Emergence of new crystalline phase in high-temperature annealed, carbon irradiated α-$KY(WO_4)_2$

R. N. Frentrop[1], V. Tormo-Marquez[2], J. Olivares[2,3], S. M. García-Blanco[1,*]

[1]Optical Sciences Group, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

[2] Centro de Micro-Análisis de Materiales, Universidad Autónoma de Madrid, E-28049-Madrid, Spain

[3] Instituto de Óptica "Daza de Valdés", Consejo Superior de Investigaciones Científicas (CSIC), Calle Serrano 121, E-28006-Madrid, Spain

*s.m.garciablanco@utwente.nl

Potassium double tungstates are very interesting crystalline materials for the fabrication of waveguide amplifiers and lasers, because they exhibit a large transparency window, long inter-ionic distances (d≈0.5 nm) and large transition cross-sections for rare-earth ions. Swift carbon ion irradiation and consecutive annealing is used to fabricate high-contrast planar waveguides in monoclinic α-$KY(WO_4)_2$. The first micro-Raman and m-lines measurements on high-temperature annealed, above amorphization threshold irradiated crystals (>$3\cdot10^{14}$ ions/cm^2) are presented. When the irradiated crystals are annealed at temperatures above 450°C, these measurements show the emergence of a polycrystalline layer with a new crystalline phase in the region amorphized by the irradiation, with a refractive index lower than that of unirradiated $KY(WO_4)_2$. Therefore, although several problems still need to be solved, this method has the potential of producing high-contrast waveguides with a step-like refractive index profile and acceptable transmission losses.

Introduction

Crystals from the potassium double tungstate family ($KY(WO_4)_2$, $KLu(WO_4)_2$, $KGd(WO_4)_2$, i.e. KREW), which have a stable monoclinic crystal phase and are therefore birefringent, exhibit several optical properties favorable for use in integrated optical devices. In particular, their high absorption and emission cross-sections [1], long inter-ionic distance between doping rare-earth ions [2] and relatively good thermal properties, makes KREW crystals interesting candidates for optical amplifiers and lasers with very high gain. In recent years, amplifiers [3] and lasers [4] have been demonstrated in low-contrast KREW waveguides with high gain and a relatively low lasing threshold. The efficiency of these devices can be improved by using high-contrast KREW waveguides, which increases mode confinement and therefore mode field intensity. However, growth of the crystal on low-index substrate materials is impossible due to lattice mismatch. Alternative methods have been investigated to fabricate these waveguides, such as lapping-and-polishing [5] and ion irradiation [6]. We have further investigated the possibility of using ion irradiation to fabricate a refractive index profile in $KY(WO_4)_2$, and in particular the effect of post-irradiation annealing to reduce optical losses. In this paper, preliminary results of high-temperature annealing of the irradiated crystals are shown. The Raman and m-lines measurements indicate the emergence of a new polycrystalline phase in the layer damaged above threshold by the ion irradiation after high temperature (>450°C) annealing.

Swift heavy ions are used to produce a layer of damage in the target material. Due to the high energy and relatively high mass of the carbon ions, the damage in the material is mostly caused by electronic interaction, e.g. ionization of the target material, although at the end of the ion path nuclear damage – caused by ballistic interactions – is present. The induced damage follows a Bragg-curve, increasing gradually up to the point where the damage build-up causes full amorphization. The depth and magnitude of the damage can be tuned by varying the ion energy and fluence, respectively. The best optical mode confinement in a planar waveguide is achieved with a refractive index profile that is close to step-like. With that aim and based on work from Merchant et al. [6] carbon ions were chosen for the irradiations. Results from simulations in SRIM 2008 (Scattering and Range of Ions in Matter) and mode calculations – using an estimated refractive index profile – in Lumerical MODE Solutions, indicate that single mode slab waveguides can be fabricated using an energy of 9 MeV. The optimal ion fluence was experimentally determined at $3{\cdot}10^{14}$ ions/cm^2 as a compromise between mode confinement and damage-induced optical losses. At this fluence, the region around the maximum electronic damage is irradiated at energies above the amorphization threshold, creating a 2 µm thick layer of amorphized $KY(WO_4)_2$ at around 2.5 µm from the surface of the crystal. An annealing step is necessary after irradiation to remove color centers and reduce scattering points caused by irradiation damage. Without this annealing step the losses in the material are too high for optical guiding. The annealing step can greatly influence the amount of modes supported by the slab because damage repair also causes the refractive index profile to change.

Experimental methods

The $KY(WO_4)_2$ crystals used in this research are 10x10x1 mm^3 (axcxb) crystals fabricated by Altechna (LT). The crystals have been polished by Altechna on one side (axc plane, with the b-axis pointing inwards), which is also the surface used for irradiation. A scratch was made on this surface with a diamond pen along the c-axis to avoid cracking of the sample during the ion irradiation. Irradiation was performed at the Centro de Micro-Análisis de Materials (CMAM) of the Universidad Autónoma in Madrid. After irradiation, the crystals were consecutively annealed at different temperatures, ranging from 150°C to 650°C, to study the effect of the annealing process. During annealing, care was taken to keep the temperature gradient around 1°C/min to avoid thermal stress to the sample.

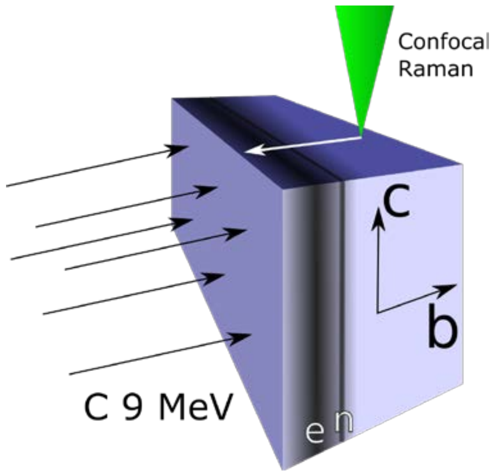

Figure 1. Schematic image of a 9 MeV carbon ion irradiated $KY(WO_4)_2$ crystal, the direction of the ion beam and the scanning direction of the confocal Raman measurements. The black gradients in the crystal give an impression of the damage profile caused by the carbon ions, where "e" indicates the electronic barrier and "n" the nuclear barrier.

Confocal Raman measurements were performed on the samples using a WiTec alpha300R/S/A microscope. The samples were polished at one endfacet (axb facet) to resolve the Raman spectra at different irradiation depths. An excitation wavelength of 532 nm was used, and an analyzing grating of 1800 gr/mm. Figure 1 shows a schematic drawing of an irradiated crystal and the Raman measurement method. M-lines measurements were performed in the Metricon 2010/M prism coupler at a wavelength of 1550 nm. At this wavelength the refractive index of the $KY(WO_4)_2$ is n≈2.

Results

Annealing of the irradiated crystals at temperatures up to 450°C results in removal of the color centers so that the original $KY(WO_4)_2$ transmission spectrum is recovered [7]. As a consequence, the optical losses are significantly lowered. A partial recovery of the original Raman spectrum of the $KY(WO_4)_2$ in not fully amorphized regions [8] can be clearly observed. However, when annealing the ($3\cdot10^{14}$ ions/cm^2) irradiated crystals to temperatures above 450°C, the Raman spectrum of the amorphized layer changes from a clearly amorphous spectrum (Figure 2a, above threshold) to a spectrum that exhibits sharp peaks, indicating recrystallization. The intensity and Raman shift of these peaks depend on the position of the focus in this layer, which indicates a polycrystalline phase. This is an interesting discovery, because besides the stable monoclinic phase there are no known stable phases for $KY(WO_4)_2$ at room temperature. It should be emphasized that in the top layer of the irradiated crystal, which is not irradiated above amorphization threshold, the Raman spectrum of the original $KY(WO_4)_2$ monoclinic phase is recovered, suggesting that a sharper interface is formed between the top layer and the recrystallized layer.

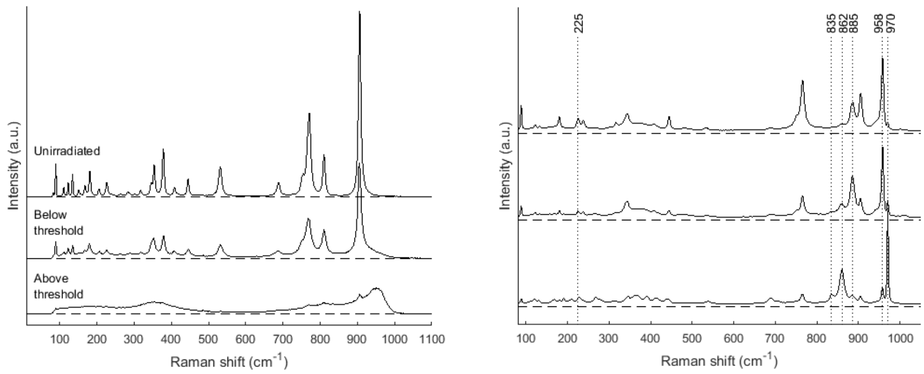

Figure 2. a) The Raman spectrum of 12 MeV carbon $3\cdot10^{14}$ ions/cm^2 irradiated $KY(WO_4)_2$ at large depth (ions never reached that depth, so unirradiated), close to the surface (below threshold damage) and at the maximum of electronic damage (above threshold damage). and after irradiation at low and high carbon ion fluence. b) Raman spectra taken at the depth of maximum electronic damage at several locations on the sample, showing the new crystalline phase in above-threshold irradiated and high-temperature annealed $KY(WO_4)_2$ and indicating the polycrystalline structure of the recrystallized layer due to the change of the spectrum with location on the sample.

The recrystallization causes cracks to appear in this layer (Figure 3). The direction of the cracks is the same over the whole sample, but does not agree with any of the crystalline or optical axes of the material. This could cause serious problems in terms of using the top layer as a waveguide, as any waveguides crossing the cracks will have large losses due to scattering and reflection.

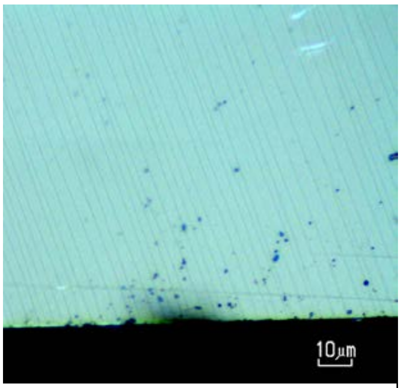

Figure 3. Optical microscope image of a high-temperature annealed crystal, focused on the recrystallized layer.

An estimation was made of the refractive index of the recrystallized layer using an m-lines scan of a crystal that was irradiated at $8\cdot10^{14}$ ions/cm^2 and subsequently annealed at 550°C. This causes the whole top layer to first amorphize and then recrystallize into the polycrystalline phase, so the bulk value of the measurement indicates the refractive index of the layer. The measurement is shown in Figure 4 and indicates a bulk refractive index value of the polycrystalline phase of 1.78. This is significantly lower than the bulk value of pure KY(WO4)2 ($n\approx2$), but also than that of the amorphous phase ($n\approx1.85$).

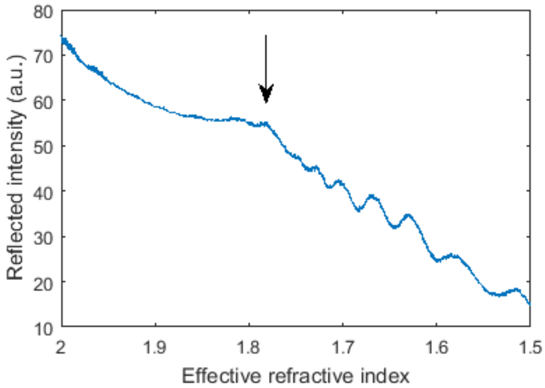

Figure 4. M-lines measurement of a recrystallized layer of irradiated KY(WO4)2 at 1550 nm, TM polarization. The bulk index is indicated with an arrow.

Conclusion

The recrystallization of the amorphized layer is potentially very interesting for the fabrication of high-contrast waveguides in $KY(WO_4)_2$. The lower refractive index compared to amorphous $KY(WO_4)_2$ and the close to step-like refractive index profile would allow for higher confinement as well as enable the fabrication of bent waveguide structures (i.e. rings, discs). The effect on waveguide performance of the recrystallized phase has to be investigated further before anything can be said about the viability, because several problems have to be overcome; the polycrystalline structure could increase scattering losses, and clear cracks are visible in the recrystallized layer that greatly reduce the usable area on the crystal and do not coincide with any of the optical axes. This research will continue with a focus on solving these problems – for example by finding strategies to relieve the stress and avoid cracks, and by increasing the annealing temperature even further to reduce scattering losses as much as possible –, because this fabrication method would be a very promising step towards the first high-contrast waveguide devices in $KY(WO_4)_2$.

Acknowledgements

This work was supported by the European Research Council through the ERC Consolidator Grant RENOS, project 648978.

References

[1] Y.-S. Yong, S. Aravazhi, S. A. Vázquez-Córdova, J. J. Carjaval, F. Díaz, J. L. Herek, S. M. García-Blanco, and M. Pollnau, "Temperature-dependent absorption and emission of potassium double tungstates with high ytterbium content," *Opt. Express*, vol. 24, no. 23, p. 26825, Nov. 2016.

[2] M. C. Pujol, X. Mateos, R. Sole, J. Massons, J. Gavalda, X. Solans, F. Dı´az, and M. Aguilo, "Structure, crystal growth and physical anisotropy of KYb(WO4)2, a new laser matrix," *J. Appl. Crystal- logr.*, no. 35, pp. 108–112, 2002.

[3] D. Geskus, S. Aravazhi, S. M. García-Blanco, and M. Pollnau, "Giant optical gain in a rare-earth-ion-doped microstructure," *Adv. Mater.*, vol. 24, no. 10, p. OP19-OP22, Mar. 2012.

[4] D. Geskus, E. H. Bernhardi, K. van Dalfsen, S. Aravazhi, and M. Pollnau, "Highly efficient Yb^{3+}-doped channel waveguide laser at 981 nm," *Opt. Express*, vol. 21, no. 11, pp. 13773–8, Jun. 2013.

[5] C. I. van Emmerik, S. M. Martinussen, J. Mu, M. Sefunc, M. Dijkstra, and S. M. García-Blanco, "Towards High Contrast Potassium Double Tungstate Rib Waveguides For Laser Applications," *IEEE Photonics Benelux Proceedings*, p. 163-166, 2016

[6] C. A. Merchant, P. Scrutton, C. Hnatovsky, R. S. Taylor, G. García, J. Olivares, A. S. Helmy, S. Member, and J. S. Aitchison, "High-Resolution Refractive Index and Micro-Raman Spectroscopy of Planar Waveguides in $KGd(WO_4)_2$ Formed by Swift Heavy Ion Irradiation," *IEEE J. Quantum Electron.*, vol. 45, no. 4, pp. 373–379, 2009.

[7] X. Mateos, R. Solé, J. Gavaldà, M. Aguiló, J. Massons, and F. Díaz, "Crystal growth, optical and spectroscopic characterisation of monoclinic KY(WO4)2 co-doped with Er3+ and Yb3+," *Opt. Mater. (Amst).*, vol. 28, no. 4, pp. 423–431, 2006.

[8] R. Frentrop, V. Tormo, M. Díaz-Híjar, J. Olivares, and S. M. García Blanco, "Low-loss slab waveguides in KY(WO_4)_2 fabricated by 12 MeV carbon ion irradiation," *IEEE Photonics Benelux Proceedings*, p. 219-222, 2016