GROWTH, SPECTRAL AND THERMAL STUDIES ON MALEIC ACID ADDED ZINC ACETATE DIHYDRATE (ZAMA) SINGLE CRYSTALS

A.Ponnuvel, A.Vijayakumar and A.Kala*
PG& Research Department Of Physics ,Govt Arts College for Men (A),Nandanam
Chennai-600 035, India.

Abstract: *Optically good quality single crystals of maleic acid added Zinc acetate dihydrate crystals (ZAMA) have been grown by slow evaporation method. The presence of various functional groups of ZAMA is confirmed by FTIR. The UV-Vis-NIR spectrum reveals the high percentage of transmission of the sample in the entire visible region. The wide range of transparency of the grown crystal is an added advantage in the field of optoelectronics applications. Thermo analytical techniques are an important experimental method for characterizing a system by measuring the changes in physico chemical properties as functions of increasing temperature with time. The study of thermal analysis is significant for knowing the different phases and stages of stability and hence the grown crystal has been subjected to thermal treatments in nitrogen atmosphere using gravimetric thermal techniques. TGA studies indicate that the crystal is structurally stable upto 150°C. Based on the data obtained from thermograms, different mechanic and non-mechanic equations are used to calculate kinetic parameters such as activation energy of the grown crystal.*

Key words: Solution Growth, Zinc acetate dihydrate, TGA, Activation energy.

1. Introduction

The numerous applications of the nonlinear optical (NLO) crystals in the vast field of Science and Technology has made the process of search of new NLO crystals and improvements in the properties of these crystals a never stopping process. Zinc acetate, a chemical compound with wide applications in many industries well known in chemical industries, has been used as a raw material for manufacturing various chemicals. Zinc acetate dihydrate crystallizes in monoclinic system with the space group C2/c. The NLO and other properties of the crystal have been improved by doping of organic impurities. NLO materials have wide range of applications in the field of telecommunications (frequency multipliers) and optical information storage devices. Maleic acid is a dicarboxylic acid, a molecule with two carboxyl groups with chemical formula $C_4H_4O_4$. An attempt is made here to find a new useful material by taking maleic acid and Zinc acetate dihydrate in 1:1 ratio. In the present work, single crystal growth of maleic acid added Zinc acetate dihydrate from solution has been reported.

2. Experimental Procedure

Analytical reagent grade (AR) samples of Zinc acetate dihydrate $Zn(CH_3COO)_2 \cdot 2H_2O$ and maleic acid ($C_4H_4O_4$) along with triple distilled water were used for the growth of single crystals. In the present study a solution of Zinc acetate dihydrate and maleic acid of equimolar ratio was prepared. The solution was stirred for 6 hours and then filtered. It was porously sealed and placed in a dust free atmosphere for slow evaporation. Optically transparent crystals of size 16 x12 x4 mm were harvested in10 days. The photograph of Zinc acetate dihydrate-maleic acid (ZAMA) as grown crystal is shown in Fig.1.

Fig.1. Photograph of the as grown ZAMA crystal

3. Spectral Analysis

Spectroscopy is a powerful technique used to study the structure of crystalline, organic and inorganic materials. Two major spectroscopic methods have been used in the present study which is Infrared and Raman spectroscopies.

4.Fourier transform infrared spectrum (FTIR)

The Fourier transform infrared spectrum (FTIR) of the crystalline sample was recorded on BRUKER IFS 66V spectrophotometer in the range 4000 - 400 cm^{-1} by KBr pellet technique. The FT-Raman spectrum was recorded in the region 3500-100 cm^{-1} using BRUKER FRA 106 FT-Raman spectrophotometer. The spectra were recorded at Sophisticated Analytical Instrumentation Facility (SAIF), Indian Institute of

Technology (IIT), Chennai, India. A spectral width of 4.29 cm^{-1} was used and the spectrum were measured with a scanning speed of 1.87 cm^{-1} per minute. The FTIR and FT-RAMAN spectra are presented in Figs.2 and 3 respectively.

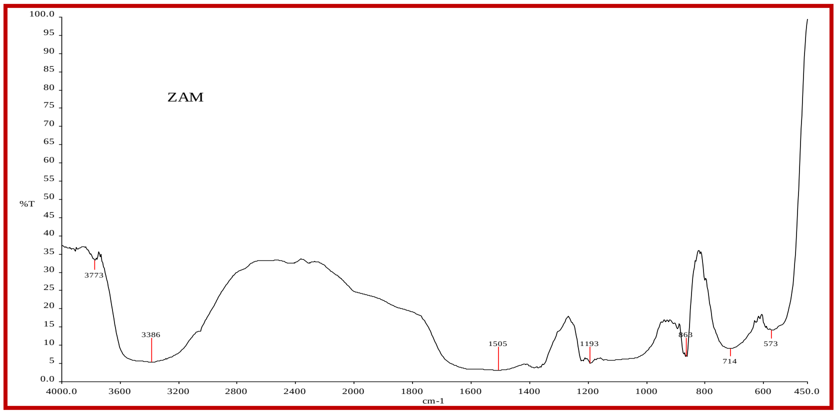


Figure.2. FTIR Spectrum of ZAMA crystal

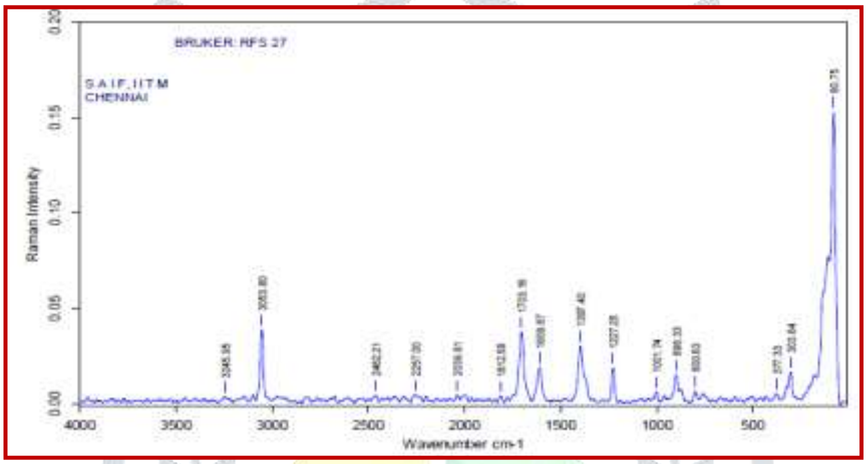


Figure.3 FT-RAMAN Spectrum of ZAMA crystal

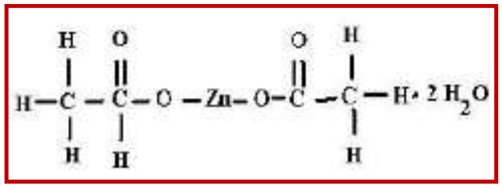
Sixteen Raman frequency shifts in the spectrum has been observed. Group theoretical analyses of the external modes of this acetate have been made. The low frequency spectrum which extends upto, ~ 50 cm^{-1} has been divided into three parts: external oscillations, low frequency hydrogen bond oscillations and vibrational frequencies of the octahedral arrangements of oxygen and water molecules around the metal ion. Zinc acetate dihydrate [$Zn(CH_3COO)_2 .2H_2O$] crystallises in the monoclinic Class space group C^6_{2h} with four molecules in the unit cell. The six nearest neighbours of a Zinc atom are four oxygen atoms and two water molecules which form a badly distorted octahedron around the zinc atom. The interna1 frequencies are made up of acetate, maleate ion frequencies and water bands. Appropriate assignments have been given for all these observed Raman and FTIR lines.

Bands due to water occur very frequently in the spectra of organic compound. When a ligand coordinates to metal atom new modes of vibration not present in the free state may become infra red active.

The stretching vibration of water molecule Zinc acetate dihydrate is expected in the region 3000-3600cm^1.

- ❖ Bands due to asymmetric and symmetric H-O-H stretching vibrations are observed in the region 3550-3200$cm^{-1}$and bands due to H-O-H bending vibration in the region 1630-1600cm^{-1}.
- ❖ Vibrational modes of coordinated water molecules such as wagging, twisting and rocking may become infrared active, the resulting bands occurring in the region 880-650 cm^{-1}. The position of the band is sensitive to the anions present since hydrogen bonds also occurs. If the water molecules are trapped certain rotational and vibrational motions become partially hindered. These bands are observed in the region 600-300cm^{-1}.
- ❖ In FTIR spectrum of ZAMA the spectral line at 3773cm^{-1} and FT-RAMAN spectrum the peak at 3245cm^{-1} are assigned to be O-H band of the water molecules. Also in the FT-Raman spectrum the peaks at 714$cm^{-1}$and moderate intensity peak at 303cm^{-1} is assigned to the vibrational mode of the water molecule.

The structure of Zinc acetate comprises two CH_3 groups and carboxylic group COO as shown in figure.



- In this region 2000-1750cm^{-1} there are a series of unusually intense overtones and combination bands.
- In general bands due to both alkene and aromatic C-H stretching occur at about 3000cm^{-1}. It must be noted that CH_2 stretching vibrations are observed at 3050-3000cm^{-1}whilst their symmetric vibration occurs at 2975cm^{-1}.
- The deformation vibration of C-H may either be perpendicular to or in the same plane containing the carbon-carbon double bonds. The absorption bands due to the out -of -plane vibrations occurs mainly at 1000-800cm^{-1} and have strong to medium intensity.
- Tri substituted alkenes absorb at 850-790 cm-1. CH_3 rocking and bending vibration is usually absorbed at 1005, 1087, 1351 and 1416cm^{-1}.
- In the spectrum of crystal the broad shoulder ranging from 2462 - 2039cm^{-1} is assigned to the CH_3 stretching mode along with overtones. The peaks at 1193 cm^{-1} and 1227cm^{-1} are assigned to CH_3 rocking and bending vibrations. The peak observed at 863cm^{-1} in FTIR spectrum and 899cm^{-1} in Raman spectrum is due to the out of plane C-H vibrations. The carbonyl groups of metal carbonyl compounds observe strongly 2710-1700cm^{-1} due to CO stretching vibrations. Bridging carbonyl compounds in which carbonyl groups associated with at lower frequency in the range 1900-1700cm^{-1}. So the functional group CO observed both in Zinc acetate and maleic acid give rise to characteristic peak at 1703 cm^{-1} which is assigned to stretching vibration of CO group.
- Alkene have a weak C=C stretching in the range 1680-1620cm^{-1} in the conjugated system the C=C stretching vibration frequency is lower than that of an isolated C=C group. Two absorption bands are normally observed, one at about 1650cm^{-1} and another less intense bands at 1600 cm^{-1}. The presence of this band maybe used to confirm the presence conjugation. Hence in the spectrum of ZAMA the spectral line at 1609cm^{-1} is due to the C=C stretching.
- Two principle absorption peaks at 1580 and 1400 cm^{-1} correspond to the asymmetric and symmetric stretching of COO vibrations of the unidentate acetate species as well as the maleic acid. In literature the C=O stretching vibrations of maleic acid give its peak at 1642cm^{-1}. In our spectrum the peak at 1505cm^{-1} should corresponds to the stretching vibration of COO group.
- The peak usually observed at 477cm^{-1} is due to O-C-O rocking vibration of pure Zinc Acetate and it appears as a shoulder. The same peak in our crystal appears at 573cm^{-1}.
- The 377 cm^{-1} line in zinc acetate dihydrate may be assigned to the totally symmetric C-C mode. The slight decrease from the usual value of 393 cm $^{-1}$ may be due to the orderly arrangement of the crystalline field in the acetate compound. The line at 303cm $^{-1}$ is the split component of the degenerate mode. But in our crystal these bands are observed to be missing. Hence it is presumed that the acetate group in suppressed by the maleate group.
- From the tentative assignments made using the FTIR and Raman spectrum leads to the conclusion that the major functional group namely C=O, C=C, COO and CH_3 are definitely present in the Zinc acetate- maleic acid single crystal. In order to confirm the presence of Zinc in the grown crystal in FT-Raman spectrum has been specifically recorded. The band in the range of 80cm^{-1} observed in the FT-Raman spectrum is a strong confirmation of the presence of Zinc in the grown crystal.
- So from the observation of the FTIR spectrum it is concluded that maleic acid has influenced the nature of KDP.

Table.1. Observed FT-IR and FT-RAMAN frequencies (cm^{-1}) of ZAMA Crystals

FTIR Wave number (cm^{-1})	FT-RAMAN Wave number (cm^{-1})	Assignment
3386	3245	O-H stretching of vibration of H_2O
-	3045	C-H Stretching
-	2462	CH_3 stretching vibration
-	2257	
-	2039	
-	1703	C=O stretching vibration
-	1609	C=C stretching vibration
1505	-	stretching of COO vibrations
-	1397	CH_3 bending vibration
1193	1227	CH_3 rocking and bending vibrations
863	899	Out of plane vibrations of C-H group
714	-	Wagging, twisting and rocking of water molecules

573	-	O-C-O rocking vibration of Zinc Acetate
-	303	vibrational mode of the water molecule
-	80	Lattice frequencies, Hydrogen band vibrations and internal frequencies of the arrangement of water molecules and Oxygen around metal ions

5.Thermal Studies

The thermal behaviour of the crystals has been investigated using Thermo gravimetric analysis (TGA) TGA study was carried out using a Perkin-Elmer thermal analyzer at Department of Chemistry, IIT Madras, to assess the thermal stability of the grown crystals. For TGA studies, the crystals were taken in an alumina crucible and were heated from 50˚C to 800˚C at a scanning rate 20˚C/min (in nitrogen atmosphere).The TGA traces for the ZAMZ crystals are presented in Figure 4.4. From TGA it is seen that the crystal is thermally stable up to 150 °C. Below 150^0C there is no detectable weight loss, Hence crystal is the thermally stable uptill 150^0C.The melting point of zinc acetate in literature is 230 ^{0}C which has decreased probably due to the addition of maleic acid.The TGA curve show that the weight loss occurs in three steps. The first weight loss is 49.8% due to the decomposition of maleic acid and the second weight loss of 7.48 % occurs due to decomposition of zinc acetate and the third weight loss of 11.74% due to the residue.The activation energy associated with the major loss is estimated using Coats-Redfern (C-R), Broido and Horowitz-Metzger method.

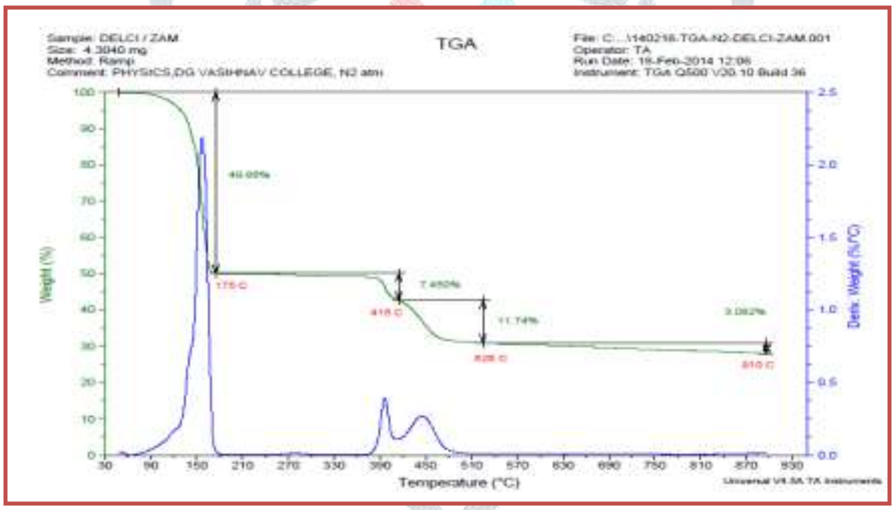


Figure.4. The TGA trace of the ZAMA crystal

6.Broido Method

Broido has developed a model and the activation energy associated with each stage of decomposition is also evaluated by this method. The equation used for the calculation of activation energy (E_a) is:

$$\ln\ln\left(\frac{1}{Y}\right)=\left(\frac{-E_a}{R}\right)\frac{1}{T}+\text{Constant} \qquad (1)$$

where

$$Y=\frac{W_t-W_\infty}{W_0-W_\infty} \qquad (2)$$

Y is the fraction of the number of initial molecules not yet decomposed; W_t is the weight at anytime t; W_∞ is the weight at infinite time (= zero) and W_0 is the initial weight. A plot of $\ln\ln\left(\frac{1}{Y}\right)$ vs. $\frac{1}{T}$ gives an excellent approximation to a straight line. The slope is related to the activation energy. The representative Broido plot is shown in Figure.5.

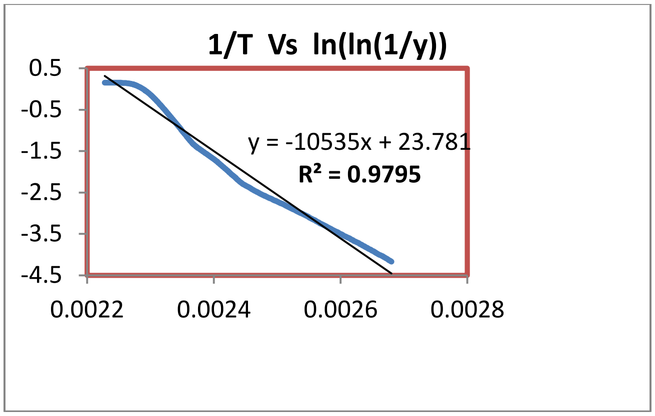


Figure.5.Broido plot

7.Approximation Method of Horowitz and Metzger

Horowitz and Metzger have demonstrated the method of calculation of energy of activation. The equation used for the calculation of energy of activation (E_a) is

$$\ln\ln\left(\frac{W_0}{W_t}\right)=\frac{E_a\theta}{RT_s^2} \quad (3)$$

The representative Horowitz and Metzger plot is shown in Figure 4.6

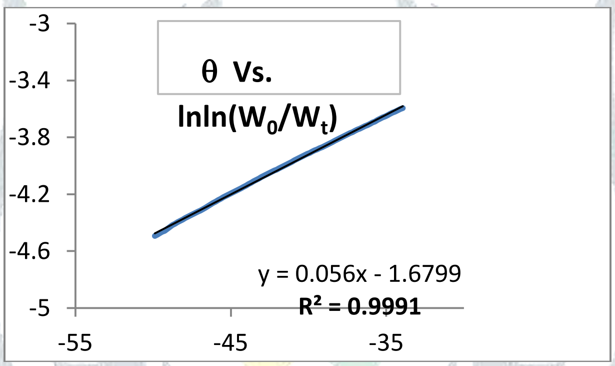


Figure.6. Horowitz -Metzger plot

where, θ is the difference between the peak temperature and the temperature at particular weight loss ($\theta = T - T_s$); W_0 is the initial weight; W_t is the weight at any time t; T_s is the peak temperature; and T is the temperature at particular weight loss. A plot of $\ln\ln\left(\frac{W_0}{W_t}\right)$ vs. θ gives an excellent approximation to a straight line. From the slope, the activation energy (E_a) is calculated.

8.Coats-Redfern Method

The Coats and Redfern method was used to evaluate kinetic data from thermogravimetric curves. Coats and Redfern graphical mode may be expressed by the following relation:

$$\log\left(\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right)=\log\frac{AR}{aE}\left(1-\frac{2RT}{E}\right)-\frac{E}{2.3RT} \quad \left(\text{for } n=0,\frac{1}{2},\frac{2}{3},\cdots\right) \quad (4)$$

$$\log\left(-\log\frac{(1-\alpha)}{T^2}\right)=\log\frac{AR}{aE}\left(1-\frac{2RT}{E}\right)-\frac{E}{2.3RT} \quad (\text{for } n=1) \quad (5)$$

where, α is the fraction of sample decomposed at time t, n is the order of decomposition reaction, a is heating rate in °C/minute, T is temperature (K), A is the frequency factor (s^{-1}), R is gas constant (8.314 J/K·mol) and E is the activation energy (kJ/mol).

$$Y=-\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] \quad \left(\text{for } n=0,\frac{1}{2},\frac{2}{3},\frac{3}{2}\text{ and }2\right) \text{ vs. } \frac{1}{T} \quad (6)$$

$$Y = -\log\left[\frac{-\log(1-\alpha)}{T^2}\right] \quad (\text{for } n=1) \text{ vs. } \frac{1}{T} \qquad (7)$$

The order of decomposition is assumed to be n = 1, since the TGA curve shows only single stage of decomposition. The plot obtained is shown in Figure 4.7. The activation energy was determined with slope of $\left(\frac{-E}{2.303}\right)$.

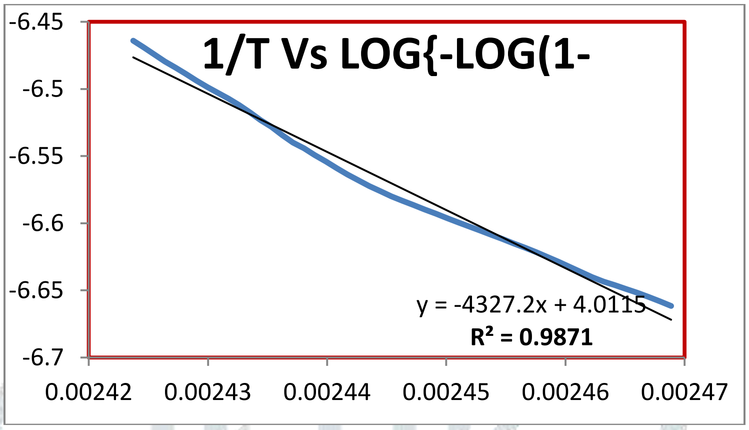


Figure.7. Coats–Redfern plot

The energy of activation was found to be 87.587 kJ/mol, 83.306 kJ/mol and 82.849 kJ/mol, respectively, for Broido, Horowitz and Metzger and Coats–Redfern methods. The thermal activation E_a with maximum R^2 of the ZAMA crystal by the Coats–Redfern method is comparable with the well-known Broido method and the approximation method of Horowitz–Metzger. The energy of activation is low, leading to the conclusion that the crystal is thermally more stable.

Conclusion

Non linear optical property is an important phenomenon in optoelectronics. The frequency conversion of the non linear optical (NLO) material has a significant impact on laser technology. Single crystals of Zinc acetate-maleic acid (ZAMA) has been grown by slow evaporation technique at room temperature. The FTIR spectrum and the FT-RAMAN spectrum of the grown ZAMA crystal have been recorded. These spectrum confirm the presence of all the functional groups and the presence of maleic acid in the grown crystal. Thermo gravimetric analysis (TGA) studies were done to assess the thermal stability of the grown crystal. The thermal stability of the grown crystal is established to be up to 150°C. The Broido, Coat-Red fern, and Horowitz-Metzger methods were used to calculate the activation energies from the thermal decomposition of Zinc acetate-maleic acid crystal.The energy of activation was found to be 87.587 kJ/mol, 83.306 kJ/mol and 82.849 kJ/mol, respectively, for Broido, Horowitz and Metzger and Coats– Red fern methods. The activation energy value calculated using the various relations are in good agreement with each other. It is observed that since the value of activation energy is lower better NLO is expected. These results indicate that the grown crystals are useful for device application.

References

[1] PA Franken, AE Hill, CW Peters, G Weinreich, *Phys. Rev Lett.* 1961;7:118.
[2] N. Bloembergen. "*Encounters in the Nonlinear Optics*", World-Scientific, Singapore, 1996.
[3] YR Shen. "*The Principles of Nonlinear Optics*", Wiley, New York, 1984:43.
[4] O Bouevitch, A Lewis, I Pinevsky, JP Wuskell, LM Loew. *Biophysical J.* 1993;65:672.
[5] DN Nikogosyan. "*Nonlinear Optical Crystal: A Complete Survey*", Springer, Heidelberg, 2005.
[6] M.H. Suhali, *Bull. Mater. Sci*. 35 (2012) 947–956.
[7] W.W. Sulkowski, A.Danch, M.Moczynski, A.Radon, A.Sulkowska, J.Borek, *J.Therm. Anal.Calorim*. 78 (2004) 905.
[8] N.Regnier, Fontaine, *J. Therm. Anal. Calorim*. 64 (2001) 789.
[9] PA Franken, AE Hill, CW Peters, G Weinreich, *Phys. Rev Lett.* 1961;7:118.
[10] N. Bloembergen. "*Encounters in the Nonlinear Optics*", World-Scientific, Singapore, 1996.
[11] YR Shen. "*The Principles of Nonlinear Optics*", Wiley, New York, 1984:43.
[12] O Bouevitch, A Lewis, I Pinevsky, JP Wuskell, LM Loew. *Biophysical J.* 1993;65:672.
[13] DN Nikogosyan. "*Nonlinear Optical Crystal: A Complete Survey*", Springer, Heidelberg, 2005.
[14] PM Rentzepis, YH Pao. *Appl. Phys. Lett.* 1964;5:156.