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Structure and site-symmetry investigation on the hexagonal $KCaY(PO_4)_2$

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Abstract

A new double phosphate, $KCaY(PO_4)_2$, isostructural with hexagonal $LaPO_4$, is reported. It crystallizes in the hexagonal system with $a = 0.6903$ nm and $c = 0.6331$ nm. Its vibrational spectra, IR and Raman spectra showed that the site symmetry of the PO_4 anion slightly deviated from D_2 toward C_2.

Keywords: Site symmetry; IR spectra; Raman spectra

1. Introduction

In recent years, double phosphates with the general formula $ABln(PO_4)_2$ (A = alkali, B = alkaline earths and Ln = rare earths) have been paid increasing attention [1–7]. Three types of these phosphates, hexagonal [3], tetragonal [5] and monoclinic [8], could be classified. They were considered to be the varieties of corresponding orthophosphates $LnPO_4$. In order to search for new and economical as well as highly efficient phosphors and to investigate the effects of the channels existing in orthophosphates and the roles of the neighboring cations on the energy transfer between activator and sensitizer and the interactions between them, we have started a series of studies based on the three kinds of host mentioned above.

It was found that phonons in the hexagonal double phosphate play a significant role in the energy transfer in the system of $KCaY(PO_4)_2$:Dy^{3+} [9]. Hence it is necessary to explore which vibrations participate into the energy migration process. We chose a representative $KCaY(PO_4)_2$ to carry out our studies; the structural data of this compound have not been reported. Its IR and Raman spectra, representative of the hexagonal double phosphates $ABLn(PO_4)_2$, are firstly reported herein.

2. Experimental

2.1. Synthesis of the samples

The raw materials, containing $(NH_4)_2HPO_4$, K_2CO_3, $CaCO_3$ (all in analytic grade) and Y_2O_3 (purity, 99.99%) were mixed together stoichiometrically with NH_4Cl as a flux and pressed into an alumina crucible; they were heated for 6 h at 300 °C followed by two heat treatments, one for 6 h at 880 C and the other for 6 h at 1020 °C. In order to obtain a single phase in shorter time, use of the flux with two interposed grindings was necessary. In comparison with the process described in [3], our synthesis process takes only one third of the time required for preparing $KCaLn(PO_4)_2$.

2.2. X-ray powder diffraction

With the help of a Rigaku X-ray diffractometer (model D/max-IIB) and single-crystal Si powder as an internal standard, the X-ray diffraction (XRD) pattern of $KCaY(PO_4)_2$ was obtained. The unit-cell parameters were calculated from a least-squares refinement of 16 stronger Cu $K\alpha_1$ reflection planes ($\lambda = 1.540\,56$ Å) collected between $2\theta = 10°$ and $2\theta = 60°$ at room temperature.

2.3. IR and Raman spectra

A Fourier transform IR spectrometer (model BIO-RAD FTS-7) was used to measure the IR spectrum of the sample covering the wavenumbers 4000–400 cm^{-1} with KBr as diluent.

The Raman spectrum was obtained with an Ar-ion laser device ($\lambda = 514.5$ nm; model Ar-ion Spectra-Physics 171). The output power was 60 mW.

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Table 1
The XRD data of hexagonal $KCaY(PO_4)_2$

d_{obs} (Å)	hkl	I/I_o	d_{calc} (Å)
5.996	100	33	5.978
4.358	101	10	4.347
3.453	110	9	3.452
2.989	200	100	2.989
2.803	102	65	2.798
2.702	201	6	2.703
2.335	112	10	2.333
2.175	202	4	2.173
2.128	211	16	2.128
2.113	003	5	2.110
1.994	300	7	1.993
1.899	031	11	1.901
1.839	212	36	1.839
1.803	113	4	1.801
1.724	203	15	1.724
1.686	302	17	1.686
1.664	221	2	1.665
1.656	310	2	1.658
1.603	311	2	1.604

Table 2
Correlations between the symmetries and vibrations for the PO_4 group

Symmetry	ν_1	ν_2	ν_3	ν_4
T_d	A_1(R)	E(R)	F_2(IR, R)	F_2(IR, R)
D_2	A(R)	2A(R)	$B_1+B_2+B_3$ all IR, R	$B_1+B_2+B_3$ all IR, R
C_2	A(IR, R)	2A(IR, R)	A+2B all IR, R	A+2B all IR, R

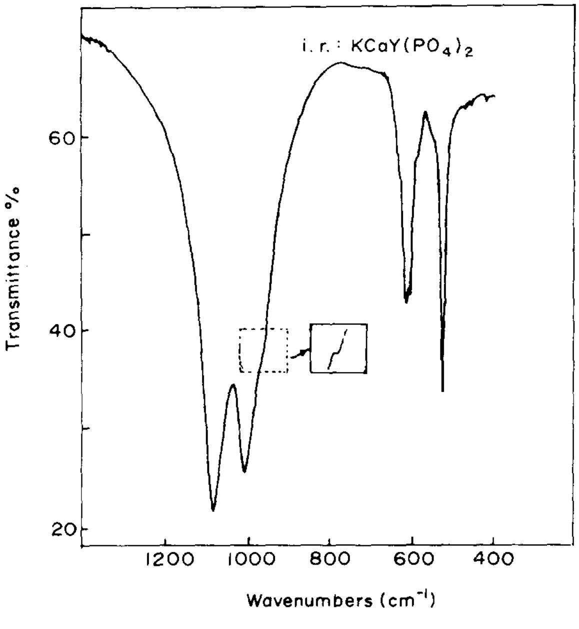

Fig. 1. IR spectrum of $KCaY(PO_4)_2$ with the KBr pellet technique at room temperature.

3. Results

3.1. Elemental, analysis data

The elemental analysis for the sample showed 17.20 wt.% P (theoretical amount, 17.30 wt.% P) 24.74 wt.% Y (theoretical amount, 24.83 wt.% Y), 10.9 wt.% Ca (theoretical value, 11.19 wt.% Ca) and 10.0 wt.% K (theoretical value, 10.92 wt.% K), which coincided with the composition $KCaY(PO_4)_2$ well. The former two elements, P and Y, were analyzed with traditional volumetric methods described in [8]; the latter two were based on an atom absorption spectrometry method.

3.2. X-ray diffraction data and cell parameters of $KCaY(PO_4)_2$

As given in Table 1 the XRD pattern for $KCaY(PO_4)_2$ is almost similar to that of $KCaDy(PO_4)_2$ [10] except for the different intensities of some reflection planes. Its cell parameters are $a=0.6903$ nm and $c=0.6331$ nm, which lie between those of $KCaDy(PO_4)_2$ and $KCaHo(PO_4)_2$ [3]. This is reasonable since the ionic radius of Y^{3+} ion is slightly larger than that of Ho^{3+} and smaller than that of Dy^{3+}.

3.3. IR and Raman spectra

The IR and Raman spectra of hexagonal $LnPO_4 \cdot 1.5H_2O$ (Ln = La–Tb) have been reported earlier [11,12]. The site symmetry for the PO_4 polyhedron was considered to be D_2 [11] or C_2 [12]. Table 2 gives the results of the group theory treatment for the PO_4 group lying in different site symmetries [12,13]. It can be seen that, for D_2 symmetry, six vibration modes corresponding to ν_3 and ν_4 would be expected. For C_2 symmetry, however, nine modes would be observed. The vibrations for Raman spectra in both D_2 and C_2 symmetry are similar to each other.

The IR and Raman spectra of $KCaY(PO_4)_2$ are shown in Fig. 1 and Fig. 2 respectively. The vibrational frequencies

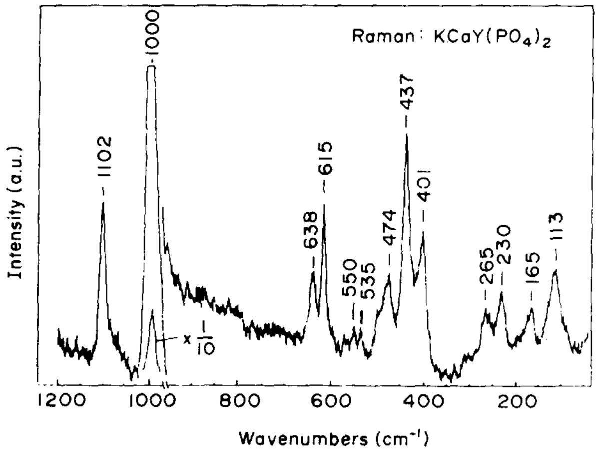

Fig. 2. Raman spectrum of $KCaY(PO_4)_2$ under Ar laser radiation with $\lambda_{ex}=514.5$ nm at room temperature (a.u., arbitrary units).

Table 3
Vibrational frequencies in the IR and Raman spectra of $KCaY(PO_4)_2$

Spectra	Composition	ν_3 (cm^{-1})	ν_1 (cm^{-1})	ν_4 (cm^{-1})	ν_2 (cm^{-1})	Rotation and translational vibration (cm^{-1})
IR	$KCaY(PO_4)_2$	1084.7 1009.6	970.4sh	615.1, 607.7sh 586.4sh, w 528.7	440vvw	–
	$LaPO_4 \cdot 1.5H_2O$ [12]	1044 1012	961sh	615 567 538	–	–
	$LaPO_4$ [11]	1100–1000	?961sh	616 565sh, w 540	?450vvw	–
Raman	$KCaY(PO_4)_2$	1102	1000vs	638 615 550w 535w	474 437 401	265 230 165 113

are summarized in Table 3. For comparison the IR vibrations of hexagonal $LaPO_4 \cdot 1.5H_2O$ are also quoted here.

4. Discussion

Early in 1950, Mooney [14] pointed out that open oxygen-lined channels along the *c* axes in hexagonal $LnPO_4$ (Ln = La–Nd) could readily accommodate a neutral molecule of water (up to a maximum, $1.5H_2O$ per unit to form $LnPO_4 \cdot 1.5H_2O$) or moderately sized ions if the charges were compensated in some way. He also suggested that the occupancy of the channels would stabilize the hexagonal phase of $LnPO_4$, and it was not possible to obtain an anhydrate hexagonal $LnPO_4$ by drying $LnPO_4 \cdot 1.5H_2O$. Instead, a monoclinic phase formed during the process of dehydration.

Considering there is not sufficient zeolithic water in hexagonal $LnPO_4$, one can expect that a short-range order in crystals would occur, i.e. (i) most of the PO_4 polyhedra have a higher symmetry (i.e. D_2), and a few PO_4 possess lower symmetry (say, deviating from D_2 and close to C_2) because of no water molecules occupying the neighboring channels and (ii) for LnO_8 polyhedra in $LnPO_4$, similarly, most have D_2 symmetry and a few show C_2. In order to maintain long-range order the PO_4 and LnO_8 polyhedra have to undergo a little adjustment, which would mean that their site symmetry slightly deviates from D_2 and is close to C_2. These deviations seem too weak to be distinguished by the XRD method (sometimes some broadened peaks may appear). With the help of vibrational and emission spectra, however, they could be revealed clearly [15]. Hence, for hexagonal $LnPO_4$ we mainly observed the vibrations of PO_4 anion pertaining to D_2 symmetry in the IR spectrum. On the contrary, the slightly distorted PO_4 polyhedron in hexagonal $LnPO_4$ must be responsible for these weak vibrations, i.e. a 961 cm^{-1} shoulder (ν_1 mode) and very very weak vibrations at about 450 cm^{-1} (ν_2, cf. Table 3).

For hexagonal $KCaY(PO_4)_2$, based on the structure of $KCaNd(PO_4)_2$ [6] and the discussion above, we can say Ca^{2+} ions replace half the Ln^{3+} in $LnPO_4$ and the K^+ ions, replacing the zeolithic water, go into the channels as the charge compensators. As a result, disorders of the superstructure and K^+ and Ca^{2+} distributions would occur besides deviation from stoichiometry. Consequently, the deviations of site symmetry for the PO_4 polyhedron in $KCaY(PO_4)_2$ are more severe to some degree than that in $LnPO_4 \cdot 1.5H_2O$. This is why besides the ν_1 mode a surplus peak at 607.7 cm^{-1} (ν_4) and several very weak vibrations at about 440 cm^{-1} (ν_2) can be observed in the IR spectrum of $KCaY(PO_4)_2$ (see Fig. 1 and Table 3).

For the Raman spectrum of $KCaY(PO_4)_2$, it seems hard to discern whether the distortions mentioned above exist or not, since the Raman activities under D_2 and C_2 symmetries are the same (cf. Table 2). However, neglecting some surplus vibrations (say, at around 535 cm^{-1} and 401 cm^{-1}, both are very weak), we did find that the vibrations for ν_4 and ν_2 as well as ν_1 are in agreement with D_2 site symmetry. These surplus weak vibrations are the proof of the deviations which lower the symmetry of PO_4 from D_2 to C_2. In addition, the ν_1-mode vibration (A_g, at 1000 cm^{-1}) seems too strong in comparison with that of orthophosphates [16]. It might be related to the large change in polarization from $LnPO_4$ to $KCaY(PO_4)_2$ or to the superimposition of ν_1 and ν_3. For the ν_3 modes we observed only one vibration (belonging to B_g) instead of three. This may be on account of the ν_3 modes pertaining to the B_g species; the other two vibrations may be too weak to be detected or overlap the ν_1 mode.

For the site symmetry of Ln^{3+} in hexagonal $KCaLn(PO_4)_2$, the emission spectrum of $KCaEu(PO_4)_2$ [7] and Eu^{3+}-doped $KCaGd(PO_4)_2$ [9] have clearly shown that the Eu^{3+} ions occupy a site symmetry sligthly deviating from D_2 and close to C_2 symmetry, i.e. the number of $^5D_0$–^7F_j (j = 0, 1, 2) emission lines was one, three and five respectively, instead of zero, three and three.

Finally, in the light of our recent work, this deviation (lower D_2 to C_2) can be observed in all hexagonal $ABLn(PO_4)_2$, i.e. they all show similar vibrational spectra and emission spectra when doped with Eu^{3+}. Further, the isomorphous substitutions of A and B by Li^+ and/or Mg^{2+} respectively would enhance this deviation [17].

5. Conclusion

For hexagonal $KCaY(PO_4)_2$ and its analogues, $ABLn(PO_4)_2$, the following conclusions can be drawn on the basis of this work.

(i) The Ln^{3+} ion in hexagonal $LnPO_4$ can be replaced by an A^+ and B^{2+} ion; meanwhile the symmetry for PO_4 and RO_8 (R = Ln or Ca) polyhedra would slightly deviate from D_2 symmetry and become close to C_2.

(ii) Vibration (IR and Raman) and emission spectra of Eu^{3+} ion are powerful techniques for determining the deviations of site symmetry in crystal lattices.

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