Materials Science-Poland, 31(1), 2013, pp. 151-157
http://www.materialsscience.pwr.wroc.pl/
DOI: 10.2478/s13536-012-0082-4

Optical, structural and electrical properties of pure and urea doped KDP crystals

B. BABU[1], J. CHANDRASEKARAN[1]*, S. BALAPRABHAKARAN[1], P. ILAYABARATHI[2]

[1]Department of Physics, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore – 641 020, Tamil Nadu, India.

[2]Research and Development Center, Bharathiar University, Coimbatore – 641 046, Tamil Nadu, India.

Single crystals of good optical quality, made of potassium dihydrogen phosphate (KDP) doped with urea were grown by slow evaporation solution growth technique at a constant temperature of 35 °C. Optical absorption and dielectric properties were studied for pure and urea doped KDP crystals. Using powder XRD studies, crystalline nature of pure and urea doped KDP crystals was confirmed. AC conductivity was measured for the grown crystals. DC electrical conductivity and photoconductivity studies were carried out for pure and urea doped KDP crystals and the differences caused by the dopant were also discussed.

Keywords: *absorption; powder XRD; dielectric; photoconductivity; potassium dihydrogen phosphate (KDP)*

1. Introduction

In recent years, second-order nonlinear optical materials have attracted much attention because of their wide applications in signal processing, frequency doubling and optical data storage. Potassium dihydrogen phosphate is a well known inorganic nonlinear optical material. Several research works have been carried out on this material because of its very high laser damage thershold and high optical nonlinearity. It is also used as a model system to recognize the mechanism of crystal growth from the solution. Worldwide it is used as a reference material for comparision of powder second harmonic generation (SHG) for a long period of time. The additives are usally added for increasing the growth rate, improving optical, mechanical as well as electrical properties of the material. N. P. Rajesh et al. [1] studied the optical transmittance and mechanical properties of the KDP crystals added with organic additives. M. Priya et al. [2] studied the electrical properties of gel grown KDP crystals added with urea and thiourea (0.002 M to 0.010 M). I. Pritula et al. [3] studied the optical transmittance, structural and spectral properties of KDP crystals doped with urea at concentrations varying from 0.2 M to 10 M. S. Goma et al. [4] doped KDP with urea with concentrations ranging from 0.002 M to 0.010 M and discussed its electrical properties along various (a, b, c) directions. In our present study we have doped KDP with 0.2 M urea and discussed the optical, structural and electrical anisotropy of KDP single crystals with urea impurities. In addition, we studied the variation in dielectric properties due to changes in temperature.

2. Crystal growth

Commercially available KDP and urea were used for the crystal growth. First, a saturated solution of pure KDP was filtered twice through Whattman filter paper to remove the impurities. Then, the KDP was doped with urea in the molar ratio of 1:0.2. The mixture solution was stirred well for about 1 h using a magnetic stirrer. The saturated solutions were taken in a crystallizing vessel and covered with thin plastic paper. Holes were made on the cover for proper evaporation of the solvent and the solution was kept in a waterbath for crystal

*E-mail: jchandaravind@yahoo.com; Tel.: +91-422-2692461; Fax: +91-422-2692676

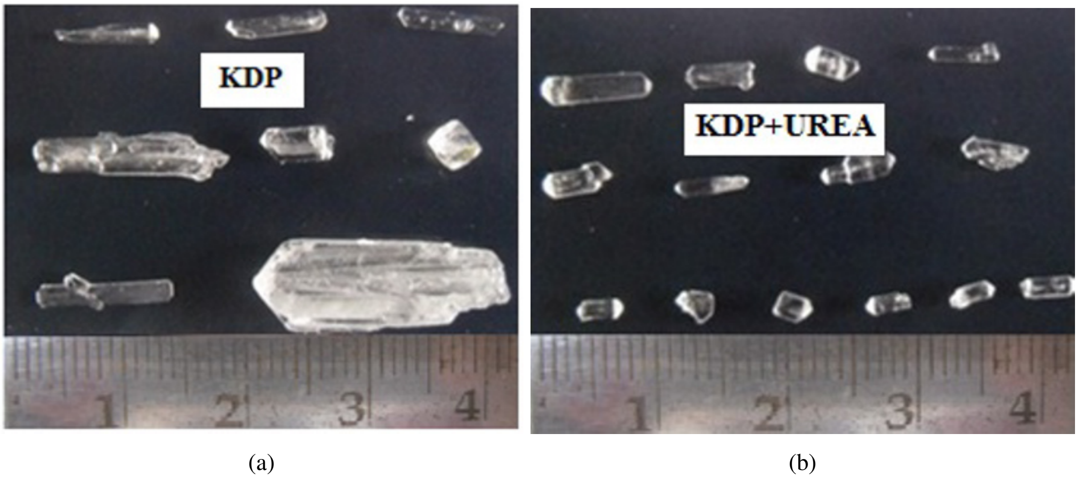


Fig. 1. As grown crystals (a) pure KDP (b) urea doped KDP.

growth. The bath temperature was maintained at a constant value of 35 °C. After 10 days, single crystals of good optical quality were obtained from the mother solution. The quality of the pure KDP and urea doped KDP crystals is shown in Fig. 1(a) and (b).

3. Results and discussion

3.1. UV-visible absorption studies

The optical absorption spectra of pure and urea doped KDP crystals were recorded using Perkin-Elmer lambda 35 spectrophotometer in a wavelength region of 200 nm to 1200 nm, which covers near ultraviolet (200 to 400 nm), visible (400 to 800 nm) and the far-infrared (800 – 1200 nm) regions. Fig. 2 shows the absorption spectra of pure and urea doped KDP crystals. From this Figure it can be seen that there is not a great difference in UV absorption cutoff wavelength but there is a difference in absorption percentage due to the dopant. In the doped crystals the absorption percentage has been changed. Crystalline purity of KDP crystals doped with urea show low percentage of absorption but an increase in their transmittance can be observed [1–3].

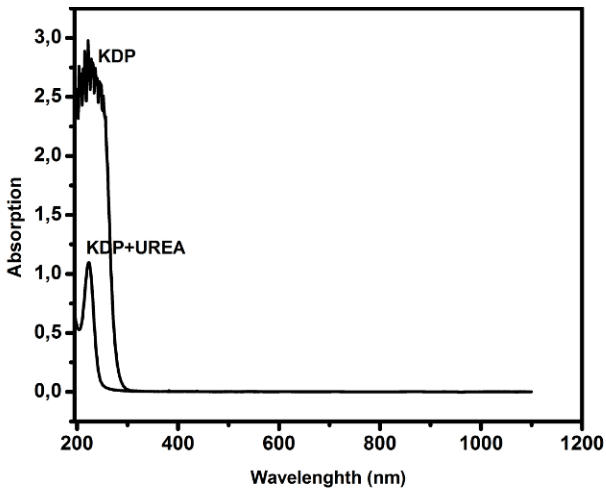


Fig. 2. UV-absorption spectra of pure and urea doped KDP crystals.

3.2. Powder XRD studies

Finely crushed powder samples of pure and urea doped KDP were subjected to the powder XRD analysis. The powder XRD patterns of pure and urea doped KDP crystals were acquired using JEOL-JDX 8030 X-ray diffractometer at a rate of 10° to 90° per min. Nickel filtered CuKa (λ = 1.5405 Å) radiation was used. The recorded spectrum is shown in Fig. 3. The sharp and specfic Bragg angle confirms the crystalline nature of the pure and urea doped KDP. It is interesting to note that there is a small shift in 2θ position and change in intensity, which is clearly shown in the

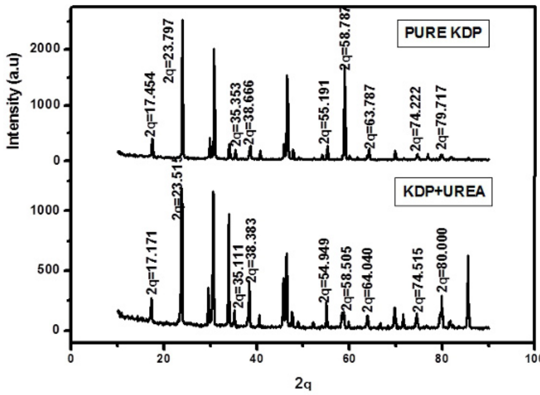


Fig. 3. Powder XRD spectrum of pure KDP and urea doped KDP crystals.

XRD spectrum. This indicates the entering of the impurity molecules into the KDP lattice, resulting in a change in the internal structure of the crystal (bond length) [3].

3.3. Dielectric studies

Generally, dielectrics are used to study the charge transport mechanism of a material. The dielectric studies of pure and urea doped KDP crystals were carried out using Hioki 3532-50 LCR meter at various temperatures, in the frequency range of 50 Hz to 5 MHz. The accuracy of this instrument is $\pm 0.08\%$. Polished crystals were placed between the copper electrodes for the measurements. The dielectric constant of the material was calculated using the given formula [5]

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A} \tag{1}$$

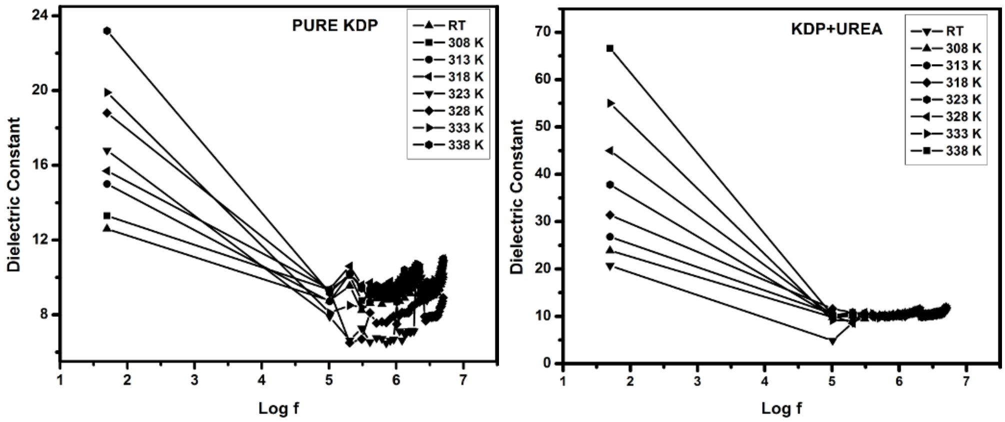
where, C is the capacitance and d is the sample thickness, A is the cross sectional area of the sample and ε_0 is the free space permitivity of the sample (8.85×10^{-12} F/m). Fig. 4 shows the dielectric constant for pure and urea doped KDP crystals. From the diagrams it can be observed that the urea added KDP crystals have high dielectric constants. However, the dielectric constant was observed to increase with an increase in temperature. The dielectric constant is very high at lower frequency range and becomes stable at higher frequency range. This may be due to the presence of all the four different types of polarization, namely electronic, ionic, orientational and space charge polarization [6]. The low value at a high frequency may be due to the significant loss of these polarizations. In our present study, the urea doped KDP crystals have higher dielectric constant rather than the pure KDP. Here, it should be noted that space charge polarization depends on the purity of the sample. So, in the present study, the considered system was dominated by the sample purity. Fig. 5 indicates that dielectric loss is inversly propotional to frequency. S. Goma et al. [4] obtained small variations in the dielectric loss values with urea concentration, ranging from 0.000 to 0.010 M. In our case (0.0 and 0.2 M), we have observed the differences in the dieletric loss with temperature but there were not considerable changes correlated with different urea doping. When temperature increased, dielectric loss also increased. Low value of dielectric loss suggests that the sample is characterized by an enhanced optical quality, suitable for device fabrication [7, 8]. The AC conductivity of the crystals was calculated by the given formula

$$\sigma_{ac} = \varepsilon_r \varepsilon_0 \omega \tan\delta \tag{2}$$

where, ε_0 is the permittivity of the free space, ε_r is the dielectric constant of the sample, $\tan\delta$ is the dielectric loss and ω is the angular frequency ($\omega = 2\pi f$). From Fig. 6 it is observed that AC conductivity has increased with the increase in temperature. Also it can be noted that AC conductivity was increased in urea doped KDP crystal.

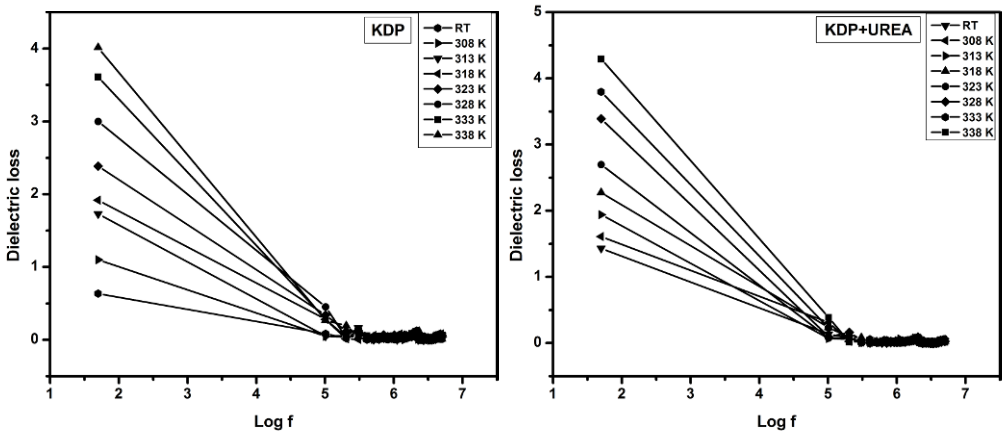
3.4. DC and photoconductivity studies

DC conductivity study has been carried out using Keithley electrometer (6517 B) in the range of 1 V to 10 V. The cut and polished samples were placed between two electrodes for the measurement. Fig. 7 shows the I-V characteristics curves. The current is linearly increasing with an increase in voltage as well as temperature. The conductivity of the samples was estimated using



(a) (b)

Fig. 4. Dielectric constant of (a) pure KDP and (b) urea doped KDP crystals.



(a) (b)

Fig. 5. Dielectric loss of (a) pure KDP and (b) urea doped KDP crystals.

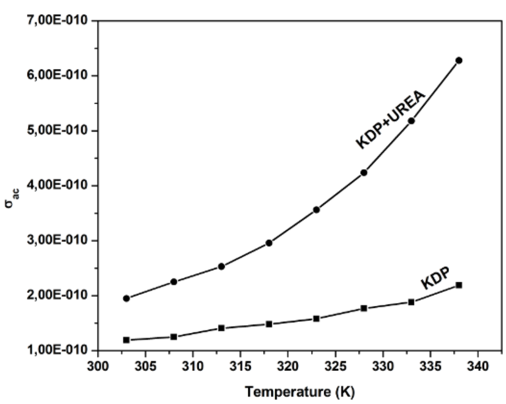
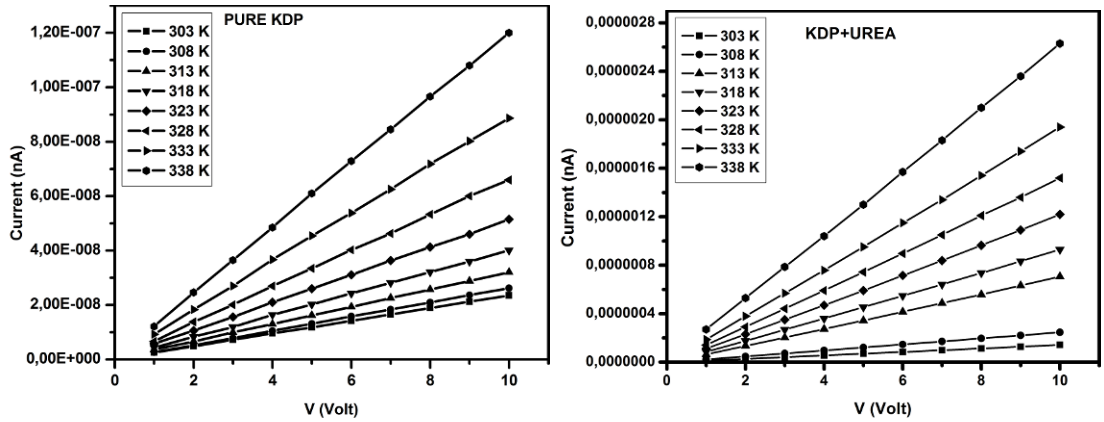


Fig. 6. AC conductivity vs. temperature for pure and urea doped KDP crystals.

the given formula [9].

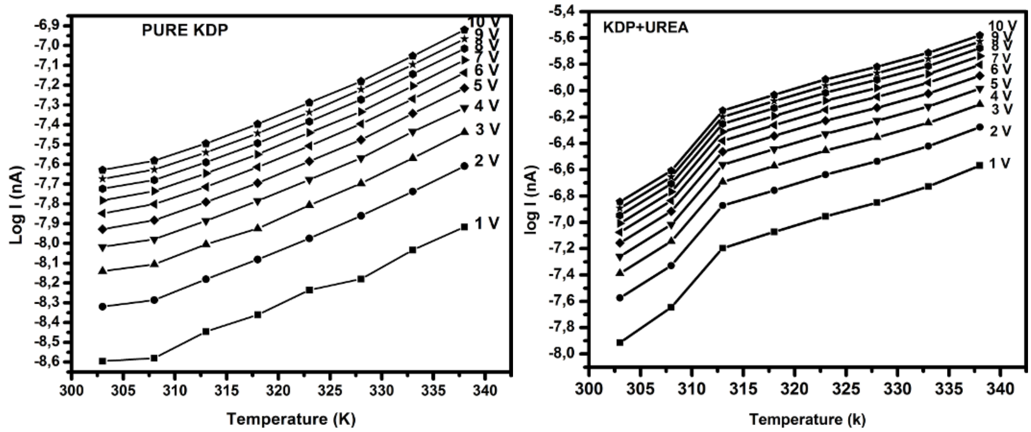
$$\sigma = [(I \times L) / (V \times A)] \tag{3}$$

where I is the current, V is the voltage, L is the thickness of the sample and A is the cross sectional area of the sample. The current is linearly increasing with applied input voltage with respect to temperature, which is shown in Fig. 8. The DC conductivity of the crystal has increased with the increase of temperature. The urea doped KDP has an increased DC conductivity, which is shown in Fig. 9. For photoconductivity study, polished crystals were taken and thin copper wire was connected on both sides of the sample with the help of silver paste (Electronic Grade).



(a) (b)

Fig. 7. I-V characteristics of (a) pure KDP and (b) urea doped KDP crystals.



(a) (b)

Fig. 8. log I vs. temperature for (a) pure and (b) urea doped KDP crystals.

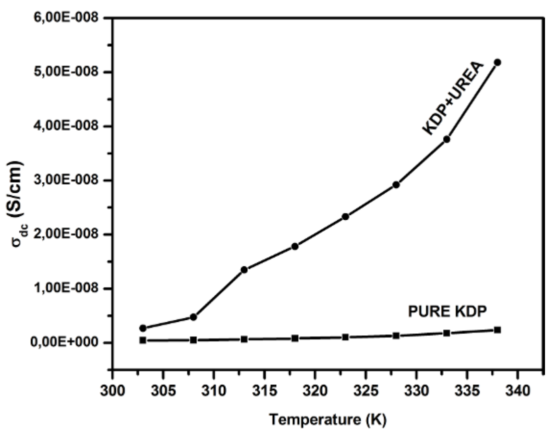


Fig. 9. DC conductivity vs. temperature.

Halogen lamp (100 W), containing iodine vapour and tungston filament was used as a radiation source for the photocurrent measurment. Fig. 10 shows the photocurrent and dark current for the applied input voltage. From the Figure it can be observed that both the crystals show the negative photoconductivity nature. It is due to the reduction of charge carriers in the presence of radiation. It can be also explained by Stockman model. According to this model the forbidden gap in the material contains two energy levels: the upper energy level is situated between the Fermi level and conduction band, the lower energy level is situated near the valence band. The lower level

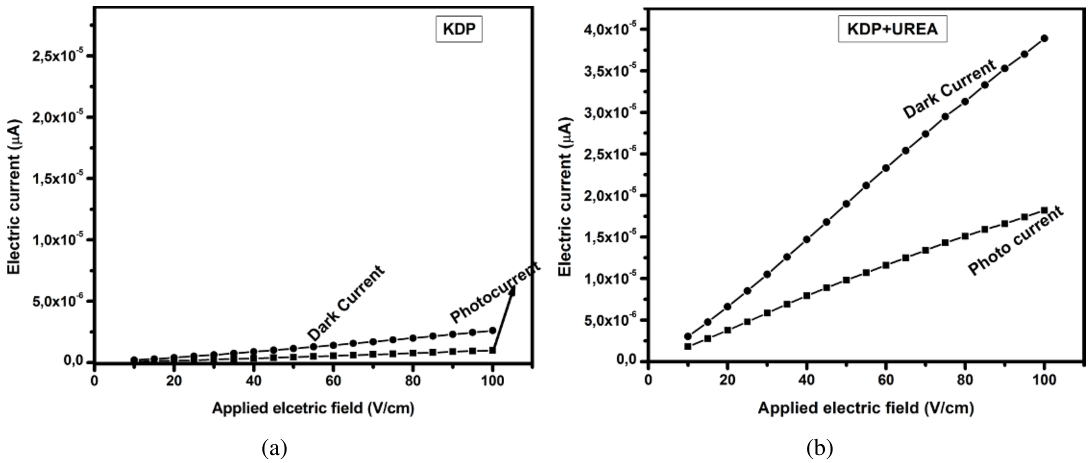


Fig. 10. Photoconductivity response: a) pure KDP crystal b) urea doped KDP crystal.

has a high capture cross-section for the electrons from conduction band and the holes from valence band. As a result, when the sample is exposed to light irradiation, the recombination of electrons and holes takes place resulting in a decrease in the number of charge carriers, thus increasing the negative photoconductivity [10]. Materials with negative photoconductivity can be used for UV and IR detector applications [11–13]. It is evident from the graph that the dopant has slightly modified both the photocurrent and the dark current of the material.

4. Conclusion

Single crystals of good optical quality, of pure and urea doped KDP were grown by solution growth technique at a constant temperature of 35 °C. In UV absorption studies both the crystals had the same absorption wavelength, but the urea doped KDP showed lower absorption percentage due to increase in transparency. The dielectric constant increased with increasing the temperature and urea doped KDP showed high dielectric constant. AC conductivity increased with dopant concentration. DC conductivity and photoconductivity studies showed that the electrical properties were improved by doping KDP with urea. The observed anisotropy of the optical, structural and electrical properties confirms that the urea molecules have occupied the sites in KDP lattice. These findings could be useful in optoelectronic applications.

Acknowledgements

The authors gratefully acknowledge the financial support from the DST, Government of India, for the major research project (SR/S2/LOP-07/2008).

References

[1] RAJESH N. P., KANNAN V., SANTHANA RAGHAVAN P., RAMASAMY P., LAN C.W., *Mater. Lett.*, 52 (2002), 326.

[2] PRIYA M., PADMA C. M., FREEDA T. H., MAHADEVAN C., BALASINGH C., *Bull. Mater. Sci.*, 24 (2001), 511.

[3] PRITULA I., KOSINOVA A., KOLYBAYEVA M., PUZIKOV V., BONDARENKO S., TKACHENKO V., TSURIKOV V., FESENKO O., *Mater. Res. Bull.*, 43 (2008), 2778.

[4] GOMA S., PADMA C. M., MAHADEVAN C. K., *Mater. Lett.*, 60 (2006), 3701.

[5] VIMALAN M., RAJESH KUMAR T., TAMIL SELVAN S., SAGAYARAJ P., MAHADEVAN C. K., *Physica B.*, 405 (2010), 3907.

[6] SINHA N., SAHAS, SINGH B. K., KUMAR K., SINGH N., GUPTA M. K., BUDAKOTI G. C., KUMAR B., *Cryst. Res. Technol.*, 44 (2009), 167.

[7] MILTON BOAZ B., BABU VARGHESE, JUSTIN RAJ C., JEROME DAS S., *Mater. Sci. Eng. (B).*, 136 (2007), 57.

[8] RAJARAJAN K., SELVAKUMAR S., GINSON P. JOSEPH, SAMIKKANNU S., VETHA POTHEHER I., SAGAYARAJ P., *Opt. Mater.*, 28 (2006), 1187.

[9] SHAKTAWAT V., JAIN N., SAXENA R., SAXENA N. S., SHARMA K., SHARMA T. P., *Poly. Bull.*, 57 (2006), 535.

[10] JOSHI N.V., *Photoconductivity*, Marcel Dekker, New York, 1990.

[11] CHEN X., SHYU D., CHOA F. S., *Proc. SPIE. Infrared Technology and Applications XXXVII*, 8012 (2011), 80123A.

[12] CHEN X., SHYU D., CHOA F. S., TRIVEDI S., *Proc. SPIE. Infrared Technology and Applications XXXVII*, 8012 (2011), 80123A.

[13] SHARMA R. K. ET AL., *Proc. SPIE. Infrared Technology and Applications XXXVII*, 8012 (2011), 80123A.

Received: 2012-03-10
Accepted: 2012-12-16