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Raman Spectroscopy of Polymorphic Orthophosphates Containing Sodium and Lanthanide Elements*

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Mixed orthophosphates ($Na_3Ln_x(PO_4)_y$) containing sodium and lanthanide elements have been prepared by several synthetic methods and have been characterized by Raman spectroscopy at both ambient and elevated temperatures, X-ray diffraction, and neutron activation analysis. The elements from La to Gd have been observed to form compounds with the stoichiometry $Na_3Ln(PO_4)_2$, which exhibit only one type of symmetry. Yttrium and the elements from Tb to Lu form compounds with the stoichiometries $Na_3Ln(PO_4)_2$ and $Na_3Ln_2(PO_4)_3$. Each compound occurs in several crystal symmetries. One of these, designated as phase γ, appears to be a new phase. © 1985 Academic Press, Inc.

I. Introduction

Conflicting data in the literature regarding the stoichiometries and crystal structures of phosphates containing alkali metals and lanthanides or actinides led us previously to examine the synthesis and characterization, mainly by Raman spectroscopy, of compounds of the type $Na_3M(PO_4)_2$ (M = Pu or light rare earths) (*1*). Our results did not confirm literature claims of the existence of compounds containing light rare earths with the stoichiometry $Na_3Ln_2(PO_4)_3$. Kizilyalli and Welch (*2*) suggested the existence of polymorphism for the double phosphates of the heavier rare earths. They observed that double phosphates of Gd and Y quenched after prolonged heating periods produced X-ray diffraction patterns that, although resembling closely those of compounds heated for shorter times at the same temperature and cooled slowly, showed distinct differences in the low-angle diffraction lines. Kizilyalli and Welch designated these compounds, respectively, β (quenched) and α (slow cooled) forms. The infrared spectra of both these forms were reported by the authors (*2*) to be very similar. The fact that the α and β forms were obtained from heating to the same temperature and gave similar ir spectra raised the question as to whether they are polymorphs, or mixtures resulting from thermal decomposition. In a recent

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extensive study of the structures of compounds with stoichiometry $Na_3Ln(XO_4)_2$ (where Ln represents the lanthanide elements and X = P, V, or As) Vlasse *et al.* (*3*) have identified five polymorphs (designated as type I, V, VI, VIII, and IX) and presented a diagram showing the fields of stability for each polymorph with respect to temperature and lanthanide element (atomic number). One of these polymorphs, the high temperature form of $Na_3Yb(PO_4)_2$ designated as type IX, was reported (*3*) to have a range of stoichiometry compatible with the general formula $Na_{3(1+x)}Ln_{(2-x)}(PO_4)_3$ where $0 \leq x \leq 0.5$. While Vlasse *et al.* (*3*) in their comprehensive paper indicate that, with exception of the phase transition V to VIII, all the other phase transitions are reversible, no experimental details are given in their references to support this conclusion.

In addition to what we perceived as an area in need of further clarification, we chose to reexamine the synthesis and phase behavior of the Na, *Ln*-containing phosphates because they can have a strong deleterious effect on the integrity of synthetic monazite matrices used to immobilize nuclear wastes. This negative effect of the presence of alkali-containing double phosphates stems from their significant hydrolyzability relative to lanthanide orthophosphates. Because our previous work with Raman spectroscopy of phosphates (*4a*) had demonstrated that this technique was a convenient way to distinguish phosphate phases and compounds with sufficient sensitivity we decided to rely heavily on Raman spectroscopy for this work.

II. Experimental

All the syntheses of the phosphate compounds in this work were made by heating intimate mixtures of powders, contained in platinum boats, in air at various temperatures from 1 hr to 4 days after which they were rapidly cooled in air, although not quenched. The following reactions were used to synthesize the compounds:

$$Ln_2O_{3+x} + 3Na_4P_2O_7 \rightarrow 2Na_3Ln(PO_4)_2 + 2Na_3PO_4 + \tfrac{1}{2}xO_2 \quad (1)$$

$$mLnPO_4 + nNa_3PO_4 \rightarrow Na_{3n}Ln_m(PO_4)_{m+n} \quad (2)$$

$$Ln_2O_{3+x} + 3Na_2CO_3 + 4(NH_4)_2HPO_4 \rightarrow 2Na_3Ln(PO_4)_2 + 3CO_2 + 8NH_3 + 6H_2O + \tfrac{1}{2}xO_2 \quad (\text{where } 0 \leq x \leq 1) \quad (3)$$

$$LnF_3 + 2Na_3PO_4 \xrightarrow{(in\ \text{KCl–NaCl}\ melt)} Na_3Ln(PO_4)_2 + 3NaF. \quad (4)$$

The reaction shown in Eq. (1) was used with all the lanthanides, while that in Eq. (2) was used primarily with holmium and other heavy lanthanides for a detailed study of compound stoichiometry. The reactions shown in Eqs. (3) and (4) were used less frequently.

Weight losses after heating were negligible; the products obtained were exposed to warm water for short times (10–20 min) to remove the soluble by-products and the excess sodium-containing starting reagents while avoiding hydrolysis. The insoluble residues were vacuum dried at 75°C. Elemental analyses of selected compounds, before and after exposure to water, showed that this treatment did not affect their stoichiometry. The lanthanide-containing starting compounds (99% purity or better) were obtained from commercial sources; in several cases a lanthanide oxide from more than one source was used to check for reproducibility of the results. All the other reagents were of analytical grade.

Portions of the solid products were analyzed for Na and *Ln* by neutron activation analysis (NAA), while the orthophosphate ion concentration was derived by material balance. An assumption was made that lanthanide oxides were absent. This assumption was very difficult to confirm due to the relatively low sensitivity for oxides of the physical methods of analysis available. X-ray powder diffraction generally has a limited sensitivity for detecting the presence of a minor phase (5–10 wt%) in a mixture. Raman spectroscopy, although sufficiently sensitive for distinguishing species among phosphate mixtures, could not detect less than 10 wt% lanthanide sesquioxides mixed with phosphates (such as $Na_3Ln(PO_4)_2$). Thus, if 5 wt% La_2O_3 were present and undetected in a mixture with $Na_3La(PO_4)_2$, the resulting analytical Na/La ratio by NAA would be 2.66 rather than the theoretical value of 3. In a few cases, orthophosphate was determined spectrophotometrically and the results confirmed those derived by material balance from NAA results. The precision of NAA (about ±4%) was not sufficiently high for determining accurately the Na/*Ln* ratios in the compounds. Thus, these ratios were used only as a guide to search for trends in attempts made to correlate values of Na/*Ln* with the various polymorphs identified by X-ray diffraction and by Raman spectroscopy. More precise values of Na/*Ln* were considered to be those in which different ratios of Na_3PO_4 and $LnPO_4$ were reacted completely [Eq. (2)] as evidenced by negligible losses on washing with water.

Most of the preparations were examined in the form of powders, these were loaded into 1.8-mm-i.d. glass tubes for Raman spectroscopy and 0.3-mm-i.d. quartz capillaries for X-ray diffractometry. In some cases pellets were pressed for Raman spectroscopy at elevated temperatures. Raman spectra were generally excited with 514.5, 488.0, or 457.9 nm radiation from an argon-ion laser. Pellets (~6 mm diam × 1.5 mm) were obtained from mixtures of $LnPO_4$ and Na_3PO_4 and of phases V and VI, and pure phases V, IX, and γ and were placed on a quartz pedestal inside a quartz test tube located in the cavity of a mini Pt-wound tube furnace. Optical ports at 90° allowed the entrance of the laser radiation and exit of the Raman radiation. This furnace is a modification of one described previously (*4b*). The result of increasing temperature on the Raman spectra was to shift most peaks to lower frequencies and to broaden the peaks to the extent that peaks close to one another ($\pm 30\ cm^{-1}$) were fused together. With our present instrumentation, the radiation emitted by the glowing sample and quartz container at ≥900°C provided a very high background which began to overlap the Raman spectrum. A Ramanor HG-2S spectrometer was used to record the spectra. The Raman instrumentation has been described in detail elsewhere (*4a*).

Holmium was used in this work to represent the heavy lanthanide elements and therefore it was used in a large number of preparations. In order to identify their X-ray powder patterns by correlation with those of phases (I, V, VI, and IX) reported by Vlasse *et al.* (*3*), the X-ray diffraction patterns of such phases were generated for holmium compounds by calculation, on the basis of reported single-crystal structure determinations of analogous compounds. In each case, structure factors were calculated using the atomic coordinates and isotropic temperature factors of these compounds directly, but with scattering factors (*5*) for Na, Ho, P, and O atoms. Predicted X-ray powder diffraction peak intensities were obtained from the squares of these structure factors by applying the appropriate Lorentz, polarization, and multiplicity factors. Line positions were calculated from estimated lattice parameters, and the patterns were plotted to scale for direct comparison with the Debye–Scherrer films.

For phase I, coordinates were taken from the structure of glaserite, $K_3Na(SO_4)_2$ (*6*), substituting Na for K, Ho for Na, and P for S. Hexagonal lattice parameters, $a = 5.293$ and $c = 6.975$, were deduced by transforming the orthorhombic cell parameters reported by Salmon *et al.* (*7*).

For phase V, coordinates were taken from $Na_3Nd(VO_4)_2$ (*8*), substituting Ho for Nd and P for V. Monoclinic lattice parameters, $a = 27.50$, $b = 5.293$, and $c = 13.95$, were deduced as described above for phase I. The angle β was assumed to be 91.4°, the observed value for $Na_3Nd(VO_4)_2$.

Coordinates for phase VI were taken from $Na_3Nd(PO_4)_2$ (*9*), substituting Ho for Nd. The lattice parameters of this orthorhombic compound were used without change: $a = 15.874$, $b = 13.952$, $c = 18.470$.

For phase IX, coordinates from $Na_3Yb(PO_4)_2$ (*10*) were used, substituting Ho for Yb. Hexagonal lattice parameters, $a = 9.19$ and $c = 21.96$, were obtained by extrapolating from the values given in the same publication for other $Na_3Ln(PO_4)_2$ compounds. The calculated powder pattern agrees with that observed by Apinitis and Sedmalis (*11*).

The powder pattern for phase VIII was taken directly from that observed for $Na_3Tm(PO_4)_2$ (*11*).

III. Results and Discussion

Several preparations with each lanthanide element were initially made at various temperatures by means of the reaction shown in Eq. (1). Subsequent preparations were made by the reactions shown in Eqs. (2)–(4). Examination of the Raman spectra obtained from these preparations revealed that the spectra of compounds of elements La to Gd (arbitrarily designated here as Group A compounds) all showed a strong resemblance to each other. The spectra of the Tb to Lu, plus Y compounds (Group B), differed both among themselves depending on the preparation temperature and also from those of Group A. Holmium was chosen as representative of the Group B compounds for more exhaustive studies because it did not exhibit any appreciable fluorescence with 514.5 nm irradiation.

a. Group A Compounds: La to Gd

Details of the syntheses of representative Group A compounds together with their Raman spectroscopy, XRD, and NAA results are shown in Table I. Considering that the products prepared by means of Eq. (2) with $Na_3PO_4/LnPO_4 = 1$ showed negligible weight loss during leaching with water and that their spectra and XRD patterns were similar, we assigned the stoichiometry $Na_3Ln(PO_4)_2$ to these compounds.

In preparations carried out in an air atmosphere, CeO_2 was found to be present in the $Na_3Ce(PO_4)_2$ product. This result was not unexpected since we had found earlier that $Na_3Ce(PO_4)_2$ heated in air was decomposed to CeO_2 and $Na_4P_2O_7$ (*12*). In the temperature range 900–1200°C all the preparations based on the reaction in Eq. (1) produced the product, $Na_3Ln(PO_4)_2$. Below 900°C, the reaction did not go to completion. For example, Raman spectra of europium preparations made at 850°C showed the presence of $EuPO_4$ and unreacted Eu_2O_3. Similar results were obtained when heavier lanthanides were substituted for the europium (see Section IIIb). These results suggest that the reaction in Eq. (1) proceeds in two steps:

$$Ln_2O_{3+x} + 3Na_4P_2O_7 \rightarrow 2LnPO_4 + 4Na_3PO_4 + \tfrac{1}{2}xO_2 \quad (1a)$$

followed by

$$2LnPO_4 + 4Na_3PO_4 \rightarrow 2Na_3Ln(PO_4)_2 + 2Na_3PO_4. \quad (1b)$$

Raman spectra of the $Na_3Ln(PO_4)_2$ compounds, where Ln = La to Gd, are shown in Figs. 1A and B and the frequencies of the major peaks are listed in Table II. Because preparations of the dysprosium compound consisted of more than one phase its spec-

TABLE I

SYNTHESIS AND IDENTIFICATION OF COMPOUNDS WITH LANTHANIDES La TO Lu, AND Y

Lanthanide element	Method of synthesis[a]	Thermal treatment temp. (°C)/time (hr)	Assignment of structure type[b]		Na/*Ln* (by NAA)
			Raman spectroscopy	XRD	
La	1	900/18	VI	VI	2.75
Pr	1	1200/21	VI	VI	2.94
Nd	4	700/5	VI	VI	—
Sm	1	1200/6	VI	VI	2.82
Eu	1	850/24	VI	VI + Eu_2O_3 + $EuPO_4$	2.62
Eu	1	1200/18	VI	VI	—
Gd	1	960/18	VI	VI	—
Gd	1	1200/6	VI	VI	—
Tb	1	1200/24	V + VI	VI	2.35
Dy	1	1200/19	V	—	—
Y	3	1200/20	IX	IX	1.93
Er	2, $m/n = 2$	1225/19	γ	—	—
Tm	1	1200/44	IX	IX	—
Yb	2, $m/n = 1$	960/19	IX	IX + NI[c]	2.42
Lu	1	1200/21	IX	IX	—
Lu	1[d]	850/96	IX	IX	—

[a] Synthesis by reaction shown in text; numbers refer to equation numbers.

[b] As defined by Vlasse *et al.* (*3*).

[c] NI, not identified extra phase.

[d] Preparation listed immediately above.

trum is not shown; however, the frequencies of its major peaks are listed. Figure 1B includes the spectra of the polymorphs of Tb, Ho, and Y (phase VI) which are similar to the compounds of La to Gd. X-ray diffraction patterns of all the Group A compounds were in accord with calculated patterns for the type VI phase as designated by Vlasse *et al.* (*3*) (low temperature, orthorhombic form of $Na_3Nd(PO_4)_2$). Although some of our syntheses were performed at temperatures above the boundary given by Vlasse *et al.* (*3*) for the formation of the glaserite structure (type I), we did not observe it in our preparations. In addition we attempted to identify the α and β forms of $Na_3Gd(PO_4)_2$ reported in (*2*) and concluded that the XRD pattern of the α form agrees well with that expected for a type VI phase reported by Vlasse *et al.* (*3*), while the pattern of the β form did not match those of any of the other phases reported by Vlasse *et al.* (*3*) nor that of the γ phase described below.

b. Group B Compounds: Y and Tb to Lu

A summary of the synthetic procedure and the experimental results for the Group B compounds are shown in Tables I and III. Raman spectra of these compounds are shown in Figs. 1B, 2, 3, and 4 and the frequencies of the major peaks are listed in Table II.

Attempts to synthesize these group B compounds at 850°C by means of the reactions in Eqs. (1) and (3) using Y, Ho, Tm, Yb, and Lu and at 950°C by means of the reaction in Eq. (2) using Tm, Yb, and Er,

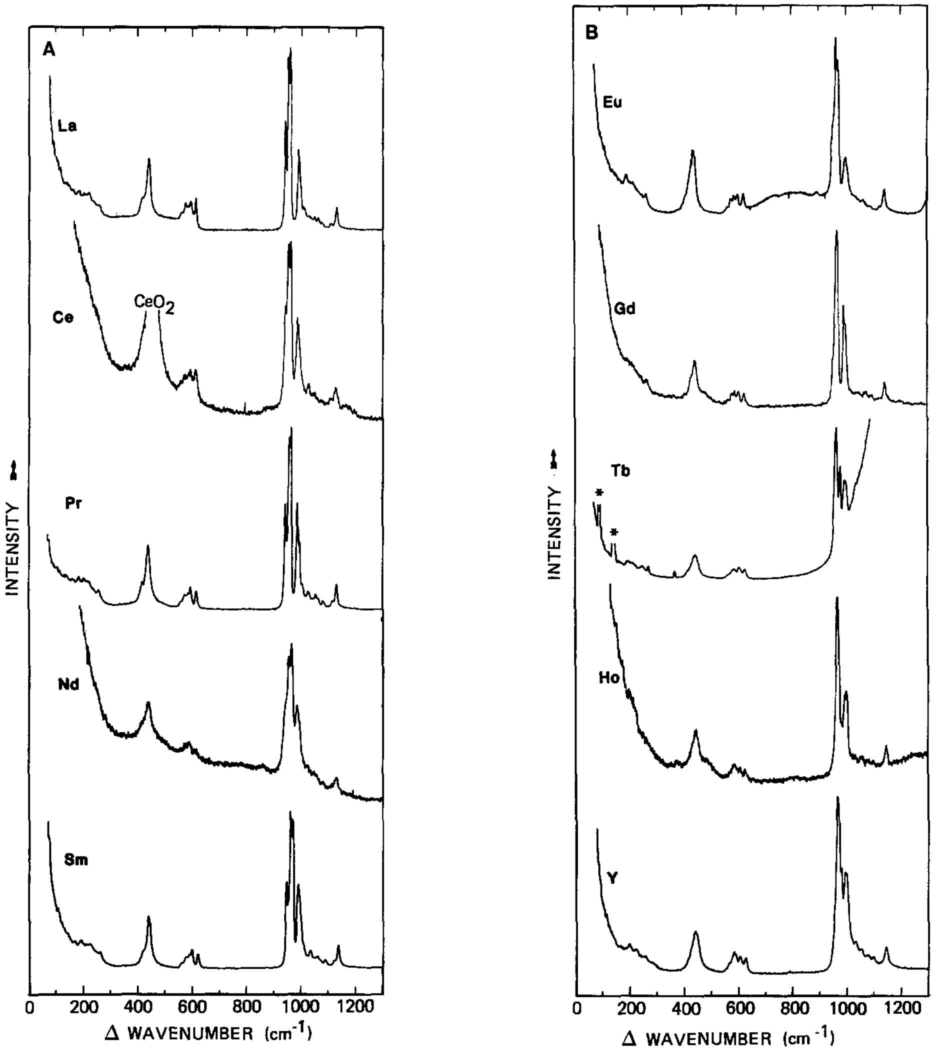

FIG. 1A. Raman spectra of compounds $Na_3Ln(PO_4)_2$ with symmetry similar to that of phase VI described in (*3*). Frequencies of major peaks are listed in Table II. Excitation: 514.5 nm. (B) Raman spectra of compounds $Na_3Ln(PO_4)_2$ with symmetry similar to that of phase VI described in (*3*). Frequencies of major peaks are listed in Table II. Excitation: 514.5 nm, except 488.0 nm (Tb). *Plasma lines.

were unsuccessful. Analyses by Raman spectroscopy indicated the presence of unreacted lanthanide oxide and lanthanide orthophosphate in the products. Presence of the latter resulted either from lack of completion of the reaction when the phosphate was used as a reagent (Eq. (*2*)) or from its formation as an intermediate (Eqs. (1A), (1B)).

Examination of the products was often complicated due to mixtures of phases. The identifications listed in Tables I and III based on analyses by Raman spectroscopy and by XRD were arrived at by iterative

TABLE II

FREQUENCIES (cm^{-1}) OF MAJOR RAMAN PEAKS OBSERVED IN SODIUM AND LANTHANIDE ORTHOPHOSPHATES

							Phase VI (Figs. 1A and 1B)							
La	418	438	576	594	614	940	951*	958*	988				1129	
Ce	—	—	575	594	612	940	952*	959*	986				1126	
Pr	419	439	574	597	617	942	956*	963*	987				1127	
Nd	418	440	565	587	615	941	955*	964*	984				1129	
Sm	419	441	578	600	617	945	960*	968*	989				1136	
Eu	—	439	581	602	620	946	961*	967*	994				1138	
Gd	—	441	583	604	622	947	961*	966*	988				1140	
Tb	—	442	587	606	626		960*	976*	994				1144	
Dy	—	432	580	610	628	945	961*	977*	993*	1027			1137	
Ho	—	442	581	610	624		966*		994				1144	
Y	—	441	581	608	626		962*	977	992				1143	
							Phase V (Fig. 2)							
Dy	417	449	587	608	656	957*	977*	992	999	1029	1052	1098	1134	
Ho	419	451	586	609	627	960*	979*	995	1002	1034	1058	1098	1137	
Y	418	452	587	610	631	961*	979*	995	1003	1034	1052	1102	1137	
							Phase γ (Fig. 3)							
Ho	414	459	554	581	627	945	980	1000*	1010*	1038	1056	1069	1142	1168
Er	416	460	555	581	631	947	981	1002*	1011*	1040	1060	1071	1143	1172
Tm	419	456	556	583	635	952	985	1004*	1012*	1040	1062	1069	1146	1173
Yb	417	459	558	584	636	953	989	1006*	1017*	1045	1068	1074	1145	1177
							Phase IX (Fig. 4)							
Ho	416	437		574	616			995*		1027*			1135	
Y	425	448		578	619			987*		1033*			1144	
Tm	429	448		578	619			991*		—			1144	
Yb	431	445		577	617			994*		1027*			1152	
Lu	—	444		580	619			1001*		—			1156	

Note. Asterisks denote most intense peaks.

comparisons, designating those products which gave reproducible simpler patterns and spectra as pure phases.

In Tables I and III we have identified four phases: types V, VI, IX, and γ. Phase γ appears to be new because its Raman spectrum and XRD pattern are significantly different from those of the other known phases. We were unable to fit the XRD pattern, listed in Table IV, to any of the known phosphate compounds including those of $NaZr_2(PO_4)_3$ (*13*) and $Na_3Sc_2(PO_4)_3$ (*14*). Because Kizilyalli and Welch have identified the existence of an oxyphosphate, $Ln_3PO_7(= Ln_2O_3 \cdot LnPO_4)$ (where Ln = La, Ce, and Gd) among the products of reaction of $LnPO_4$ with Na_2CO_3 (*15*) and of $GdPO_4$ with excess Na_3PO_4 (*2*), we sought to confirm that our phase γ was not an oxyphosphate. Raman spectra of La_3PO_7, and products of the reaction of $HoPO_4$ with various amounts of Ho_2O_3 at temperatures up to 1500°C, were obtained and compared to phase γ. The spectra of these products were markedly different from that of phase γ. The Raman spectrum of phase γ (Fig. 3) appears to be unique and is characterized by a large number of peaks. The XRD patterns of phase γ did not match the data of the oxyphosphates listed in (*13*). From the composition of the starting mixtures used to prepare phase γ, and the limited number of analytical results, we conclude tentatively that phase γ has a stoichiometry very

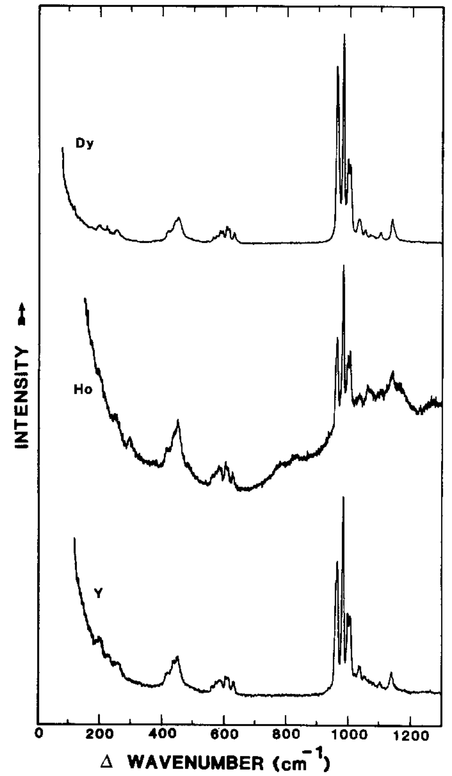

FIG. 2. Raman spectra of compounds $Na_3\mathit{Ln}(PO_4)_2$ with symmetry similar to that of phase V described in (*3*). Frequencies of major peaks are listed in Table II. Excitation: 514.5 nm.

close to $Na_3\mathit{Ln}_2(PO_4)_3$. This stoichiometry corresponds to that given by Vlasse *et al.* (*3*) for phase IX ($Na_{3(1+x)}\mathit{Ln}_{(2-x)}(PO_4)_3$, where $0 \leq x \leq 0.5$) if x is set equal to zero. Thus, one may speculate that phase γ is a polymorph of phase IX. Attempts to identify the structures of the α and β forms of $Na_3Y(PO_4)_2$ reported in (*2*) by comparison of their XRD patterns with patterns calculated for phases I, V, VI, VIII, and IX (*3*) and for γ were not successful. The XRD pattern of the β form resembles that of phase I, the glaserite structure, while neither analogy nor resemblance was found for the α form. These results are the reverse of those found for Gd compounds, as discussed above.

Some of the results listed in Tables I and III were acquired during attempts to determine the reversibility of transformations by additional thermal treatment of some of the compounds. The lack of reproducibility encountered for the reversibility of some transitions may have been due to the fact that preparations were not quenched, although they were cooled rapidly. This led us to explore the use of Raman spectroscopy at high temperatures for the identification of the various polymorphs at those temperatures.

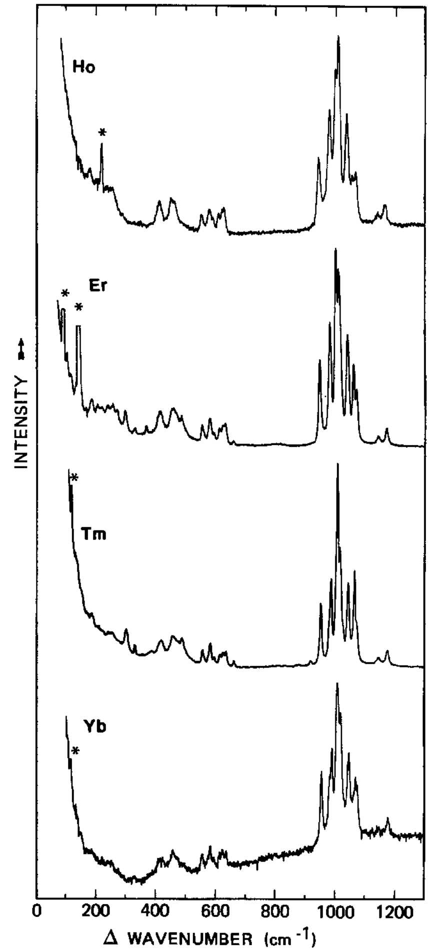

FIG. 3. Raman spectra of compounds $Na_3Ln(PO_4)_2$ with symmetry designated that of phase γ. Frequencies of major peaks are listed in Table II. Excitation: 457.9 nm (Er), 488.0 nm (Ho) and 514.5 nm (Tm, Yb). *Plasma lines.

TABLE III

SYNTHESIS AND IDENTIFICATION OF HOLMIUM COMPOUNDS

Method of synthesis[a]	Thermal treatment temp. (°C)/time (hr)	Assignment of structure type[b]		Na/*Ln* (by NAA)
		Raman spectroscopy	XRD	
2, *m*/*n* = 1	1020/67	V + VI	VI	2.82
2, *m*/*n* = 0.67	1020/67	V + VI	VI	2.89
1	1200/6	V	V	—
1[c]	900/18	V + VI	VI + NI[d]	2.46
VI[e]	900/72	V + trace Ho_2O_3 and $HoPO_4$	V + NI	2.28
2, *m*/*n* = 1	1200/21	V + VI	VI + NI	—
1	1200/17	V + VI	V	2.41
1	1030/146	V + VI	VI + NI	—
1	960/19	VI + trace Ho_2O_3	VI + NI	2.24
2, *m*/*n* = 1	1030/146	V + VI	VI + NI	—
2, *m*/*n* = 0.5	1030/80	VI	VI + NI	—
2, *m*/*n* = 2	1225/68	γ + trace $HoPO_4$	γ	1.35
[f]	1200/20	γ	γ	1.44
2, *m*/*n* = 2	1200/39	γ + trace $HoPO_4$	γ	—
2, *m*/*n* = 2	1020/137	IX	IX	1.51
2, *m*/*n* = 2	1200/21	IX	IX	1.81
2, *m*/*n* = 1.5	1200/59	IX	IX	1.95
2, *m*/*n* = 1.33	1200/20	V + VI	V	2.21
2, *m*/*n* = 1	1225/68	V + VI	V	2.57
1[g]	900/20	V	—	—

[a] Synthesis by reaction shown in text; numbers refer to equation numbers.

[b] As defined by Vlasse *et al.* (*3*).

[c] Preparation listed immediately above.

[d] NI: not identified extra phase.

[e] Previously fired 20–90 hr at 800–950°C.

[f] Phase IX + $Na_4P_2O_7$.

[g] Previously fired at 1200°C.

We selected $HoPO_4$ to establish the effect of temperature on its Raman spectrum because this compound has many sharp peaks at ambient temperature, and because it has no polymorphs at higher temperatures. The spectrum of $HoPO_4$ was recorded at 500, 750, and 910°C; nearly all the peaks were present at these temperatures and about half of them shifted to lower frequencies with increasing temperature. Such shifts are consistent with theory and with results obtained by others (*16*). A list of the frequencies (cm^{-1}) at 25°C and the average shift (cm^{-1}/K) follows: 140 (−0.009); 293 (−0.015); 484 (−0.011); 998 (−0.022); and 1055 (−0.034). The spectra of a mixture $Na_3PO_4 : HoPO_4$ were recorded at several temperatures while heating at about 1°C/min. The spectra indicated, by the disappearance of the $HoPO_4$ peaks, that the reaction was completed between 900 and 1000°C. The temperature was lowered to 915 ± 15°C and held for 18 hr. Although at this temperature the background radiation was

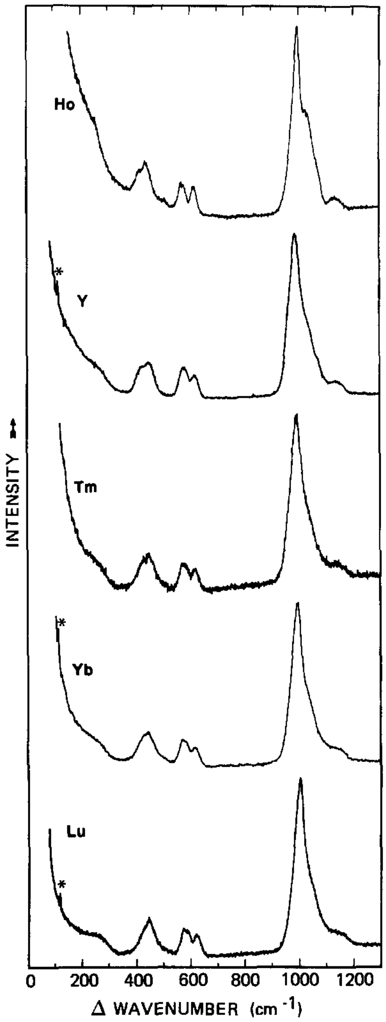

FIG. 4. Raman spectra of compounds $Na_3Ln_2(PO_4)_3$ with symmetry similar to that of phase IX described in (*3*). Frequencies of major peaks are listed in Table II. Excitation: 514.5 nm, except 488.0 nm (Ho). *Plasma lines.

not excessive, the broad intense peak present at ~970 cm^{-1} did not allow for an unequivocal distinction between phases V and VI. If, however, we assume that the shift observed for $HoPO_4$ can be used to correct the position of the broad peak at ~900°C to room temperature, we conclude that it would be located at 987 cm^{-1}, which is much closer to phase V (983 cm^{-1}) than to VI (963 cm^{-1}). On cooling to room temperature the spectrum obtained was unequivocally that of phase V. A mixture of phases V and VI of $Na_3Ho(PO_4)_2$, based on its room temperature Raman spectrum, behaved interestingly during heating. At 465°C the original three most intense peaks had broadened into one peak with two shoulders and its frequency shifted to a higher value, remaining unchanged up to 940°C. We interpreted this as the conversion of phase VI, present in the mixture, to phase V; this was confirmed by the spectra

TABLE IV

X-RAY POWDER DIFFRACTION DATA FOR PHASE γ OF $Na_3Ln_2(PO_4)_3$[a]

Intensity[b]	*d* (Å)	Intensity[b]	*d* (Å)
M	6.34	VW	2.149
M	4.77	VW	2.118
M	4.68	VW	2.086
M	4.29	VW	2.059
W	3.996	Tr	2.015
W+	3.882	VW	1.988
W+	3.808	W	1.986
M	3.604	W+	1.963
W	3.398	W	1.922
W+	3.197	VW	1.894
Tr	3.151	W	1.868
Tr	3.056	Tr	1.842
S	2.976	VW	1.812
M+	2.930	W	1.773
W	2.828	W	1.765
M	2.737	W	1.746
VW	2.705	Tr	1.718
W	2.658	W+	1.690
W	2.624	Tr	1.607
VW	2.563	W	1.593
VW	2.514	VW	1.573
Tr	2.473	VW	1.562
W	2.422	VW	1.544
VW	2.243	Other very weak lines to *d* = 0.92 Å were observed.	
VW	2.200		

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[a] Obtained with 11.4-cm-diam Debye–Scherrer camera and Cu : $K\alpha$ radiation; line intensities were estimated visually.

[b] S = strong, M = medium, W = weak, VW = very weak, and Tr = trace.

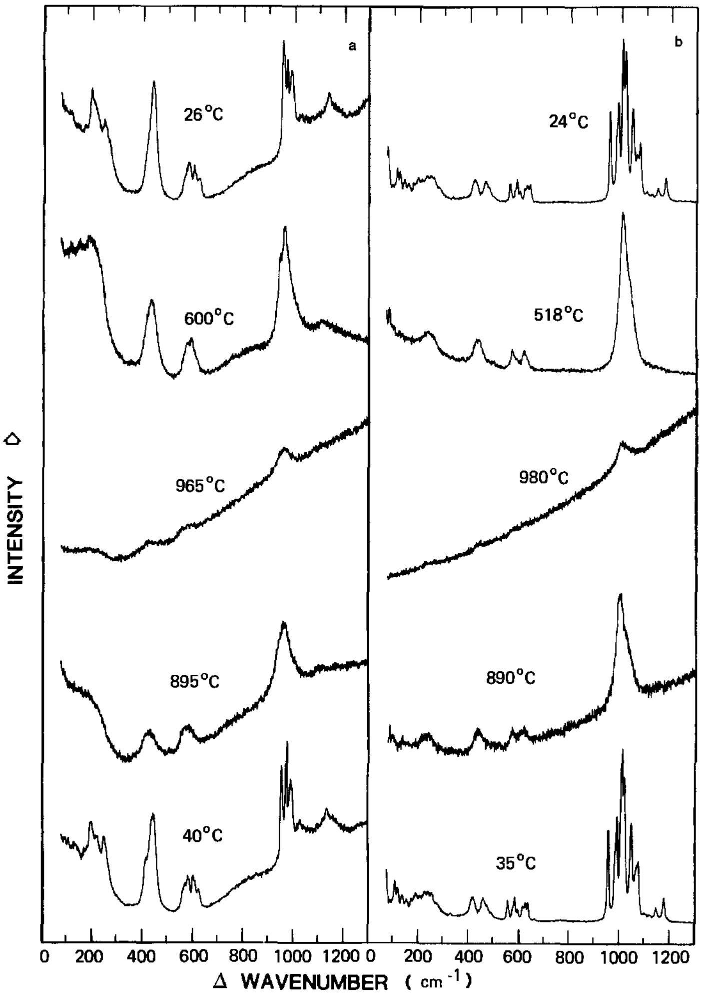

FIG. 5. Raman spectra, from top, at increasing and then decreasing temperatures of (a) mixture of phases V and VI of $Na_3Ho(PO_4)_2$ where the disappearance of phase VI can be inferred from the shift of the main peak to higher frequencies; (b) $Na_3Yb_2(PO_4)_3$ (the conversion of phase γ to IX and black to γ can be seen as a function of temperature).

obtained on cooling to 250°C and room temperature. The sequence of spectra with both increasing and decreasing temperature is shown in Fig. 5a.

A pellet of phase V with composition $Na_3Dy(PO_4)_2$ was heated and kept 18 hr at 1050°C while spectra were recorded at various temperatures. At 750°C the spectrum showed that its three peaks fused into a single one which was located at $\sim$16 cm^{-1} lower than the most intense of the three peaks at room temperature. On cooling to room temperature the spectrum of phase V was obtained. This result together with that obtained from the mixture of phases V and VI of $Na_3Ho(PO_4)_2$ indicates that phase V is the more stable form at room temperature for lanthanides heavier than Tb.

The effect of increasing the temperature, up to 900°C, on phase γ $Na_3Yb_2(PO_4)_3$ was to change significantly its Raman spectrum to that of phase IX. On cooling to room temperature the spectrum indicated that phase IX was converted to γ. The corresponding spectra showing these changes are shown in Fig. 5b. The effect of increasing and then decreasing temperature on $Na_3Lu_2(PO_4)_3$ with the structure of phase IX was to convert it into a mixture of phase IX and exsoluted $LuPO_4$. The results indicate that in general phase IX is stable at temperatures above 500°C while phase γ is stable at lower temperatures. However, the fact that phase IX was observed with stoichiometry $Na_3Ln(PO_4)_2$ for Ln = Tm and Tb and with $Na_3Ln_2(PO_4)_3$ for Ln = Y, Ho, and Lu, while the latter compound exsolutes $LuPO_4$ upon heating, suggests that the value of x in $Na_{3(1+x)}Ln_{(2-x)}(PO_4)_3$ (which can vary between 0 and 0.5) may be dependent on the temperature. This is quite reasonable on the basis that such stoichiometry may represent solid solutions in the system $LnPO_4$–$Na_3Ln(PO_4)_2$.

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