Appl. Phys. B 67, 559–562 (1998)

Applied Physics B
Lasers
and Optics

# Electro-optic properties of $LiKSO_4$ and $LiK_{1-x}Rb_xSO_4$ crystals

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Received: 16 March 1998/Revised version: 2 June 1998

**Abstract.** The electro-optic properties of $LiK_{1-x}Rb_xSO_4$ for $x$ varying between 0 and 0.50 were investigated by an ac modulation method based upon the Sénarmont arrangement. The electro-optic coefficient $r_c$, and for the first time the coefficients $r_{41}$ and $r_{51}$ were determined with good accuracy in pure $LiKSO_4$ around room temperature at a wavelength of 633 nm. The frequency dependence of the electro-optic coefficient $r_c$ was measured in the frequency range from 1 kHz up to 1 MHz. The values of the factor of merit $n_e^3 r_c$ of the mixed crystals $LiK_{1-x}Rb_xSO_4$ were obtained for the first time, for the concentrations $x = 0.05, 0.10, 0.20$, and 0.50. The electro-optic properties are shown to be affected by the random presence of the rubidium ions in this disordered system.

**PACS:** 78.20.Jq; 78.20.Nv; 61.43.-j

In the last years, an increasing interest has been devoted to the research of new optical materials for opto-electronic devices, particularly for external modulation of laser beams. Lithium potassium sulfate ($LiKSO_4$) has been pointed out as a promising material for these applications, since it presents good optical quality, suitable electro-optic (EO) effect and fairly low dielectric permittivity [1]. A great number of experimental works have been devoted to the study of the physical properties of this crystal. It has been shown that it presents a very rich sequence of structural phase transitions, leading to different phases with pyroelectric and ferroelastic properties, EO effects, and, possibly, incommensurate structures [2–7]. The EO properties of $LiKSO_4$ were first studied by Sliker in 1964, who observed an effect three times higher than that of quartz [1]. Later, the temperature dependence of the EO coefficient $r_c$ in the low-temperature range was reported in the literature [6].

The room-temperature structure of $LiKSO_4$ has an hexagonal symmetry belonging to the space group $P6_3$ ($C_6^6$) with two formula units per unit cell [8, 9]. The lithium ions are surrounded by tetrahedrally coordinated oxygens, each one belonging to a different sulfate group; conversely each sulfate group is associated with four lithium ions. The potassium ions are localized along the $c$ hexagonal axis. Owing to the polar character of its room temperature symmetry, this crystal is pyroelectric and presents optical activity along the $c$ axis in this phase [10].

Recently we started a systematic study of the physical properties of mixed crystals of $LiK_{1-x}Rb_xSO_4$ ($x \leq 0.50$) by means of different experimental techniques: Raman scattering, birefringence and electrical conductivity measurements, differential scanning calorimetry, and neutron powder diffraction [11–13]. These studies showed that this system presents a sequence of phase transitions similar to that of the pure crystal ($x = 0$). The presence of rubidium ions in the potassium sites introduces a large change of the transition temperatures and leads to the smearing of the first-order transitions. At room temperature, the crystals with $x \leq 0.25$ present an average hexagonal symmetry with the point group 6 ($C_6$), analogous to the $LiKSO_4$ crystal [11]. On the other hand, the crystals with $x \geq 0.25$ are isomorphous with the trigonal low-temperature phase of the $LiKSO_4$, which belongs to the point group $3m$ ($C_{3v}$) [13].

In this work, we present accurate measurements of the EO coefficients $r_c$, $r_{41}$ and $r_{51}$ of $LiKSO_4$ by using an accurate ac modulation method. We show the frequency dependence of the EO coefficient $r_c$ in the frequency range 1 kHz to 1 MHz. We also investigate the EO properties of the mixed crystals $LiK_{1-x}Rb_xSO_4$ in order to study their optical characteristics in comparison with the pure system ($x = 0$). The figure of merit $n_e^3 r_c$ (the refractive indices of the mixed crystals are unknown) of these crystals was obtained, at room temperature, for the concentrations $x = 0.05$, 0.10, 0.20, and 0.50 and for an electric field modulation frequency of 1 kHz.

## 1 Electro-optic effect

The linear EO properties of the crystals with the hexagonal symmetry 6 ($C_6$) are described by four coefficients $r_{13}$, $r_{33}$, $r_{41}$ and $r_{51}$ [14]. For this symmetry, the corresponding indicatrix in the presence of an electrical field $\boldsymbol{E} = (E_1, E_2, E_3)$ can be written in the principal axes system of the crystal $(x, y, z)$ as:

$$\left(1/n_o^2 + r_{13}E_3\right)\left(x^2 + y^2\right) + \left(1/n_e^2 + r_{33}E_3\right) z^2 \\ + 2\left(r_{41}E_1 + r_{51}E_2\right) yz + 2\left(r_{51}E_1 - r_{41}E_2\right) xz = 1\,, \qquad (1)$$

where $n_o$ and $n_e$ are the ordinary and extraordinary principal refractive indices, respectively. Hereafter we consider only the absolute value of the EO coefficients.

If the light beam is propagating along the $x$ axis and the electrical field is applied along the $z$ axis, the field-induced birefringence in the $(y, z)$ plane is given by:

$$\Delta n_{yz}(E) = \frac{n_e^3 r_c E_3}{2}, \tag{2}$$

where the effective coefficient $r_c$ is defined by:

$$r_c = r_{33} - \left(n_o^3/n_e^3\right) r_{13}. \tag{3}$$

The EO coefficient $r_{41}$ can be determined when the electric field is applied along the $x$ axis and the light beam is propagating along the $y'$ axis. This new coordinate system $(y', z')$ is obtained by a 45° rotation of the principal axes around $x$. Thus, the coefficient $r_{41}$ is related to the field-induced birefringence by [15]:

$$\Delta n'_{xz'}(E) = \frac{n_{oe}^3 r_{41} E_1}{2}, \text{ with } \quad n_{oe} = \left(\frac{2n_o^2 n_e^2}{\left(n_o^2 + n_e^2\right)}\right)^{1/2}. \tag{4}$$

In the same way, the EO coefficient $r_{51}$ (which is, owing to the symmetry, equal to $r_{42}$) can be obtained when the electric field is applied along the $y$ axis, and the light is propagating along the $y''$ axis, which corresponds to the $y$ axis rotated at 45° around the $x$ axis:

$$\Delta n''_{xz''}(E) = \frac{n_{oe}^3 r_{51} E_2}{2}, \tag{5}$$

where $n_{oe}$ is determined by (4) above. The sample configurations used for the measurement of the coefficients $r_c$, $r_{41}$ and $r_{51}$ are shown in Fig. 1a.

Finally, the field-induced phase shift for each component of the light polarization can be expressed by

$$\Gamma_i(E) = \frac{2\pi L_i}{\lambda} \Delta n_i(E), \tag{6}$$

where $L_i$ is the crystal length along the light propagation direction, $\lambda$ the wavelength of the light beam, and $\Delta n_i(E)$ the field-induced birefringence in the light path.

## 2 Experimental procedures

The ac modulation method used for the determination of the EO coefficient is based on the Sénarmont arrangement, as depicted in Fig. 1a [16]. The sample is placed between a linear polarizer and a quarter-wave plate, the latter being followed by a linear analyzer. Each optical component (including the sample) is oriented at 45° relative to its predecessor, except the analyzer, located at an azimuthal angle $\beta$ with respect to the principal axes of the sample. Under these conditions, the optical transmission factor of the lossless system is:

$$T = I/I_o = (1/2)\left[1 - \sin(\Gamma - 2\beta)\right], \tag{7}$$

where $I_o$ and $I$ are, respectively, the input and output light intensities and $\Gamma$ is the total phase shift introduced by the sample. If only an ac electric field is applied on the sample, the total phase shift $\Gamma$ can be expressed as [15]:

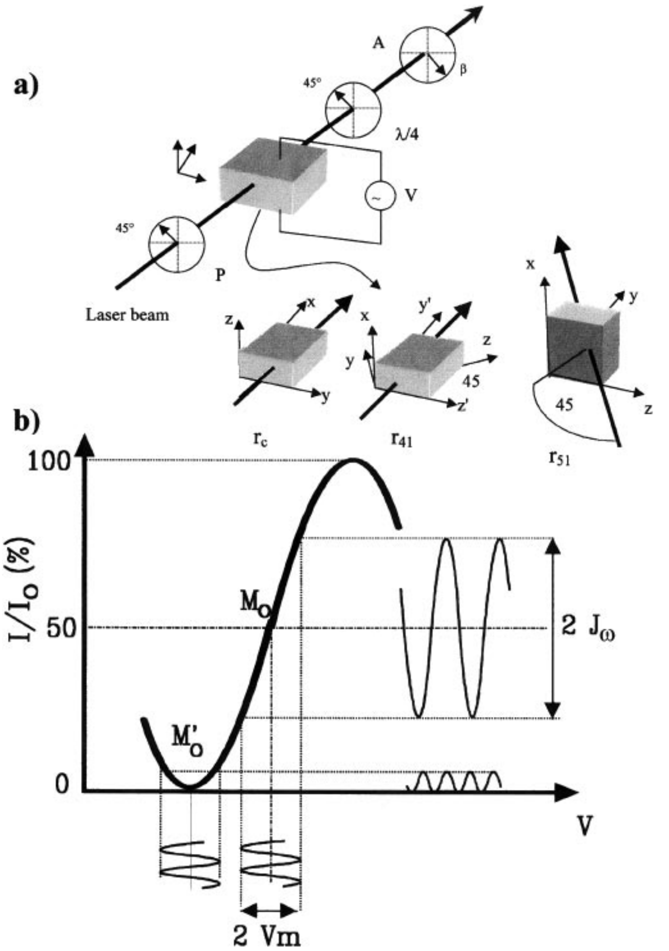

**Fig. 1.** **a** Sénarmont arrangement and sample configurations for measuring the EO coefficients $r_c$, $r_{41}$, and $r_{51}$. The optical elements are indicated by P: linear polarizer; $\lambda/4$: quarter-wave plate, and A: analyser. **b** Optical transmission function of the Sénarmont setup with the two particular working points

$$\Gamma = \Gamma(0) + \Gamma_m \sin \omega_m t, \tag{8}$$

where $\Gamma(0)$ represents the spontaneous phase shift of the crystal and $\Gamma_m$ the amplitude of the induced phase shift due to the ac field at the $\omega_m = 2\pi f$ angular frequency.

In order to obtain the EO coefficients, the azimuthal angle of the analyzer is adjusted to a particular point (see Fig. 1b), called $M'_0$ $(\beta = \Gamma(0)/2 + k\pi/2)$ with $k = 0, \pm1, \pm2\ldots$, so that the phase shift owing to the spontaneous birefringence of the crystal is compensated. Under these conditions, when the induced phase shift $\Gamma_m$ is very small, (7) can be expanded in Bessel functions, limited to the first-order term:

$$T = \frac{1}{2} + \frac{\Gamma_m}{2} \sin \omega_m t \quad \text{for } k = 0, \pm2, \pm4\ldots,$$
$$T = \frac{1}{2} - \frac{\Gamma_m}{2} \sin \omega_m t \quad \text{for } k = 0, \pm1, \pm3\ldots. \tag{9}$$

The sinusoidal term of (9) corresponds to the output-modulated signal defined by the modulation coefficient $m$ as:

$$\Gamma_m = \frac{2J_\omega}{I_0} = m\,, \tag{10}$$

where $J_\omega$ is the amplitude of the output-modulated signal. Finally, using the equations above, the EO coefficients can be obtained by:

$$r_c = \frac{\lambda d m}{\pi L n_e^3 V}, \quad r_{41} = \frac{\lambda d' m'}{\pi L' n_{oe}^3 V'}, \quad r_{51} = \frac{\lambda d'' m''}{\pi L'' n_{oe}^3 V''}, \tag{11}$$

where $m$, $m'$, and $m''$ are the modulation coefficients, $d$, $d'$, and $d''$ the inter-electrode spacings, $V$, $V'$, and $V''$ the amplitudes of the applied voltages.

The frequency dispersion of the $r_c$ coefficient was measured for modulation frequencies varying between 1 kHz and 1 MHz and using the 633 nm wavelength of a HeNe laser. Owing to their very low values, and thus to a poorer accuracy, the EO coefficients $r_{41}$ and $r_{51}$ were measured only at one frequency (1 kHz). In both cases the amplitude of the ac voltage was 130 V. In order to obtain the temperature dependence of the spontaneous birefringence, and thus the value of the thermo-optic coefficient, we used the compensation of the phase shift [16] $\Gamma(T) = (2\pi L/\lambda)\Delta n(T)$ that is induced by a variation of the temperature $T$. In this case, the compensation is achieved step by step by appropriate rotations $\delta\beta = \delta\Gamma/2$ of the analyser in order to track the extinction of the light or the double-frequency point $M_0$ (Fig. 1b) of the optical modulation. For all measurements, silver paste electrodes were applied to the surfaces of the samples. In the case of $r_{51}$ coefficient, the sample was electroded with semi-transparent evaporated gold coating.

Single crystals of $LiK_{1-x}Rb_xSO_4$ were grown by slow evaporation of aqueous solutions containing the salts of $Li_2SO_4{:}H_2O$, $Rb_2SO_4$ and $K_2SO_4$ in molar ratios $x = 0$, 0.05, 0.10, 0.20, and 0.50. Transparent crystal of $LiKSO_4$ ($x = 0$) were obtained in the form of hexagonal bipyramids with direct identification of the $z$ axis. The $x$ axis was defined as perpendicular to the $z$ axis and parallel to a natural face of the crystal. The morphology of the mixed crystals was the same as presented by the pure crystal, except the crystal $x = 0.50$, which was hexagonal-rod type. The Rb concentrations in the crystals were confirmed by X-ray fluorescence analysis. The investigated samples were cut from untwined regions and polished for optical measurements. Typical sample dimensions were 8 mm × 6 mm × 1 mm.

## 3 Results and discussions

### 3.1 *Pure* $LiKSO_4$ *crystal*

The EO coefficients of $LiKSO_4$ were determined from (4), (10), and (11), using ordinary and extraordinary refractive indices of 1.4705 and 1.4703, respectively [17]. The measured values of the coefficients $r_c$, $r_{41}$ and $r_{51}$ for a modulation frequency of 1 kHz are reported and compared with those of literature in Table 1. In the case of the $r_c$ coefficient, our measured value is 30% and 40% smaller than the previously reported ones [1, 6], respectively. This difference could be related to the experimental method utilised by those authors, who used the compensation of the phase shift $\Gamma(V_{dc}) = (2\pi L/\lambda)\Delta n(V_{dc})$ induced by dc electrical voltage [16]. Within this method and before applying the dc voltage the analyser angle is adjusted to compensate the natural phase shift $\Gamma(0)$. Consequently, only the dc voltage-induced phase shift is in principle measured. In fact, $\Gamma(0)$ can vary with the temperature (thermo-optic effect) during the measurements and thus introduce an error in the value of $\Gamma(V_{dc})$. In order to determine the thermo-optic effect and to estimate the additional errors in the EO coefficients due to the thermo-optical contributions, the temperature change of the spontaneous birefringence in the $(y, z)$ plane was measured around room temperature. The results, plotted in Fig. 2, yield a linear temperature variation of the birefringence, with a slope equal to $\delta\Delta n/\delta T = 2.32 \times 10^{-6}\,°C^{-1}$, which can be considered as a rather weak thermo-optic coefficient. Nevertheless, a simple calculation with the sample dimensions used in the case of [6], leads to a phase shift $\Gamma(T)$ equal to 0.6°, which could be due to a variation of temperature of 0.1 °C. This value has to be compared with the 11.3° of the phase shift $\Gamma(V_{dc})$ induced by a voltage of 5 kV [6]. This indicates that even small fluctuations of temperature during measurements could give rise to a non-negligible source of errors in the determination of the EO coefficients. Thus, this effect could explain the dis-

**Table 1.** Room-temperatute electro-optic coefficients $r_c$, $r_{41}$, and $r_{51}$ of $LiKSO_4$, for a modulation frequency below piezoelectric resonances, and for a wavelength of 633 nm. ($\lambda = 546$ nm in the case of Sliker results)

| Authors | $r_c$ /pm/V | $r_{41}$ /pm/V | $r_{51}$ /pm/V |
|---|---|---|---|
| Present results | $1.1 \pm 0.06$ | $0.14 \pm 0.015$ | $0.29 \pm 0.03$ |
| Fujimoto [6] | $1.9 \pm 0.15$ | – | – |
| Sliker [1] | $1.6 \pm 0.16$ | – | – |

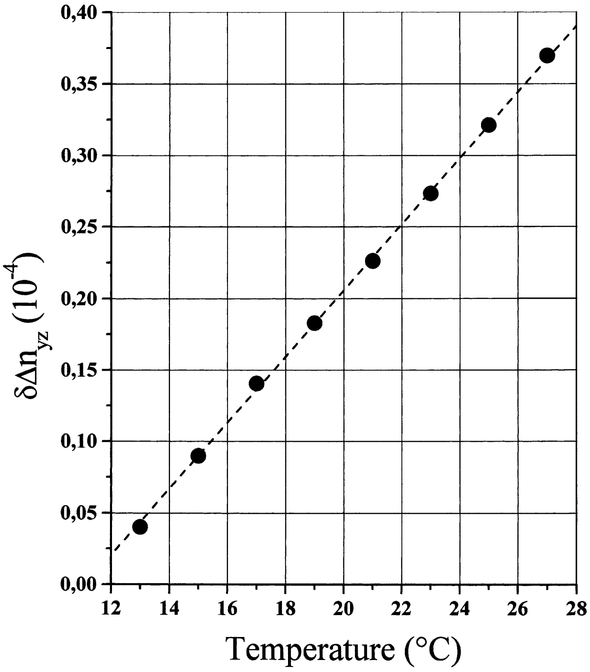

**Fig. 2.** Temperature dependence of the variation of the spontaneous birefringence $\delta\Delta n_{yz}$ in the $(y, z)$ plane. The slope of the *curve* gives the value of the thermo-optic coefficient which is equal to $2.32 \times 10^{-6}\,°C^{-1}$

crepancy between our value of the $r_c$ coefficient and those of other authors listed in Table 1.

The dependence of the $r_c$ coefficient of $LiKSO_4$ on the modulation frequency was investigated for an applied voltage $V = 100\,V_{pp}$. The EO coefficient presented a nearly constant value up to 200 kHz, beyond which two sharp peaks appeared at frequencies around 570 and 650 kHz. These peaks originate from the piezoelectric resonances in the crystal.

Our results allow us to conclude that $LiKSO_4$ could be an interesting material for specific modulation applications, since it presents a low dielectric permittivity and a weak thermo-optic effect around room temperature. Nevertheless, we observe that this crystal possesses relatively weak EO coefficients, which limits the range of possible technological applications.

### *3.2* $LiK_{1-x}Rb_xSO_4$ *mixed crystals*

Now we present a first study of the EO properties of the mixed crystals $LiK_{1-x}Rb_xSO_4$. From measurements obtained at a frequency of 1 kHz the figure of merit $n_e^3 r_c$ is plotted in Fig. 3 as a function of the concentration of rubidium. The value of $n_e^3 r_c$ remains nearly constant for small amounts of rubidium ($x \leq 0.05$), and then strongly decreases with increasing the rubidium concentration. It is interesting to note that the value is the same for the crystals with $x = 0.10$ and $x = 0.20$, which have the same hexagonal structure as pure $LiKSO_4$, and slightly smaller for the trigonal crystal $x = 0.50$.

The non-monotonous dependence of $n_e^3 r_c$ on the rubidium amount merits attention. It cannot be explained by a modification of crystal symmetry, but rather by a smaller deformation of the lattice and by a change of ionic polarizabilities due to the introduction of rubidium ions in the lattice.

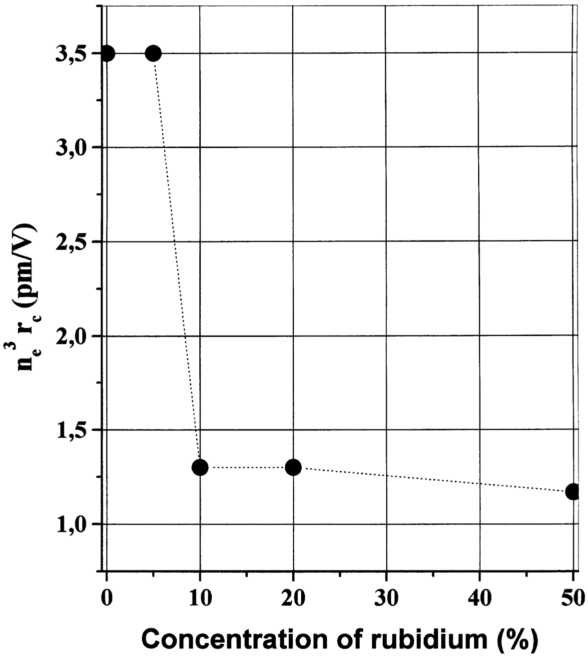

**Fig. 3.** Figure of merit $n_e^3 r_c$ of $LiK_{1-x}Rb_xSO_4$ measured for a frequency of 1 kHz, a wavelength of 633 nm and at room temperature as a function of the concentration of rubidium ($x$)

The EO properties in pure $LiKSO_4$ probably originate from the ionic polarizabilities of the sulfate group, and partly from the lithium ion. The substitution of potassium ions by larger rubidium ions causes both a smaller deformation of the lattice and of polarizable ions, and thus a decrease of the EO properties at low frequencies (below piezoelectric resonances). This is proved by the value of $n_e^3 r_c$ found for $x \geq 10\%$, which is close to the purely electronic contribution ($\approx 1$ pm/V), as derived from the second-harmonic generation coefficients [18, 19] in pure $LiKSO_4$.

## 4 Conclusions

The EO coefficients $r_c$, $r_{41}$, and $r_{51}$ have been determined for the hexagonal room-temperature phase of $LiKSO_4$. Although the obtained values were not very large for technological interest, the low dielectric permittivity and thermo-optic effect around room temperature are in favour for applications in optical modulators. In addition, the EO response has been measured between $1–10^3$ kHz. The results reveal that the EO response is frequency independent up to 500 kHz just below the piezoelectric resonances.

The factor of merit $n_e^3 r_c$ of $LiK_{1-x}Rb_xSO_4$ mixed crystals has been determined for the first time thanks to a very sensitive method. The obtained values are nearly 30% of that of the pure crystal, with a small dependence on the rubidium amount. This suggests that the ionic contribution to the EO effect is nearly cancelled by the randomly distribution of the rubidium ions in the lattice.

*Acknowledgements.* This work was partially supported by the Brazilian agency Conselho Nacional de Desenvolvimento Cientifico e Tecnologcio.

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