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Optical Characterization of Gel Grown Pure and Mixed KDP-ADP Crystals

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ABSTRACT:
Single crystals of pure and mixed KDP-ADP of high quality are grown by gel method.UV-Vis. optical transmission spectrum showed the UV cutoff wavelength of mixed KDP-ADP crystal decreases with increasing concentration of ADP. The NLO property of the mixed KDP-ADP crystals is lesser than that of the pure KDP and higher than that of ADP. Photoconductivity study confirms that the pure and mixed KDP-ADP crystals exhibit positive photoconductivity. The absence of absorption bands in the visible region and the wide bandgap of the grown crystal attest to the suitability of the grown crystal for photonic and optical applications.

Keywords: Gel growth; Characterization; UV-Vis. NIR spectroscopy: SHG; Photoconductivity

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I. INTRODUCTION

Ammonium dihydrogen phosphate (ADP) is an interesting material with varied application as a piezo-electric material in transducer devices, nonlinear optics (NLO), electro-optics, and as monochromators for X-ray fluorescence analysis[1-6]. ADP was among the first matetrial that were used and exploited for their non-linear optical (NLO) and electro-optic (EO) properties[7]. They are widely used as the second, third and fourth harmonic generator in Nd:YAG and Nd:YLF lasers. Studies on ADP crystals still attract interest because of their unique nonlinear optical, dielectric and antiferroelectric properties[8-10].

Current interest is focused on to find the materials, which have suitable nonlinear optical properties for, use as the active media in efficient second harmonic generators, tunable parametric oscillators and broadband electro-optic modulators. Growth of large single crystal is a slow and difficult process. Hence, it is highly desirable to have some technique of screening crystal structures to determine whether they are non-centrosymmetric and it is also equally important to know whether they are better than those currently known. Kurtz and Perry [11] proposed a powder SHG method for comprehensive analysis of the second order nonlinearity. Employing this technique, Kurtz and Perry surveyed a very large number of compounds.Photo detection technology is becoming more and more important in military applications, particularly in guided weapons and communication through fiber optics. Infrared developments are based on solid-state photonic devices. Further developments in these fields demand a good understanding of the basic principles of photoconductivity processes.In this paper, the authors report theUV-Vis-NIR Spectroscopy, photoconductivity and surface morphology studies are investigated and reportedfor the high quality single crystals of pure and mixed KDP-ADP are grown by gel method.The nonlinear optical property of the single crystal has been confirmed by SHG test.

II. EXPERIMENTAL STUDY

2.1. UV-Vis-NIR Spectroscopy

Ultraviolet-visible spectroscopy (UV/ VIS) is also known as electronic spectroscopy. Ultraviolet (200 - 400 nm) and visible (400 –800 nm) absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. It uses light in the visible and adjacent near ultraviolet (UV) and near infrared (NIR) ranges. In this region of energy, space molecules undergo electronic transitions. The ultraviolet spectrum of a molecule results from transitions between electronic energy levels accompanied by changes both in vibrational and rotational states.

The region from 10-200 nm can be studied in evacuated systems and is termed as “vacuum ultraviolet”. The range from 200-380 nm is the portion of the spectrum normally covered by the term ultraviolet. The atmosphere is transparent in this region and quartz optics may be used to scan from 200-380 nm. The excitation of electrons from p & d orbitals, π-orbitals and particularly π-conjugated systems occurs above 200 nm and gives rise to readily accessible and informative spectra.

The spectral range, which is accessible with most instruments, is from 200 nm to 800 nm and this entire region is often referred to as ultraviolet spectrum although it includes the visible region (380 to 780 nm). A tungsten filament lamp is generally used for the visible region of the spectrum. Conjugation of double bonds lowers the energy required for the transitions and absorption moves to longer wavelength.An energy level diagram showing electronic transitions is depicted in Figure 1.1.

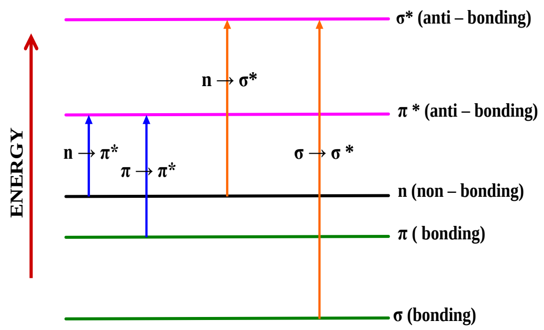


Figure 1.1: Energy level diagram with electronic transitions

2.2 Optical Bandgap

Though ionic crystals absorb strongly in the ultra-violet region and reveal interesting features in respect of band-to-band transitions, a study on this aspect was first made on semiconductor crystals [12]. In the case of crystalline materials, the absorption edge is observed in the short wavelength range [13]. This low wavelength data are related to interband . Hence, in the present work an attempt was made to analyze optical absorption data obtained on single crystals of pure and mixed KDP-ADP at room temperature.

The optical energy gap (E_g) can be calculated from the well-known quadratic equation [14] which is often called Tauc law

$\alpha h\nu = A(h\nu - E_g)^n$ (1.1)

where $h\nu$ = incident photon energy,

α = absorption coefficient,

E_g = band gap of the material,

A = constant that depends on the electronic transition probability and

For direct allowed transition n = ½, indirect allowed transition n = 2.

2.3. NLO test – Kurtz and Perry Powder SHG Method

The nonlinear optical property of the grown single crystal is tested by passing the output of Nd:YAG Quanta ray laser through the crystalline powder sample. The schematic of the experimental setup used for SHG studies is shown in Figure 1.2. A Q-switched, mode locked Nd:YAG laser was used to generate about 6 mJ/pulse at the 1064 nm fundamental radiation.

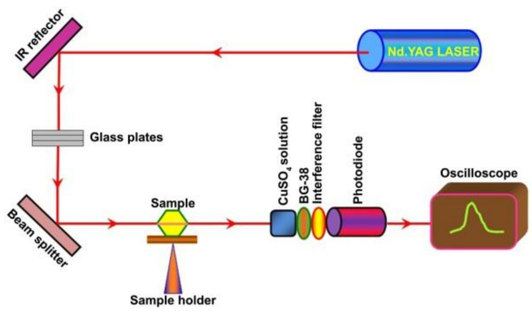


Figure 1.2: Schematic experimental setup for SHG efficiency measurement

2.4. Photoconductivity Studies

Photoconduction, as the name suggests, includes the generation and recombination of charge carriers and their transport to the electrodes. When photons of energy greater than that of the band gap of the material are incident upon a photoconductive material, electrons and holes are created in the conduction and valence bands, respectively increasing the conductivity of the sample. But this statement is only partially true. In a doped material, for example, the impurity atom absorbs the photon of slightly less energy than that of the band gap and free electron is created in the conduction band [15].

The crystal sample is well-polished and surfaces are cleaned with acetone. This is attached to a microscope slide and two electrodes of thin copper wire (0.14 cm diameter) are fixed on to the specimen at some distance apart using silver paint. After this it is annealed at a temperature of 100 °C to perfect dryness. A d.c. power supply, a Keithley 485 picoammeter and the prepared sample are connected in series. The applied field is increased from 0 to 2000 Vcm-1. The sample is covered with a black cloth to avoid exposure to any radiation. The current (dark) is measured. To measure the photoconductivity, light from a 100 W halogen lamp is focused onto the sample. The current is noted for varying applied fields.In few cases, it has been observed that when radiation of certain energy is incident on a photoconductor, a decrease in current is observed instead of the expected increase; this phenomenon is called “negative photoconductivity”. The variation in the mobilities of charge carriers is generally very small and hence can be ignored.

This means that either the number of free charge carriers or their life time is substantially reduced by incident radiation [16].

III. RESULTS AND DISCUSSION

3.1. UV-Vis. Analysis

The transmission spectrum plays a vital role in identifying the potential of a NLO material because a given NLO material can be of utility only if it has a wide transparency window without any absorption in UV and visible region.Optical transmittance spectra were recorded at room temperature using PerkinElmer Lambda 35 spectrophotometer on ~2 mm thick plates in the Z-cut plateswith highly transparent, defect free single crystals of pure and mixed KDP-ADP. The UV–Visible transmittance spectra were recorded in the wavelength region 200–1100 nm of pure KDP and ADP and mixed KDP-ADP crystals are shown in Figure 1.3. From Figure 1.4 it shows the transparency in the visible spectral range of the samples. The crystal is highly transparent in the near UV, Visible and near IR regions. From the spectrum it is observed that the transmittance percentage of mixed KDP-ADP and pure ADP crystals are higher than that of the pure KDP crystal. The transmittance is higher than 90 % above 310 nm and it increases further as the wavelength increases towards the visible and NIR regions, which is an essential parameter for NLO application. Thus, the large transmittance window in the entire visible –NIR region enables very good optical transmission of the second harmonic frequencies of Nd:YAG laser. The optical transparency range is almost the same in all the crystals and there is a marked change in the onset wavelength and also in the percentage transmittance for mixed KDP-ADP crystals. The cut-off wavelength is slightly reduced for increasing ADP concentration in KDP from 0.2 to 1 mole. The low value of cut-off wavelength and the large transmittance window are the most desirable properties of the crystals used for NLO applications. The absorption coefficients (α) have been calculated using the following formula:

$$\alpha = \frac{1-(T+R)}{L} \qquad (1.2)$$

where T is the measured value of transmittance, L is the length of the sample in Z-direction and R is the total reflection ratio of the two polished surfaces normal to the incident light (R = 0.08 at 1.05 μm).

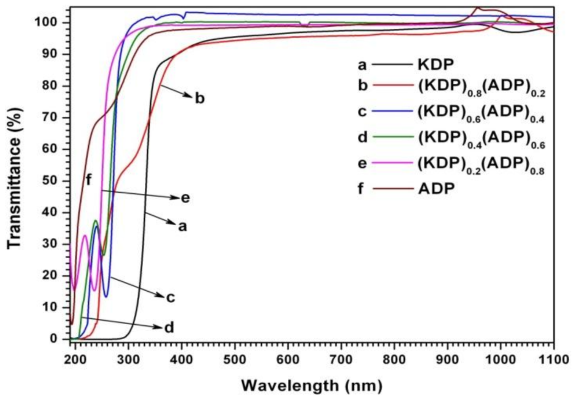


Figure 1.3: UV-Vis. optical transmission spectrum of pure and mixed KDP-ADP single crystals

Figure 1.4 shows the plots of $(\alpha h\upsilon)^2$*vs*hυ for pure and mixed KDP-ADP crystals. The bandgap energy of the pure KDP crystal is found to be 3.63 eV. This indicates that pure KDP is a higher band gap energy material. From Figure 1.4, it is evident that KDP crystal has UV cutoff at 341 nm. The UV cutoff wavelength of mixed KDP-ADP crystal decreases with increasing concentration of ADP. It reveals that the UV cutoff wavelength of mixed KDP-ADP crystals can be tuned by adjusting

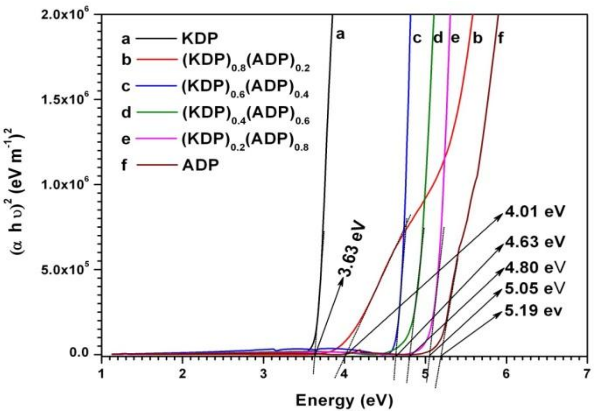


Figure1.4: Optical bandgap measurements of pure and mixed KDP-ADP single crystals the concentration of ADP from 0.2 to 1 mole which makes it suitable for fabricating optoelectronic devices as per our needs. A UV cut-off below 300 nm is sufficiently low for SHG laser radiation at 1064 nm or other applications in the blue region. The absence of absorption bands in the visible region and the wide bandgap of the grown crystal attest to the suitability of the grown crystal for photonic and optical applications [17]. The calculated bandgap energy and UV cutoff wavelength of all the grown crystals are presented in the Table 1.1.

Table 1.1: Optical bandgap energy values and cutoff wavelength values of pure and mixed KDP-ADP single crystals

Sample name	Optical bandgap energy (eV)	Cutoff wavelength (nm)
KDP	3.63	341
$(KDP)_{0.8}(ADP)_{0.2}$	4.01	309
$(KDP)_{0.6}(ADP)_{0.4}$	4.63	267
$(KDP)_{0.4}(ADP)_{0.6}$	4.80	258
$(KDP)_{0.2}(ADP)_{0.8}$	5.05	245
ADP	5.19	239

3.2. NLO Studies

A Q switched Nd:YAG laser beam of wavelength 1064 nm was used within an input beam energy of 6.5 mJ/pulse and pulse width of 8 ns, the repetition rate being 10 Hz. The SHG radiations of 532 nm (green light) emitted were collected by a photo multiplier tube (PMT-Philips Photonics model 8563) and the optical signal incident on the PMT was converted into voltage output at the CRO (Tektronix-TDS 3052). The second harmonic generation developed in the pure and mixed KDP-ADP crystals grown in the present work has been confirmed by the emission of green radiation from the powder sample. The output power from the pure KDP and different concentration of ADP -KDP crystals was compared to that of urea crystal and the results are presented in Table 1.2. The amplitude of the green radiation is found to be decreased when the concentration of ADP increased in the mixed crystals. Thereby, the NLO property of the mixed KDP-ADP crystals is lesser than that of the pure KDP and higher than that of ADP.In the case of $(KDP)_{0.6}(ADP)_{0.4}$ and $(KDP)_{0.4}(ADP)_{0.6}$ crystals, the SHG efficiency is less than the efficiency of $(KDP)_{0.8}(ADP)_{0.2}$ and $(KDP)_{0.2}(ADP)_{0.8}$ crystals. This may be due to the deterioration of crystalline perfection [18].

Table 1.2: The obtained SHG data and efficiency values of pure and mixed KDP-ADP single crystals

Sample name	Input power (mJ)	Output power (mV)	SHG efficiency (compared with KDP)
KDP	6.5	53	-
$(KDP)_{0.8}(ADP)_{0.2}$	6.5	47.2	0.89 times
$(KDP)_{0.6}(ADP)_{0.4}$	6.5	12.4	0.23 times
$(KDP)_{0.4}(ADP)_{0.6}$	6.5	18.8	0.35 times
$(KDP)_{0.2}(ADP)_{0.8}$	6.5	26.3	0.49 times
ADP	6.5	7.5	0.14 times

3.3. Photoconductivity Analysis

The experiment was performed at room temperature. The variation of photo current (I_{ph}) and dark current (I_d) with applied field of pure and mixed KDP-ADP crystals are shown in Figures 1.6 - 1.11. The current increased when the sample was illuminated and it decreased suddenly when the illumination was stopped. It is observed from the plot that the dark current is less than the photo current for all the grown crystals in the present study, thus revealing that the pure and mixed KDP-ADP crystals exhibits positive photoconductivity [16]. In general positive photoconductivity is attributed to generation of mobile charge carriers caused by the absorption of photons [5].

Figure 1.5: Field dependent conductivity of pure KDP single crystal

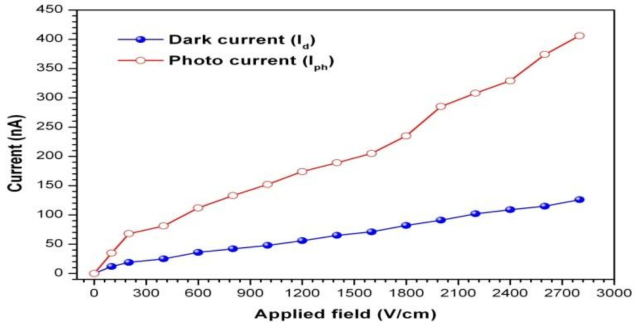


Figure 1.6: Field dependent conductivity of $(KDP)_{0.8}(ADP)_{0.2}$single crystal

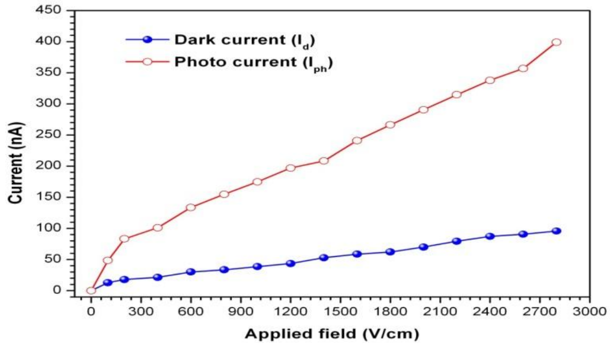


Figure 1.7: Field dependent conductivity of $(KDP)_{0.6}(ADP)_{0.4}$single crystal

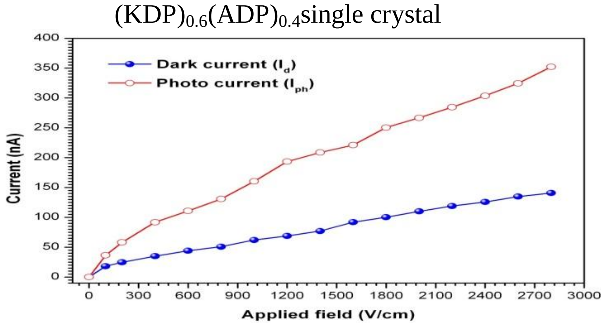


Figure 1.8: Field dependent conductivity of $(KDP)_{0.4}(ADP)_{0.6}$single crystal

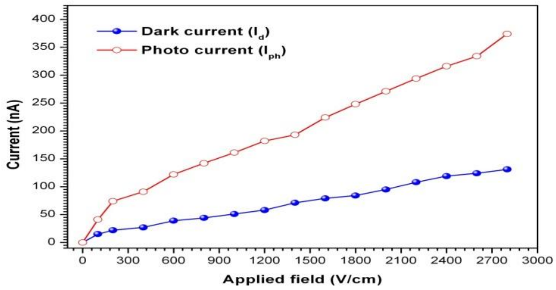


Figure 1.9: Field dependent conductivity of $(KDP)_{0.8}(ADP)_{0.2}$single crystal

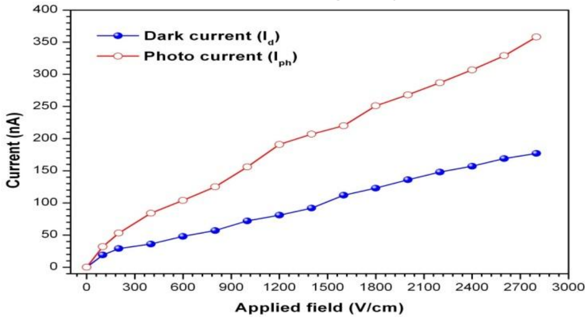
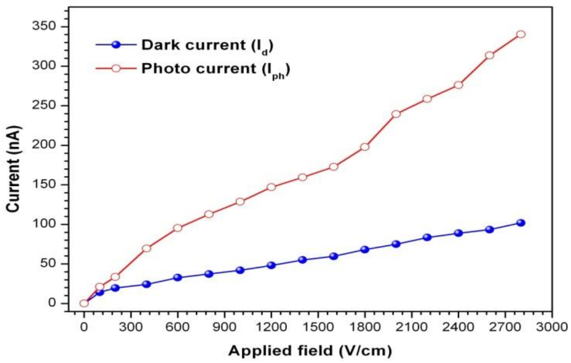


Figure1.10: Field dependent conductivity of ADP single crystal



When a semiconductor or insulator absorbs radiation of sufficient quantum energy, there is an increase of electrical conductivity called photoconductivity. Photoconductors are useful for varying electric current by means of light. Photoconductivity results if the effect of light is primarily either to increase the density of free carriers or if the effect of light is to decrease the resistance of barriers in the material. When barriers are not present, the absorption of radiation producing photoconductivity ionizes either host-crystal atoms or impurity atoms, producing free electrons and free holes, or free charge carriers of just one sign, respectively. It is the change in the density of free charge carriers throughout the photoconductor which is responsible for the photoconductivity. When barriers to the flow of electrons are present, there are regions of photoconductor with a high density of free carriers separated from other similar regions by narrow regions with lower density of free carriers. The latter regions, often in the form of space-charge layers, prohibit the flow of charge carriers from one region of the photoconductor to another. The action of light in this case is to decrease the height of the barrier, thus permitting greater charge carrier flow between different regions of the photoconductor [15].

IV. CONCLUSION

Single crystals of pure and mixed KDP-ADP of high quality are grown by gel method.UV-Vis. optical transmission spectrum showed the UV cutoff wavelength of mixed KDP-ADP crystal decreases with increasing concentration of ADP. The NLO property of the mixed KDP-ADP crystals is lesser than that of the pure KDP and higher than that of ADP. It is observed from the plot that the dark current is less than the photo current for all the grown crystals in the present study, thus revealing that the pure and mixed KDP-ADP crystals exhibits positive photoconductivity. The absence of absorption bands in the visible region and the wide bandgap of the grown crystal attest to the suitability of the grown crystal for photonic and optical applications.

REFERENCES

[1]. Ram Kripal, SantwanaShukla, PrashantDwivedi, EPR and optical studies of Cu2+ doped ammonium dihydrogenphos-phate single crystals, Physica B 407 (2012) 656-663.

[2]. P. Rajesh, K. Boopathi, P. Ramasamy, Investigations on the solubility, growth, structural, optical, mechanical, dielectric and SHG behaviour of ammonium acetate doped ammonium dihydrogen phosphate crystals, J Crystal Growth 318 (2011) 751-756.

[3]. K. Srinivasan, A. Cantoni, G. Bocelli, Compositional de-pendence of morphology and lattice parameters during growth of K1-x(NH4)xH2PO4 mixed crystals, Cryst. Res. Technol. 45(7) (2010) 737-746.

[4]. R. AnandaKumari, Growth and characterization of NLO crystal, Ind. J. Pure & Appl. Phys. 47 (2009) 369-371.

[5]. Y. Asakuma, Q. Li, H. M. Ang, M. Tade, K. Maeda, K. Fukui, A study of growth mechanism of KDP and ADP by means of quantum chemistry, Appl. Surface Sci. 254(15) (2008) 4524-4530.

[6]. XiueRen, DongliXu, DongfengXue, Crystal growth of KDP, ADP, and KADP, J Crystal Growth 310 (2008) 2005-2009.

[7]. DongfengXue and HenrykRatajczak, Effect of hydrogen bonds on physical properties of

ammonium dihydrogen-phosphate crystals, J Molecular Structure: Theochem. 716 (2005) 207-210.

[8]. K. Sethuraman, R. Ramesh Babu, R. Gopalkrishnan, P. Ra-masamy, Unidirectional growth of 〈1 1 0〉 ammonium dihydrogen orthophosphate single crystal by Sankarana-rayanan–Ramasamy method, J Crystal Growth 294 (2006) 349-352.

[9]. A. P. Voronov, V. I. Salo, V. M. Puzikov, G. N. Babenko, A. D. Roshal, V. F. Tkachenko, Hybrid organic-inorganic crys-tals based on ammonium dihydrogen phosphate and ammo-nium salicylate, J Crystal Growth 335 (2011) 84-89.

[10]. P. Rajesh, P. Ramasamy, Binay Kumar, G. Bhagavanna-rayana, Effect of cobalt and DL-malic acid on the growth rate, crystalline perfection, optical, mechanical, dielectric, pie-zoelectric properties and SHG efficiency of ADP single crystals, Physica B 405 (2010) 2401-2406.

[11]. Kurtz S.K. and Perry T.T. (1968) *J. Appl. Phys*., **39**, 3798–38l3.

[12]. Arora. S. K., Trivedi T.R. and Patel.V.A., (2002) *ScriptaMaterialia*, **47**, 43-647.

[13]. Korashy A. El, ZahedH.El- and Radwan M., (2005) *Physica B*, **334**, 75-8

[14]. Tauc J. (1974) '*Amorphous and Liquid semiconductors'*, J. Tauc Ed. Plenum, New York.

[15]. Bube R.H. (1981), '*Photoconductivity of Solids*', Wiley Interscience, New York.

[16]. Joshi V.N. (1990), '*Photoconductivity*', Marcel Dekker, New York.

[17]. Rao K.V., Smakula A., (1965) *J.Appl. Phys*. **36**, 3953.

[18]. Bhagavannarayana G., Parthiban S.,Meenakshisundaram S., (2008) *Cryst.Growth Des.***8**, 446.

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