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VIBRATIONAL SPECTRA OF ARSENATES AND PHOSPHATES
OF THE TYPE $\text{KCaLn}(\text{XO}_4)_2$

Key words: IR spectra, Raman spectra, factor group analysis, influence of cations.

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ABSTRACT

The infrared and Raman spectra of polycrystalline samples of different compounds of the types $\text{KCaLn}(\text{AsO}_4)_2$ and $\text{KCaLn}(\text{PO}_4)_2$, belonging to the hexagonal LaPO_4 structural modification, were recorded and discussed. A complete vibrational assignment, based on a factor group analysis, is proposed. The influence of the different lanthanide cations on the internal vibrations of the XO_4 groups is briefly discussed and some comparisons with related compounds are also made.

It is well known that simple lanthanide arsenates, phosphates, vanadates and chromates (V) of the type LnXO_4 belong to two different structural types.

The compounds with the bigger cations adopt the monoclinic monazite-like structure, whereas those with the smaller cations crystallize in the tetragonal zircon-structural type^{1,2}. In the limiting region between the two structural types some dimorphic phases are found. These are PmAsO_4 ³, TbPO_4 ⁴, $\text{LaVO}_4/\text{CeVO}_4$ ^{5,6} and PrCrO_4 ⁷ respectively.

On the other hand, lanthanum phosphate and other lighter lanthanide phosphates can exist as $\text{LnPO}_4 \cdot 0.5 \text{H}_2\text{O}$ in a metastable hexagonal modification⁸.

A series of triple arsenates and phosphates of the type $\text{ABLn}(\text{XO}_4)_2$, with $\text{A} = \text{K, Rb, Cs}$; $\text{B} = \text{Ca, Sr}$; Ln = trivalent lanthanide cation, belonging also to this last mentioned structural type have been prepared and characterized recently⁹⁻¹¹. Therefore, it seems interesting to investigate the vibrational behaviour of these new materials in order to extend our knowledge on the spectroscopic properties of lanthanide compounds in different crystalline environments.

In order to start a systematic study of this type of phases we have prepared a number of arsenates and phosphates of K/Ca with different lanthanide cations, i.e., $\text{KCaLn}(\text{AsO}_4)_2$ with $\text{Ln} = \text{Nd, Sm, Eu, Gd, Dy, Ho}$ and $\text{KCaLn}(\text{PO}_4)_2$ with $\text{Ln} = \text{Sm, Eu, Gd, Dy, Ho, Er}$. Compounds with other lanthanide cations could not be obtained in adequate purity grades.

Structural Characteristics

As stated above, the prepared compounds are isostructural with the hexagonal LaPO_4 form. A complete structural analysis of one of these phases, namely $\text{KCaNd}(\text{PO}_4)_2$, was published some years ago¹². The space group is $\text{P6}_222 (\text{D}_4^4, \text{Nr.180})$ and one $\text{K}_{1.5}\text{Ca}_{1.5}\text{Nd}_{1.5}(\text{PO}_4)_3$ formula in the unit cell.

The structure is built up by chains of edge sharing $(\text{Ca}, \text{Ln})_8$ -polyhedra and tetrahedral XO_4 -groups interconnected by corner sharing. The structure is also characterized by the presence of large tunnels which run parallel to the crystallographic c axis. The larger K^+ ions can be accommodated in these tunnels.

As it was expected the volume of the unit cell diminishes regularly, as the Z-value of the incorporated lanthanide cation increases. The volume contraction is more pronounced in the case of the phosphate series, due probably to the smaller size of the PO_4^{3-} ion.

Analysis and Discussion of the Spectra

In the investigated compounds the tetrahedral oxo-anion lies on sites of D_2 -symmetry. This fact implies a total removal of degeneracies of all the vibrational modes, but the symmetric stretching and bending modes remain infrared-inactive.

As the unit cell contains three XO_4 -groups it seems appropriate to analyze the vibrational behaviour of the full cell through a correlation with the factor group D_6 .

Table 1 shows the correlation between the point group of the "free" ion with its site-symmetry and also with the corresponding factor group.

As typical examples of the measured spectra, Fig. 1 shows the IR spectrum of $\text{KCaEu}(\text{AsO}_4)_2$ whereas Figures 2 and 3 show the Raman spectra of $\text{KCaSm}(\text{AsO}_4)_2$ and $\text{KCaDy}(\text{PO}_4)_2$ respectively. The other substances show very similar spectra.

In the IR spectra, the ν_3 region usually shows three well defined bands or two bands and a shoulder. No evidences were found for the ν_1 band, in agreement with the predictions of Table 1. On the other hand, in the deformation region, only two of the three pre-

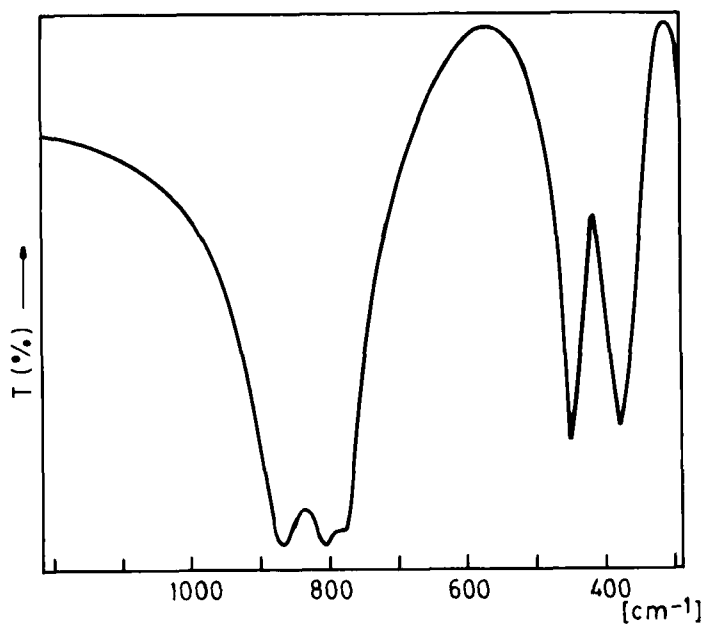


FIG.1. Infrared Spectrum of $\text{KCaEu}(\text{AsO}_4)_2$

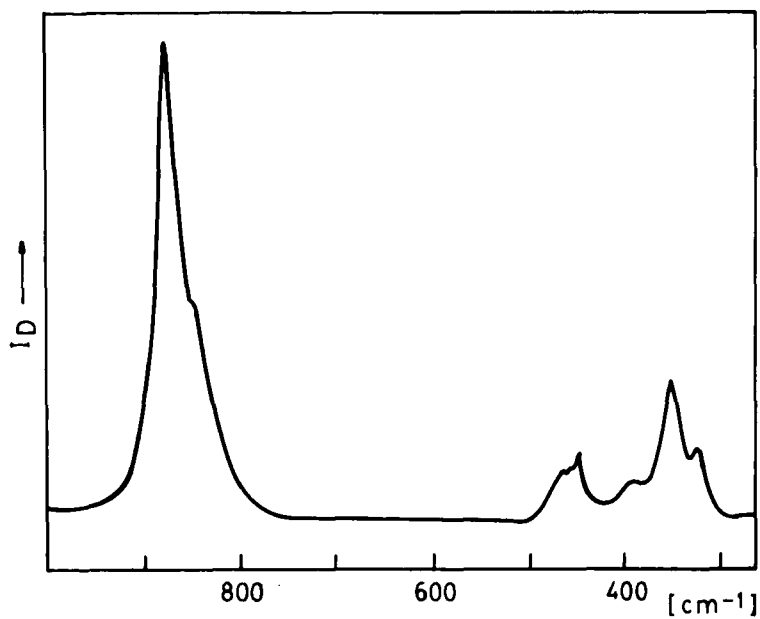


FIG.2. Raman Spectrum of $\text{KCaSm}(\text{AsO}_4)_2$

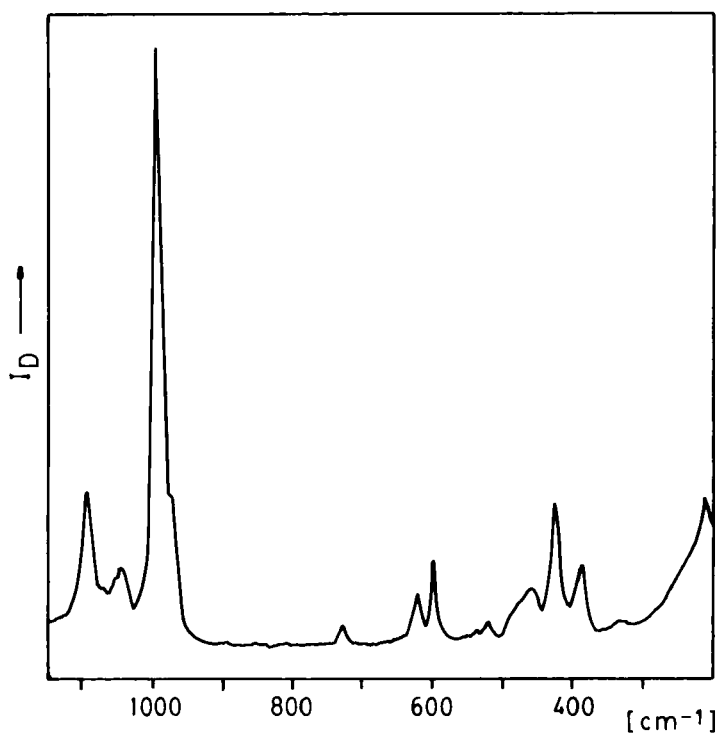


FIG.3. Raman Spectrum of $\text{KCaDy}(\text{PO}_4)_2$

TABLE 1
Correlation Between the Point Group T_d , the
Site-Symmetry D_2 and the Factor Group D_6

Mode	T_d	D_2	D_6
ν_1	A_1	A	$A_1 + E_2$
ν_2	E	2A	$2A_1 + 2E_2$
ν_3	F_2	$B_1 + B_2 + B_3$	$A_2 + B_1 + B_2 + 2E_1 + E_2$
ν_4	F_2	$B_1 + B_2 + B_3$	$A_2 + B_1 + B_2 + 2E_1 + E_2$
<u>Activity:</u>			
IR	F_2	$B_1; B_2; B_3$	$A_2; E_1$
Raman	$A_1; E; F_2$	$A; B_1; B_2; B_3$	$A_1; E_1; E_2$

dicted ν_4 -components are observed, although in some cases one of these bands is rather asymmetric. The ν_2 mode satisfies also the site-symmetry and factor group predictions and could not be observed in any of the IR spectra.

In the Raman spectra, the two components expected according to the factor group analysis for the ν_1 mode are always observed although that of lower frequency is usually weak or badly defined. In the phosphates, ν_3 can be generally observed as a triplet of lines of weak or medium intensity, but it remains unobserved in all the arsenates. In these cases these bands are probably overlapped by the stronger ν_1 -components (remember also that in the "free" AsO_4^{3-} ion ν_3 and ν_1 are practically coincident¹³). The Raman spectra in the deformation region shows ν_2 and ν_4 as strong and medium intensity doublets respectively. However, in the case of the phosphates, two additional weaker lines, located at higher frequencies, are seen near the ν_2 -doublet (cf. Fig. 3), in agreement with the factor group predictions. In most cases, some other weak lines, probably assignable to external (lattice) or combinational modes, are also distinguished in this region.

Tables 2 and 3 show the values measured in all the investigated compounds together with the proposed assignments.

In conclusion, the general spectroscopic behaviour clearly indicates important factor group effects, which suggest important interactions between the XO_4 -anions in the unit cell, a point of view which is supported by the structural characteristics of this structural type.

Furthermore, it is interesting to investigate in some detail the influence of the different lantha-

TABLE 2
Assignment of the IR and Raman Spectra
of the $\text{KCaLn}(\text{AsO}_4)_2$ -Phases (values in cm^{-1})

Ln	Mode	IR	RAMAN
Nd	ν_1 :	---	871vs, 845m
	ν_2 :	---	~ 345w
	ν_3 :	875vs, 810vs, 788sh	---
	ν_4 :	455vs, 385vs	~445 w
Sm	ν_1 :	---	875vs, 847sh
	ν_2 :	---	385w, 345s, 320m
	ν_3 :	865vs, 810vs, 785sh	---
	ν_4 :	450vs, 390vs	461m, 452m, 445m
Eu	ν_1 :	---	876vs, 844sh
	ν_2 :	---	344s, 319w
	ν_3 :	865vs, 805vs, 780m	---
	ν_4 :	445vs, 375vs	460w, 445m
Gd	ν_1 :	---	878vs, 845m
	ν_2 :	---	335m, 340m, 312m
	ν_3 :	870vs, 815vs, 795sh	---
	ν_4 :	440vs, 373vs	462w, 437m
Dy	ν_1 :	---	881vs, 840sh
	ν_2 :	---	387w, 348s, 322m
	ν_3 :	870vs, 812vs, 795sh	---
	ν_4 :	455vs, 395vs	463w, 448sh
Ho	ν_1 :	---	882vs, 840sh
	ν_2 :	---	347s, 320m
	ν_3 :	870vs, 815vs, 797sh	---
	ν_4 :	452vs, 393vs	462m, 444m

vs = very strong; s = strong; m = medium; w = weak;
sh = shoulder

TABLE 3
Assignment of the IR and Raman Spectra
of the $\text{KCaLn}(\text{PO}_4)_2$ -Phases (values in cm^{-1})

Ln	Mode	IR	RAMAN
Sm	ν_1 :	---	991vs, 977sh
	ν_2 :	---	485sh, 458w, 428s, 388m
	ν_3 :	1075vs, 1000vs, 941m	1091s, 1060sh, 1048m
	ν_4 :	605vs, 530vs	625m, 600m
Eu	ν_1 :	---	993vs, 974m
	ν_2 :	---	478sh, 458w, 427s, 390m
	ν_3 :	1075vs, 1000vs, 940m	1095m, 1055w
	ν_4 :	600vs, 517vs	626m, 601m
Gd	ν_1 :	---	995vs, 978m
	ν_2 :	---	484sh, 460m, 430s, 390m
	ν_3 :	1087vs, 1010vs, 965m	1095s, 1057sh, 1047m
	ν_4 :	610vs, 530vs	627m, 602s
Dy	ν_1 :	---	997vs, 977sh
	ν_2 :	---	478sh, 462w, 431s, 393m
	ν_3 :	1085vs, 1010vs, 965s	1097s, 1057sh, 1048m
	ν_4 :	625vs, 560vs	627m, 603s
Ho	ν_1 :	---	997vs, 975m
	ν_2 :	---	466w, 432s, 393m
	ν_3 :	1090vs, 1010vs, 960sh	1099m, 1060w
	ν_4 :	615vs, 535vs	629w, 604m
Er	ν_1 :	---	1000vs, 985sh
	ν_2 :	---	476w, 464w, 434m, 396w
	ν_3 :	1087vs, 1010vs, 975m	??
	ν_4 :	615vs, 530vs	630w, 605w

vs = very strong; s = strong; m = medium; w = weak
sh = shoulder

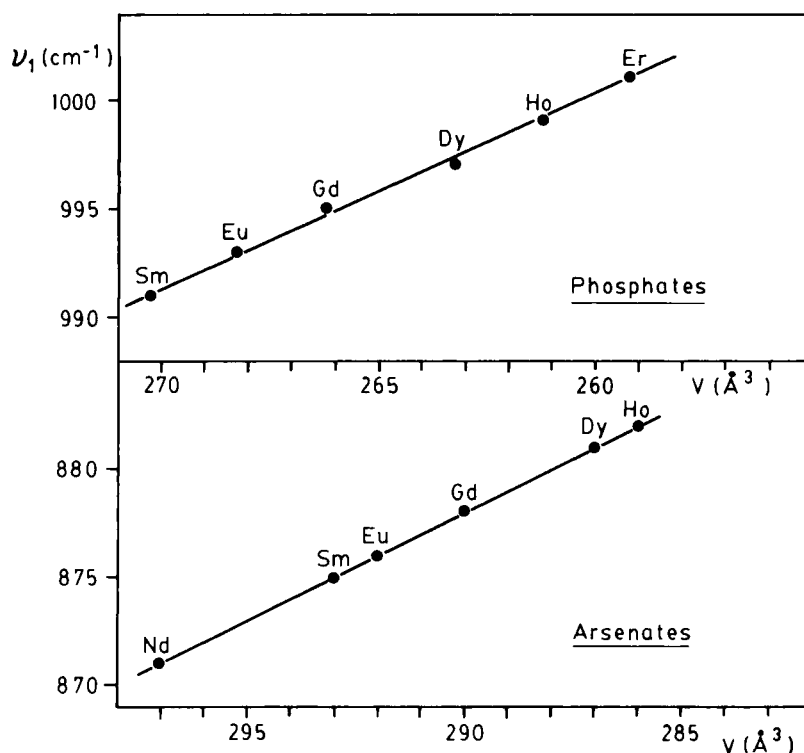


FIG.4. Dependence of the ν_1 -stretching mode of the XO_4 -groups from the unit cell volume.

nide cations on the internal vibrations of these XO_4 -anions. As in other cases, in which this aspect was analyzed, the value of the symmetric stretching modes, obtained from the Raman spectra seems the most suitable for such study, due to its high intensity and very good definition (cf. for example¹⁴⁻¹⁶).

A plot of the higher-frequency component of this stretching mode as a function of the unit cell volume shows a linear relation between both values as can be seen from Fig.4 for the two investigated series of com

pounds. This behaviour implies, that as a direct consequence of the volume diminution from Nd to Ho, the X-O bonds are reinforced and generate the observed increase in the stretching vibration, following the same direction. A totally similar behaviour was found and extensively discussed, in the case of the lanthanide orthovanadates, LnVO_4 , belonging to the zircon-structural type^{17,18}. The present results confirm also our previous statement: for oxoanions joined to lanthanide cations, the effect of the contraction in the unit cell dimensions overrides that of the increase of the effective nuclear charge of the cations.

It is also interesting to notice that a similar dependence of ν_1 from the cell dimensions has been recently observed in a large series of phosphates belonging to the eulytite-structural type¹⁹.

Finally, it is interesting to compare the values of Tables 2 and 3 with those reported for simpler orthophosphates²⁰ and orthoarsenates²¹ of the lanthanides. Despite the different structural types involved, the frequency values are found in very similar ranges.

EXPERIMENTAL

1.Syntheses of the compounds. The compounds were prepared by solid state reactions between appropriate amounts of CaCO_3 , K_2CO_3 , As_2O_5 (or $(\text{NH}_4)_2\text{HPO}_4$) and the respective lanthanide oxide⁹⁻¹¹. Maximum heating temperature was 900°C and the heating time around 48 hs.

2.Spectra. The IR spectra were recorded on a Perkin Elmer 580 B spectrophotometer using the KBr-pellet technique. Raman spectra of the crystal powders sealed in glass capilars were obtained on a SPEX-Ramalog 1403-double monochromator spectrometer equipped with a SCMP controll unit and employing the 488 nm-line of an argon-ion laser for excitation.

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