INFRARED AND RAMAN SPECTRA OF CAK₃H(PO₄)₂

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Abstract

Even though we tried to get a deuterated analogue of $K_3CaH(PO_4)_2$ we did not have success, therefore we focused on the specters of protiated analogue of the said compound. The structure of $K_3CaH(PO_4)_2$ is determined by x-ray diffraction. [1]. The compound crystallizes in the monoclinic system (space group $C2/m$ respectively C_{2h}^3) with two-unit formulas in the elementary cell. The structure of this compound characterizes with the existence of symmetrical dimers $[H(PO_4)_2]$, similar like the $Mg_2KH(PO_4)_2 \cdot 15H_2O$ and $Mg_2KH(AsO_4)_2 \cdot 15H_2O$ [7]. The IR and Raman spectra are recorded at room temperature and at the boiling temperature of liquid nitrogen (LNT).

Keywords: Potassium calcium hydrogen phosphate, X-ray diffraction, Infrared spectroscopy; Raman spectroscopy

1. Introduction

We have discussed in detail the vibrational spectra of $CaK_3H(PO_4)_2$. Unfortunately, we didn't succeed in getting a deuterated analog of the compound. This made it harder to analyze the vibrational spectra of this compound. Therefore, we mainly focused our analyzes on the vibrational spectra of $MgNa_3H(PO_4)_2$ [24]. With that we had in mind that $CaK_3H(PO_4)_2$ and $MgNa_3H(PO_4)_2$ are not isostructural compounds, even though both compounds belong to the same glaserit type of structure. Respectively, it was found that $MgNa_3H(PO_4)_2$ crystalizes in the triclinic crystal system, the centrosymmetric space group $P1$ respectively Ci[1] [25], whereas $CaK_3H(PO_4)_2$ crystalizes the monoclinic system (space group $C2/m$ respectively C₂ₕ³).

The FTIR spectra recorded at room temperature and lower temperature the Raman spectra recorded at room temperature of $CaK_3H(PO_4)_2$ indicate that they differ from those of $MgNa_3H(PO_4)_2$ [24], even though it was expected of them to be very similar. As we can see the are some strips that are sensitive to temperature, which in the infrared LNT spectra are found in 1490, 1190, 940, 800 and 475 cm⁻¹. All of these strips can be described as the vibrations in which the proton takes part. According to the intensity, the strips in 1490 and 1190 cm⁻¹ can be described as δ (OH) and γ (OH) modes, the strip with weak intensity in 940 cm⁻¹ vibrations of HPO_4, whereas the strips around 800 and 475 cm⁻¹ width, the vibrations of the OHO group from the symmetrical dimer $[H(PO_4)_2]$.

## 2. Body of Manuscript

The infra-red specter was recorded with the infrared interferometer Perkin-Elmer System 2000 FT-I in the zone from 4000 to 380 cm-1 with a resolution from 2 to 4 cm-1, there were collected r 32 infrared spectra (FT-IR) furie- transforming. Different techniques were used to get the substance ready to be recorded, like the recordings in the suspensions of different oils and tablets of KBr. Otherwise, the spectra were recorded at different temperatures, from room temperature (RT) to the boiling point of liquid nitrogen (LNT). For the

recordings of the infrared spectra at the boiling point of liquid nitrogen, the cell for low temperature used P / N 21525 with KBr tablets, in which the substance that is prepared for the recording is placed. For the making and processing of the FT-IR spectra, the GRAMS ANALYST 2000 GRAMS 32 programs were used.

THE Raman spectra are recorded at room temperature with the mikroraman spectrometry LabRam 300 (Horiba Jobin-Yvon) using a He-Ne laser (red) at 633 nm and Nd: YAG laser (green) 532 nm. To focus the laser we used an Olympus MplanN microscope with the ability to zoom up to 50x. The spectra were recorded in a zone from 4000 up to 100 cm-1, and there were 15-30 spectra accumulated with a resolution of 2 cm-1. To get the Raman spectra and to process them LabSpec [6] dhe GRAMS 32 [5] programming packets. Rentgen diffractograms of compounds were obtained using the Rigaku Ultima IV diffractometer with CuKα radiation while using a 40 kV generator and a current of 40 mA. The prepared samples were placed in a carrier from calcium or glass while using a D/tex detector in the 2θ from 5 in 80 ° with a recording velocity of 10 ° / min.

3. Table Figures and Equations
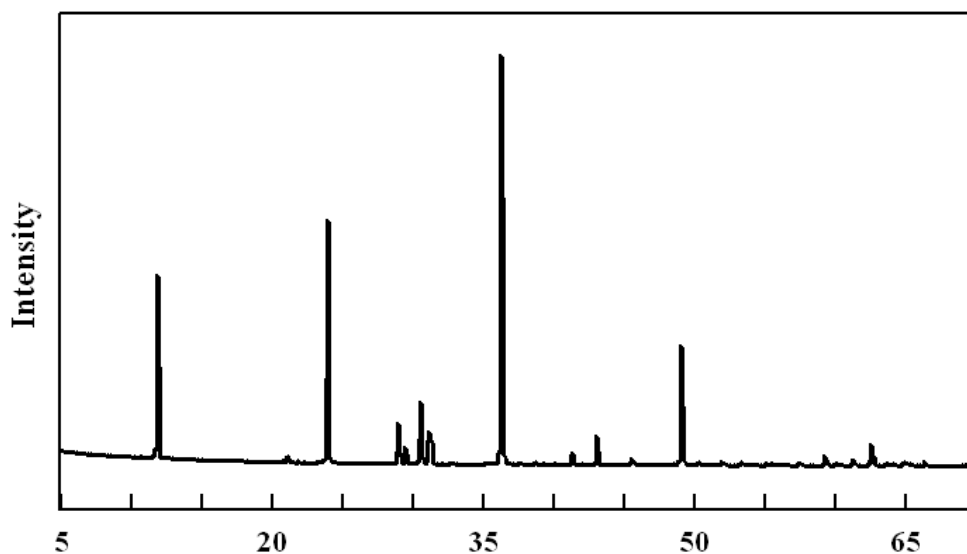
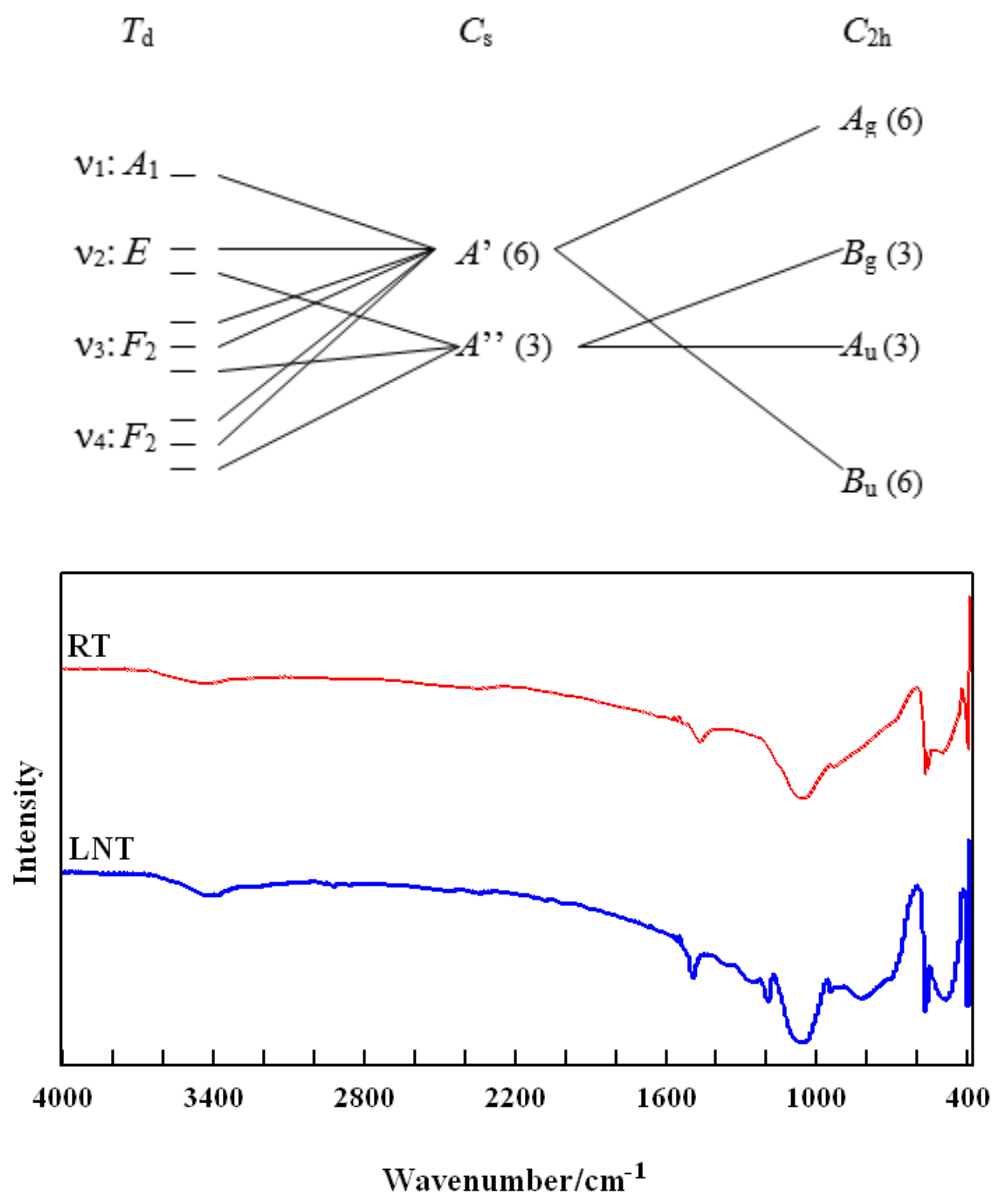**Figure 1**. Roentgenogram of the analyzed sample of $CaK_3H(PO_4)_2$

Table 1. Some interatomic distances and angles in the structure of **$CaK_3H(PO_4)_2$** [1]

Interatomic distance/ pm		angles / °	
P–O(1)	152,6(2)	O(1)–P–O(2)	108,5(1)
P–O(2)	156,0(2)	O(1)–P–O(3)	111,0(1)
P–O(3)	153,2(1)	O(2)–P–O(3)	108,2(1)
Ca–O(1)	234,8(1)	O(3)–P–O(3)	109,8(1)
Ca–O(3)	231,8(1)		
K(1)–O(1)	288,8(2)		
K(1)–O(2)	312,5(2)		
K(1)–O(3)	302,6(2)		

Table 2. The results of the elementary cell vibration analyzes for the inner modes of $PO_4{}^{3-}$ of $CaK_3H(PO_4)_2$.

T_d C_s C_{2h}

A_g (6)

$v_1: A_1$ —

$v_2: E$ = A' (6) B_g (3)

$v_3: F_2$ = A'' (3) A_u (3)

$v_4: F_2$ =

B_u (6)

RT

Intensity

LNT

4000   3400   2800   2200   1600   1000   400

Wavenumber/cm^{-1}

Figure 2. FTIR spectra of $CaK_3H(PO_4)_2$ recorded in room temperature (upper graph) and in low temperature (lower graph).
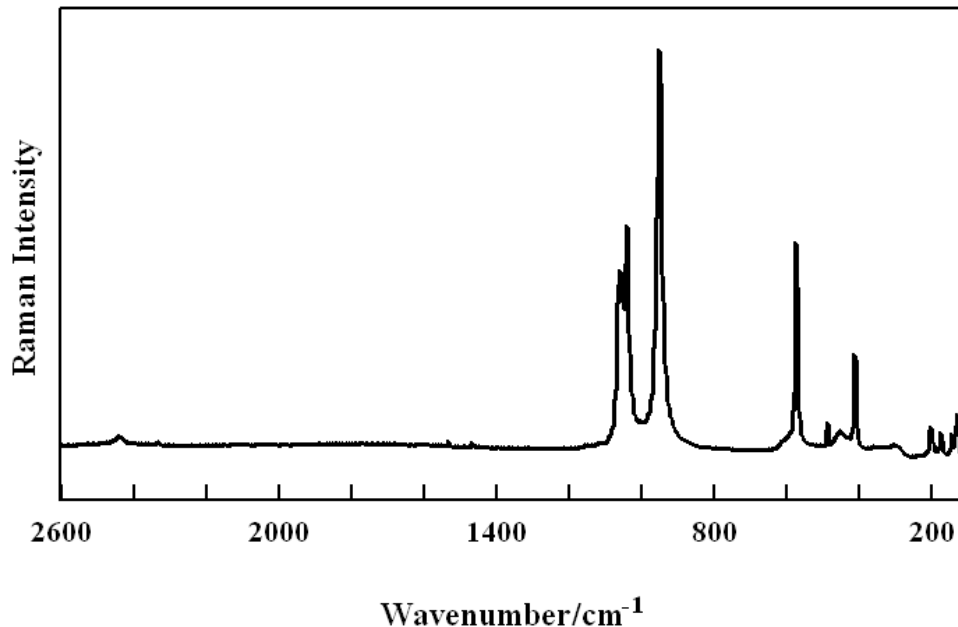
Figure 3. Raman spectra of $CaK_3H(PO_4)_2$ recorded in room temperature

FTIR spectra recorded at room temperature and low temperature and the Raman spectra of $CaK_3H(PO_4)$ recorded at room temperature are shown in Fig. 2 and 3. From the spectra, we see that they differ from those of $MgNa_3H(PO_4)_2$ [24], even though it was expected of them to be very similar. As we can see there are some strips sensitive to temperature, which in the LNT infrared spectra are found in 1490, 1190, 940, 800, and 475 cm^{-1}. All these strips can be described as the vibrations in which the proton takes part. According to the intensity, the strips in 1490 and 1190 cm^{-1} can be described as δ (OH) and γ (OH) modes, the strip with low intensity in 940 cm^{-1} vibrations of HPO_4, whereas the strips that are wide around 800 dhe 475 cm^{-1} vibrations of the OHO group from the symmetrical dimmer $[H(PO_4)_2]$.

According to the position and the high intensity, we can certainly describe the unsymmetrical wide strip to the vibrations of $\nu_3(PO_4)$, The burning strips with low intensity in the Raman spectra are shown in 1055 and 1037 cm^{-1} . The more intense strip in 948 cm^{-1} with high reliability can be described as the $\nu_1(PO_4)$ mode. The two strips in 567 and 555 cm-1, and one in 570 cm^{-1} in the Raman spectra we describe the $\nu4(PO4)$ vibrations. While the strips that are around 400 and 410 cm^{-1} that are seen in the infrared and Raman spectra, can be described as the $\nu_2(PO_4)$ modes. The strips under 200 cm^{-1} come from the net's modes.

4. Conclusions

Hydrogen-containing salts are of wide scientific interest due to their ferroelectric and antiferroelectric properties as well as their conductive properties.
Here we have to emphasize that the precise recording of the strips that come as a result of the vibrations in which the acidic proton takes part can't be made without the spectra of the deuterated analogues.

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