Crystal structure, thermal behaviour, vibrational spectroscopy and optical properties of new compounds $K_2Ca(HAsO_4)_2 \cdot 2H_2O$ with kröhnkite-type chain

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Abstract. The new kröhnkite compound called potassium calcium-bis-hydrogen arsenate dihydrate $K_2Ca(HAsO_4)_2 \cdot 2H_2O$ was obtained by hydrothermal method and characterized by X-ray diffraction, infrared spectroscopy, Raman scattering, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis and optical (photoluminescence and absorption) properties. It crystallizes in the triclinic space group $P\bar{1}$ and unit cell parameters $a = 5.971(3)$ Å, $b = 6.634(3)$ Å, $c = 7.856(4)$ Å, $\alpha = 104.532(9)°$, $\beta = 105.464(9)°$ and $\gamma = 109.698(9)°$. The structure of $K_2Ca(HAsO_4)_2 \cdot 2H_2O$ built up from this infinite, $(Ca(HAsO_4)_2(H_2O)_2)^{2+}$, was oriented along an axis resulting from the association of CaO_6 octahedra alternating with each two $HAsO_4$ tetrahedra by sharing corners. Each potassium atom links two adjacent chains by three oxygen atoms of $HAsO_4$ tetrahedra. TGA and DSC have shown the absence of phase transition. The existence of vibrational modes corresponding to the kröhnkite is identified by the IR and Raman spectroscopies in the frequency ranges of 400–4000 and 20–4000 cm^{-1}, respectively. The photoluminescence measurement show one peak at 507 nm, which is attributed to band–band (free electron–hole transitions) and (bound electron–hole transitions) emissions within the AsO_4 inorganic part.

Keywords. Kröhnkite; X-ray diffraction; vibrational studies; thermal analysis; photoluminescence absorption.

1. Introduction

The present study is an extension to our work on the crystal structures of the mineral kröhnkite, $Na_2Cu^{II}(SO_4)_2 \cdot 2H_2O$ [1]. Kröhnkite-type compounds contain infinite $[M(XO_4)_2 \cdot 2H_2O]$ chains, where M is a divalent (Mn, Fe, Co, Ni, Cu, Zn or Cd) or a trivalent (Al, Fe or In) cation and X is pentavalent (P or As) or hexavalent (S, Se, Cr or Mo), containing infinite octahedral–tetrahedral chains [2,3]. The compounds are reported to form triclinic crystals (space group $P\bar{1}$) with similar lattice parameters [4].

Indeed, recent single-crystal X-ray diffraction data of $K_2Mg(CrO_4)_2 \cdot 2H_2O$ [5] and $K_2Cd(CrO_4)_2 \cdot 2H_2O$ [6] have confirmed the statement that both compounds are isostructural and can be assigned to the structural type A (see classification in [2]) of compounds containing kröhnkite-type chains.

In this study, we report the description structure of new monoarsenate (IV) associated with calcium and potassium

cations to give $K_2Ca(HAsO_4)_2 \cdot 2H_2O$ formulation. The structure contains kröhnkite-type chains of type A with $HAsO_4$ tetrahedra, rarely encountered in the literature. Only four compounds are reported in the literature. The vibrational behaviour of $HAsO_4^{2-}$ guest ions in $K_2Ca(HAsO_4)_2 \cdot 2H_2O$ is described. Finally, the results of the thermal analysis are discussed.

2. Experimental

2.1 *Synthesis*

Crystals of $K_2Ca(HAsO_4)_2 \cdot 2H_2O$ were prepared by the hydrothermal synthesis.

A mixture of K_2CO_3 (solubility: 1120 g l^{-1}), $CaCO_3$ (solubility: 0.013 g l^{-1}) and H_3AsO_4 (solubility: 16.7 g per 100 ml) was placed in a Teflon vessel, which was filled with 80% water

and enclosed in a stainless steel bomb. The mixture was heated at 180°C under autogenous pressure for 72 h.

The title compound was prepared according to the following chemical reaction:

$$K_2CO_3 + CaCO_3 + 2H_3AsO_4 \longrightarrow K_2Ca(HAsO_4)_2 \cdot 2H_2O + Ca(OH)_2 + 2CO_2.$$
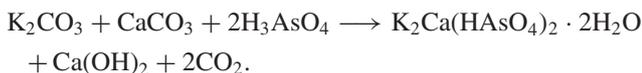
2.2 *X-ray data collection*

A single crystal was carefully selected under polarising microscope and mounted on MicroMount needle (MiTeGen). X-ray single crystal data were collected at room temperature on an APEX II Quazar diffractometer (4-circle Kappa goniometer, IμS microfocus source (MoKα), CCD detector). The structure was solved by direct methods with SHELXS-97 and SHELXL-97 programs included in WINGX package [6–8]. The hydrogen atoms were located in the Fourier maps and constrained in distance and angle (DFIX and DANG options). The assignments of atoms in metal environments (M = K, Ca and As) were based on M–O distances and thermal motion considerations. The crystal data and refinement details are given in table 1. The final atomic coordinates and U_{eq} are given in tables 2 and 3. Interatomic distances and bond angles are listed in table 4. The crystallographic projections were drawn with diamond [8].

2.3 *Infrared measurement*

The Fourier transform infrared (FTIR) spectrum of the title compound was recorded in the range of 4000–400 cm^{-1} with samples in KBR pellets using Perkin–Elmer FTIR spectrometer. The resolution of the spectrum was ±2 cm^{-1}.

2.4 *Raman scattering*

Furthermore, the Raman spectrum was measured with a LABRAMHR 800 triple monochromator under a 50*LF objective microscope. A He–Ne ion laser operating at about 20 mW was used (on the sample) as an excitation source (514.5 nm) with spectral steps of 3 cm^{-1}.

2.5 *Thermal behaviour*

Thermal stability was measured by using TGA (Perkin–Elmer, model: Pyris 6 TGA) in alumina crucible under a nitrogen flow of 20 ml min^{-1} with a heating scan rate of 10°C min^{-1} over the temperature range of 30–800°C. The analyses were performed by Perkin–Elmer software.

Thermal properties were measured by using DSC (Perkin–Elmer, model: Pyris Diamond) in aluminium caps under a nitrogen flow at a heating/cooling rate of 10°C min^{-1} over the temperature range of 30–450°C. The analyses were performed by Perkin–Elmer software.

Table 1. Summary of crystallographic data of $K_2Ca(HAsO_4)_2 \cdot 2H_2O$.

Crystal data	
Formula	$K_2Ca(HAsO_4)_2 \cdot 2H_2O$
Compound name	Potassium calcium calcium-bis[(hydrogen arsenate)]
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
a (Å)	5.971(3)
b (Å)	6.634(3)
c (Å)	7.856(4)
α (°)	104.532(9)
β (°)	105.464 (9)
γ (°)	109.698 (9)
V (Å^3)	261.7(2)
Z	1
Formula weight (g mol^{-1})	434.17
μ (mm^{-1})	2.702
ρ_{cal} (g cm^{-3})	2.754
Experimental details	
Diffractometer	Bruker APEX II
Temperature (K)	296(2)
Θ range (°)	2–30.5
Limiting indices	$-8 \leq h \leq 8$
	$-9 \leq k \leq 9$
	$-11 \leq l \leq 11$
Collected reflections	4799
Unique reflections [(R(int)]	1475
Parameters	79
Goodness-of-fit on F^2	1.096
Final R indices	0.0255
R indices (all data)	0.0680
Largest diff. peak and hole/e (Å^{-3})	$-0.739/0.891$

Table 2. Fractional atomic coordinates and equivalent isotropic displacement in $K_2Ca(HAsO_4)_2 \cdot 2H_2O$.

Atom	x	y	z	U_{iso}
As1	0.02656(4)	0.37497(4)	0.23721(3)	0.01143(9)
K1	0.34931(11)	0.02212(10)	0.22988(8)	0.02170(13)
Ca1	0.500	0.500	0.000	0.01216(14)
O1	0.1763(3)	0.3228(3)	0.0940(3)	0.0196(4)
O2	−0.2835(3)	0.3027(3)	0.1222(3)	0.0189(4)
O3	0.0570(3)	0.2390(3)	0.3902(2)	0.0179(4)
O4	0.1825(3)	0.6707(3)	0.3759(3)	0.0196(4)
OW1	0.6906(4)	−0.1846(3)	0.2930(3)	0.0201(4)

2.6 *Absorption and photoluminescence measurements*

A Perkin–Elmer LS 55 spectrometer exciting with 350 nm radiation were used to record the room temperature photoluminescence spectrum. Optical absorption spectrum of

Table 3.   Anisotropic displacement parameters in $K_2Ca(HAsO_4)_2 \cdot 2H_2O$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
As1	0.01066(13)	0.01209(14)	0.01354(13)	0.00510(10)	0.00201(9)	0.00624(9)
K1	0.0236(6)	0.0223(3)	0.0269(3)	0.0141(3)	0.0127(2)	0.0124(2)
Ca1	0.0111(3)	0.0126(3)	0.0141(3)	0.0056(2)	0.0057(2)	0.0057(2)
O1	0.0218(9)	0.0209(9)	0.0230(9)	0.0099(8)	0.0165(7)	0.0095(7)
O2	0.0123(7)	0.0212(9)	0.0232(9)	0.0081(7)	0.0041(7)	0.0099(7)
O3	0.0219(9)	0.0172(9)	0.0166(8)	0.0087(7)	0.0063(7)	0.0105(7)
O4	0.0194(8)	0.0112(8)	0.0258(9)	0.0037(7)	0.0119(7)	0.0038(7)
OW1	0.0187(8)	0.0162(9)	0.0197(9)	0.0052(7)	0.0024(7)	0.0062(7)

Table 4.   Selected inter-atomic distances (Å) and bond angles in $K_2Ca(HAsO_4)_2 \cdot 2H_2O$.

Bond lengths (Å)		Angles (°)	
As–O$_4^{3-}$ anion			
As1–O1	1.6541(17)	O1–As1–O2	113.53(10)
As1–O2	1.6632(18)	O1–As1–O3	110.35(9)
As1–O3	1.6825(18)	O1–As1–O4	107.85(9)
As1–O4	1.7488(19)	O2–As1–O3	109.77(9)
		O2–As1–O4	108.79(9)
		O3–As1–O4	106.27(9)
Calcium coordination			
Ca–O1	2.3082(18)		
Ca–O1^{vi}	2.3082(18)		
Ca–O2^{iii}	2.3274(19)		
Ca–O2^{vii}	2.3274(19)		
Ca–OW1^{viii}	2.357(2)		
Ca–OW1^{ix}	2.357(2)		
Potassium coordination			
K1–O1	2.838(2)		
K1–OW1	2.822(2)		
K1–O2^{i}	2.882(2)		
K1–O2^{iii}	2.831(2)		
K1–O3	2.9426(19)		
K1–O4^{iv}	2.851(2)		

Symmetry codes: (i) $-x, -y, -z$; (ii) $x-1, y, z$; (iii) $x+1, y, z$; (iv) $x, y-1, z$; (v) $-x+1, -y+1, -z+1$; (vi) $-x+1, -y+1, -z$; (vii) $-x, -y+1, -z$; (viii) $-x+1, -y, -z$; (ix) $x, y+1, z$.

the spin-coated films was deduced from direct transmission measurements performed using a conventional UV–Vis spectrophotometer (Hitachi, U-3300).

3.   Results and discussion

3.1   *Structure description*

The asymmetric unit of $K_2Ca(HAsO_4)_2 \cdot 2H_2O$ is built by an $HAsO_4$ anion, calcium and potassium. The main geometrical features like bond distances and angles are reported in table 4.

As we can see in figure 1, the structure of this compound consists essentially anionic entities of $HAsO_4$, these tetrahedrals are located in (0 1/4 3/4), between these groups and the cationic entities of potassium and calcium are intercalated.

The atomic arrangement of $K_2Ca(HAsO_4)_2 \cdot 2H_2O$ represents a new structure type among the large group of compounds [2,3,9] with the general formula $A_2Me(XO_4)_2 \cdot 2H_2O$, containing kröhnkite-type chains. This infinite $[Ca(HAsO_4)_2(H_2O)_2]$ was oriented along an *a* axis resulting from the association of CaO_6 octahedra alternating with each two $HAsO_4$ tetrahedra by sharing corners. Each potassium atom links two adjacent chains by three oxygen atoms of $HAsO_4$ tetrahedra (figure 1).

The majority of such compounds belong either to the monoclinic kröhnkite structure type (P21/c, 'type D' in the A–G classification according to the refs [2,3,9,10]), or to the closely related triclinic collinsite structure type P-1, 'type A'.

The calcium is surrounded by four equatorial oxygen atoms common to adjacent $HAsO_4$ tetrahedra ($d_{Ca-O} \approx 2.33$ Å) and by two opposite water molecules in axial position ($d_{Ca-Ow} \approx 2.33$ Å). The mean Ca–O distance of 2.33 Å is similar to data from related compound, e.g., 2.28 Å in $CdCrO_4 \cdot 2H_2O$ [5].

The general features of the potassium environments of the studied compound are very similar to those found in the literature. In fact, they are six-coordinated atoms with K–O bonds < 2.82 Å (not listed in [3]), and have virtually identical mean ⟨K–O⟩ distances.

Each potassium atom links two adjacent chains by four oxygen atoms of $HAsO_4$ tetrahedral and two oxygen atoms to molecule water. The two water molecules in $K_2Ca(HAsO_4)_2 \cdot 2H_2O$ are involved in well-defined hydrogen bonds with Ow···O distances ranging between 2.688 and 2.724 Å (table 5).

The AsO_4 group is fairly regular, with a small bond-length distortion (table 4), O–As–O angles ranging between 106.27(9) and 113.53(10)°, and an average As–O bond length of 1.68715 Å, very close to the average value in arsenates (⟨As–O⟩ = 1.682 Å; [11]). The As–O distances are in good agreement with several phases containing monoarsenate groups known in the literature [12,13].

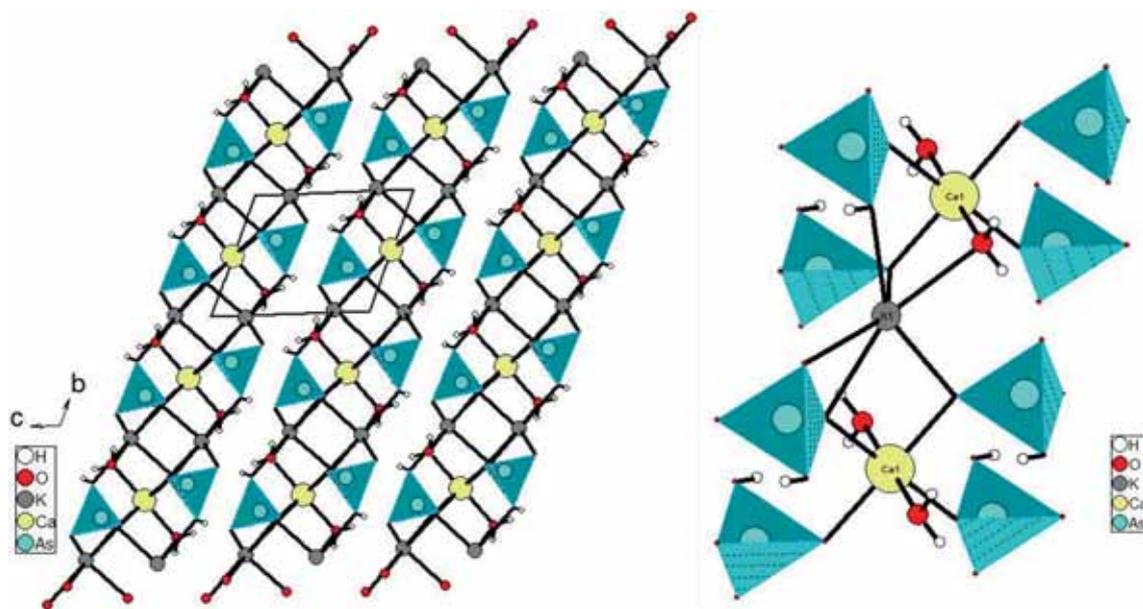**Figure 1.** Projection (left) and view of kröhnkite-type infinite chain in $K_2Ca(HAsO_4)_2 \cdot 2H_2O$.

Table 5. Bond lengths (Å) and angles (°) in the hydrogen-bonding scheme.

D–H$\cdots$A	D–H	H$\cdots$A	D$\cdots$A	D–H$\cdots$A
O3–H1$\cdots$O4	0.720	1.973	2.688	172.20
O2–HW1$\cdots$O4	0.840	1.926	2.724	158.26
O4–H3$\cdots$O2	0.719	2.031	2.670	148.37

Symmetry codes: (i) $[-x, -y, -z+1]$; (ii) $[-x+1, -y, -z+1]$; (iii) $[-x, -y, -z]$; (iv) $[x-1, y, z]$.

3.2 Vibrational studies

To provide more information on the crystal structure, we have studied the vibrational properties of our compound using infrared absorption and Raman scattering.

The computed wavenumbers and their IR and Raman intensities corresponding to different modes are listed in table 6 with detailed assignments. In addition, the IR and Raman spectra are presented in figures 2 and 3, respectively.

3.2a *Vibration of $HAsO_4^{2-}$ anion*:
The normal modes of vibration in isolated AsO_4 tetrahedra with an ideal T_d symmetry were widely studied [14]. The ν_1 and ν_3 symmetric and asymmetric stretching modes are observed in 1200–900 cm^{-1} region, whereas the ν_2 and ν_4 symmetric and asymmetric bending modes are distinguished in 600–400 cm^{-1} domain [14,15].

The medium band at 870 cm^{-1} in Raman spectrum is assigned to the asymmetric stretching $\underline{\nu}_3$ mode of the arsenate ion. In IR spectrum, this mode also appears as a single

Table 6. IR and Raman frequencies (cm^{-1}) and band assignment at room temperature.

IR (cm^{-1})	Raman (cm^{-1})	Intensity	Assignments
435	437	s	$\nu_2(AsO_4)$
452			
472			
590	540	m	$\nu_4(AsO_4)$
628	629		
669			
748	753	m	$\gamma(H_2O)$
775	—	s	$\nu_1(AsO_4)$
—	855	s	$\nu_3(AsO_4)$
870			
1202	1219	m	$\delta(As-O-H)$
1227			
1774	1762	m	$\delta(O-H\cdots O)$
	1782		
2184	2335	m	
2205			$\nu(OH)$ "A + B + C"
2658	2736	m	$\nu(OH)$ "A + B + C"
3419	3443	w	$\nu(OH)$ "A + B + C"

s, strong; m, medium; w, weak; δ, in-plane bending; γ, out-of-plane bending; ν, stretching.

medium band at 855 cm^{-1}. The wavelength is 863 cm^{-1}, which is similar to data of compound related, for example, 831 cm^{-1} in $NH_3(CH_2)_6HAsO_4 \cdot 2H_2O$ [16].

We distinguish the ν_1 (AsO_4) by intense Raman bands at $\sim$775 cm^{-1}.

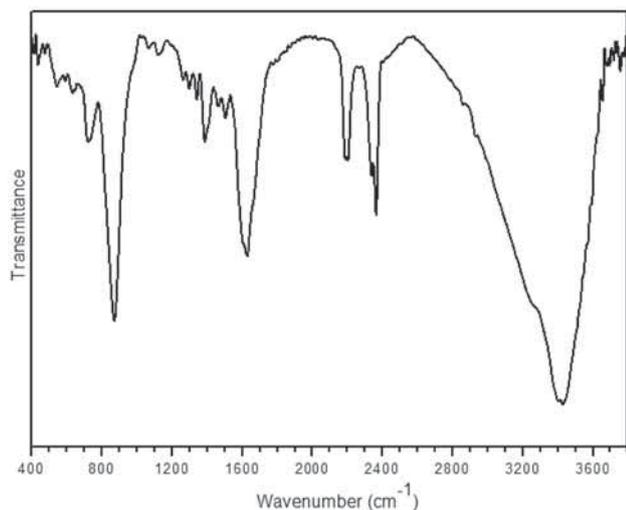This can be explained by the presence of two different As–O distances in AsO_4^{3-} groups.

Figure 2. IR spectra of $K_2Ca(HAsO_4)_2 \cdot 2H_2O$.

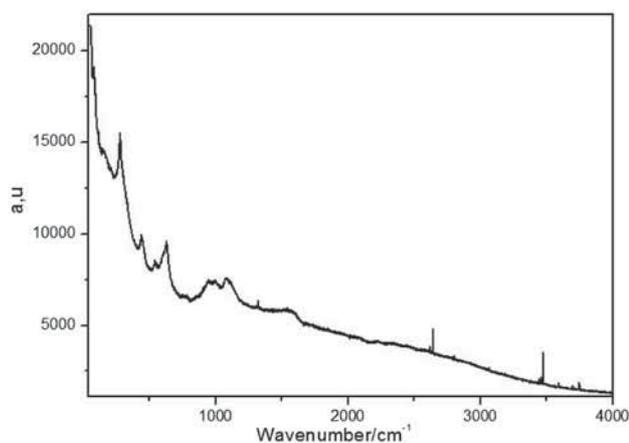**Figure 3.** Raman spectra of $K_2Ca(HAsO_4)_2 \cdot 2H_2O$.

In fact, Debrus *et al* [17], when performed an X-ray diffraction study on the title crystal, revealed four different As–O bond values in the $HAsO_4^{2-}$ groups, which can be classified as As–O and As–OH types. Taking into account, the effect of intermolecular interactions on geometrical parameters, we have considered the cluster built up from two acids $[H_2AsO_4]^-$, water molecule linked by O–H$\cdots$O hydrogen bonds and mineral group.

The distances of these bond distances are between 1.65 and 1.75 Å, respectively. The greatest distance corresponds to lowest wavenumber at 855 and 870 cm^{-1}.

The major peaks observed in the region between 435 and 669 cm^{-1} are associated with ν_2 and $\nu_4 AsO_4^{3-}$ tetrahedra ($\nu_4 > \nu_2$). The two weak bands near 1227 and 1202 cm^{-1} in IR and 1219 cm^{-1} in Raman can be assigned to the δ(As–O–H) bending vibration. Third vibrational modes associated with the hydroxyl groups are taken into consideration. There should be three such modes, O–H stretching, As–O–H in plane bending and As–O–H out-of-plane bending.

These wave numbers are in good agreement with monoarsenate groups known in the literature [18–20].

3.2b *The vibration of water molecule*: The broad lines at 3419, 2658 and 2205 and 3443, 2736 and 2335 cm^{-1} in IR and Raman, respectively, can be assigned to the A–B–C bands of OH stretching vibrations in the title compound [21–24]. Accordingly, the observed band at 1774 cm^{-1} in infrared and two pictures in Raman at 1762 and 1782 cm^{-1} are assigned to the δ(HOH) mode of the water molecule. In the IR spectrum, a very weak band appears at 748 cm^{-1} and the corresponding Raman band is also observed as a medium band at 753 cm^{-1}. These bands are attributed to the O–H out-of-plane deformation.

3.3 *Thermal behaviour*

The TGA curve shows that the compound is in the range from 30 to 800°C (figure 4). The first interval of temperature, 70–100°C, corresponds to the departure of two water molecules (calc. 8% and exp. 8.5%). As shown in figure 5, this thermal phenomenon is attributed to the endotherm at 90°C.

The second weight loss occurs over the temperature range of 270–494°C. Approximately, 4% of the mass is lost, which corresponds to one molecule of water per formula unit. This result is well confirmed by the consistent peak at 157°C in DSC [25]. Finally, the third weight corresponds to $Ca(OH)_2$ degradation, gives rise to the endothermic peak located at 498°C well-confirmed by the consistent peak at 481°C in DSC [26].

3.4 *Optical study*

The title compound exhibits strong blue luminescence at 507 nm (2.44 eV) when excited at 376 nm, which can be observed even with the naked eye at room temperature. The luminescence originates from the electronic transition in the AsO_4 tetrahedra. A simple model illustrating
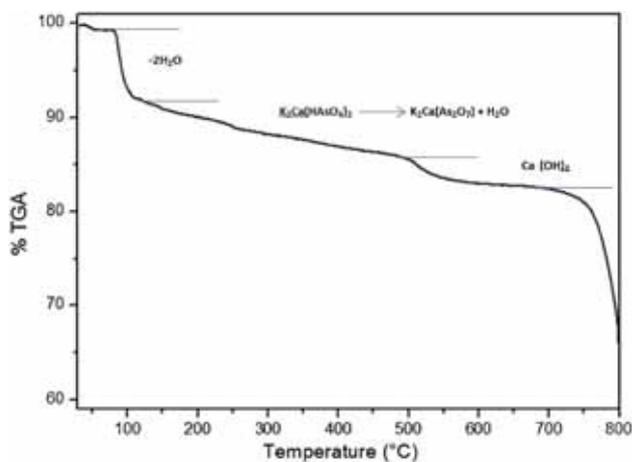

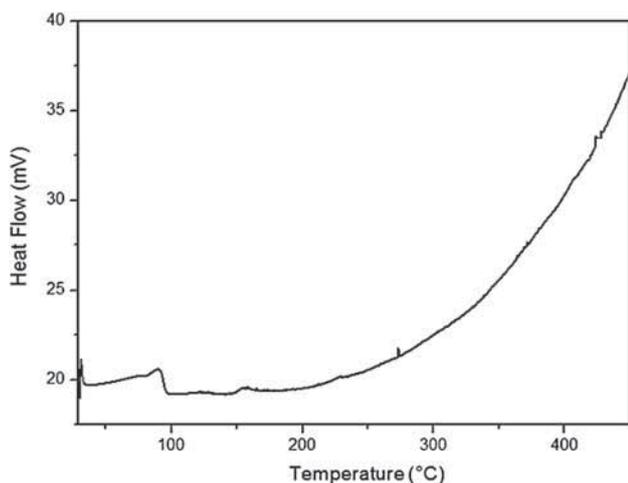**Figure 4.** TGA curves of $K_2Ca(HAsO_4)_2 \cdot 2H_2O$.

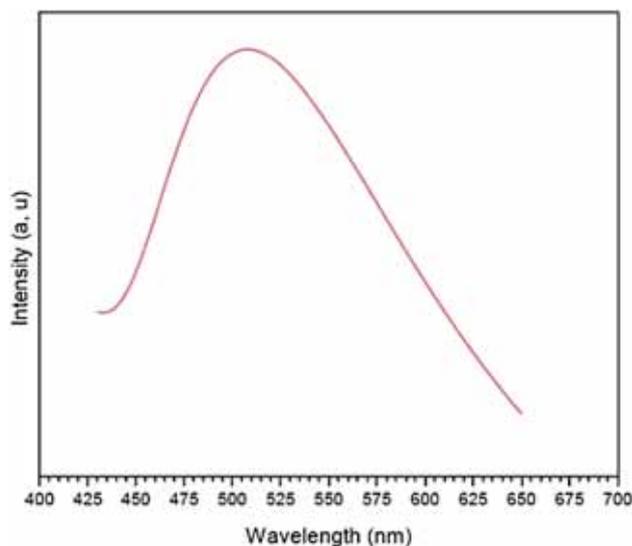**Figure 5.** DSC curve of $K_2Ca(HAsO_4)_2 \cdot 2H_2O$.

Figure 6. Luminescent excitation of $K_2Ca(HAsO_4)_2 \cdot 2H_2O$.

the formation and recombination process of the exciton in $(C_5H_7N_2)_2CuCl_4 \cdot H_2O$. Under the excitation of 376 nm irradiation, an electron $(-)$ is excited from the valance band (VB) composed of As $(3d)$ + O $(2p)$ orbitals to the conduction band (CB) formed by the As $(4p)$ orbital, leaving a hole $(+)$ in the VB. The electron $(-)$ and the hole $(+)$ move freely in the CB and VB, forming an exciton. The recombination of the electron and hole in the exciton yields a green emission at 507 nm. This result suggests potential uses for this material as UV detection and non-linear optical materials (figure 6).

4. Conclusions

The chemical preparations, crystalline structure determination, thermal analysis and the vibrational study of a new

potassium calcium-bis-hydrogen arsenate dihydrate K_2Ca $(HAsO_4)_2 \cdot 2(H_2O)$ were described. This compound belongs to the triclinic system with $P\bar{1}$ space group. The vibrational properties of this structure were studied by infrared and Raman spectroscopies. The thermal analysis of this compound was studied by DSC and TGA in the temperature range between 30 and 800°C. The optical properties were investigated by photoluminescence measurement. A strong green excitonic emission was observed at room temperature.

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