Cs^+-K^+ Exchange in Z-Cut $KTiOPO_4$ Crystal Covered with Chromium Masking Layer *

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Cs^+–K^+ ion exchanges are performed on z-cut $KTiOPO_4$ crystals with chromium coating covered. The temperature of ion exchange is 430° C, and the time range from 15 min to 30 min. The dark mode spectra of the samples are measured by the prism coupling method. The channel structures on the samples are observed by a microscope and the near field pattern of the channel waveguides are measured by the end-fire coupling method. The refractive index of the samples increases and the increments at surface are modulated due to the existence of Cr film. In the region covered by Cr film, the refractive index of the samples at the surface increases dramatically in a shallow layer. The results of energy dispersive x-ray spectra indicate that in the region covered with Cr film, Cr ions participate in the ion exchange process, and enhance the refractive index. The results may provide a possibility that achieves index enhancement and Cr doping synchronically.

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Potassium titanyl phosphate ($KTiOPO_4$, KTP) is a very promising nonlinear optical crystal because of its excellent optical properties and high damage threshold.[1] A combination of high nonlinear coefficient, wide transparency range and broad angular as well as thermal acceptance make it very attractive for different nonlinear optical and waveguide applications.[2−4] A waveguide for nonlinear optical effect, such as second-harmonic generation, is desirable since it enhances the conversion efficiency and enables miniaturization of the laser source.[5]

Fabrication of KTP waveguide has been reported by ion exchange, which is performed by immersing z-axis-oriented KTP crystal in Rb, Cs or Tl nitrate bath.[6] Ion exchange is also an important alternative method for fabricating periodically poled KTP (ppKTP) structure, which is a key part in frequency doubling of semiconductor diode laser.[5,7] A typical method of fabricating KTP channel waveguide or ppKTP is to immerse z-cut KTP in molten $RbNO_3$, permitting rubidium ions to enter the KTP substrate in exchange for potassium ions.[8] Adding $Ba(NO_3)_2$ to the melt with different molar ratio was found to provide a way of controlling the diffusion rate and achieving periodic domain inversion. Compared to Rb–K exchange, Cs–K exchange has high diffusion rate and results in large refractive index enhancement, therefore is more conducive to the formation of waveguides. However, reports on channel waveguide structure in KTP by ion exchange in molten $CsNO_3$ are very few, probably because of the high molten point of $CsNO_3$ (414°C), which make it difficult to find a suitable metal material to be the masking layer. Because of the excellent chemical stability of Cr film, it has been used as mask material in many cases.[9,10] In this Letter, we report the investigation of fabricating channel structure on KTP crystals with Cr mask by ion exchange in molten $CsNO_3$, and discuss the properties of the formed waveguide and the method of incorporation of Cr ion into a KTP waveguide by ion exchange.

Z-cut KTP crystals are provided by the School of Chemistry and Chemical Engineering, Shandong University. The samples with size of $10\times10\times1.5\,mm^3$ are optically polished on the up-surface and cleaned with O plasma before deposition. A 200–400-nm-thick Cr film is applied to the up-face of the KTP samples by sputtering and patterned using standard photolithography techniques to produce an 8-μm channel structure with a period of 100 μm. In order to prevent the crack of the substrate, the samples are first gradually heated in a preheating oven nearly to the temperature of the melt before being immersed, then the crystals are immersed in the molten $CsNO_3$ at 430°C. After the diffusion time of 15 min and 30 min respectively, the KTP samples are removed from the melt rapidly and cooled gradually down to room temperature to prevent the crack of the samples. The prism-coupling (model 2010 prism coupler (Metricon, USA)) and the end-fire coupling method were employed to investigate the properties of the both planar and channel waveguides probably formed. A polarizing micro-

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scope was used to observe the channel structure after ion exchange processing. The energy dispersive x-ray (EDX) spectra were used to observe and analyse the constituent of samples after ion exchange.

After both 15 min and 30 min ion exchange process, no Cr coating can be found on the surface of the samples. The molten salt looks a bit yellow-green colour. It may be due to the existence of Cr oxide, such as Cr_2O_3. Because $CsNO_3$ has a strong oxidation effect, Cr can be oxidized in the exchange process and then dissolved in molten salt. Especially when the temperature is high (430°C), the molten salt contains much dissolved oxygen. In order to examine the face that the absent of Cr coating after ion exchange is not due to Cr in-diffusion or the poor adhesion of Cr to KTP crystal, one as-deposition sample with patterned Cr coating is firstly annealed at 300°C for 30 min and 430°C for 15 min, respectively. No noticeable difference can be found on the surface of annealed sample from that of the as-deposition sample. Since the Cr coating sheds in the ion exchange process, the Cs^+ substituting K^+ may occur in the area of KTP surface with Cr coating.

After ion exchange finished, the samples are measured using conventional prism-coupling method and the results are compared with that of the KTP without Cr coating, which is performed under the same ion exchange temperature for 15, 30 and 120 min, respectively. Figure 1 shows the dark mode spectra of the sample with Cr coating after ion exchange in $CsNO_3$ at 430°C for 30 min and the KTP sample without the Cr film exchanging for 30 and 120 min. The index profiles can be reconstructed by inverse Wenzel–Kramers–Brillouin (iWKB) method,[11] as shown in Fig. 2.

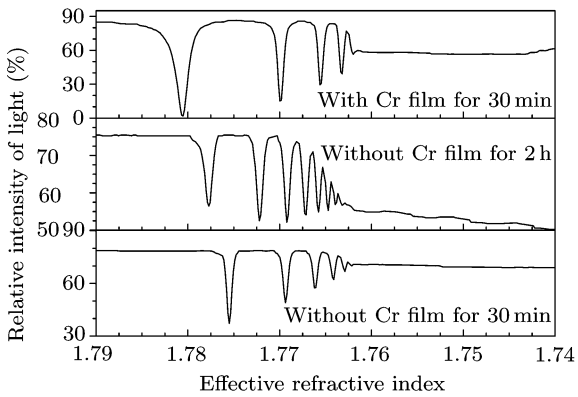

Fig. 1. Dark mode spectra of the sample with Cr coating for exchange 30 min compared with that of the sample without Cr coating.

The refractive index distribution for Cs ion exchange KTP waveguide can be successfully approximated with the exponential function[12]

$$n(z) = n_0 + \Delta n \exp(-z/D), \qquad (1)$$

where n_0 is the index of substrate; Δn is the maximum index increment; D is the effective diffusion depth. Using Eq. (1) to fit the refractive index profiles of samples with and without Cr coatings after ion exchange, the waveguide parameters are obtained and shown in Fig. 2. From the results it can be found that under the same ion exchange condition, the surface index of KTP with Cr coating is higher than that of the sample without Cr coating. The value is even larger than the saturated surface index after normal ion exchanged in $CsNO_3$ for 120 min. The result means that the index modulation by ion exchange is enhanced because of the existence of Cr oxide. The similar results are obtained for n_y and n_z, except that the dark mode spectrum of index n_y shows a somewhat extraordinary profile, which is shown in Fig. 3. It can be found that a very broad dip appears in the left side of the profile for the samples after ion exchange for both 15 min and 30 min. The possible explanation is that n_y on the sample surface increases dramatically because of

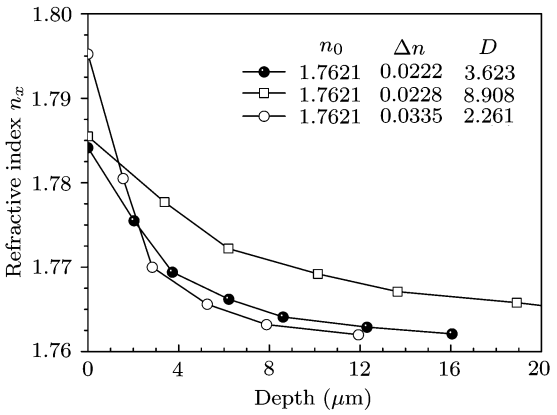

Fig. 2. Refractive index profiles for the samples with and without Cr coating after exchange in $CsNO_3$ melt: closed circles: without Cr film exchange for 30 min, open circles: with Cr film exchange for 30 min, squares: without Cr film exchange for 120 min.

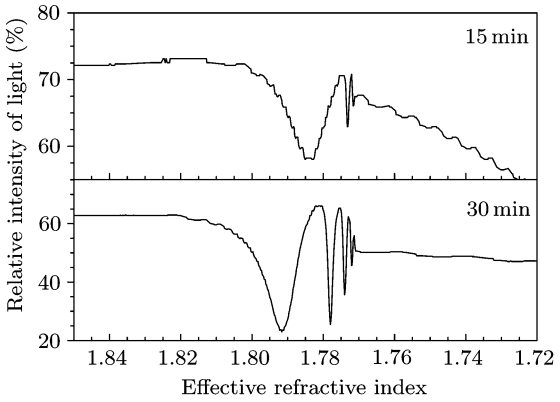

Fig. 3. Relative intensity of the reflected light versus the effective refractive index n_y of the incident light.

the existence of Cr coating, whereas the increment of n_y is limited in such a shallow layer so that the waveguide mode with large index can not be confined well.

Beam propagation method (BPM) is used to reconstruct the refractive index profiles n_y based on step functions. The results are shown in Fig. 4, which gives a good coincidence with the above analysis. Table 1 lists the structure parameters and the calculated and measured mode indices.

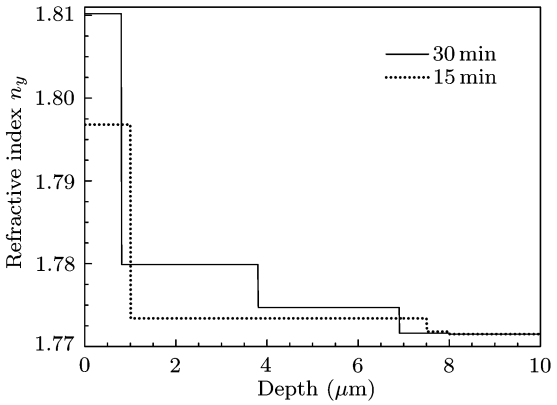

Fig. 4. Refractive index profiles of the samples with Cr coating after exchange 15 and 30 min reconstructed by BPM based on step functions.

Table 1. Profile structure parameters of n_y and mode indices for samples with Cr coating. Y: index; D: depth.

Sample	Adjustable parameters	Calculated mode index	Measured mode index
30 min	$Y_1 = 1.8102$, $D_1 = 0.8$	1.7915	1.7917
	$Y_2 = 1.7799$, $D_2 = 3.8$	1.7777	1.7780
	$Y_3 = 1.7747$, $D_3 = 6.9$	1.7742	1.7740
	$Y_4 = 1.7716$, $D_4 = 8.0$	1.7714	1.7721
15 min	$Y_1 = 1.7968$, $D_1 = 1.0$	1.7839	1.7839
	$Y_2 = 1.7734$, $D_2 = 7.5$	1.7732	1.7731
	$Y_3 = 1.7718$, $D_3 = 0.5$	1.7719	1.7715

As is found above, the refractive index increases on the entire surface of the samples but is modulated periodically by the pattern of Cr coating. Channel waveguide is formed as well, and is demonstrated by end-fire coupling measurement. The light confinement near the top surface of the sample may be degraded because of lacking of enough index contrast on the two sides of the channel structure. However, it can be improved by removing the thin layer near the sample surface. The channel structure in our experiment observed is given in Fig. 5(a) and the near-field pattern measured at the wavelength 1.55 μm is shown in Fig. 5(b). Because the depth of waveguide is deep enough, three guiding modes are excited in the perpendicular direction.

For investigating the function of Cr coating in the ion exchange process, the constituent of sample at top surface is analysed using EDX technique and the results are shown in Fig. 6. The dotted and solid line represent the EDX spectra from the sample areas with Cr film and without Cr film (channel structure), respectively. The enlarged plot in the range from 4 keV to 7 keV is inset in Fig. 6. Several coincidence strong peaks are found in both spectra, which correspond to the constituent elements of KTP, such as K, P, Ti and Cs. Au is detected because a thin Au coating is deposited on the sample surface for conduction. In addition, a small peak from element Cr is found only in the EDX spectra with Cr film, while no Cr is found in the channel structure (see the inset in Fig. 6). This

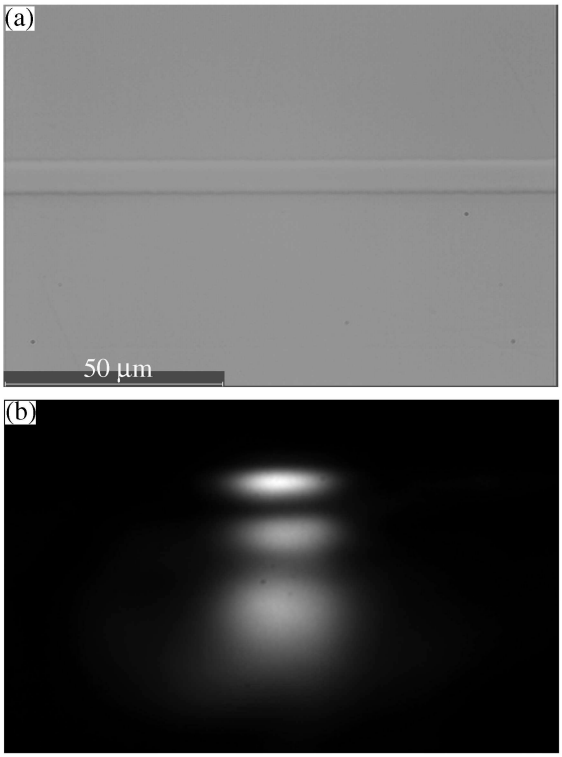

Fig. 5. Channel structure observed by a microscope and the near-field pattern of the TE mode in channel waveguide at 1.55 μm.

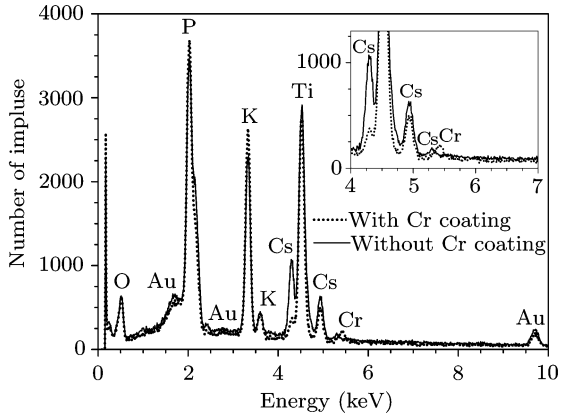

Fig. 6. EDX spectra of samples with and without Cr coating after exchange for 30 min.

means that an amount of Cr involves in the exchange process when Cr film is deposited on the KTP surface. Although some Cr ions exist in the molten salt, these Cr ions do not involve the ion exchange process. It can be supposed that in the region covered by Cr film, chromium may be doped into KTP in ionic form, e.g. Cr^{3+} or Cr^{4+}, to substitute the Ti^{4+} in KTP crystals. Although the process of Cr incorporation in the present experiment is unclear, it provides a method of doping Cr ions directly into KTP waveguides by ion exchange.

In summary, Cs^{+}–K^{+} ion exchanges have been produced on $KTiOPO_4$ crystals with a chromium masking layer on top surface. The temperature and time of ions exchange are 430°C and 15 or 30 min. Waveguides with index increasing are fabricated and the dark mode spectra are measured by the prism coupling method. The channel structure is formed and the near-field pattern is observed. The refractive index increments at the surface are modulated due to the existence of Cr film and the refractive index of the sample covered by a Cr coating increases dramatically in a shallow layer. The results of EDX spectra indicate that in the region covered with Cr film, Cr ions are doped into KTP waveguides and the refractive index increment is enhanced. The present work provides a possible method to achieve the index increment and Cr doping in fabricating waveguides simultaneously. Further investigation on the characters of the waveguide and ion exchange process will be carried out later.

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