

Study of the Diffused Reflectance and Microstructure for the Phase Transformation of KNO_3

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Optical, micro-structural, thermal and electrical properties of the investigated potassium nitrate (KNO_3) samples were characterized by various techniques such as X-ray analysis, scanning electron microscopy, UV-VIS-NIR absorption and differential scanning calorimetry. The presence of structural phase transition is checked by differential scanning calorimetry, electrical and X-ray analysis measurement. The thermal energy required for such transformation is calculated and found to be 46.2 J/g. The activation energies of the electrical conduction for KNO_3 were found to be 0.236 eV for phase II and 0.967 eV for phase I. The optical band gaps of KNO_3 for the higher photon energy are calculated and equal to 5.03 and 5.01 eV for II and I phases, respectively and at lower photon energy, the values are equal to 3.84 and 3.80 eV for II and I phases, respectively. The data which leads to the interpretation of electronic spectra of potassium nitrate is possible to assume that the long wavelength part of absorption band corresponds to $n-\pi^*$ transition. Then, the short-wavelength part is probably due to the transition in a higher excited state of symmetry $\pi-\pi^*$. The mean values of crystalline sizes are determined by scanning electron microscopy analysis. Such information can considerably aid in understanding the process of transformations near the phase crystal modifications at 129 °C.

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1. Introduction

Phase transitions are important in most areas of solid state science. They are interesting academically, e.g. a considerable slice of current research in solid state physics concerns soft mode theory, which is one aspect of phase transitions, and they are important technologically, e.g. in the synthesis of diamond from graphite, the processes for strengthening of steel and the properties of ferroelectricity and ferromagnetism [1].

Polymorphism is often characterized as the ability of a substance to exist as two or more crystalline phases that have different arrangements and/or conformations of the molecules in the crystal lattice [2, 3]. The methods available for the physical characterization of the solid material, it is generally agreed that the crystallography, the microscopy, the thermal analysis, the spectroscopy, e.g., IR, and, and optical properties are the most useful methods for characterization of polymorphs. If a crystalline material is capable of existing in two or more polymorphic forms (e.g. diamond and graphite), the process of transformation from one polymorph to another is a phase transition. The instability of the lattice systems, related to the phase transitions, has been attributed to soft modes or anomalous fluctuations in order-disorder configurations of constituents of the crystals [4]. The phase

transformation of AgNO_3 was studied by optical, microstructure and thermal measurements [5]. Previous studies show that the origin of the orientational disorder observed in KNO_3 , AgNO_3 and NaNO_3 and the resulting order-disorder phase transition [5]. AgNO_3 has a topological link with the aragonite structure of KNO_3 II. When there are sufficiently large thermal liberations of NO_3 ions, the structure of phase II (of AgNO_3) can be converted homogeneously to the high temperature NaNO_3 structure of phase I [5].

There has been only little information on the electronic properties of the crystals near the phase transition points [6]. To understand the microscopic structure in the phase transition of the dielectric crystal, it is important to investigate the anomaly related to the electronic state near the transition points [4].

Molecular electronic transitions take place when electrons in a molecule are excited from one energy level to a higher energy level. The energy change associated with this transition provides information on the structure of a molecule and determines many molecular properties. In the last few years, much attention has been paid round the studies on the structure and properties of alkali nitrate crystals during and after phase transformation. Such studies are of great interest from both scientific and technological stand points. It is quite obvious that investigation and interpretation of the various physical properties of such crystals depends on the changes in electronic properties near the phase transformations of the crystal.

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KNO_3 has several different phases depending on temperatures. When KNO_3 is heated from room temperature through the transition point $\approx 129^\circ\text{C}$, KNO_3 transforms from orthorhombic (phase II, $Pnma$) to trigonal structure (phase I, $R3m$) [4]. On cooling from the phase I, KNO_3 passes through another trigonal phase (phase III, $R3m$), in the temperature range from ≈ 124 to 100°C , before reverting to the phase II. (The phase III exhibits ferroelectric properties [7].) Infrared [8, 9] and Raman spectra [10] of KNO_3 have been measured, in order to study the lattice dynamics of the different phases. Ultraviolet absorption of KNO_3 at ≈ 4.1 eV was measured by Cleaver et al. [11] and was attributed to the intramolecular electronic transition in the NO_3^- ion [12, 13]. Potassium nitrate (KNO_3) is an excellent additive for fertilizers, as it contains two important nutrients needed by plants. It is commonly used in black powder gunpowder. (KNO_3) is as a thermal storage medium. Sodium and potassium nitrate salts are stored in molten state with the solar energy collected by the heliostats at the GEMASOLAR Thermosolar Plant in Spain. The dosimetric properties of KNO_3 are appropriate for radiation dosimetry applications. Pellets of potassium nitrate appear to be an effective dosimeter for the quality control in routine irradiations [14].

There were no detailed results on optical properties for phase II or I of KNO_3 and there were no detailed results on thermal-microstructure and optical results for phase II or I of KNO_3 . In order to overcome these deficiencies, a program of sample measurement was undertaken in which various analyses including scanning electron microscopy (SEM), UV-Vis-NIR absorption and differential scanning calorimetry (DSC) were carried out.

2. Experimental

For the phases preparation of KNO_3 , the first phase (II) (at low temperature) is used as received at room temperature, while the second phase (I) (at high temperature phase) was prepared above the phase transition point i.e. 140°C . The tube furnace was used to heat up the sample at 140°C .

The material used in the present work was ultra pure potassium nitrate powder KNO_3 obtained from BDH, England. For thermal analysis measurements DSC a Shimadzu system type-50 was used to perform high precision thermal analysis. The heating rate is $5^\circ\text{C}/\text{min}$. All functions are incorporated into a single compact instrument including detector, temperature, gas control and computer interface.

For electrical measurements the samples were prepared in the form of pellets. The thickness of potassium nitrate sample is 1.5 mm. The electrical measurement (electrical resistance R), are carried out by an RLC bridge type (Philips 6304). X-ray diffraction patterns are carried out by X-ray machine type, Shimadzu LabX XRD-6000 with $\text{Cu } K_\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation and secondary monochromator. The X-ray diffraction patterns are carried out and taken at some selected temperatures.

The images patterns for KNO_3 samples are taken by SEM type which is instrument JSM-6360 where acceleration voltage (kV) = 20 and where image is SEI. The material used as a 100% standard in the presented investigations is BaSO_4 as a reference.

For diffused reflectance (DR) measurements, Shimadzu UV-VIS-NIR spectrophotometer model (UV-3600) was used to measure the DR in the wavelength range 230–800 nm by using integrating sphere attachments. The diffused reflectance measurements are carried out at selected temperatures.

3. Results and discussion

3.1. Thermal, electrical, X-ray and thermal-microstructure measurements

The results for thermal and electrical measurements of KNO_3 samples are given where a sample of KNO_3 is analyzed at first by DSC. Figure 1 shows DSC thermogram for KNO_3 sample during heating run starting from room temperature up to 240°C . The thermogram shows at first no variation up to 120°C . The sample seems to be stable against thermal agitation up to 120°C , then a sudden drop at 129°C . This clearly indicated an endothermic phase transition at 129°C . The energy required for such transformation is found to be 46.2 J/g . Further, heating of KNO_3 up to 240°C gives no change and the sample seems to be stable against thermal agitation up to 240°C .

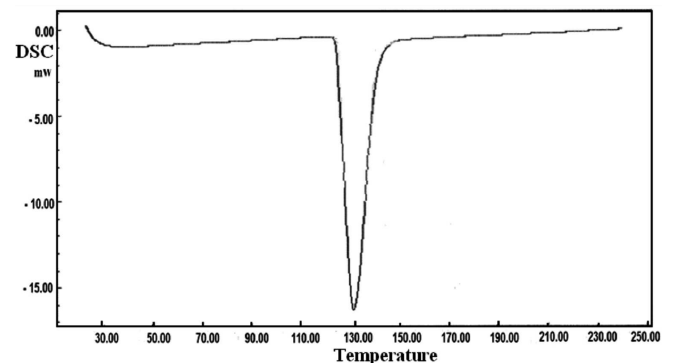


Fig. 1. DSC thermogram for the endothermic phase transition at 129°C in KNO_3 .

The phase transition which is detected here by DSC is also checked by studying the variations in the electrical resistivity for potassium nitrate with temperature as shown in Fig. 2a,b.

Figure 2a shows the temperature dependence of the dc resistivity (ρ) during the phase transition for KNO_3 . It is clear that the electrical resistivity decreases gradually with temperature up to $\approx 129^\circ\text{C}$; after this temperature, ρ decreases quickly.

Figure 2b shows the relation between $1000/T$ and $\ln \rho$ which is drawn in order to obtain the activation energy of the electrical conduction for KNO_3 before and after the phase transition process [15]. Accordingly, the activation energy values are calculated and found to be 0.236 eV for phase II (phase II, i.e. from room temperature up to the transition temperature point $\approx 129^\circ\text{C}$)

and 0.967 eV for phase I (phase I, i.e. above the transition temperature point).

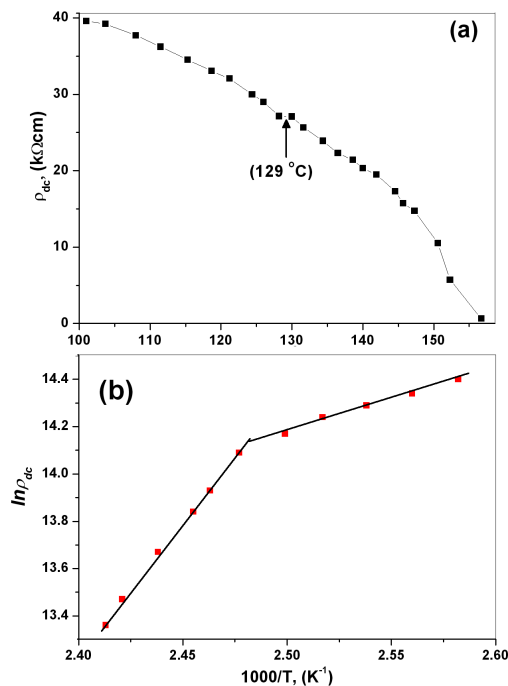


Fig. 2. (a) The variation of resistivity with temperature and (b) The variation of $\ln \rho$ with $1000/T$ for KNO_3 sample.

The lattice instability appearing at the II \rightarrow I phase transition of NO_3^- has been studied by structural analyses, infrared absorption, and the Raman scattering measurements [4]. In both the phases II and I, the nitrate ions have two orientations, and lie slightly above and below the plane. The K atoms are slightly shifted to either sides of the plane for phase II, but lie on these planes for phase I. During the II \rightarrow I phase transition; layers of the K atoms and NO_3^- groups are shifted and are repacked by accompanying the change in the configuration and orientation of NO_3^- [4].

According to DSC and dc resistivity measurements for KNO_3 , an X-ray analysis is carried out before and after the phase transition temperature point (129°C) to confirm the presence of phase transition. The obtained results are given in Fig. 3a and b, where in Fig. 3a the X-ray diffraction pattern at room temperature represents (phase II) while in Fig. 3b X-ray pattern represents (phase I) after the heat treatment at 129°C . It is clear that X-ray analysis shows the presence of phase transition in KNO_3 due to the structure change. This structural phase transition is accompanied by a variation in the electronic state in the crystal during the phase transformations [16, 17]. The difference between the two diffraction patterns for phase I and phase II mainly related to the thermal heat treatment of the sample at 129°C . This heat treatment revealed large changes of the intensity of the peaks accompanied by the changes in the preferred orientation.

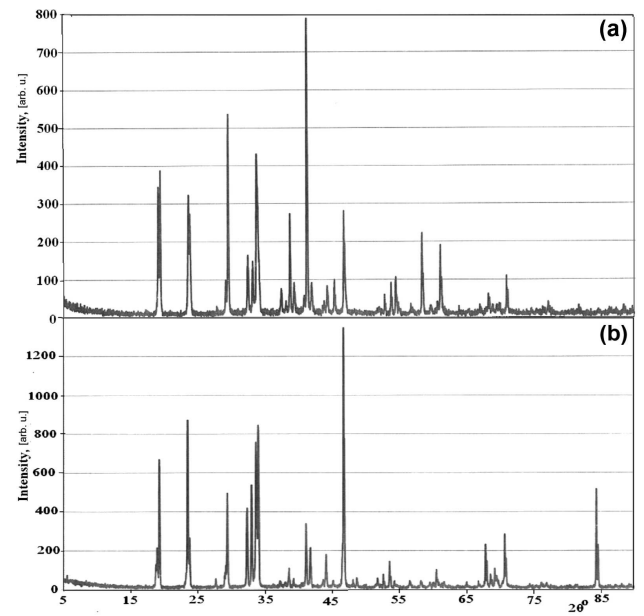


Fig. 3. (a) X-ray diffraction patterns for crystalline KNO_3 at room temperature (phase II), and (b) X-ray diffraction patterns for crystalline KNO_3 above transition temperature (phase I).

Many substances in the solid state undergo a phase transition associated with a change in structure during the transition; the arrangement of the atoms is modified and is associated with a change in the symmetry of the crystal. This change in symmetry is characterized by going from a phase with specified symmetry to another phase with a different symmetry induced by displacement of atoms in the solid [1].

The change in the configuration and orientation of NO_3^- in the KNO_3 crystal is induced by the structural phase transition. As the temperature is raised [4], the nitrogen atom deviates largely from the coplanar arrangement of the nitrogen and oxygen atoms within each NO_3^- ion. As the NO_3^- ions are collinear in the phase I, they can be easily in dynamic disorder between the two equilibrium positions. In this disordered phase, however, the rotation of NO_3^- is not completely free [4].

3.2. SEM analysis

A SEM is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. The SEM is routinely used to generate high-resolution images of shapes of objects.

The SEM images of KNO_3 samples are shown in Fig. 4. The SEM image of KNO_3 for phase I and phase II are obtained. The samples are formed from cluster of spheres with varying sizes. The phase I and phase II samples show a spherical grain of varying particle sizes, i.e., the size of particles varies with increasing temperature.

The mean values of crystalline sizes of phases I and II are determined, for phase II are between 3.09 to 3.17 μm and for phase I are between 3.35 to 3.76 μm . It is shown from two images for KNO_3 that the crystalline size for phase I is greater than that for phase II. The presence of $\text{II} \rightarrow \text{I}$ phase transformations in KNO_3 is supported and confirmed by electrical and X-ray analysis measurements.

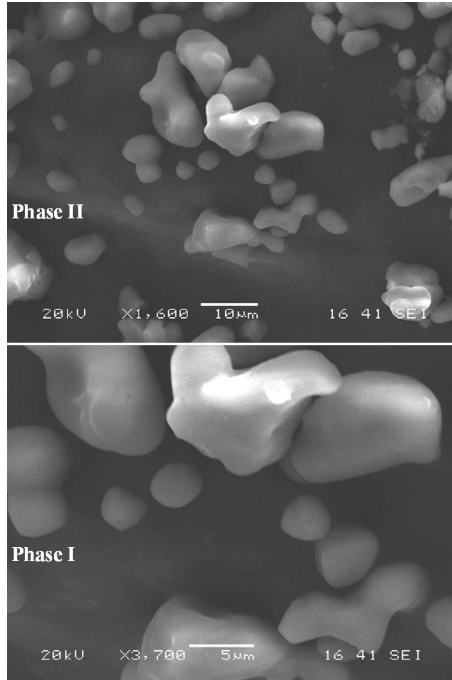
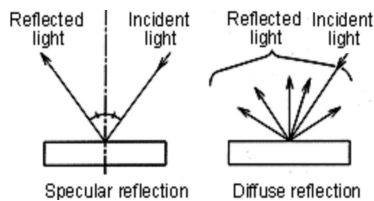


Fig. 4. SEM images for phases II and I for KNO_3 .

The surface morphology of KNO_3 samples changes due to the effect of the transformation temperature on the studied sample. This can be attributed to the changes in the intensity of the XRD patterns or due to the changes in the preferred orientations of the planes inside the samples through the transformation process.

3.3. Optical properties of potassium nitrate (KNO_3)

Diffuse reflection is the reflection of light from a surface such that an incident ray is reflected at many angles rather than at just one angle as in the case of specular reflection. A surface built from a non-absorbing powder such as plaster, or from fibers such as paper, or from a polycrystalline material such as white marble, reflects light diffusely with great efficiency. Many common materials exhibit a mixture of specular and diffuse reflection. Diffuse reflection from solids is generally not due to surface roughness. A flat surface is indeed required to give specular reflection, but it does not prevent diffuse reflection [18].



Since light cannot penetrate opaque (solid) samples, it is reflected on the surface of the samples. As shown in the above figure, incident light reflected symmetrically with respect to the normal line is called “specular reflection”, while incident light scattered in different directions is called “diffuse reflection”. Diffuse reflectance is an excellent sampling tool for powdered or crystalline materials in the mid-IR and NIR spectral ranges. It can also be used for analysis of intractable solid samples. Diffuse reflectance is an excellent sampling technique as it eliminates the time-consuming process of pressing pellets for transmission measurements.

Factors related to high spectral quality for diffuse reflectance sampling are particle size, refractive index, homogeneity and packing.

Diffused reflectance (DR) spectroscopy is a spectroscopic technique based on the reflection of light in the UV–VIS–NIR region by using powdered samples. The spectrum of DR is a ratio of the light scattered from an infinitely thick layer and the scattered light from an ideal non-absorbing reference sample is measured as a function of the wavelengths [19–22]. The Kubelka–Munk theory is generally used for analyzing the diffuse reflectance spectra obtained from weakly absorbing samples. In this case the Kubelka–Munk equation at any wavelength becomes [23]:

$$F(R) = \frac{(1 - R)^2}{2R}, \quad (1)$$

where R is the measured diffused reflectance of the KNO_3 samples of two phases and $F(R)$ is the so-called Kubelka–Munk function which corresponds to the absorbance. The Kubelka–Munk function $F(R)$ values were converted to the linear absorption coefficient by the relation [24, 25]:

$$\alpha = \frac{F(R)}{t} = \frac{\text{Absorbance}}{t}, \quad (2)$$

where t is the thickness of KNO_3 powders. The value of the optical band gap E_g can be calculated using the fundamental absorption which corresponds to electron excitation from the valence band to the conduction band. The optical band gap of KNO_3 of different phases (II, I) can be determined by the following equation [26, 27]:

$$\alpha h\nu = A(h\nu - E_g)^n. \quad (3)$$

We modify this equation to be suitable to use the Kubelka–Munk function and its related linear absorption coefficient as follows:

$$(\alpha h\nu) = \left(\frac{F(R)h\nu}{t} \right) = A(h\nu - E_g)^n, \quad (4)$$

where A is an energy independent constant and E_g is the determined optical band gap of KNO_3 of different phases (II, I) powders, n is a constant which determines the type of optical transitions and for indirect allowed transition, $n = 2$ and for direct allowed transition, $n = 1/2$.

Figure 5 shows the plot of the diffused reflectance for KNO_3 for phase I and phase II. It is clear that the diffused reflectance (DR) for phase I and for phase II of

KNO_3 samples increases with increasing wavelength (λ). At lower wavelengths, DR of the two plots of (II and I) phases are approximately superimposed on each other. At higher wavelengths the DR of phase I is higher than II, which can be attributed to structure modifications from (phase II) to (phase I). We should mention that all the equations were programmed by using Excel sheet software and all graphs were graphed by origin 7.

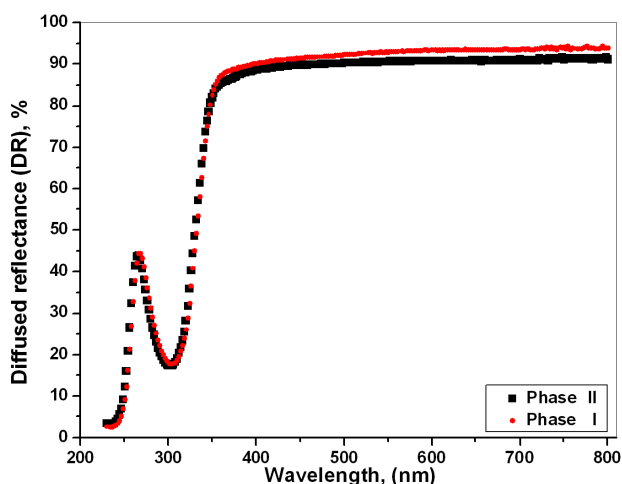


Fig. 5. Diffused reflectance as a function of wavelengths for the different phases (II and I) of KNO_3 sample.

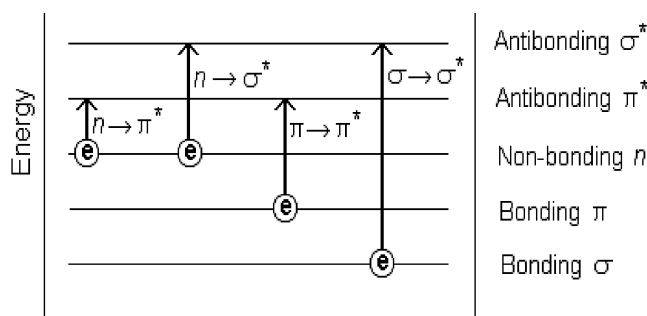


Fig. 6. The schematic representation for the molecular excited states.

A molecule or ion will exhibit absorption in the visible or ultraviolet region when radiation causes an electronic transition within its structure. Thus, the absorption of light by a sample in the ultraviolet or visible region is accompanied by a change in the electronic state of the molecules in the sample. The energy supplied by the light will promote electrons from their ground state orbitals to higher energy, excited state orbitals or antibonding orbitals. The electronic transitions in some compounds and some other compounds can be determined by ultraviolet-visible spectroscopy, provided that transitions in the ultraviolet (UV) or visible range of the electromagnetic spectrum exist for this compound [28, 29]. The molecular electronic transitions exist: $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \sigma^*$ and $n \rightarrow \pi^*$ as shown in Fig. 6.

The analysis of experimental data [30], which leads to the interpretation of electronic spectra of alkali nitrate crystals. It is possible to assume that the long wavelength part of absorption band corresponds to $n \rightarrow \pi^*$ transition. Then the short-wavelength part is probably due to the transition in a higher excited state of symmetry $\pi \rightarrow \pi^*$.

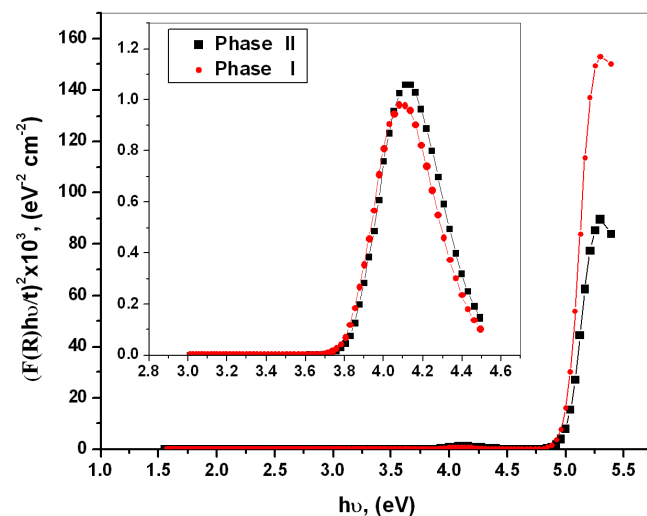


Fig. 7. Plotting of $(F(R)hv/t)^2$ as a function of photon energy (hv) for the different phases (II and I) of KNO_3 sample.

The optical band gap of the samples was determined from the plots of $(F(R)hv/t)^2$ as a function of photo energy hv as show in Fig. 7. Extrapolating of the linear part of this figure to x -axis (photon energy) i.e. $hv = 0$, one can determine the value of the energy gap of KNO_3 of (II, I) phases. It is clear from this figure and its set that there are two band gaps for the studied KNO_3 (II and I) phases as follows:

- (1) At the higher photon energy, the values of the energy band gap equal 5.03 and 5.01 eV for II and I phases, respectively.
- (2) At lower photon energy, the values of the energy band gap equal 3.84 and 3.80 eV for II and I phases, respectively.

Based on McEwen's molecular orbital calculations [12, 13, 31] for a nitrate ion NO_3^- the absorption band from 3.40 to 4.50 eV has been assigned to the $n \rightarrow \pi^*$ transition, and the stronger absorption band above 4.80 eV has been assigned to the $\pi \rightarrow \pi^*$ transition. The position of the $n \rightarrow \pi^*$ absorption peak does not shift with photon energy for phases I and II for KNO_3 . It is shown that at higher wavelengths, the energy band gap decreases for phases I and II than that for at lower wavelengths. This indicates that the optical band gap of KNO_3 change strongly for phase I and phase II. It is expected that the changes of the band gap of KNO_3 for phase I and II which are due to the increase of temperature may be due to the presence of phase transition. By a coupling between the intramolecular vibration and the intramolecular electronic transition of the NO_3^- ion,

the transition probability of the $n \rightarrow \pi^*$ transition is seriously influenced by the structural phase transition of KNO_3 . So we have observed the singularity of the absorption spectrum for phases II and I, i.e., before and after phase transition temperature as given in previous figures. Increasing the temperature, especially near the transition point, considerably increases the probability of reorientations of the molecules. At the phase transition, the character of the reorientations qualitatively changes, which should lead to a change of the characteristics of the material [5].

To confirm or support the results which depend on the calculations of the optical constants of KNO_3 for phases I and II, we calculate the absorption index (k) which depends on the diffused reflectance data from the equation $k = \alpha\lambda/4\pi$ [23]. By plotting of the absorption index against wavelength is shown in Fig. 8. It is shown that the absorption index of KNO_3 for phases I and II is very small (10^{-5} – 10^{-4}). These lower values of the absorption index comply with the calculations of the optical constants based on the diffused reflectance.

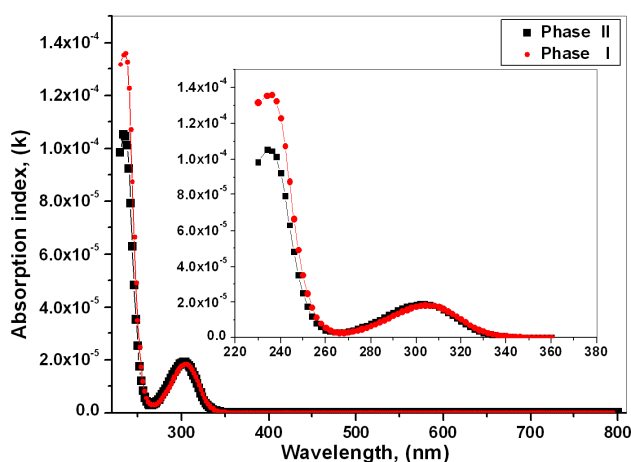


Fig. 8. Plotting of absorption index k as a function of wavelengths for the different phases (II and I) KNO_3 sample.

The absorption spectra have been ascribed to the intramolecular electronic transition in NO_3^- . Therefore, it indicates the anomalies in the electronic transition near the structural phase transition point [5].

The optical modes of lattice vibrations in the NO_3^- crystal composed of NO_3^- and K^+ ions are classified into three modes: ionic, covalent, and rotational modes [32]. The three modes have been observed by infrared absorption and Raman scattering [4], and show anomalous temperature dependence near transition point. These results show the anomalous behaviour of the intramolecular vibration modes of NO_3^- near the II \rightarrow I phase transition of KNO_3 .

4. Conclusion

Potassium nitrate samples were successfully investigated by various techniques such as X-ray analysis, SEM,

UV–VIS–NIR absorption, electrical resistivity, and DSC that support the presence of structural phase transition. The surface morphology, optical, thermal and electrical properties for phases II and I of KNO_3 were investigated. Such information can considerably aid in the understanding of the process of transformations among crystal modifications (II \rightarrow I) near the transition temperature (129°C). Potassium nitrate undergoes a phase transition associated with a change in its structure during the transformations; the arrangement of the atoms is modified and is associated with a change in the symmetry. This change in symmetry is characterized by going from a phase with specified symmetry to another phase with different symmetry induced by displacement of atoms. The structural phase transition induces a variation in the electronic state in the crystal. During the II \rightarrow I phase transition, layers of the K atoms and NO_3^- groups are shifted and are repacked by accompanying the change in the configuration and orientation of NO_3^- . The absorption of light by a sample in the ultraviolet or visible region is accompanied by a change in the electronic state of the molecules in the sample. The data which leads to the interpretation of electronic spectra of alkali nitrate crystals corresponds to $n\text{--}\pi^*$ transition and $\pi\text{--}\pi^*$ transition.

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