

Optical Characterization of (TMA)₂**ZnCl**₄ **Single Crystals in the Normal Phase**

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Abstract

The transmittance (T) and the reflectance (R) were measured for $(TMA)_2ZnCl_4$ single crystals and hence the absorption coefficient (α), extinction coefficient (K_{ex.}), refractive index (n), real and imaginary dielectric constants (ε' , ε'') of $(TMA)_2ZnCl_4$ crystals were calculated as a function of photon energy. The analysis of the spectra behavior of the absorption coefficient in the absorption region revealed indirect transition. The dispersion of the refractive index is discussed in terms of the single oscillator Wemple-DiDomenico model. The single oscillator energy (E₀), the dispersion energy (E_d), the lattice dielectric constant (ε_L) and the ratio of free charge carrier concentration to the effective mass (N/m*) were estimated. The FTIR spectra were recorded to study the functional groups of the as grown and annealed samples.

Keywords

(TMA)₂ZnCl₄ Single Crystals, Optical Band Gap, Refractive Index, Dispersion Parameters, FTIR Spectroscopy

1. Introduction

The A_2BX_4 type crystals (with A = K, NH₄, Rb; B = Zn, Co; X = Cl, Br) have been interested because of their incommensurately modulated structures and the successive phase transitions [1]. In the recent past, the study of incommensurate phases in matter has grown explosively with the discovery of over a hundred materials exhibiting incommensurate properties. Many of these materials belong to the ferroelectric A_2BX_4 family [1], which exhibit in addition to the well-known normal-commensurate phase transitions one or several intermediate incommensurate phases. In these phases a local atomic property (like spontaneous polarization in ferroelectrics) is modulated with a period which is incommensurate with the underlying lattice periodicity [2].

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The compounds belonging to TMA family have attracted much interest because of exhibiting some peculiar characteristics associated with the phase transition. Among them $[N(CH_3)_4]_2ZnCl_4$ (hereafter (TMA)_2ZnCl_4) with β -K₂SeO₄ type structure as the normal (or prototype) phase at the high temperature region. (TMA)_2ZnCl_4 exhibits a sequence of structural phase transitions. It turns incommensurate when cooled through a first-order phase transition occurring at T_{INC} = 296 K, becomes ferroelectric by lock-in of the incommensurate modulation at T_{C-F} = 279 K, and at T_{C2} = 276.3 K another first-order ferroelectric phase transition takes place at 181 K is monoclinic, phase V between 181 K and 163 K is monoclinic or triclinic, and phase VI, which is stable below 163 K, is orthorhombic. The highest temperature phase, Phase I, has Pmcn symmetry. In this phase one unit cell contains four formula units consisting of two inequivalent types of tetramethylammonium ions [3].

Many investigations have been performed on (TMA)₂ZnCl₄ crystals including studies of the effect of electric field and mechanical stress (uniaxial or shear stress) on dielectric permittivity and spontaneous polarization by Styrkowiec and Czapla [4]. They concluded that, the electric field shifts the transition point T_{c1} , (IC) to higher temperature and the transition point T_{c2} (ferroelectric ferroelastic) lower. It is found that the dielectric constant and the shift of the transition point are dependent on the uniaxial stresses and this stress can also induce a change of the crystal symmetry. Linear birefringence (LB) behavior of $[N(CH_3)_4]_2 ZnC1_4$ and $[N(CH_3)_4]_2 CuC1_4$ was studied in the critical region on normal-incommensurate phase transition by Kim et al. [5]. The temperature dependences of birefingence and dielectric permittivity of $[N(CH_3)_4]_2ZnC1_4$ and $[N(CH_3)_4]_2CoC1_4$ are measured by Sveleba et al. [6]. The long-periodic commensurate phases appear within the incommensurate phase under the influence of external electric fields (E) and mechanical stresses. In the other hand Sveleba et al. [7] investigated the optical birefringence, optical indicatrix rotation, and residual intensity of $[N(CH_3)_4]_2ZnCl_4$ crystals doped with Ni²⁺ in the parent and incommensurate phases. Their temperature dependences obtained are nonlinear in a wide temperature range. It is shown that the nature of this nonlinearity is related to the presence of local spatial regions of the correlated motion of tetrahedral groups. Studies on the behaviour of the modulation wave vector in $[(CH_3)_4)N]_2ZnC1_{4-x}Br_x$ compounds as a function of composition (x) and temperature were performed by Vogels *et al.* [8]. Time evolution of dielectric permittivity in $[N(CH_3)_4]_2 ZnC1_4$ crystals was measured at the fixed temperature by Styrkowiec [2]. In both incommensurate (II) and Ferroelectric (III) phases, a longterm relaxation of permittivity has been confirmed.

Little attention has been paid to the study of optical properties near the absorption edge of $(TMA)_2ZnCl_4$ crystal. This contribution reports the results of investigation of some optical properties of $[N(CH_3)_4]_2ZnCl_4$ crystals in the normal phase. Another goal of the present work is to get some information about the vibration bands by Fourier transform infrared (FTIR) spectroscopic studies.

2. Experimental

 $(TMA)_2ZnCl_4$ single crystals were grown using the solution growth technique from saturated solutions by slow cooling from 45°C to 35°C instead of isothermal evaporation. The raw material used for growth was obtained by mixing aqueous solutions of tetramethylammonium chloride ($C_4H_{12}NCl$) and Zinc chloride ($ZnCl_2$) in stoichiometric amounts. Typically the growth runs lasted from 30 - 50 days. During this period the average cooling and growth rates were 0.2°C/day and 0.3 mm/day, respectively. After an initial capping period, the crystal grew clear to heights ranging from 10 to 15 mm each. From the as grown crystals specimens were formed into b-plates with size of about 0.8 mm in thickness and 36 mm² in area using a wet thread saw. The specimens used for optical measurements were clear, transparent and free from any noticeable defects. More details about the grown crystals are shown elsewhere [9].

The optical transmittance was recorded at room temperature using Shimadzu UV-VIS dual beam scanning spectrophotometer in the energy range 2.1 - 6.4 eV. The incident unpolarized light was nearly perpendicular to (010) plane. The surrounding medium was air. The relative specular reflectance was measured at an incident angle of 5°, while the sample was placed horizontally facing downward and was illuminated from the bottom.

The FTIR spectra were recorded in the range 400 - 4000 cm^{-1} employing a NICOLET FTIR 6700 spectrometer by the KBr pellet method to study the functional groups of the samples.

3. Results and Discussions

3.1. Optical Transmittance

Transmission spectrum is very important for any nonlinear optical (NLO) material, because a nonlinear optical

material can be of practical use only if it has wide transparency window. **Figure 1** shows the variation of the optical transmission (T) and reflectance (R) spectrum as a function of wavelength for $(TMA)_2ZnCl_4$ single crystal recorded in the range 190 to 900 nm at room temperature. From Figure 1, the lower cut off wavelength is obtained and listed in Table 1. UV-Vis-NIR spectrum, reveal that, $(TMA)_2ZnCl_4$ crystal is conveniently transparent from 300 to 900 nm with about 60% of transmittance and there is almost a steady transmittance in the visible region. The high transmission or low absorption in the region 300 - 900 nm makes the material to obtain low reflectance and refractive index which is a suitable property for antireflection coating solar thermal devices and nonlinear optical applications.

Electronic transitions between the valence band and the conduction band in crystals starts at the absorption edge that corresponds to the energy difference between the lowest minimum of the conduction band and the highest maximum of the valence band. The value of the energy gap depends in a rather subtle way on the structure and the actual values of the pseudopotential in the crystal. The optical behavior of a material is generally utilized to determine its optical constants for example the absorption coefficient α . The absorption coefficient (α) was calculated by means of the ratio recording technique in order to eliminate the reflection losses. This was achieved by placing a thin crystal in the way of reference beam, and another thicker one in the way of the sample beam. Assuming that the change in reflection with thickness is negligible, the ratio of the transmittance of two samples of different thicknesses is given by [10]:



$$\ln T_{1-2} = \alpha \Delta d \tag{1}$$

Figure 1. Spectral variation of transmission and reflectance of (TMA)₂ZnCl₄ single crystal.

Table 1. Optical constants for (TMA)₂ZnCl₄ crystal in the normal phase.

Physical quantity	Value	
Optical energy gap $E_s^{opt.}$	5.903 eV	
Cut off wavelength	195.016 nm	
Optical conductivity $\sigma_{opt.}$	$2.933 \times 10^{10} \ s^{-1}$	
Electrical conductivity $\sigma_{ele.}$	$16.423 (\Omega \cdot m)^{-1}$	
Electric susceptibility χ_c	0.164	
Lattice dielectric constant ε_L	10.10	
The ratio of carrier concentration to effective mass N/m^*	$2.05\times 10^{59}~(m^3{\cdot}kg)^{-1}$	
Molar polarizability α_p	$1.37\times 10^{21}~\text{cm}^3\!/\text{mole}$	

where T is the transmittance and d is the crystal thickness.

Figure 2(a) shows the spectral response of the total absorption coefficient (α) for $(TMA)_2ZnCl_4$ crystal. The α -hv dependence exhibits a long tail at the low energy part. It can be seen that the absorption increases slowly with increasing photon energy in the range below hv = 6.1 eV. At photon energies hv > 6.1 eV, the spectra showed a steeper increase of the absorption coefficient. It can be assumed that this increase in $\alpha(hv)$ is due to the onset of interband transitions at the fundamental edge.

The relationship between absorption coefficient α and photon energy $h\nu$ can be expressed as [11]:

$$\left(\alpha h\nu\right)^{1/m} = A\left(h\nu - E_g^{opt.}\right) \tag{2}$$

where A is a constant nearly independent of photon energy and $E_g^{opt.}$ is the optical energy gap. Here *m* represents an index that can take any of the values: 2, 3/2, 1/2 or 3 depending on the type of transition responsible for the absorption. For allowed direct transition m = 1/2 while m = 3/2 for forbidden direct transition. For allowed



Figure 2. (a) The photon energy dependence of α and (b) The photon energy dependence of $(\alpha hv)^{1/2}$ (inset shows the linear fit and the value of optical energy gap $E_g^{opt.}$) for (TMA)₂ZnCl₄ single crystal.

indirect transition m = 2 and for forbidden indirect transition m = 3. The range within which this equation is valid is very small and hence it becomes too difficult to determine exactly the value of the exponent m [12]. In a small energy range, the dependence of $(\alpha h v)^{1/2}$ on hv for (TMA)₂ZnCl₄ samples is shown in Figure

In a small energy range, the dependence of $(\alpha hv)^{l/2}$ on hv for $(TMA)_2ZnCl_4$ samples is shown in Figure **2(b)**. The dependence of $(\alpha hv)^{l/m}$ on photon energy hv for onset gaps was plotted for different values of m and the best fit was obtained for m = 2. This indicates that the optical absorption obeys Equation (2) with m = 2 which means that $(TMA)_2ZnCl_4$ crystal is an indirect material and the fundamental edge is due to allowed indirect transitions. By extrapolating the straight lines to the value, where $(\alpha hv)^{l/2} = 0$, value of E_g^{opt} was determined. The obtained value is 5.903 eV. This value has good agreement with those calculated by El-Korashy [13] which reported direct band gap energy value of 5.89 eV at 300 K (the normal paraelectric phase) for this crystal.

3.2. Optical Constants

The reflectance of the surface (R) is written in terms of refractive index (n) [14] as:

$$R = \frac{(n-1)^2 + K_{ex.}^2}{(n+1)^2 + K_{ex.}^2}$$
(3)

The optical constants (n, K_{ex}) were determined from the transmission (T) and reflection (R) spectrum. The absorption coefficient α is related to extinction coefficient K_{ex} , by:

$$K_{ex.} = \frac{\alpha\lambda}{4\pi} \tag{4}$$

Figure 3 shows the plot of extinction coefficient (K_{ex}) as a function of photon energy (hv). From the graph, it is clear that extinction coefficient (K_{ex}) value increases with increase in the photon energy. The dependence of refractive index (n) on the energy is also shown in **Figure 3** and it is seen that the refractive index decreases as the photon energy increases. Thus, the extinction coefficient (K_{ex}) and refractive index (n) depend on the photon energy. It is understood that the higher value of photon energy will enhance the optical efficiency of the material. Hence, by tailoring the photon energy, one can achieve the desired material for optical device fabrication.

The complex dielectric constant $\begin{pmatrix} \epsilon \\ \epsilon \end{pmatrix}$ is related to the refractive index and the extinction coefficient as:

$$\dot{\varepsilon} = \varepsilon' - i\varepsilon'' \tag{5}$$

$$\varepsilon' = n^2 - K_{ex.}^2$$
 and $\varepsilon'' = 2nK_{ex.}$ (6)

where ε' and ε'' are the real and imaginary parts of the complex dielectric constant, respectively.



Figure 3. Extinction coefficient (K_{ex}) and refractive index (*n*) versus photon energy for (TMA)₂ZnCl₄ single crystal.

The variation of the imaginary ε'' part of the dielectric constant with photon energy preserves the same dependence of the absorption coefficient while the behavior of ε' , the real part of the dielectric constant, and the refractive index is the same as shown in Figure 4.

The optical conductivity is a measure of the frequency response of the material when irradiated with light is given by the relation [15]:

$$\sigma_{opt.} = \frac{\alpha nc}{4\pi} \tag{7}$$

where c is the velocity of light. The electrical conductivity is related to the optical conductivity by the relation:

$$\sigma_{ele.} = \frac{2\lambda}{\alpha} \sigma_{opt.} \tag{8}$$

The energy dependence of the optical and electrical conductivities is illustrated in Figure 5. The obtained results for extinction coefficient and optical conductivity are in fair agreement with those obtained by Girisun *et al.*



Figure 4. The dependence of the real ε' and imaginary ε'' parts of the dielectric constant on the photon energy for $(TMA)_2 ZnCl_4$ single crystal.



Figure 5. The dependence of the optical $\sigma_{ont.}$ and electrical $\sigma_{ele.}$ conductivities on the photon energy for (TMA)₂ZnCl₄ single crystal.

[15] for tristhiourea zinc sulphate (ZTS) and by Raj *et al.* [16] for L-Alaninium Malate (LAM) single crystals. The high magnitude of optical conductivity $(1.45 \times 10^{10} \text{ s}^{-1})$ and the low extinction coefficient (10^{-5}) confirms the presence of very high photo response nature of the material. This makes the material more prominent for device applications in information processing and computing.

For further analysis of the experimental results, the electric susceptibility χ_c can be calculated according to the relation [17]:

$$\varepsilon_r = \varepsilon_0 + 4\pi \chi_c = n^2 - K_{ex.}^2 \tag{9}$$

$$\chi_c = \frac{\left(n^2 - K_{ex.}^2 - \varepsilon_0\right)}{4\pi} \tag{10}$$

where ε_0 is the dielectric constant in the absence of any contribution from free carriers. The energy dependence of the electric susceptibility is similar to that of the imaginary ε'' part of the dielectric constant. χ_c -hv relationship is depicted in **Figure 6**, then the value of electric susceptibility χ_c calculated near the energy gap at 5.9 eV is listed in **Table 1**.

Lattice dielectric constant ε_L and contribution of charge carriers (*N*) can be calculated by the fitting of the linear part of the relation [18];

$$n^{2} = \varepsilon_{L} - \left(\frac{e^{2}}{4\pi^{2}\varepsilon_{0}c^{2}}\right) \left(\frac{N}{m^{*}}\right) \lambda^{2}$$
(11)

where *e* is electronic charge, *c* is the velocity of light and N/m^* is the ratio of carrier concentration to effective mass, **Figure 7** shows the fitting of Equation (11) near the absorption edge. When the carrier concentration increases, the energy gap decreases, then the refractive index increases [19].

The molar polarizability α_p of (TMA)₂ZnCl₄ single crystals can be deduced according to the Clausius-Mossotti local-field polarizability model [20] from the relation:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{L\rho}{3M} \alpha_p \tag{12}$$

where *L* is the Avogadro's number, ρ is the density of material and *M* molecular weight. The photon energy dependence of $\binom{n^2-1}{\binom{n^2+2}{2}}$ is shown in Figure 8. From the extrapolation, the molar polarizability α_p value is deduced and listed in Table 1.













3.3. Dispersion Characterizations

The dispersion of refractive index of $(TMA)_2ZnCl_4$ has been fitted to Wemple and DiDomenico (WDD) model which is based on single oscillator formula [21] [22].

$$n^{2} - 1 = \frac{E_{d}E_{0}}{E_{0}^{2} - (h\nu)^{2}}$$
(13)

where E_0 is single oscillator energy or average energy gap and E_d is dispersion energy and $h\nu$ is the photon energy. Factor E_d depends on the imaginary part of dielectric constant (ε'') whereas E_0 does not. Due to this reason E_d is very nearly independent of E_0 , and E_0 is related to the bond energy of chemical bonds present in the system. Oscillator parameters calculated from the linear fit of $(n^2 - 1)^{-1}$ and $(h\nu)^2$ around the absorption edge as depicted in **Figure 9**. From the intercept (E_0/E_d) and the slope $(1/E_0E_d)$, the dispersion parameters E_d and E_0 are calculated and given in **Table 2**. The dispersion plays a significant role with respect to optical communication and spectral dispersion [23]. The values of static refractive index (n_0) have been calculated by extrapolating the WDD dispersion equation for $h\nu \rightarrow 0$ and listed in **Table 2**.

The moments of optical dispersion spectra M_{-1} and M_{-3} , can be evaluated using the relationships [24]:

$$E_0^2 = \frac{M_{-1}}{M_{-3}} \tag{14}$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \tag{15}$$

The zero-frequency refractive index (static refractive index) is obtained using Equation (13), by putting hv = 0, *i.e.* based on the expression:

$$n_0^2 - 1 = \frac{E_d}{E_0} \tag{16}$$

Furthermore the values of static refractive index zero-frequency refractive index n_0 are also calculated and recorded in Table 2.



Figure 9. Plot of $(n^2 - 1)^{-1}$ as a function of $(hv)^2$ (inset shows the linear fit of the linear part of the curve near the optical energy gap) for $(TMA)_2ZnCl_4$ single crystal.

Table 2. Normal dispersion of $(TMA)_2 ZnCl_4$ single crystals.			
Physical quantity	Value		
Single oscillator energy E_0	6.55 eV		
Dispersion energy E_d	2.06 eV		
Moment of the optical dispersion spectra M_{-1}	$0.314 (eV)^2$		
Moment of the optical dispersion spectra M_{-3}	$7.323 \times 10^{-3} (eV)^{-2}$		
Static refractive index n_0	1.314		
Oscillator strength S ₀	$2.61 \times 10^{-5} \text{ (nm)}^{-2}$		
Oscillator wavelength λ_0	157.87 nm		

The values of dispersion parameters and the optical moments gathered in Table 2, are strongly agree with Wemple [21] and DiDomenico [22].

The refractive index *n* can also be analyzed to determine the oscillator strength S_0 for (TMA)₂ZnCl₄ crystals. The refractive index is represented by a single Sellmeier oscillator at low energies [25]:

$$\frac{n_0^2 - 1}{n^2 - 1} = 1 - \left(\frac{\lambda_0}{\lambda}\right)^2$$
(17)

where λ_0 is the oscillator wavelength. If we put $S_0 = (n_0^2 - 1)/\lambda_0^2$. We can rewrite Equation (17) as:

$$\frac{1}{\left(n^{2}-1\right)} = \frac{1}{\lambda_{0}^{2}S_{0}} - \frac{1}{\lambda^{2}S_{0}}$$
(18)

 S_0 is the average oscillator strength. The plotting of $(n^2 - 1)^{-1}$ versus λ^{-2} shows linear part edge as shown in **Figure 10**. The intersection with $(n^2 - 1)^{-1}$ axis is $1/\lambda_0^2 S_0$ and the slope is $1/S_0$. Hence, the values of S_0 and λ_0 were determined and listed in **Table 2**.

3.4. Fourier Transform Infrared Spectroscopy

FTIR spectra carried out in the range 400 - 4000 cm⁻¹ of as grown (TMA)₂ZnCl₄ crystals and crystals annealed for 1 and 2 hours in the paraelectric phase at 150°C have been assigned in **Table 3** and the functional groups have been identified (**Figure 11**). The band observed at 950 cm⁻¹ is assigned to C-N stretching mode of vibration. The rocking of CH₃ is assigned to the bands observed at 1071 and 1280 cm⁻¹. The band at 1415 cm⁻¹ is assigned to the in-plane bending mode of CH₃ and the out-of-plane bending is assigned to the band at 1487 cm⁻¹. Symmetric and asymmetric stretching of CH₃ is observed at 2952 and 3022 cm⁻¹ respectively. The band observed around 3435 cm⁻¹ and 1635 cm⁻¹ are assigned to the O-H stretching and bending vibration of water molecule present in the KBr compound. The values assigned were in close agreement with the assignments made by Ganguly *et al.* [26], as shown in **Table 3**.

The FTIR spectra for specimens annealed at different temperatures in the normal phase (Figure 11), shows the same peaks assigned for the as grown crystal have been observed (Table 3). There is a slight shift in the peak positions because of the hydrogen bonding. There is no significant variation in the vibration frequencies with thermal annealing. With increasing annealing duration, the absorption peaks centered at 949.78, 1287.27,



Figure 10. Plot of $(n^2 - 1)^{-1}$ as a function of λ^{-2} (inset shows the linear fit of the linear part of the curve near the optical energy gap) for (TMA)₂ZnCl₄ single crystal.

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Assignment	Wavenumber (cm ⁻¹)			
Assignment	Annealed at 150°C for 2 h	Annealed at 150°C for 1 h	As grown	
C-N-C (skeletal bending)	454.16	456.62	457.05	
	458.02			
Symmetric stretching of C-N	949.78	949.78	949.78	
CH ₃ Rocking	1286.89	1287.31	1287.27	
O-H bending	1384.33	1384.59	1384.66	
Symmetric bending of CH ₃	1415.63	1415.58	1415.52	
Asymmetric bending of CH ₃	1484.25	1484.89	1483.98	
Symmetric stretching of CH ₃	2957.37	2958.49	2957.35	
Asymmetric stretching of CH ₃	3024.71	3025.2	3023.88	
O-H Vibration of water molecule	3443.77	3477.09	3476.12	

Table 3 Characteristic frequencies of various functional groups of (TMA)₂7nCl, crystal



1415.52 and 3023.88 cm⁻¹ decreases in intensity, while the peaks at 1597 and 1636 cm⁻¹ increase in intensity. Another significant spectral feature observed is the transformation of sharp peaks as at 457.05, 1287.27 and near 3470 cm⁻¹ to a broad hump with increasing the annealing duration. Also there is a complete removal of some peaks such as the peaks centered at 2366 cm⁻¹ and 2758 cm⁻¹ which decrease in intensity and then vanish completely.

Sveleba *et al.* [6] showed that, the temperature dependences of the birefringence $\delta(\Delta nc)$ for [N(CH₃)₄]₂ZnCl₄ crystal specimen annealed at 370 K for 1.5 h brought about a reduction of the rate of nonlinear variation of $\delta(\Delta nc)$ with the temperature. Also deviations from linear temperature dependences are observed in the dielectric permittivity temperature dependence measurements. They attribute this behavior to fluctuation processes and/or the appearance of a new phase state of the crystal.

4. Conclusions

1. Optical transmission studies showed that $(TMA)_2ZnCl_4$ crystal was optically transparent in the entire visible region with a lower cut-off below 256 nm. From the data the absorption coefficient (α) and the optical band gap E_{α}^{opt} was deduced (Figure 2). The type of transition was allowed indirect one.

2. The refractive index (*n*) was calculated as a function of photon energy. Values of the optical and electrical conductivities (σ_{opt} . & σ_{ele}) and the lattice dielectric constant (ε_L) and the ratio of free charge carrier concentration to the effective mass (N/m^*) were estimated at room temperature for samples of (TMA)₂ZnCl₄ and listed in Table 1.

3. The refractive index values have been fitted to the single oscillator Wemple-DiDomenico (WDD) model. The single oscillator energy (E_0), the dispersion energy (E_d), Static refractive index n_0 , Moments of the optical dispersion spectra M_{-1} and M_{-3} , Static refractive index n_0 and the Oscillator strength S_0 are calculated and presented in Table 2.

4. FTIR spectra was measured for the as grown and annealed crystals as shown graphically in **Figure 11**. CH₃, C-N and C-N-C groups are identified (**Table 3**) by the frequency assignments. For annealed samples, some absorption peaks decrease or increase in intensities. There is a transformation of some sharp peaks to broad humps.

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