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Growth, characterization and optical properties of potassium iodide (KI) doped potassium hydrogen phthalate (KHP) single crystals for optoelectronic applications

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Potassium iodide (KI) doped potassium hydrogen phthalate (KHP) single crystals were grown by slow evaporation technique using millipore water as a solvent. The grown single crystals were analyzed by powder X-ray diffraction and the analysis confirmed that KI-doped KHP crystallizes in orthorhombic system with space group $Pca2_1$. The functional groups were identified by FT-IR technique which showed slight shift in vibrational frequencies, indicating inclusion of dopant into the crystal lattice. The UV-Vis spectral studies revealed the optical transparency of the doped crystals in the entire visible region. The optical band gap values were estimated from Tauc plots. Kurtz-Perry powder test was employed for second harmonic generation efficiency studies of the grown crystals.

Keywords: *crystal growth; optical nonlinearity; Tauc plot; second harmonic generation*

1. Introduction

Nonlinear optical (NLO) crystals have proven to be efficient candidates for a number of applications such as second harmonic generation (SHG), frequency mixing, electro-optic modulation, data storage etc. NLO interaction demands, in general, a material which is optically transparent to the incident light and generates radiation, possesses a quadratic susceptibility of sufficient magnitude, allows for the phase matching and withstands high intensity laser radiation. Hence, nonlinear optics is material-limited field, with practical advances largely controlled by the progress in making available improved NLO materials. It has led to the investigation of a wide variety of materials namely, inorganic crystals, organic crystals, polymers, metal-organic complexes and semi-organics for their nonlinear optical properties. The search for materials having high optical nonlinearity of organics and physical robustness of inorganics has led to the development of a class of compounds known as semi-organics. Semi-organic NLO materials have higher optical quality, large nonlinearity, good mechanical strength compared to inorganic and organic NLO materials and are good candidates for applications in the field of optoelectronics [1]. One of the advantages of semi-organics is that the bonding schemes are three dimensional, unlike in polar organic crystals, which results in stubbier habit. Potassium hydrogen phthalate crystal is an excellent semi-organic nonlinear optical material, well-known for its application in the long-wave X-ray spectrometers [2]. KHP exhibits excellent optical, piezoelectric, nonlinear optical and elastic properties investigated in detail by earlier researchers [3–8]. KHP having chemical formula $K[C_6H_4COOH.COO]$ belongs to alkali acid series and has orthorhombic symmetry with space group $Pca2_1$ [9]. KHP having good platelet morphology with (0 1 0) cleavage plane consisting of high and low growth steps has been studied by optical microscopy [10]. KHP possesses piezo-electric, pyroelectric, elastic, nonlinear optical properties which are desirable for optoelectronics. They are also advantageous for long term stability in devices [11–16]. The studies showed that SHG efficiency can be enhanced by organic dopants in tris thiourea zinc(II) sulfate (ZTS), ammonium dihydrogen phosphate (ADP) and KHP single crystals [17, 18]. It has been reported that ZTS single crystals doped with inorganic impurity, like potassium

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iodide alter their physical and chemical properties and doped ZTS nonlinear crystals may find applications in optoelectronic devices [19]. Previous studies reported urea doped potassium dihydrogen orthophosphate crystals grown by slow evaporation from aqueous solution, having low value of dielectric permittivity [20]. Impurities, like urea. Ni^{2+}, Mg^{2+} in ZTS material improved its crystalline perfection [21, 22]. Investigations on doping of rare earth elements revealed their influence on the mechanical, electronic and optical properties of KHP crystal [23]. Studies of the effect of alkali metal ions on KHP showed observable changes in morphology and the improvement in SHG efficiency [24, 25]. It has been reported that KCl inorganic salt doped ZTS has different surface morphology than pure ZTS crystal [26]. Laser damage threshold studies showed a considerable reduction in damage threshold and increased SHG efficiency of KDP crystals doped with La^{3+} ions [27]. Studies on potassium carbonate as additive in KDP showed a decrease in the value of dielectric constant due to occupying by the additive interstitial positions, which favored frequency conversion [28]. It has been reported that Mn doped ZTS showed a change in angular position of XRD peaks due to lattice stress generated by the doping. SHG efficiency of ZTS doped with Mn, enhanced greatly at suitable dopant concentration but too high concentration did not cause any significant change due to deterioration of crystalline perfection [29]. The earlier reports showed that various dopants play a vital role in improving the crystalline perfection and optical properties of NLO material for device applications. In the present study, effect of KI with different concentrations on KHP crystals have been investigated with the help of powder X-ray diffraction, Fourier transform infrared spectroscopy, ultraviolet-visible spectral analysis and Kurtz-Perry powder test second harmonic generation measurements.

2. Experimental

2.1. Crystal growth

The analytical reagent (AR) KHP and KI chemicals have been used for the crystal growth using millipore water as a solvent. A saturated KHP solution was prepared under slightly acidic conditions (pH ~ 4.9). Potassium iodide of 1 %, 5 % and 10 % molar concentrations was added (5 mL each) to the supersaturated solution of KHP. The resultant solutions were stirred for 5 h using a magnetic stirrer for homogeneous mixing and then the solutions were transferred to clean Petri dishes covered with a thin polythene sheet having perforations, and kept in dust free chamber for slow evaporation. Small crystals began to grow in 4 days to 5 days and grew larger in a time of about 15 days to 20 days. Photograph of the grown undoped and doped crystals are shown in Fig. 1. The approximate size of the grown crystals, which had platelet morphology, was 10 mm × 8 mm × 3 mm. Large optically transparent single crystals were selected to carry out various characterizations.

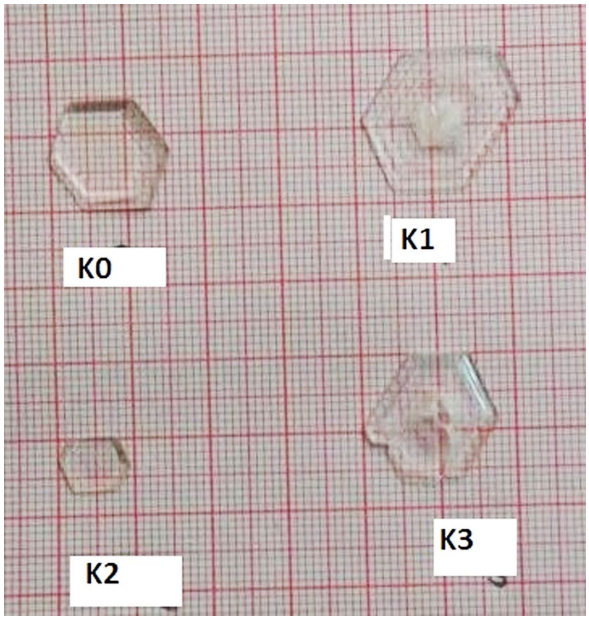


Fig. 1. Photographs of grown crystals: K0-undoped, K1: 1 mol % KI doped, K2: 5 mol % KI doped and K3: 10 mol % KI doped.

2.2. Characterization

The powder X-ray diffraction (PXRD) study was carried out in the 2θ range of 5° to 70° using Rigaku-Miniflex diffractometer with CuKα (λ = 1.5418 Å). The Fourier transform

infra-red (FT-IR) spectra were recorded for all grown crystals in the range of 400 cm^{-1} to 4000 cm^{-1} using Bruker-Alpha spectrometer by KBr pellet method. Optical transparency of the grown crystals was studied using Varian Cary 5000 UV-Vis-NIR spectrometer in the range of 200 nm to 1000 nm. The second harmonic generation test was carried by Kurtz-Perry powder method using an Nd:YAG laser with the wavelength of 1.064 μm and SHG generated by randomly oriented microcrystals packed in a microcapillary tube was measured by photomultiplier tube. The frequency doubling was confirmed by emission of green color radiation.

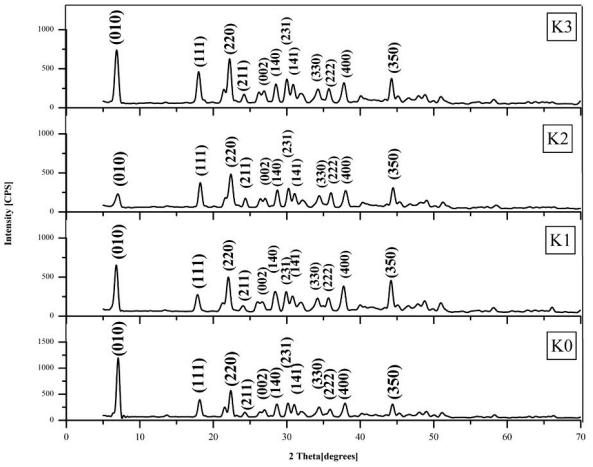


Fig. 2. Powder XRD pattern of undoped and KI doped KHP crystals.

3. Results and discussion

3.1. Powder XRD analysis

The undoped and KI doped KHP single crystals were subjected to powder X-ray diffraction study in the 2θ range of 5° to 70° using Rigaku Miniflex 600 (5^{th} generation) X-ray diffractometer with a wavelength $\lambda = 1.5406$ Å. Analysis of the data confirmed that undoped and KI doped KHP crystallize in orthorhombic system with a space group $Pca2_1$. The estimated lattice parameters which are shown in Table 1 are in agreement with previously reported values [4, 23]. From the spectrum, a change in relative intensity of the peaks and a shift in the angular position of the peaks was observed. Hence, it is reasonable to believe that the dopant has entered the crystalline matrix without much distortion and produced lattice strain. The unit cell volume changed with dopant concentration without any systematic variation and the crystalline structure remainded unaltered [22, 25]. The powder XRD spectra of the samples are shown in Fig. 2.

3.2. FT-IR spectral studies

The FT-IR spectral analysis was carried out in the range of 400 cm^{-1} to 4000 cm^{-1}. The spectra of undoped and KI doped KHP are shown in Fig. 3. As a result of KI doping, the shift in characteristic vibrational frequencies is observed. The broadening or narrowing of some absorption peaks in FT-IR spectra of doped KHP can be seen in comparison to undoped spectrum and this may be due to the considerable lattice strain generated by KI dopant. It indicates incorporation of the dopant into the KHP crystalline matrix [19, 23, 28]. C=C asymmetric stretching at 1943 cm^{-1}, 1945 cm^{-1}, 1942 cm^{-1} and 1936 cm^{-1} and C=O symmetric stretching at 1974 cm^{-1}, 1570 cm^{-1}, 1566 cm^{-1}, 1572 cm^{-1} for undoped, 1 mol%, 5 mol%, 10 mol% KI doping, respectively, show the effect of the dopant. Some important characteristic vibrational frequencies were identified and agreed with the earlier reported values [23, 25]. Some of the stretching frequencies are given in Table 2.

3.3. UV-Vis spectral studies

The UV-Vis analysis was carried in the range of 200 nm to 1000 nm for the grown crystals and the spectra are shown in Fig. 4. It has been found that, the undoped and KI doped KHP crystals are optically transparent in the entire visible and near infrared region which makes them potential candidates for optoelectronic device fabrication. The good transmittance of the doped crystals in the entire visible region ensures their suitability for second harmonic generation. It is also observed that, the cut-off wavelength for undoped and doped crystals is about 320 nm and remains unchanged [25].

Table 1. Lattice parameters.

Lattice parameters	Pure KHP [Å]	KHP + 1 mol% KI [Å]	KHP + 5 mol% KI [Å]	KHP + 10 mol% KI [Å]
a	9.752	9.524	9.732	9.516
b	13.224	13.354	13.446	13.505
c	6.610	6.654	6.586	6.608
Volume of unit cell [$Å^3$]	852.42	846.27	861.82	849.21

Table 2. FT-IR frequencies assignments of undoped and KI doped KHP crystals.

Functional groups	Undoped KHP [cm^{-1}]	KHP + 1 mol% KI [cm^{-1}]	KHP + 5 mol% KI [cm^{-1}]	KHP + 10 mol% KI [cm^{-1}]
C=O symmetrical stretching	1574	1570	1566	1572
C–C=O stretching	1095	1096	1091	1089
C=C stretching	1375	1377	1381	1385
O–H stretching	2482	2485	2485	2475
C=C asymmetric stretching	1943	1945	1942	1936
C–O carboxylic stretching	1282, 1142	1280, 1147	1284, 1145	1280, 1144
C=C–C out of plane ring deformation	559	559	559	558
C=C stretching	1675	1677	1675	1677
O–H stretching (hydrogen bonding)	3451	3460	3451	3446
C–C stretching	770	772	768	768

Decrease in the optical transparency for 10 mol% KI doping is observed due to inclusion of KI into the lattice which is favoring the promotion of electrons in π, σ and n-orbitals for excitation [27, 30]. The optical energy gap of undoped and KI doped KHP crystals was calculated from the Tauc relationship [31] and the Tauc plots are shown in Fig. 5:

$$ah\nu = B(h\nu - E_g)^{1/2} \quad (1)$$

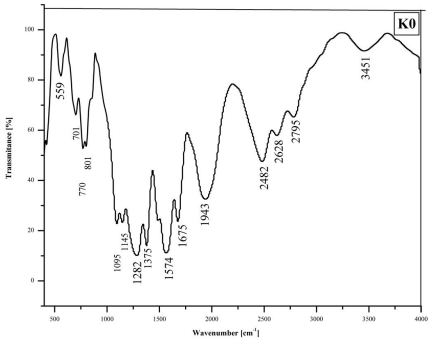
and

$$a = \frac{1}{d\log(\frac{1}{T})} \quad (2)$$

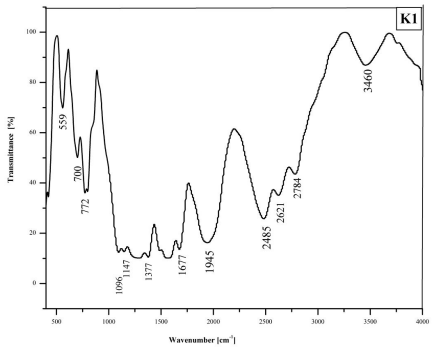
where a is an absorption coefficient, hν is the energy (h is a Planck constant equal to 6.625×10^{-34} $J{\cdot}S^{-1}$ and ν is the frequency of incident photon in Hz), E_g is the value of the optical energy gap between the valence band and the conduction band, T is the transmittance, and d is the thickness of the crystal. The factor B depends on the probability of transition and is supposed to be a constant within the optical frequency range (an energy-independent constant). From the Tauc plot, the optical band gaps were found to be 4.121 eV, 4.090 eV, 4.118 eV and 4.116 eV for undoped, 1 mol%, 5 mol% and 10 mol% KI doped KHP crystals, respectively.

3.4. Second harmonic generation (SHG) studies

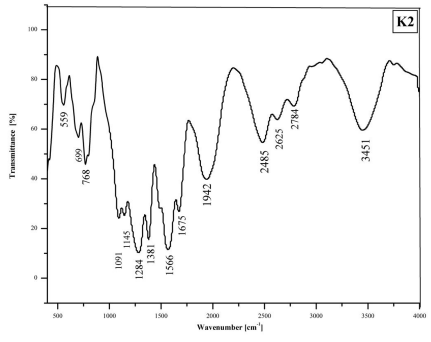
Second harmonic generation (SHG) test was performed on the samples by Kurtz-Perry powder technique [32]. An Nd:YAG Q-switched laser of 1064 μm radiation with input of 1.2 mJ/pulse was



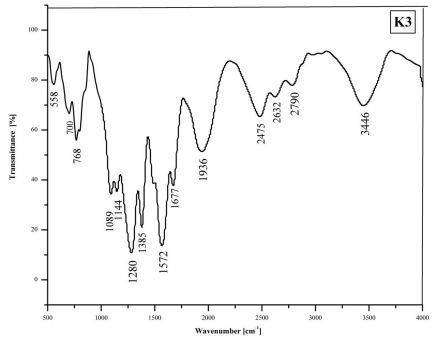
(a)



(b)



(c)



(d)

Fig. 3. FT-IR spectra of undoped and KI doped KHP crystals.

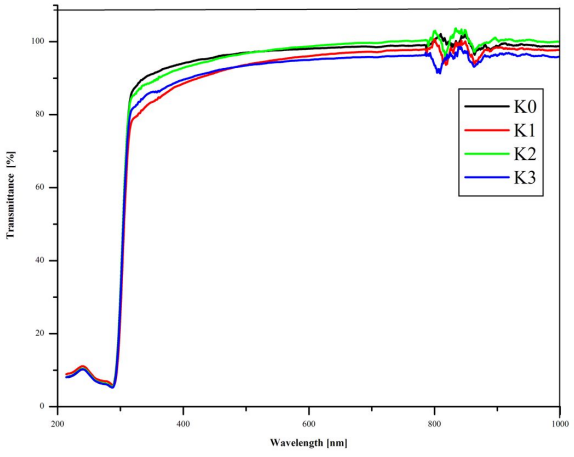


Fig. 4. UV-Vis spectra of undoped and KI doped KHP crystals.

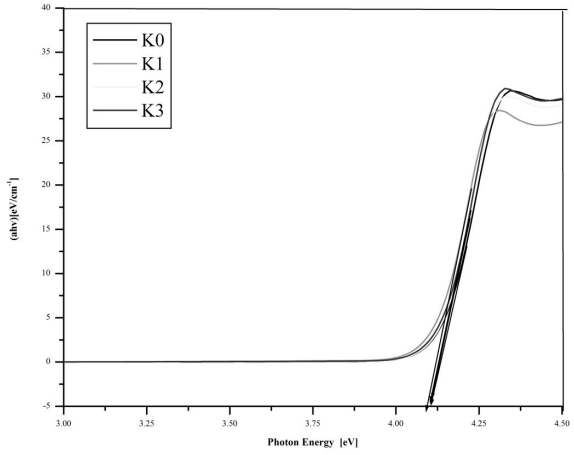


Fig. 5. Tauc plots of undoped and KI doped KHP crystals.

used as an optical source and directed on finely powdered sample filled in microcapillary tube. The SHG output intensities for undoped and KI doped KHP are tabulated in Table 3 with urea and KDP as reference. It is observed that the SHG efficiency is concentration dependent. Many materials with higher molecular nonlinearity have been identified. Attainment of SHG effect requires favorable alignment of the molecules within the crystal structure which can be achieved by facilitating nonlinearity in the presence of solvent. The SHG can be enhanced by attaining the molecular alignment through formation of complexation [25].

The enhancement in crystalline perfection could lead to an increase in NLO efficiency. KHP crystal has linear and NLO properties with centrosymmetric crystal structure, and according to the theory, it is not expected to exhibit SHG property. SHG is normally related to favorable molecular alignment facilitating nonlinearity [18]. The SHG property exhibited by undoped and doped KHP crystal is due to the p-electron cloud movement from the donor to acceptor molecules in the center of inversion symmetry or the local non-centrosymmetry caused by defects. Previous studies reported that SHG was exhibited by KHP [18]. From the data, it is observed that the SHG efficiency of KI doped KHP decreased due to the deterioration of crystalline perfection. The decrease in SHG output is due to non-favorable molecular alignment through formation of complexation of KI dopant into crystalline matrix and the disturbance of charge transfer at higher dopant concentration [33–35].

Table 3. Second harmonic generation output.

Sample	SHG output [mV]
Input beam energy	1.20 J/pulse
Urea (reference)	95
KDP (reference)	40
KHP undoped	46
1 M% KI doped KHP	46
5 M% KI doped KHP	40
10 M% KI doped KHP	44

4. Conclusions

Single crystals of undoped and KI-doped KHP have been grown by slow evaporation method at room temperature. The powder XRD studies confirmed the changes in the intensity and minor shift in peak positions due to the incorporation of KI into the crystal lattice of KHP. The lattice parameters were estimated. The FT-IR studies showed slight shift in positions of the vibrational frequencies of functional groups. The UV-Vis studies revealed that the doped KHP crystal have good optical transmittance in the entire visible region which is desirable for optoelectronic applications. The powder SHG test confirmed the NLO properties of undoped and doped KHP crystals. The decrease in SHG output is due to the disturbance of charge transfer at higher dopant concentration.

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References

[1] Rajashekaran R., Mohankumar R., Jayavel R., Ramasamy P., *J. Cryst. Growth*, 252 (2003), 317.
[2] Kejalakshmy N., Srinivasan K., *J. Phys. D: Appl. Phys*, 36 (2003), 1778.
[3] Loiacono G.M., Osborne W.N., *J. Cryst. Growth*, 43 (1978), 401.
[4] Kejalakshmy N., Srinivasan K., *Opt. Mater.*, 27 (2004), 389.
[5] Bairava Ganesh R., Kannan V., Meera K., Rajesh N.P., Ramasamy P., *J. Cryst. Growth*, 282 (2005), 429.
[6] Ecolivet C., Miniewicz A., Sanquer M., *J. Phys. Chem. Solids*, 53 (1992), 511.
[7] Miyashita Y.O., Murakami A., Aoki K., Yamaguchi S., *Proc. SPIE- Inter. Soc. Opt. Eng.*, 1503 (1991), 436.
[8] Miniewicz A., Bartkiewicz S., *Adv. Mater. Opt. Electron.*, 2 (1993), 157.
[9] Enculescu M., *Physica B*, 405 (2010), 3722.
[10] Beck L., Stemmler P., Legrand F., *Rev. Sci. Instrum.*, 66 (1995), 1601.
[11] Shankar M.V., Verma K.B.R., *Ferro. Lett*, 21 (1996), 55.
[12] Sirdeshmukh D.B., Srinivas K., *J. Mater. Sci.*, 21 (1986), 4117.
[13] Ester G.R., Halfpenny, *J. Cryst. Growth*, 187 (1998), 111.
[14] Niraimathi V., Aroumoji P.M., Anbarasan G., Rajarajan G., *J. Opt. Adv. Mater*, 15 (2015), 205.
[15] Raju R.K., Dharmaprakash S.M., Subhash H.J., Jayanna H.S., *Mater. Res. Innov.*, 22 (2018), 200.
[16] Benedict J.B., Wallace P.M., Reid P.J., Jang S.H., *Adv. Mater.*, 15 (2003), 1068.
[17] Bhagavannarayana G., Kushwaha S.K., *J. Appl. Cryst.*, 43 (2010), 154.
[18] Bhagavannarayana G., Parthiban S., Meenakshisundaram S., *J. Appl. Cryst*, 39 (2006), 784.
[19] Krishnan C., Selvarajan P., Freeda T.H., Mahadevan C.K., *Physica B*, 404 (2009), 289.
[20] Goma S., Padma C.M., Mahadevan C.K., *Mater. Lett.*, 60 (2006), 3701.
[21] Kumaresan P., Moorthy Babu S., Anbarasan P.M., *Mat. Res. Bull.*, 43 (2008), 1716.
[22] Praveen V.N., Vijayan N., Mahadevan C.K., Bhagavnnarayana G., *Mater. Manuf. Processes*, 23 (2008), 816.

[23] SUDHAHAR S., KRISHNA KUMAR M., JAYARAMAKRISHNAN V., MURALIDHARAN R., MOHAN KUMAR R., *J. Mater. Sci. Technol.*, 30 (2014), 13.
[24] RAMSAMY G., PARTHIBAN S., MEENAKSHISUNDARAM S., MOJUMDAR S.C., *J. Therm.Anal. Calorim.*, 100 (2010), 861.
[25] DEEPA G., FREEDA T.H., MAHADEVAN C.K., *Indian J. Phys.*, 76 (2002), 369.
[26] KRISHAN C., SELVARAJAN P., FREEDA T.H., *J. Mater. Lett.*, 62 (2008), 4414.
[27] KANNAN V., BAIRAVA GANESH R., SATHYALAKSHMI R., RAJESH N.P., RAMASAMY P., *Cryst. Res. Technol.*, 41 (2006), 678.
[28] DHANRAJ P.V., MAHADEVAN C.K., BHAGVANNARAYANA G., RAMASAMY G., RAJESH N.P., *J. Cryst. Growth*, 310 (2008), 5341.
[29] BHAGAVANNARAYANA G., KUSHWAHA S.K., PARTHIBAN S., MEENAKSHISUNDARAM S., *J. Cryst. Growth*, 311 (2009), 960.
[30] FREEDA T.H., MAHADEVAN C.K., *Bull. Mater. Sci.*, 23 (2000), 335.
[31] MOTT N.F., DAVIS E.A., *Electronic Processes in Non-crystalline Materials*, Oxford Clarendon, London, 1979.
[32] KURTZ S.K., PERRY J.J., *J. Appl. Phys.*, 39 (1968), 3798.
[33] MEENAKSHISUNDARAM S., PARTHIBAN S., SARATHI N., *J. Cryst. Growth*, 293 (2006), 376.
[34] VASUDEVAN G., ANBUSRINIVASAN P., MADHURAMBAL G., MOJUMDAR S.C., *J. Therm. Anal. Calorim.*, 96 (2009), 99.
[35] PRAKASH T.J.J., EKADEVASENA S., *J. Mater. Sci: Mater. Electron.*, 28 (2017), 7393.

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