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Temperature dependence of the optical parameters for potassium zinc chloride crystals doped with lithium ions

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Abstract

Temperature dependence of the optical parameters near the absorption edge of K_2ZnCl_4:yLi$^+$crystals, where $y = 0.00\%$, 0.34%, 0.86%, 0.94%, 1.13% and 1.29% is reported over the temperature range from 276 to 350 K. An analysis of the absorption spectrum reveals that the type of transition is the indirect allowed one. The absorption edge shifted towards lower energy with increasing temperature. As a necessity, the validity of the Urbach rule of the modified K_2ZnCl_4:yLi$^+$ crystals has been checked. In the region of the absorption edge, the Urbach parameters, the temperature dependence of the optical energy gap and the steepness parameter were evaluated as functions of both temperature and y concentration.

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Keywords: K_2ZnCl_4:yLi$^+$ crystals; Optical parameters; Temperature dependence

1. Introduction

Numerous materials with the general formula A_2BX_4, where A and B are cations and X is an anion, are isomorphous with the β-K_2SO_4 (space group Pmcn at high temperatures) are currently of interest because of their unusual ferroelectric properties [1]. K_2ZnCl_4 crystal, abbreviated (KZC), undergoes a sequence of phase transitions from the initial paraelectric phase (PE) at 553 K to an incommensurate phase (IC), then to the commensurate (C) ferroelectric phase (FE) at 403 K [2,3]. At room temperature it crystallizes in the orthorhombic space group ($Pna2_1$) with four molecules and unit cell $a = 12.38$, $b = 7.247$ and $c = 8.91$ Å [4]. The existence of incommensurate superstructure phases makes it important to grow these crystals (and others) and investigate their physical properties. Incommensurate (IC) materials have attracted much attention, because they constitute an intermediate class between crystalline and non-crystalline systems in that they exhibit perfect long-range order without translational periodicity at least in one direction. This intermediate class gives rise to many new phenomena that were not observed in crystals. On the other hand, a variety of effects that appear in the mentioned crystals do not have any analogies in the usual periodically arranged systems. The latter enables the application of IC materials in various optical devices [5].

Crystals of KZC grown from an aqueous solution near room temperature, consist of large domains and are particularly suited for the observation of polarization reversal by etching, powder and nematic liquid crystal techniques [6]. KZC crystals that were transformed completely to the IC phase by heating and then cooling to room temperature contain many domain walls, depending on the rate of cooling, and show complicated domain configurations [7].

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Many papers may be interested by potassium zinc chloride due to their unusual ferroelectric properties. There already exist some investigations which include theoretical, thermal, dielectric and spectroscopic properties of A_2BX_4 crystals [8–11]. The doping of impurities into KZC crystals through growth from solutions containing various materials results in modification of the crystal form. The effects on the electrical and optical properties of doping with metal ions, such as Ni^{2+}, Mn^{2+} and Co^{2+} at various concentrations have been studied [12–15]. There have been practically no reports available in respect of concentration dependence of optical constants in K_2ZnCl_4:yLi^+ crystals hereafter (KZC:Li). From this point of view, an attempt has been made to grow and characterize some KZC:Li doped crystals.

The aim of the present work is to obtain an insight into changes that may be produced on the type of optical transition, the optical energy gap and Urbach parameters of KZC crystals as a result of internal action, by doping with Li^+ in different concentrations, and external action, by variation of sample temperature.

2. Experimental

KZC:yLi^+ crystals were grown from an aqueous solution containing KCl, LiCl and $ZnCl_2$, respectively, by slow evaporation method at 306 K. To compensate its absorbent an excess of $ZnCl_2$ was added. Slow growing from solution in water has long been a standard method for growing large pure crystals of inorganic or organic substances. Slow growing increase the degree of internal order. And having a perfect crystal completely regular, free of defects and dislocations. Crystals of KZC:yLi^+ of $\sim$6 cm^3 were grown by this technique. In this case a multi-jars crystallizer was used so that the crystals with different (y) concentrations grew under the identical conditions. The actual concentrations (y) in the crystals were 0.00%, 0.34%, 0.86%, 0.94%, 1.13% and 1.29% as measured by the atomic absorption technique using an atomic absorption spectrometer, Pye Unicam, type Sp 1900. Crystals thus obtained, in a period of about nine weeks, were transparent, colorless of different morphologies, with well defined edges and free from visible cracks were chosen to prepare the samples. The sample is then reduced in thickness until it is convenient for transmittance measurements.

A Shimadzu UV–Vis-2101 PC dual beam scanning spectrophotometer was used to record the optical transmittance of the samples. Unpolarized monochromatic light in the energy range 3.4–6.4 eV was used. The surrounding medium was air and the measurements were done at different temperatures starting from 276 K and up to 350 K. The temperature of the sample was controlled using an ultra thermostat (Mgw Lauda type K2R, Germany) and it was measured with an accuracy of ±0.1 K. The direction of the incident unpolarized light was nearly perpendicular to the (0 1 0) plane. The expected overall error in the absorption coefficient was $\sim$2%.

3. Results and discussions

3.1. Crystals growing and morphology

Full-faced, transparent (except near the seed region), colorless KZC:yLi^+ doped crystals weighing 4–6 g were grown in 50–70 days. We carried out two or three growth experiment at each y_s. Fig. 1 shows some of the as-grown KZC:yLi^+ doped crystals. Furthermore, the external volume of crystals decreases with increasing Li^+ concentration in the solution. Moreover, the crystal growth ceases completely when the Li^+ concentration is greater than 10% in the solution.

3.2. Absorption coefficient

The absorption coefficient α was determined from the transmittance T_λ and the reflectance R_λ using the relation [16]:

$$\alpha = -\frac{1}{d}\ln\left[\frac{T_\lambda}{(1-R_\lambda)^2}\right] \quad (1)$$

where d is sample thickness and nearly equals 0.1 cm. In the above equation we can neglect R_λ compared to unity (i.e. $R_\lambda \ll 1$) and becomes:

$$\alpha = -\frac{1}{d}\ln[T_\lambda] \quad (2)$$

Results of the absorption coefficient (α) against photon energy ($h\nu$) in the energy range from 3.44 to 6.35 eV at room temperature for K_2ZnCl_4:yLi^+crystals with y = 0.00%, 0.34%, 0.86%, 0.94%, 1.13% and 1.29% Li^+ concentration are presented in Fig. 2a. The dependence shows continuous increase in α with increasing $h\nu$. Near the absorption edge α increases more rapidly with $h\nu$. It is clear that doping KZC crystal with Li^+ions affects both the magnitude of α and the shape of the α–$h\nu$ dependence at all energies.

To study the band gap nature and to estimate the value of the energy gap E_g, the following equation from the model proposed by Bardeen et al. [17], was used:

$$(\alpha h\nu)^n = A(h\nu - E_0) \quad (3)$$

where n is an index determined by the nature of the electron transition during the absorption process, ($n = 2$ for allowed direct transition, and $n = 1/2$ for allowed indirect transition) and A is a constant nearly independent of photon energy, known as the disorder parameter [18]. The transition energy E_0 is equal to E_g for direct transitions and $E_g \pm E_p$ for indirect transitions, where E_p is the energy of the associated phonon. The absorption coefficient in the present study can be reasonably well fitted by Eq. (3) with $n = 1/2$. This means that the optical transition in KZC:Li crystals is of the indirect type and that the fundamental edge is due to allowed indirect transitions.

The plot of $(\alpha h\nu)^{1/2}$ against the photon energy $h\nu$ at room temperature is shown in Fig. 2b and every line