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Growth and Characterization of Crystals for Room Temperature I.R. Detectors and Second Harmonic Generation Devices

Submitted by

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1.0 Introduction

One of the major objective of this program was to modify the triglycine sulfate (TGS) crystals with suitable dopants and variants to achieve better pyroelectric properties and improved infrared detectivities (D*), and higher Curie transition temperature compared to undoped TGS crystals. Towards these objectives, many promising dopants, both inorganic and organic, were investigated in the last few years. These dopants gave significant improvement in the D* value of the infrared detectors fabricated from the grown crystals (Clarkson-CCDS-Reports) with no significant increase in the Curie temperature (49^{o} C). The IR detectors were fabricated at EDO/Barnes Engineering Division, Shelton, CT.

In the last one year many TGS crystals doped with urea were grown using the low temperature solution crystal growth facility. It is found that doping with urea, the normalized growth yield increased significantly compared to pure TGS crystals and there is an improvement in the pyroelectric and dielectric constant values of doped crystals. This gave a significant increase in the materials figure of merits. The Vicker's hardness of 10 wt% urea doped crystals is found to be about three times higher in the [010] direction compared to undoped crystals.

This report describes in detail the results of urea doped TGS crystals. No work is performed on the growth of L-arginine sulfate (LAP) crystals.

2. Experimental Procedures

2.1 Growth of UrTGS crystals

Single crystals of pure and doped TGS crystals were grown from aqueous solution by temperature lowering technique using modified reciprocating crystallizer.[4] Saturated solution of TGS at 40 ^{o}C was prepared using BDH Optran grade crystalline powder.The amount of dopants were 5 and 10 wt % of urea in the growth solution. The growth solution containing urea or pure TGS solution was equilibrated in the

crystallizer at 42 ^{o}C for 48 hours. The temperature of the crystallizer was maintained within +0.01 ^{o}C using a YSI. 72 proportional temperature controller. The appropriate polyhedral TGS seed crystals grown by slow evaporation technique were affixed to the seed holder with the Dow Corning silicone adhesive. The dimensions of various faces of the seed crystals were measured and recorded. The seed holder and the seed crystals were preheated to 42 ^{o}C before insertion into the growth cell. Seed crystal surfaces were allowed to dissolve slightly before the temperature was lowered to the correct saturation temperature and held there for 24 hours. Afterwards, the solution temperature was lowered at a programmed rate which increased from initial 0.1 ^{o}C per day to 0.2^{o}C per day in order to maintain a constant supersaturation. All the growth parameters were kept identical so as to balance out the effect of growth parameters on the properties of resulting crystals. After completion of the growth runs, the crystals were removed from the growth solution and slowly cooled to room temperature in an preheated oven to avoid any thermal shock. The dimensions of the various faces of the grown crystals were remeasured. Transparent and optical quality crystals were obtained.

2.2 Dielectric, pyroelectric and microhardness measurements

Thin slices of samples were cleaved perpendicular to the b-axis of doped and undoped crystals. These samples were lapped and polished using fine grit 5-3 micron alumina polishing paper and iso-propyl alcohol as a lubricant. Silver electrodes were thermally evaporated under vacuum onto major faces (010) of the crystal. A 1659 Gen.Rad. RLC bridge was used to measure the sample capacitance and dissipation factor during heating cycle from room temperature to 54 ^{o}C. The pyroelectric current in these samples was measured by the direct method of Byer and Roundy.[5] The detailed calculation of electrical parameters are described elsewhere.[6] Vickers hardness was measured using a Leitz miniload machine with a load of 0.49N for a dwell time of 15s. Freshly cleaved or wire saw cut and polished surfaces (010) and (001) were primarily tested.

2.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of undoped TGS and urea doped TGS crystals was taken with a Perkin Elmer FTIR spectrometer attached with a microscope.

3. Results and Discussions

Table I describes the average growth data of pure and urea doped TGS (UrTGS) crystals. It can be seen from Table I that normalized growth yield of 5 and 10wt% urea doped TGS crystal is significantly higher than undoped TGS crystals. This has implications in growing larger TGS crystals in the same amount of time with other growth parameters remaining constant. The axial growth velocity along [010] direction is three times compared with [001] direction in all the crystals studied. However, the axial growth velocity along [010] direction of 10 wt% urea doped TGS crystals is fifteen times higher as compared to growth velocity along [010] direction in pure TGS crystals. These experimental data show that the growth characteristics of urea doped TGS crystals are quite different from pure TGS crystals. The growth habits of undoped and urea doped crystals are shown in Fig.1. The crystal morphology of urea doped crystals is essentially the same as undoped TGS crystals. Table IIA shows the values obtained for dielectric constant and loss, and pyroelectric coefficient for undoped TGS crystals and Table IIB gives the same values for urea doped crystals. The calculated values of various figures of merit using above parameters are also presented in Table IIA and Table IIB. The values of dielectric constant and pyroelectric coefficient of undoped TGS crystals are in good agreement with literature values.[1] However, the pyroelectric properties of 10 wt% and 5 wt% urea doped TGS crystals are higher than pure TGS crystals which make them more suitable for infrared devices. This is because urea being a dipolar impurity, going into TGS lattice creating a higher dipole moment, thereby increasing the pyroelectric coefficient. The properties of TGS crystals vary widely in the literature because their physical properties depend on various factors, such as growth conditions, history of the sample, method of measurement, and finally the growth pyramid from where the sample has been cut.

Urea in UrTGS crystals was not quantitatively measured. However, it was indirectly established by dielectric and pyroelectric, and Fourier Transform Infrared Spectroscopy (FTIR) measurements. Infrared absorption was maesured in undoped and urea doped TGS crystals. Figures 2-4 show percentage transmission as a function of wavelength for undoped TGS crystal, 5 wt% urea doped, and 10 wt% urea doped TGS crystals respectively. It can be seen from Figures 3 and 4 that increasing the percentage of urea in the growth solution has increased the absorption due to the N-H stretch at about 3200 Cm^{-1}. This indicates the incorporation of urea in TGS crystals. The peak at 3200 Cm^{-1} in the case of pure TGS crystal as seen in Fig. 2 is due to the O-H stretch.

Similar effects of doping were seen by Fang et al.,[4] in TGS crystals doped with 4-nitroaniline, although the change in the pyroelectric coefficient in our case is much larger. The calculated figures of merit (F_V , high voltage responsivity; F_i , high current responsivity; F_D , responsivity for detectors) for urea doped crystals are higher than undoped TGS crystals as seen in Table IIA and IIB. However, actual use of above crystals in infrared detectors or vidicons will determine if predicted improvement in signal to noise ratio is realized.

The Vickers hardness for undoped and urea doped TGS crystals is given in Table III. In the case of undoped TGS crystals the hardness in [010] and [001] directions is within fifteen percent of each other. On the other hand in crystals doped with 10 wt% urea, the hardness has increased about three times in the [010] direction compared to undoped crystals, while in crystals doped with 5 wt% urea, the hardness increase is only two times in the [010] direction. The increase in the hardness in the [001] direction is not very significant. This large increase in the hardness in urea doped crystals in the [010] direction may be attributed to the fact that, urea could intercalate into the TGS lattice, which is not all that compact. The increase in hardness primarily in the 'b' direction [010] may be due to the formation of new H-bonds. The H-bond network of undoped TGS is quite extensive, mostly crisscrossing in the 'a' and 'c' directions [7]. Urea would probably disrupt the crystal lattice, but it would require lot of energy to break this H-bond network. So one would not expect much change in the

hardness in the 'a' and 'c' directions. Intercalation may push the lattice apart in the b-direction [010] somewhat, although any energy cost should be minimal considering the stabilization of the lattice by the additional H-bonds in the b-direction [010]. The increase in hardness in urea doped crystals will have significant effect in machining these crystals for device purposes, where [010] face is used for infrared detector fabrication.

The enhancement of the above mentioned properties makes urea doped UrTGS crystals more suitable for various infrared detecting devices.

4. Summary

Urea doping in TGS crystals have increased the pyroelectric and dielectric constant in TGS crystals. By selecting dipolar impurity like urea, the materials figures of merit of TGS crystals for device applications have increased significantly. Urea doped crystals have much higher normalized growth yield. Doping with urea has increased the hardness of TGS crystals in the [010] direction, which will be extremely useful in device fabrication, where [010] face is used for fabrication of infrared detectors.

5. Acknowledgements

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6. References

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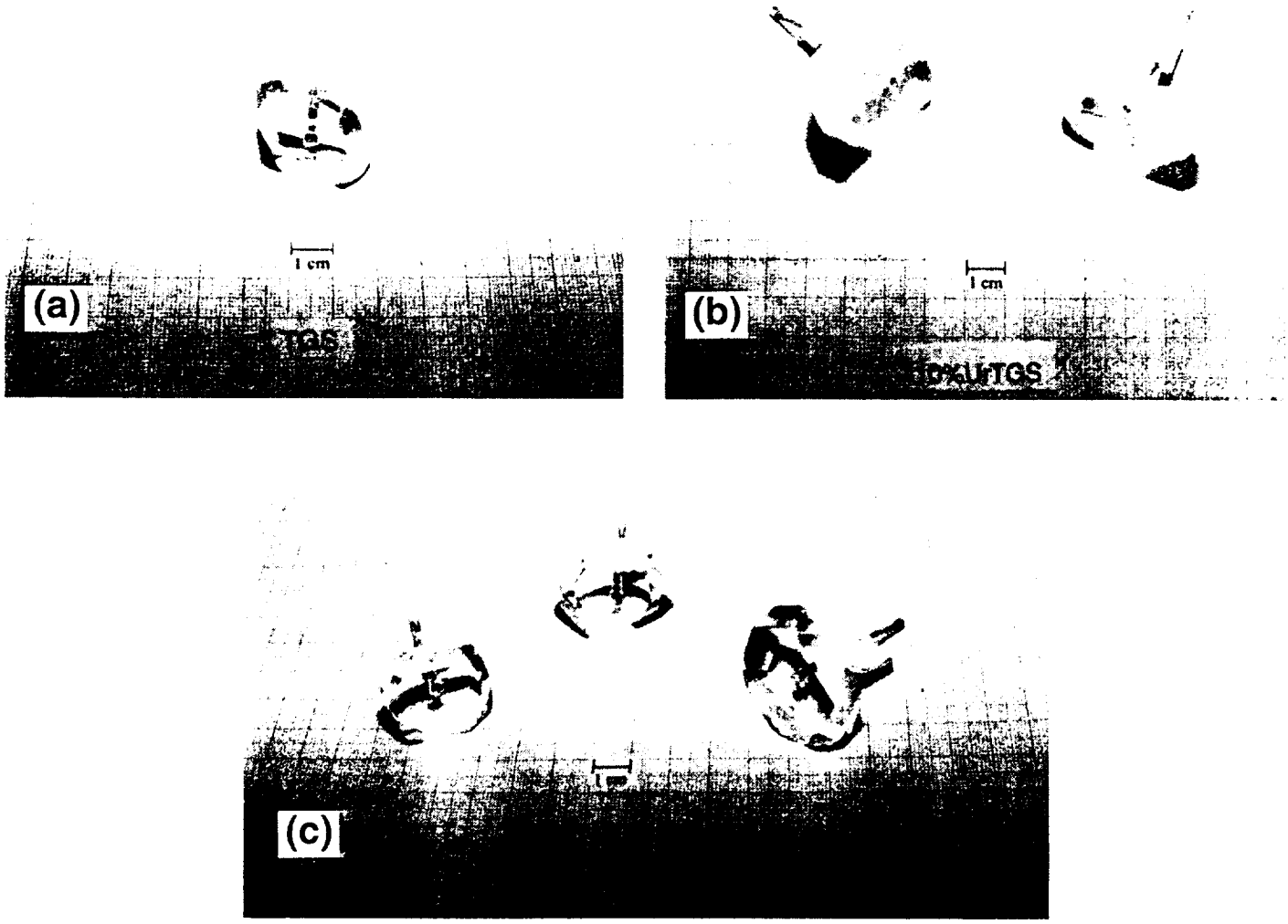
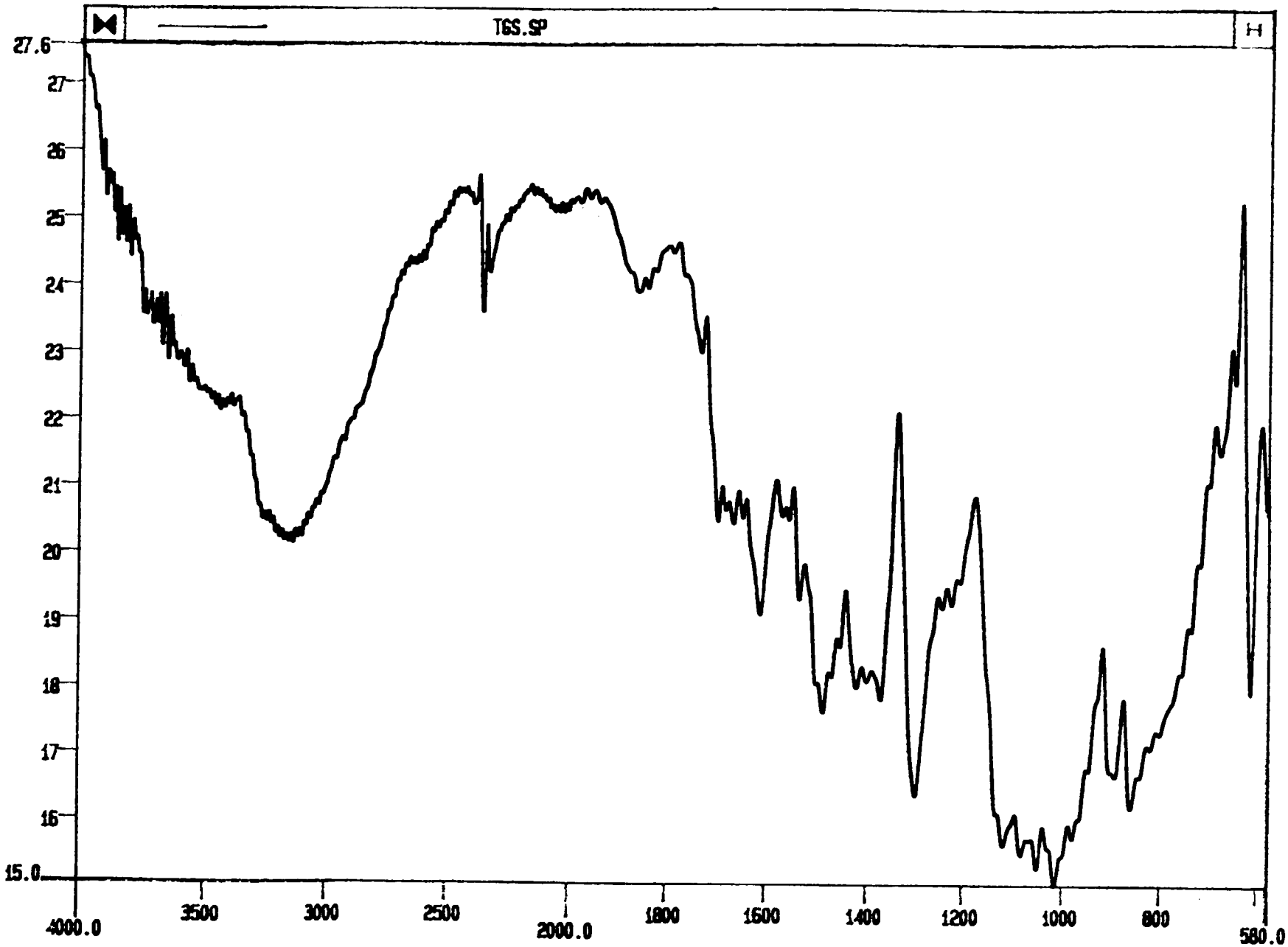
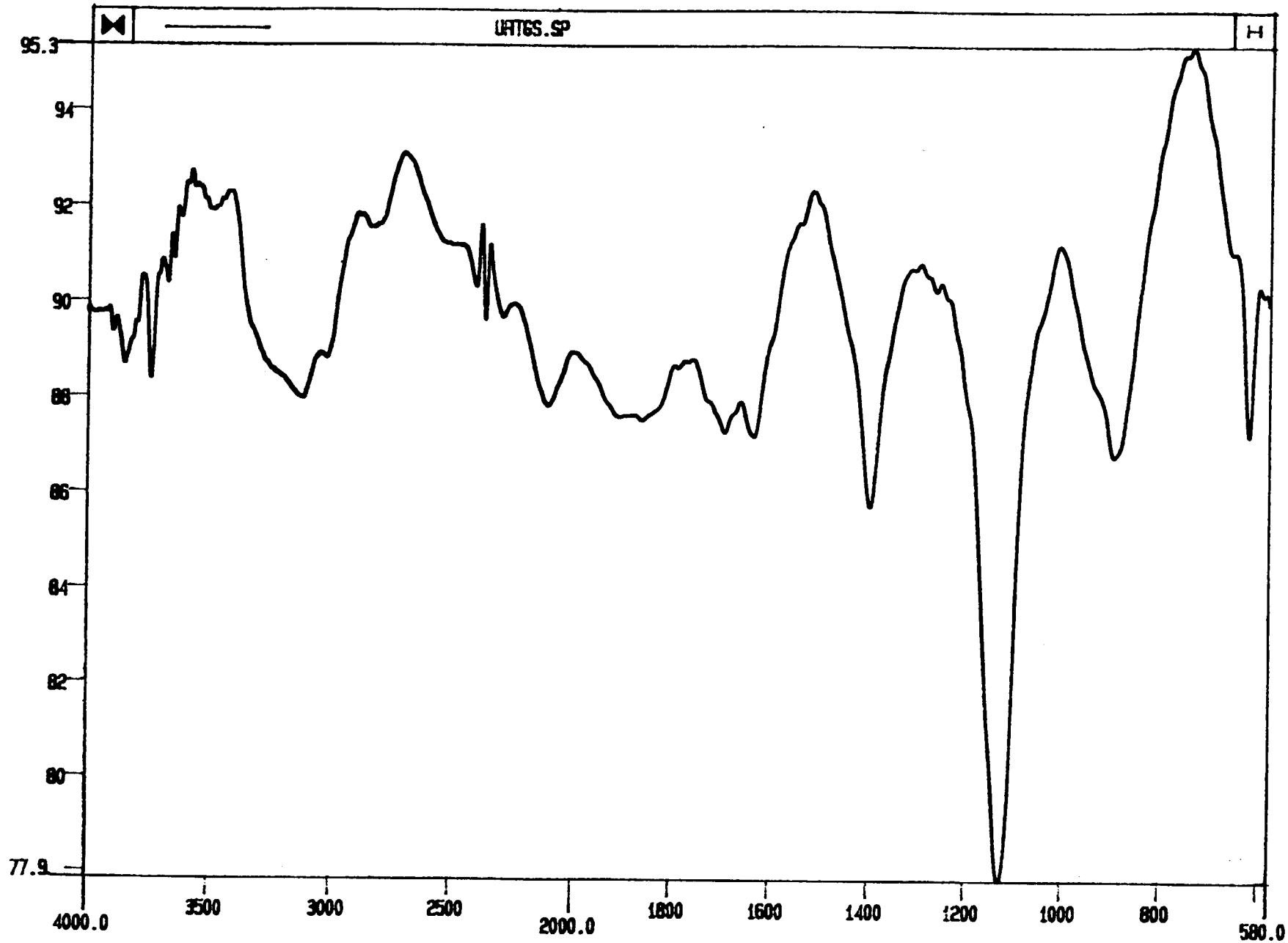


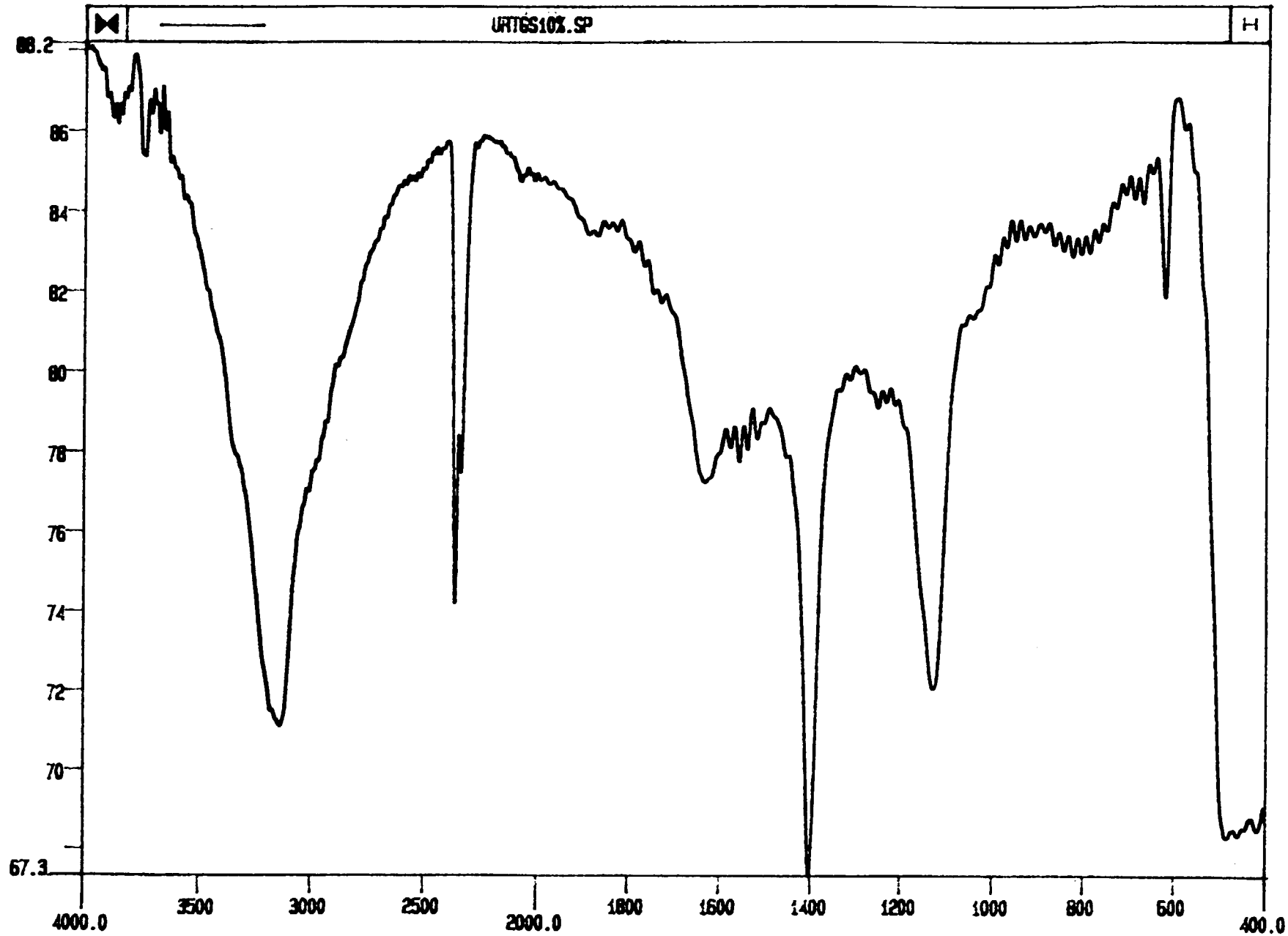
FIGURE 1. MORPHOLOGY OF TGS CRYSTALS: (a) UNDOPED, b) 10 WT% UREA DOPED, (c) 5 WT% UREA DOPED.



FTIR of Pure TGS Crystals (Figure 2)



FTIR of 5 Wt% Urea doped TGS Crystal (Figure 3)



FTIR of 10 Wt% Urea doped TGS Crystals (Figure 4)

Table I Growth Data of TGS crystals

Crystals	Normalized growth yield (gm/d/°C)	Axial growth velocity (mm/d/°C)		
		V[010]	V[001]	v[010]/v[001]
TGS	0.120	0.218	0.061	3.57
10%URTGS	3.08	3.27	1.06	3.08
5%URTGS	0.604	0.767	0.251	3.06

Table II A Material Figure of Merit of TGS Crystals

Crystal	Temp. (°C)	Fi=p nc/(cm)²°C	ε′	Tan δ	Fv=p/ε′ nc/(cm)²°C	Fvid= p/(ε′)$^{1/2}$ nc/(cm)²°C	F_D= p/(ε″)$^{1/2}$ nc/(cm)²°C
TGS	35	45.0	70	0.0105	0.64	5.4	52.3
	40	80.0	105	0.0088	0.75	7.8	83.0
	45	160.0	250	0.004	0.64	10.0	152.6

Table II B Material Figure of Merit of TGS Crystals

Crystals	Temp. (°C)	$F_i=p$ nc/(cm)^2°C	ε'	Tanδ	$F_V=p/\varepsilon'$ nc/(cm)^2°C	$F_{vid}=p/(\varepsilon')^{1/2}$ nc/(cm)^2°C	$F_D=p/(\varepsilon'')^{1/2}$ nc/(cm)^2°C
URTGS (10wt% Urea)	35	351.3	70.58	0.0105	4.97	41.82	836.42
	40	404.2	110.8	0.0023	3.64	38.49	798.80
	45	534.0	235.0	0.0037	2.27	34.90	572.96
URTGS (5 wt% Urea)	35	240.5	92.74	0.2081	2.59	24.97	54.75
	40	321.7	143.3	0.2252	2.25	26.88	56.63
	45	384.2	422.8	0.2616	0.91	18.69	36.53

Table III Microhard ness Data of TGS

Crystals	Vicker Hardness number gm/(μm)2	
	(001)	(010)
TGS	102.78	89.0
10%URTGS	123.8	278.3
5%URTGS	123.8	178.2