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The Vibrational Spectra of α-Alkaline Earth Pyrophosphates*,†

B. C. CORNILSEN

Department of Chemistry and Chemical Engineering, Michigan Technological University, Houghton, Michigan 49931

AND R. A. CONDRATE, SR.

Division of Engineering and Science, New York State College of Ceramics, Alfred University, Alfred, New York 14802

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Raman spectra and middle infrared absorption spectra (4000–200 cm^{-1}) were measured for α-$Ca_2P_2O_7$, α-$Sr_2P_2O_7$, and α-$Ba_2P_2O_7$. These spectra were interpreted using factor group analyses, and band assignments were made. Noncoincidences in the infrared and Raman spectra of α-$Sr_2P_2O_7$ indicated that this material possesses the centrosymmetric space group D_{2h}^{16}-*Pnma* rather than the noncentrosymmetric space group, C_{2v}^{9}–*Pna*2_1. The similarities between the vibrational spectra of α-$Ba_2P_2O_7$ and α-$Sr_2P_2O_7$ suggested that α-$Ba_2P_2O_7$ is isostructural with α-$Sr_2P_2O_7$. Differences were noted in the vibrational spectra of monoclinic α-$Ca_2P_2O_7$ and the two orthorhombic α-phases, α-$Sr_2P_2O_7$ and α-$Ba_2P_2O_7$, which were related to differences in their crystal structures. The $P_2O_7^{4-}$-anions of all three compounds contained nonlinear P–O–P bond angles.

Introduction

Alkaline earth pyrophosphates are interesting solid-state materials which display several reversible and irreversible phase transformations. This occurrence is not surprising because of the configurational flexibility of the pyrophosphate anion (*1*). Many investigators have measured and analyzed the infrared spectra of alkaline earth pyrophosphates for structural information (*2–12*). However, none of these studies have included their Raman spectra. Only the Raman spectra of α- and β-$Mg_2P_2O_7$ have been reported (*13*). This lack of Raman data can lead to a misinterpretation of their vibrational spectra with respect to structure. In this paper, both the infrared and Raman spectra are reported for the α-phases of several alkaline earth pyrophosphates. These spectra are interpreted using factor group analyses, and band assignments are made. The analyses present related structural information for the α-phases.

Experimental

Preparation of Materials

The preparation of α-$Ca_2P_2O_7$ involved a three-step chemical process. First, $CaHPO_4$ was prepared by a method described by Ranby *et al.* (*14*). Approximately 15.0 g of $CaCl_2$ was dissolved in 10 ml of boiling water. A hot concentrated $NH_4H_2PO_4$ solution was slowly added dropwise to an excess of hot $CaCl_2$ solution. The resulting $CaHPO_4$ pre-

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cipitate was washed with distilled water and dried with acetone. γ-$Ca_2P_2O_7$ was then prepared by the decomposition of $CaHPO_4$ at 718°C (*14–16*). Finally, α-$Ca_2P_2O_7$ was prepared by sintering pressed pellets of γ-$Ca_2P_2O_7$ at 1300°C for approximately 20 hr (*14–17*). The pellets which were formed by pressing powders at 25 000 psi possessed high structural integrity.

α-$Sr_2P_2O_7$ was prepared by a two-step procedure. First, $SrHPO_4$ was formed by mixing solutions of $SrCl_2$ and $(NH_4)_2HPO_4$ (*14*, *18*, *19*). Two different $SrHPO_4$ phases may be isolated depending upon the temperature of the reacting solutions. The β-phase is formed below 25°C, while the α-phase is formed above this temperature. α-$Sr_2P_2O_7$ was then formed in this study by decomposition of either α- or β-$SrHPO_4$ at 800°C (*18*, *19*).

α-$Ba_2P_2O_7$ was prepared by a two step chemical process (*2*, *3*). First, $Ba_2P_2O_7 \cdot H_2O$ was precipitated by adding $Na_4P_2O_7$ solution to a warm solution of $BaCl_2$. Then the resulting precipitate was dehydrated at 440°C in order to form α-$Ba_2P_2O_7$.

Wet chemical and emission spectrographic analyses were used to determine the stoichiometry and the concentrations of the major constituents present and to demonstrate the low concentrations of impurities. The X-ray diffraction patterns were characteristic of the various α-phases.

Infrared Measurements

Infrared spectra were measured on a Perkin–Elmer Model 621 double-beam grating spectrophotometer with a CO_2 and H_2O purging device. Both KBr pellet and nujol mull techniques were used to obtain infrared spectra (4000–200 cm^{-1}). The instrument was calibrated with polystyrene film and indene. Wavenumber accuracy is within ±2 cm^{-1} for narrow bands.

Raman Measurements

Raman spectra were measured using a Spex Industries Model 1401 double monochromator and a Coherent Radiation Laboratory Model 51 argon ion laser. The 4880-Å exciting line was used to obtain the illustrated spectra. However, these spectra were checked for plasma lines, ghosts or fluorescence by using the laser line at 5145 Å. Normal 90° collection optics were used for spectral measurements. Raman spectra were measured for both powders and sintered pellets. The spectrophotometer was calibrated using indene and the plasma lines of the laser. Wavenumber accuracy was within ±2 cm^{-1} for sharp bands.

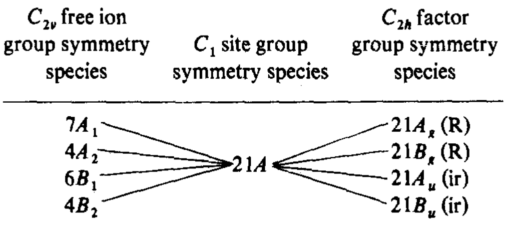
Results and Discussion

Crystal Structures and Spectral Predictions for α-Alkaline Earth Pyrophosphates

α-$Ca_2P_2O_7$ possesses a primitive unit cell with a monoclinic structure. Its space group is $P2_1/n$-C_{2h}^5 with four molecular units per primitive unit cell (*20*). α-$Mg_2P_2O_7$ possesses a similar space group ($P2_1/c$-C_{2h}^5) (*21*, *22*). In each case, the $P_2O_7^{4-}$-anions are located on C_1-sites. Correlation of the symmetry species for the C_{2v}-free ion group to the C_{2h}-factor group via the C_1-site group leads to the spectral predictions summarized in Table I.

TABLE I

FACTOR GROUP PREDICTIONS FOR α-$Ca_2P_2O_7$ USING SPACE GROUP $P2_1/n$–C_{2h}^5



Activities	Free ion	Site group	Factor group
Raman	21	21	42
Infrared	17	21	42
Coincidences	17	21	0

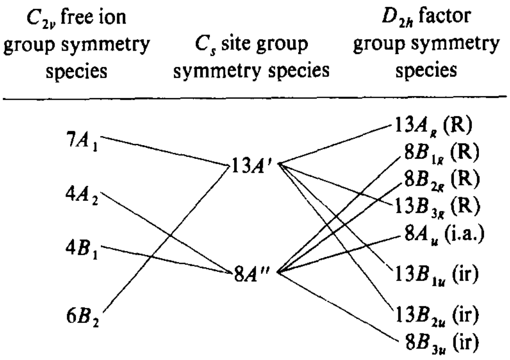
Only accidental coincidences should occur between the infrared and Raman bands of these centrosymmetric materials.

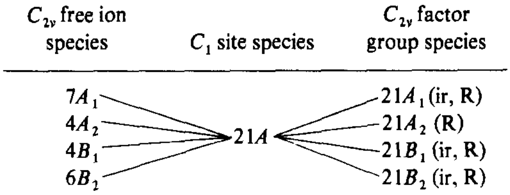
The primitive unit cell of α-$Sr_2P_2O_7$ possesses an orthorhombic structure. Two different analyses of single-crystal X-ray diffraction data indicated two different crystal structures, a centrosymmetric structure with the space group *Pnma*–D_{2h}^{16} and a noncentrosymmetric structure with the space group *Pna*2_1–C_{2v}^{9} (*23*, *24*). Four molecular units are found in the primitive unit cells of each structure. An EPR study of Mn^{2+}-doped α-$Sr_2P_2O_7$ suggests that the structure of the α-phase is centrosymmetric (*25*). However, this prediction depends upon the assumption that the added dopant does not perturb the crystal structure. The spectral predictions for the two possible crystal structures using factor group analyses are listed in Table II. The major difference between the predictions for the two structures is that no coincidences are expected between infrared and Raman bands for the centrosymmetric structure whereas some coincidences are expected for the noncentrosymmetric structure.

No X-ray diffraction analysis with single crystals has been reported for α-$Ba_2P_2O_7$. X-Ray powder diffraction patterns have been interpreted in terms of an orthorhombic structure (*14*). A theoretical powder pattern has been calculated in this study using the cell parameters reported by Ranby *et al.*, and the atomic coordinates for the centrosymmetric space group of α-$Sr_2P_2O_7$ (*14*, *23*). The calculated X-ray powder diffraction pattern agrees with both the pattern observed in this study and the pattern reported by Ranby *et al.* (*14*), suggesting a similarity in the crystal structures for α-$Sr_2P_2O_7$ and α-$Ba_2P_2O_7$.

TABLE II

SPECTRAL PREDICTIONS FOR α-$Sr_2P_2O_7$ USING SPACE GROUPS *Pnma*–D_{2h}^{16} AND *Pna*2_1–C_{2v}^{9}





Factor group	D_{2h}	C_{2v}
Raman active:	42	84
Infrared active:	34	63
Coincidences:	0	63

Interpretation of the Vibrational Spectra of α-$Ca_2P_2O_7$

The infrared spectrum of α-$Ca_2P_2O_7$ is illustrated in Fig. 1 while its Raman spectrum is illustrated in Fig. 2. Its empirical band assignments are listed in Table III. These assignments are made empirically with respect to those reported earlier for the $Mg_2P_2O_7$ polymorphs (*13*). The degree of mixing of the various modes of motion (stretching, bending, etc.) has not been determined for the various vibrational fundamentals of α-$Ca_2P_2O_7$ and the remaining pyrophosphates by normal coordinate analysis, and must be considered in a later study in order to understand the exact nature of these fundamentals. Impurity bands noted by earlier investigators for β-$Ca_2P_2O_7$ at ca. 950 and 727 cm^{-1} are not observed in the illustrated infrared spectrum (*2*, *9*). More than 22 bands are observed for the internal modes indicating that a site group model for the $P_2O_7^{4-}$-anion is inadequate, and that a factor group model must be applied. In general,

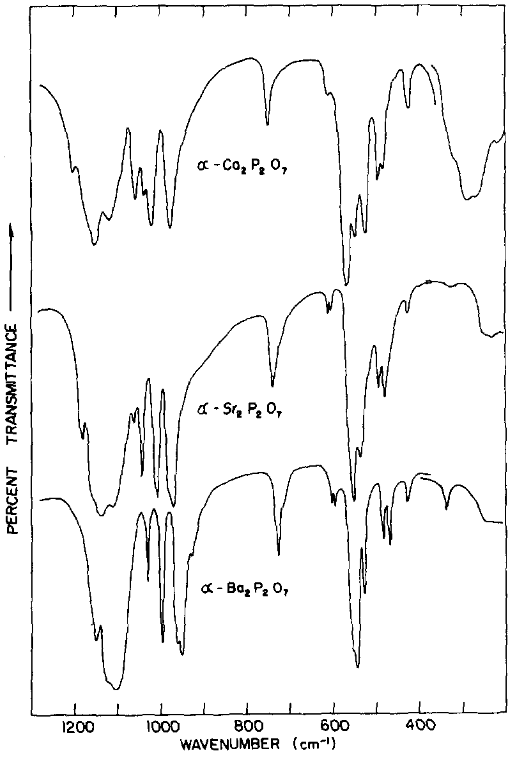


FIG. 1. The infrared spectra of α-$Ca_2P_2O_7$, α-$Sr_2P_2O_7$, and α-$Ba_2P_2O_7$.

noncoincidences are apparent between a majority of the infrared and Raman bands, which is consistent with the predictions of the applied centrosymmetric factor group model. Even though α-$Ca_2P_2O_7$ and α-$Mg_2P_2O_7$ possess similar factor groups, observed spectral features such as band shapes, relative intensities of bands, band locations, and band numbers are somewhat different. Apparently, these differences for the two monoclinic crystals can be related to differences in their unit cell parameters and the distortion of the structure of the $P_2O_7^{4-}$-anion. The P–O–P bond angles are 130 and 144° for α-$Ca_2P_2O_7$ and α-$Mg_2P_2O_7$, respectively. Also, the structure of the $P_2O_7^{4-}$-anion for α-$Mg_2P_2O_7$ deviates further from an eclipsed C_{2v}-type configuration of terminal PO_3 units than for α-$Ca_2P_2O_7$. These angular differences for the anions strongly influence the unit cell parameters. Differences were noted earlier in the vibrational spectra of $CaHfO_3$ and $SrHfO_3$ which possess similar crystal structures with the same space group (*26*). The spectral differences for the latter materials were related to the degree of monoclinic distortion of the crystal structure.

The band assignments made in this investigation for α-$Ca_2P_2O_7$ are consistent with those made earlier for α-$Mg_2P_2O_7$ (see Table

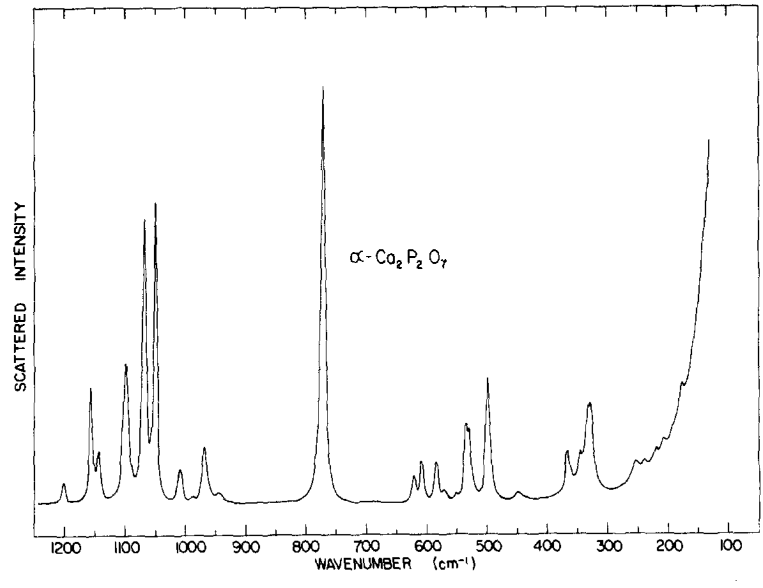


FIG. 2. The Raman spectrum of α-$Ca_2P_2O_7$.

TABLE III

BAND ASSIGNMENTS FOR VARIOUS α-ALKALINE EARTH PYROPHOSPHATES (cm^{-1})

α-$Mg_2P_2O_7$		α-$Ca_2P_2O_7$		α-$Sr_2P_2O_7$		α-$Ba_2P_2O_7$		
ir (*25*)	Raman (*13*)	ir	Raman	ir (*2*)	Raman	ir (*9*)	Raman	Assignments
1211	1192	1205	1210	1186	1197	1156	1167	$\nu^a_{PO_3}$
1193	1144	1165	1163	1163	1153	1126	1164	
1133	1126	1155	1152	1144	1128	1109	1128	
1118	1113	1120	1105	1117	1099		1102	
1105							1090	
1081	1089	1060	1074	1068	1068	1034	1049	$\nu^s_{PO_3}$
	1064	1041	1055	1049				
1052	1005	1025	1015	1014	1042	1003	1004	$\nu^a_{PO_3}$
			995		1009			
982	972	980	974	989	968	969	953	ν^a_{POP}
			953	979		958		
761	748	752	775	749	768	736	753	ν^s_{POP}
740								
638	641	619	629	621	623	609	617	δ_{PO_2}
587	617	605	616	613	611	603	605	
558	583	580	591	563	571	564	570	
509	559	570	579	548	556	556	552	
454	494	553	558	503	531	539^2	534	
437	464	533	542	489	497	487	485	
(388)	413	500	537	434	482	472	443	
(360)	398	490	504	(338)	447	431	350	
(348)	380	430	455		360	(337)	336	
	354	325	373		336			
			352					
			337					

III) (*13*). For instance, the intense band in the Raman spectrum at 775 cm^{-1} can be assigned to the symmetric bridge P–O stretching mode. This mode was observed at 748 cm^{-1} for α-$Mg_2P_2O_7$ (*13*). Two Raman bands (1055 and 1074 cm^{-1}) were observed for α-$Ca_2P_2O_7$ in the symmetrical terminal P–O stretching region. The $P_2O_7^{4-}$-free ion model with C_{2v}-symmetry predicts two symmetrical terminal P–O stretching modes belonging to the A_1-symmetry species. Apparently, the two observed Raman bands are Raman-active factor group components of these free-ion modes. The same modes were observed earlier in the Raman spectrum at 1064 and 1089 cm^{-1} for α-$Mg_2P_2O_7$ (*13*). Similar relationships observed between the other infrared and Raman bands of α-$Ca_2P_2O_7$ and α-$Mg_2P_2O_7$ can be used in the assignment of the remaining internal vibrational modes for the $P_2O_7^{4-}$-anion of α-$Ca_2P_2O_7$.

Interpretation of the Vibrational Spectra of α-$Sr_2P_2O_7$ and α-$Ba_2P_2O_7$

The infrared and Raman spectra of α-$Sr_2P_2O_7$ are illustrated in Figs. 1 and 3, respectively. The empirical band assignments are listed in Table III. Noncoincidences are observed between most infrared and Raman bands. Therefore, similarly to the interpretat-

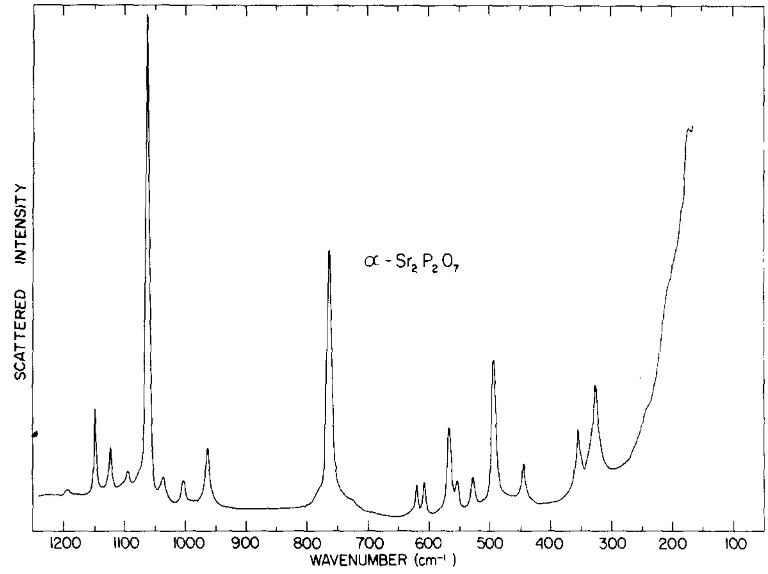


FIG. 3. The Raman spectrum of α-$Sr_2P_2O_7$.

tion of the EPR data for doped α-$Sr_2P_2O_7$, our interpretation of the observed vibrational data suggests that the centrosymmetric space group is the most probable space group for α-$Sr_2P_2O_7$ (*25*). The band features for the Raman spectrum of α-$Sr_2P_2O_7$ are different than those of α-$Ca_2P_2O_7$. For instance, only one factor-group split component is observed for the symmetric terminal P—O stretching mode of α-$Sr_2P_2O_7$. Earlier, two split bands were observed for α-$Ca_2P_2O_7$. Also, in contrast to α-$Ca_2P_2O_7$, the band associated with the symmetric terminal P—O stretching mode of α-$Sr_2P_2O_7$ is more intense than the band associated with the symmetric bridge P—O stretching mode. The two above-mentioned spectral differences can be explained if one assumes that the bands associated with the symmetric terminal stretching modes of the C_{2v}-free ion model are overlapped for α-$Sr_2P_2O_7$. Apparently, this overlap results because of the orthorhombic arrangement of the $P_2O_7^{4-}$-anions in the crystal structure of α-$Sr_2P_2O_7$. The remaining band assignments for α-$Sr_2P_2O_7$ are consistent with those made for both α-$Ca_2P_2O_7$ and α-$Mg_2P_2O_7$.

The infrared and Raman spectra of α-$Ba_2P_2O_7$ are shown in Figs. 1 and 4, respectively. Observed band maxima are listed in Table III. The same differences in the vibrational spectra noted for α-$Sr_2P_2O_7$ with respect to α-$Ca_2P_2O_7$ are also observed in the case of α-$Ba_2P_2O_7$. For instance, only one strong band is observed in the Raman spectrum of α-$Ba_2P_2O_7$ which can be assigned to the symmetric terminal P–O stretching mode. Also, this Raman band is more intense than the band belonging to the symmetric bridge P–O stretching mode. These spectral observations for α-$Ba_2P_2O_7$ fortify the interpretation that the above-mentioned differences in the vibrational band features for monoclinic α-$Ca_2P_2O_7$ and orthorhombic α-phases can be related to the differences in their crystal structures.

The band features of both the infrared and the Raman spectra of α-$Sr_2P_2O_7$ and α-$Ba_2P_2O_7$ are strikingly similar. A one-to-one correlation seems to exist between most of their bands. Several of the expected bands might not be observed because they are hidden behind intense bands. For instance, the Raman

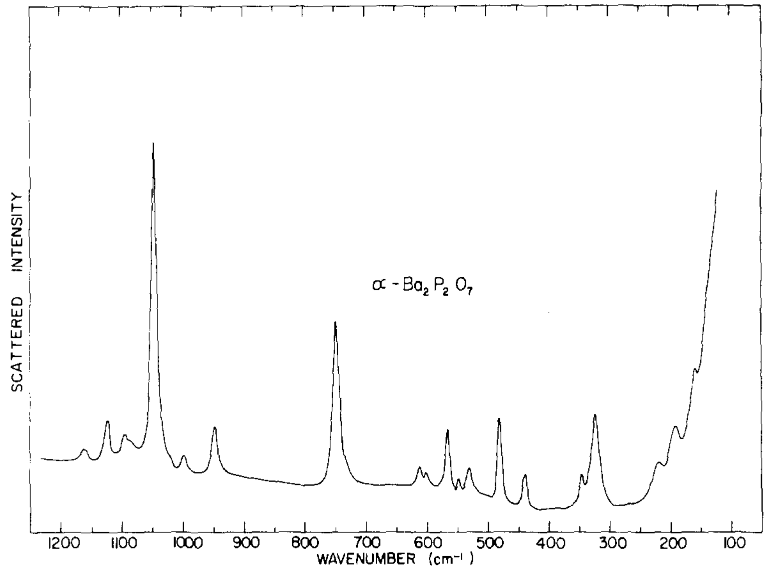


FIG. 4. The Raman spectrum of α-$Ba_2P_2O_7$.

band of α-$Ba_2P_2O_7$ related to the Raman band at 1042 cm^{-1} for α-$Sr_2P_2O_7$ might not be observed because it is hidden behind the strong band at 1049 cm^{-1} for α-$Ba_2P_2O_7$. This spectral interrelation suggests that their factor group and, therefore, their space groups are similar. The interpretation is consistent with the ability to calculate the *d*-spacing locations and relative intensities of peaks in the powder X-ray diffraction pattern of α-$Ba_2P_2O_7$ using the atomic coordinates for the space group of α-$Sr_2P_2O_7$. The band assignments for α-$Ba_2P_2O_7$ are consistent with those for the other α-alkaline earth pyrophosphates.

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