\text{exc}} = 350$ nm).

luminescent properties. The rigid framework of the magnesium and zinc polyphosphates contrasts with the less compact structure of the barium polyphosphate. Silver atoms are located in off-centered positions of distorted octahedra. Such position allows the luminescence of single silver ions to be observed. The emissions occur in the UV range. The large volume of the silver site of the barium polyphosphate is consistent with the larger Stokes shift deduced from the

luminescence spectra. The additional visible emission observed only in the zinc polyphosphate cannot be attributed to silver pairing but is tentatively assigned to a new zinc-silver luminescent center by comparison with a similar emission due to the silver pairs in AgPO_3 .

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