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Research Article

Keywords: Absorption, gap energy, Urbach energy.

Posted Date: September 27th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-932638/v1>

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UV-Visible characterization of Zinc and Potassium Zinc pyrophosphate

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Abstract

New $\text{Zn}_2\text{P}_2\text{O}_7$, $\text{K}_2\text{ZnP}_2\text{O}_7$ and $\text{KZn}_{1.5}\text{P}_2\text{O}_7$ compounds were synthesized with conventional solid solid reaction method. The optical properties have been studied by using UV-Visible spectrophotometer. The optical band gaps (E_g) were found to be 3.76 eV, 3.39 eV and 3.59 eV respectively. Optical parameters such as refractive index, Cauchy's parameters and conductivity were deduced. The refractive index fitting in the visible range and the dispersion parameters (E_0 and E_d) of these compounds were estimated using the Wemple–DiDomenico model.

Keywords: Absorption, gap energy, Urbach energy.

Introduction

Diphosphates are technologically important because of their various properties like fluorescent, luminescent, semiconductor, catalytic, dielectric, magnetic, and ion-exchange [1]. Therefore, systematic preparative and structural studies on pyrophosphate with general formula $\text{A}_{2-2x}\text{B}_{1+x}\text{P}_2\text{O}_7$ (with $0 \leq x \leq 1$) have been undertaken during the last years. In this paper we will interest with $\text{Zn}_2\text{P}_2\text{O}_7$, $\text{K}_2\text{ZnP}_2\text{O}_7$ and $\text{KZn}_{1.5}\text{P}_2\text{O}_7$ compounds. These samples are characterized by different structural arrangement. The $\text{Zn}_2\text{P}_2\text{O}_7$ structure reveals twelve form groups per mesh formed by three types of phosphorus and three types of Zn^{2+} cation, it can be described by the alternation of anionic and cationic layer in (0, 1, 0) direction. The anionic layer is formed by infinite chains of dimer $\text{P}_2\text{O}_7^{4-}$, which develop in the a direction. These chains are formed by two types of P_2O_7 groups gathered by clusters of two. The first

group is formed by two inequivalent phosphorus atoms (P1 and P2). The other is constituted by a single type of phosphorus. The two-dimensional cationic layer is shaped by crowns of polyhedra of the Zn^{2+} cation [2].

The $\text{KZn}_{1.5}\text{P}_2\text{O}_7$ structure contains the tetrahedral framework anion $[\text{ZnP}_2\text{O}_7]^{2-}$ which consists of $[\text{P}_2\text{O}_7^{4-}]$ diphosphate groups sharing common vertices with the adjacent $[\text{ZnO}_4]$ tetrahedral. This structure is characterized by the absence of any correlation between the Zn-O and P-O bond lengths and the coordination of the O atom by the K cations. This suggests that the K-O ionic bond weakly affects the sufficiently strong P-O and Zn-O bonded interactions [3].

The $\text{K}_2\text{ZnP}_2\text{O}_7$ structure is made up of $[\text{ZnP}_2\text{O}_7]$ layers consisting of corners sharing $[\text{P}_2\text{O}_7]$ groups and $[\text{ZnO}_4]$ tetrahedral, and the sodium atoms are located between the layers in 7- or 8-fold coordinated sites [4].

In previous works we studied the electrical and dielectrical properties of these three compounds and we determined the conduction mechanisms within each sample [5,6,7].

In the present work, we present and discuss their optical properties.

Experimental method

The studied compounds were prepared by conventional solid state reaction [5-7].

Zinc diphosphate $\text{Zn}_2\text{P}_2\text{O}_7$ was carried out by solid state reaction techniques. Stoichiometric quantities of ZnO, and $\text{NH}_4\text{H}_2\text{PO}_4$ were ground, mixed, and progressively heated first to 573 K with a heating step of $10^\circ/\text{min}$ to expel NH_3 , water and CO_2 , and then to 923 K ($10^\circ/\text{min}$). Mixed potassium zinc diphosphate $\text{K}_2\text{ZnP}_2\text{O}_7$ was obtained in a powder state from starting compounds (K_2CO_3 , ZnO and $\text{NH}_4\text{H}_2\text{PO}_4$) by means of solid state technique. The reagents are carefully mixed and progressively heated up to 573 K for 12 h to allow water, ammonia, and carbon dioxide vapors to evolve. After a final grinding, the powder is heated at 873 K for 12 h [8]. Then, a polycrystalline sample of the $\text{KZn}_{1.5}\text{P}_2\text{O}_7$ compound was prepared by the solid-phase reaction of $\text{Zn}_2\text{P}_2\text{O}_7$ with $\text{K}_2\text{ZnP}_2\text{O}_7$ according to the following reaction:

Stoichiometric proportions of $\text{Zn}_2\text{P}_2\text{O}_7$ and $\text{K}_2\text{ZnP}_2\text{O}_7$ are weighed and ground for 5 h; the powder is then pressed in tablet form 8 mm in diameter, to favor the mechanisms of condensation in the solid state reaction. The obtained pellets were fritted at 923 K for 12 h with a heating step of $5^\circ/\text{min}$.

The optical absorption spectra of our pyrophosphates samples were measured at room temperature using a UV-vis spectrophotometer (HITACHI, U-3300) in the wavelength range of 200–900 nm.

Optical properties

Optical absorption and optical energy gap

The skeleton covalency of the material are found by the UV-Vis spectroscopic technique, which relates the electronic contribution to the electrical conductivity. One of the most direct methods for probing the band structure of materials is to study their absorption spectra.

The experimental UV-Vis absorption spectra of $K_2ZnP_2O_7$, $KZn_{1.5}P_2O_7$ and $Zn_2P_2O_7$ compounds measured at room temperature in the wavelength region 200–800 nm is shows in Figure 1. The prominent peak centered at 216 nm, 221 nm and 219 nm respectively for $K_2ZnP_2O_7$, $KZn_{1.5}P_2O_7$ and $Zn_2P_2O_7$ compounds can be assigned to arise due to

$O^{2-} \longrightarrow Zn^{2+}$ charge transfer band [8]. These absorption spectra reveal a broad band having its maximum intensity at 350 nm for the three cited samples. This absorption band of PO_4^{3-} is caused by a charge transfer from the oxygen legends (O^{2-}) to the central phosphor atom (P^{5+}) [9]. This result is hopeful because these materials possess an excitation wavelength in the UV region. The P^{5+} ion has a closed-shell electronic structure. Considering the electronic structure of the PO_4^{3-} ion, one electron charge transfer process from the oxygen 2p orbital to the 3s orbital of the P^{5+} ion is involved in the excitation phenomenon.

To calculate the optical band gap of these phosphor materials, the absorption spectra so obtained for each sample was then converted into a remission function [10]:

$$\alpha = \frac{2,303}{d} A$$

With (α) the absorption coefficient, (A) is the absorbance and (d) is the thickness of the pellet. It is thus possible to work with the reflectance according to Kubelka–Munk (K–M) function [11] given by:

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty}$$

Where R_∞ is the diffused reflectance.

The energy band gap E_g of materials is related to the absorption coefficient (α) near the band edge by the Tauc equation [12] as:

$$(\alpha h\nu) = B(h\nu - E_g)^n$$

Where B is an energy-independent constant. So, $F(R_\infty)$ being proportional to α , yields:

$$[h\nu F(R_\infty)] = B(h\nu - E_g)^n$$

Depending on the mechanism of inter-band transitions, the index (n) takes different values. Those values may be equal to 1/2, 2, 3/2, and 3 for the allowed direct, allowed indirect, forbidden direct, and forbidden indirect transition, respectively. Figures 2 a, b and c show the variation of $(\alpha h\nu)^{1/n}$ versus the photon energy $h\nu$ for direct and indirect allowed transition. The values of the optical band gap energy E_g are normally obtained by screening of the linear part of the curve to intersect the x -axis at zero absorption [13]. For the three studied compounds the best fit is obtained for $n = 2$ proving the indirect transition. The calculated values of optical band gap energy E_g are summarized in Table 1. These values show that we can classify our samples as a semiconductor.

It is generally accepted that absorption edge depends on the oxygen bond strength in the material forming network, this process changes the oxygen bonding in network and any difference of this bond varies the absorption characteristics [14]. This explains the increasing of the optical band gap with increasing $\langle \text{Zn} - \text{O} \rangle$ distance.

Urbach energy

The disorder in crystallization of the material can be measured by the Urbach energy. Furthermore this energy evaluates the density of localized states in the band. There are absorption tails at energies smaller than E_g , and the absorption coefficient α can exhibit exponential behavior as [15]:

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_u}\right)$$

Where α_0 is a constant and E_u is an energy which is interpreted as the width of the tail of localized states in the forbidden band gap. To calculate E_u , a curves were plotted between $\ln(\alpha)$ and photon energy ($h\nu$) as shown in figure 3. The value of Urbach energy (E_u) is normally calculated by considering the reciprocal of the slope of the linear portion in the lower photon energy region of these curves [16]. The obtained E_u energies are given in table 1. It is noted that the founded Urbach energies are almost the same for all studied compounds. Furthermore, these values prove the presence of disorder in our pyrophosphate materials. This result can be explained by the existence of defects and grain boundary in these materials.

Refractive index

Accurate knowledge of the refractive index and its frequency dependence is very important. This index n was approximately calculating by using the following equation [17]:

$$n = \left[\frac{4R}{(R-1)^2} - k^2 \right]^{\frac{1}{2}} - \frac{R+1}{R-1}$$

Where k is the extinction coefficient. It is a measure of the fraction of light lost due to scattering and absorption per unit distance of the penetration medium. The extinction coefficient can be estimated from the values of α and λ as [18]:

$$k = \frac{\alpha\lambda}{4\pi}$$

The spectral distributions of the values of n versus wavelength (λ) for the titled pyrophosphates are shown in Figure 4. For each sample the behavior of the refractive index present peaks similar for that corresponding to the absorption spectra. This result is due to high energy transition [19]. In the range of (600–800) nm the n values decrease with increasing wavelength. This is in good agreement with the Cauchy theory [20]:

$$n = n_0 + \frac{A}{\lambda^2} + \frac{B}{\lambda^4} + \frac{C}{\lambda^6}$$

The fit (line) of experimental data was added in Figure 4. It demonstrates that these samples have a normal dispersion for the visible wavelength range. Cauchy's parameters are gathered in table 2.

The Wemple - DiDomenico model is the simplest general model to describe the interaction of optical radiation with a solid, this is the classic Lorentz model. For this model, valence electrons are assumed to be bonded to specific atoms in the solid by harmonic forces that tend to restore the valence electrons in specific orbits around the atomic nuclei. The solid is considered as a set of atomic oscillators, each with its own frequency. We assume that upon excitation of the oscillators at their own frequencies (Resonance Frequency) a resonance process occurs. In quantum physics, these frequencies correspond to those necessary to produce transitions from the valence band to the conduction band. The model of the single oscillator consists in considering one oscillator with a dominant contribution and with the energy parameters E_d and E_0 . Wemple-DiDomenico describes the refractive index by the following equation [21]:

$$n^2 = 1 + \frac{E_0 E_d}{E_0^2 - (h\nu)^2}$$

Where E_0 is the oscillation energy and E_d is the dispersion energy or dispersive energy.

The evolution of the refractive index ($n(\lambda)$) versus wavelength λ (Figure 4) in the transparency zone of our materials proves the validity of the harmonic oscillator. Using the Wemple-DiDomenico dispersion equation we can determine the dispersion parameters of the compounds. The parameters E_0 and E_d for our compounds were calculated from the slope of the linear part of the curve of $(n^2-1)^{-1}$ as a function of $(h\nu)^2$ as shown in Figure 5. Their values

are summarized in table 3. The usual situation in insulators and semiconductors is to find an inverse correlation between the refractive index and the characteristic oscillation energy E_0 . In semiconductors, this correlation works very well, and even extends to an analogous correlation with the band gap energy [22]. Under the same model, the refractive index can be analyzed to determine the average oscillator wavelength λ_0 and oscillator length strength S_0 of the studied samples. These values can be obtained using this equation:

$$n^2 - 1 = \frac{S_0 \lambda_0^2}{1 - (\frac{\lambda_0}{\lambda})^2}$$

Figure 6 shows the variation of $(n^2 - 1)^{-1}$ versus λ^{-2} for the three pyrophosphates, we obtain S_0 and λ_0 values from the linear fit of these spectra. The obtained values are listed in table 3.

Optical Conductivity

The optical response of material is mainly studied in terms of the optical conductivity (σ_{opt}) which can be obtained from the absorption coefficient (α) and refractive index (n) using the following equation [23]:

$$\sigma_{opt} = \frac{\alpha n c}{4\pi}$$

Where c is the light velocity.

Figure 7 shows the variation of the optical conductivity as a function of photon energy for the studied samples. It is very clear that this conductivity increases with increase in photon energy. We can say than, this increase in optical conductivity causing to the increase in the absorption coefficient. We can also prove that the $K_2ZnP_2O_7$ compound has the highest optical conductivity. This result can be explained by the smallest gap energy of the $K_2ZnP_2O_7$ sample.

Conclusions

In this paper, we have studied the optical properties of new compounds: $K_2ZnP_2O_7$, $KZn_{1.5}P_2O_7$ and $Zn_2P_2O_7$, prepared by conventional solid state reaction. Optical band gap and Urbach energies of our samples were estimated from theoretical fits. The $K_2ZnP_2O_7$ has the smaller optical gap energy, this explain the height optical conductivity of this material. The dispersion of these pyrophosphates compounds were studied using the Wemple–DiDomenico method. The oscillator energy E_0 and the dispersion energy E_d were calculated. These materials can be used in laser compounds and electronic devises.

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Figures captions:

Fig 1: Optical absorption spectra of $\text{Zn}_2\text{P}_2\text{O}_7$, $\text{K}_2\text{ZnP}_2\text{O}_7$ and $\text{KZn}_{1.5}\text{P}_2\text{O}_7$ measured at room temperature.

Fig 2 (a) , (b) and (c): plots $(\alpha h\nu)^2$ versus $h\nu$ for the tree studied samples.

Fig 3: $\ln(\alpha)$ versus photon energy $h\nu$ for all titled compounds.

Fig 4: Refractive index as function as wavelength of our studied compounds.

Fig 5: Plots of $(n^2-1)^{-1}$ versus $(h\nu)^2$ of the $\text{K}_2\text{ZnP}_2\text{O}_7$, $\text{KZn}_{1.5}\text{P}_2\text{O}_7$ and $\text{Zn}_2\text{P}_2\text{O}_7$ respectively.

Fig 6: variation of $(n^2 - 1)^{-1}$ as function as λ^{-2} .

Fig 7: Variation of optical conductivity versus photon energy.

Tables captions:

Tab 1: Values of gap-energy and Urbach energy for different compounds.

Tab 2: Cauchy's parameters of the tree studied samples.

Tab 3: Calculated values of dispersion parameters of all compounds.

	E_g (eV)	E_u (eV)	$\langle \text{Zn-O} \rangle$ (Å)
$\text{K}_2\text{ZnP}_2\text{O}_7$	3.39	0.27	1.95
$\text{KZn}_{1.5}\text{P}_2\text{O}_7$	3.59	0.26	1.97
$\text{Zn}_2\text{P}_2\text{O}_7$	3.76	0.3	3.28

Tab.1

	n_0	A (μm) ⁻²	B (μm) ⁻⁴	C (μm) ⁻⁶
$\text{K}_2\text{ZnP}_2\text{O}_7$	2.92	0.106	- 0.012	0.001
$\text{KZn}_{1.5}\text{P}_2\text{O}_7$	3.16	0.199	- 0.088	0.0008
$\text{Zn}_2\text{P}_2\text{O}_7$	3.17	0.460	- 0.364	0.007

Tab.2

	S_0 (μm) ⁻²	λ_0 (μm)	E_0 (eV)	E_d (eV)
$\text{K}_2\text{ZnP}_2\text{O}_7$	0.32	0.13	0.91	5.36
$\text{KZn}_{1.5}\text{P}_2\text{O}_7$	0.27	0.57	0.2	18.1
$\text{Zn}_2\text{P}_2\text{O}_7$	0.14	0.24	0.42	38.4

Tab.3

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

Fig.6

Fig.7