Journal of Crystal Growth 78 (1986) 24–30
North-Holland, Amsterdam

GROWTH AND EXCITON LUMINESCENCE OF ZnSe AND ZnS_xSe_{1-x} SINGLE CRYSTALS

Xi-Min HUANG
Changchun Institute of Physics, Changchun, People's Rep. of China

and

Kenzo IGAKI
Department of Materials Science, Faculty of Engineering, Tohoku University, Sendai 980, Japan

Received 1 December 1985; manuscript received in final form 14 May 1986

High-quality single crystals of ZnSe and ZnS_xSe_{1-x} were grown by a sublimation method. The very strong peak of free exciton emission, sharp lines of bound excitons and a fine reflection spectrum are observed, showing the high-quality of the grown crystals. High-purity ZnSe with excess zinc vacancies through a previous heat-treatment under the saturation pressure of selenium was doped with Al at a low temperature. A marked increase of the intensity of the luminescence lines related to Al_{Zn} was observed.

1. Introduction

Recently, deep interest has been focussed on ZnSe and ZnS_xSe_{1-x} crystals because of their direct wide gaps, suitable for the development of blue light emitting diodes. In order to reach this target, high-quality and large single crystals of ZnSe and Zns_xSe_{1-x} must be grown. Many workers have attempted to grow large and high-quality crystals of these materials [1–7], but the purity and the quality require further improvement. Crystals often contain traces of impurities such as Al, Ga, In, Cl and F, and these impurities are substitutional type simple donors with shallow levels. These shallow donors give a number of bound exciton luminescence lines in a complex way at low temperature, and play an important role in determining n-type conductivity of the ZnSe crystals.

Electrical measurements are not readily applicable for these wide band-gap semiconductors because of their very low electrical conductivity and give no information on the impurity species. However, many sharp exciton emission lines, observed at liquid helium temperature, provide an extensive source of experimental data which contributes to the identification of the impurities and defects in these semiconductors [8–12]. The exciton emission spectra have been increasingly employed and have become a very powerful experimental tool for the evaluation of the crystal quality. In order to identify the chemical origin of the bound exciton emission in ZnSe, very sharp lines of bound exciton spectra must be obtained with high spectral resolution of at least 0.05 meV on high quality single crystals. In order to avoid line broading, small amounts of impurities on a level of 0.01 ppm must be added to high-purity ZnSe single crystals.

The purpose of the present investigation is to grow high purity ZnSe and ZnS_xSe_{1-x} large single crystals by the sublimation method, and to evaluate these crystals by optical spectroscopy at low temperature and to identify the I_2^{Al}, I_{2a}^{Al} and I_{2b}^{Al} lines using the back-doping method. For this purpose the raw materials Se and S were refined by the vacuum evaporation method and a growth chamber of special shape was designed to obtain single crystals. The results of the exciton emission spectra are described.

RYSTALS

peak of free exciton
f the grown crystals.
selenium was doped
observed.

:h contributes to
:s and defects in
exciton emission
iployed and have
:ntal tool for the
In order to iden-
: bound exciton
:s of bound exci-
ith high spectral
on high quality
d line broading,
a level of 0.01
ırity ZnSe single

ıvestigation is to
Se_{1-x} large single
nethod, and to
l spectroscopy at
the I_2^{Al}, I_{2a}^{Al} and
method. For this
d S were refined
ıod and a growth
:signed to obtain
exciton emission

---

2. Experimental procedures

2.1. Refining method

The refining equipment for S or Se is shown in fig. 1. About 0.4 mol of S with nominal purity 6N grade (or Se of 5N up grade) were introduced into the quartz ampule as shown in fig. 1. After flushing with high purity argon, the ampule was sealed off at a pressure of 10^{-3} Torr. One end of the ampule with the specimen was kept in a furnace at 20°C above the melting point and the other end was immersed in liquid nitrogen. For about one week, dendritic crystals of S or Se were grown on the inner wall of the quartz tube over a 30 mm length just above the furnace; then the quartz tube with the specimen was lifted about 35 mm and the refining run was continued for three weeks. Refined specimens were analysed by an ion micro analyser (IMA) *.

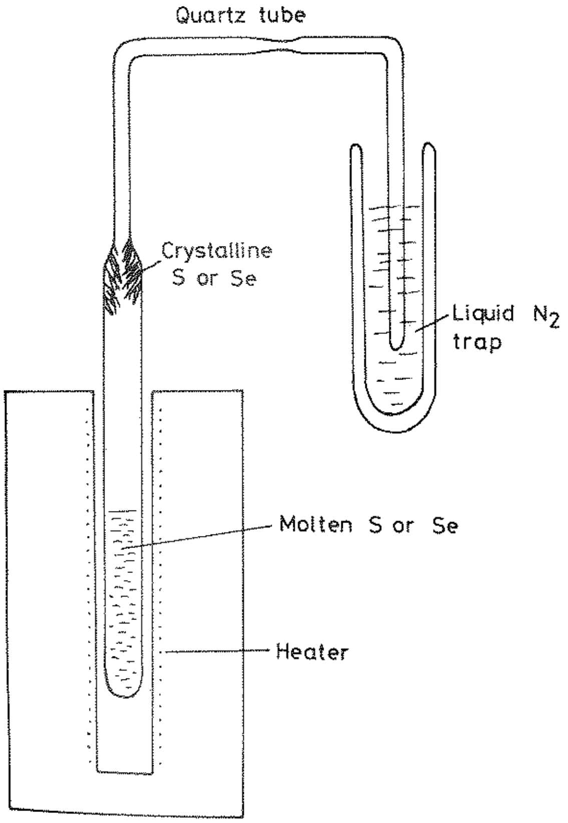

Fig. 1. Experimental arrangement for the refining of S or Se.

2.2. Synthesis of the source specimen

About 1/20 mol of ZnSe polycrystals were synthesized at 1000°C by the chemical reaction of pure Zn (Cominco, 6N grade) and refined Se. ZnS polycrystals were prepared by a similar procedure. Synthesized ZnSe and ZnS were refined through vapor phase transport two or three times under a controller partial pressure of Zn corresponding to the minimum total pressure [5]. The method used here for a polycrystal of homogeneous ZnS_xSe_{1-x} solid solution was similar to that reported earlier [6].

2.3. Growth of single crystals

The schematic construction of the apparatus used to grow ZnSe single crystals is shown in fig. 2. The fused quartz tube consists of the source chamber (s) containing refined ZnSe polycrystals, the Zn reservoir (r) containing high purity Zn and the growth chamber (c) which has a special shape as shown in fig. 3. The end of the growth chamber consists of a broad head with a neck of diameter about 1 mm. In the case of growing ternary single crystals of ZnS_xSe_{1-x}, no reservoir is used, and appropriate amounts of S and Se for the desired composition are introduced in the quartz tube. The temperature difference ΔT between the temperature of the source chamber (T_s) and that of the growth chamber (T_c) is 3–5°C. In the case of $T_c = 1000$°C, the Zn reservoir temperature (T_{Zn}) is fixed at 450°C from the condition of the minimum total pressure.

2.4. Al-doping and photoluminescence

Aluminium was vacuum deposited on both surfaces of a wafer specimen taken from the growth ZnSe single crystals on cleaving along the {110} cleavage plane, after previous heat-treatment in

---

* Measurements were cordially performed at the Semiconductor Laboratory, Sharp Co. Ltd., Japan.

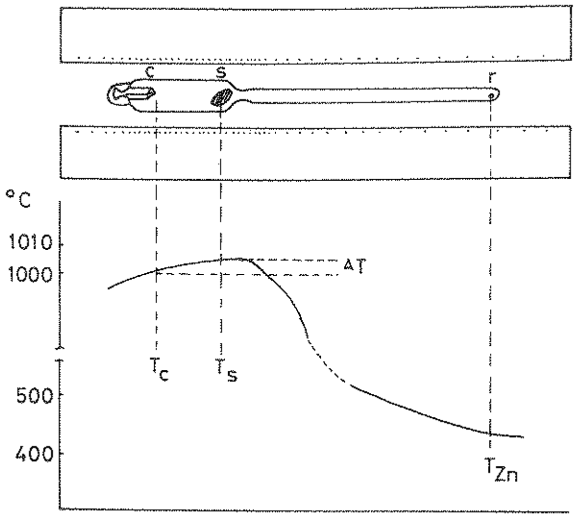

Fig. 2. Schematic construction of growth ampule and an example of temperature profile.

the Se saturation vapor pressure at 700°C for 72 h. The Al-deposited wafer was sealed in a quartz ampule and doped with Al by diffusion at 300°C for 48 h in argon atmosphere; then the ampule was quenched in water. To remove the Al remaining on the surface, the wafer was dipped in 12N NaOH at 95°C for 2 min and etched at 95–100°C for 2 min by an etching solution consisting of three parts of a saturated aqueous solution (at 60°C) of $K_2Cr_2O_7$ and two parts of concentrated H_2SO_4.

The photoluminescence and reflection spectra were measured on samples immersed in liquid helium and cooled to 2 K. A 2 kW Xe lamp through UV filters was used as the excitation source. Spectra were recorded using a J.Y. U-1000 double monochromator with a reciprocal dispersion of 0.2 nm/mm and an HTVR-106 UH photomultiplier.

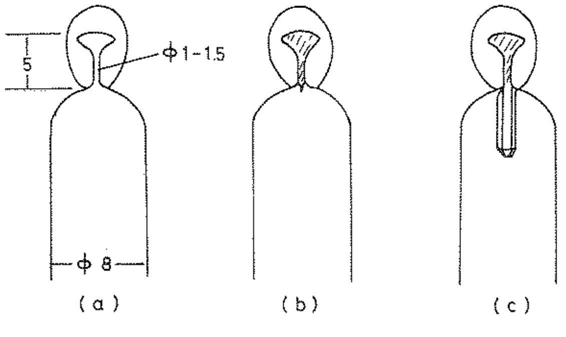

Fig. 3. Schematic illustrations of the growth chamber and the grown crystal. Marker represents 1 cm.

3. Results and discussion

3.1. IMA analysis of sulfur

The analytical results obtained through IMA are shown in table 1. Data are represented by the relative value of the ion current and ND indicates that the measured value is lower than the detection limit. The concentrations of Al, Si, As and Se in the refined sulfur sample are 5–10 times lower than that of the residue in the second runs as shown in table 1. This result shows the effectiveness of the refining method adopted in the present study.

3.2. Crystal growth

On keeping $\Delta T = 3$–5°C, a few nuclei had been formed at the end of the growth chamber shown in fig. 3a, but a single nucleus among them was able to grow preferentially through the neck part of growth chamber, and thereafter a single crystal in the shape of a hexagonal column was grown free of the constraint from the vessel wall. Figs. 3b and 3c show a schematic illustration of the growth behaviour. Fig. 4 shows a pale yellowish-green ZnS_xSe_{1-x} ($x = 0.04$) transparent single crystal. An X-ray diffraction study revealed that the six columnar planes were $\{110\}$ planes and the growth direction was $\langle 111 \rangle$. The growth rate was about 0.5 mm/day for $\Delta T = 5$°C; the growth duration was 3 weeks. Using this type of growth chamber, large single crystals were obtained reproducibly.

3.3. Photoluminescence spectra of the undoped ZnSe crystals

The near band-edge photoluminescence spectrum (solid line) and the reflection spectrum (dotted line) of the as-grown, undoped ZnSe are

---

Table 1
Analytical result
Sample
Residue, second
Upper portion, f
Middle portion,
Lower portion, f
Middle portion,
ND means "not

Fig. 4. Photogra
crystal growr

shown in fig.
mum of the r
2.802 eV. Th
ported by Hit
peak at 2.802
be due to the
tons, because
mum of the r

Table 2
Energies of boun
Spectral line
and
donor level
I_2
I_3
$I_{2\beta^*}$
E_d
β^* = a, b, c, d.

Table 1
Analytical results of sulfar by IMA

Sample	Relative value of the ion current					
	$^{23}Na^+$	$^{27}Al^+$	$^{28}Si^+$	$^{75}As^+$	$^{80}Se^+$	$^{32}S^+$
Residue, second run	ND	8.5×10^{-3}	5.4×10^{-2}	4.5×10^{-2}	1.2×10^{-3}	1.0
Upper portion, first run	ND	1.5×10^{-3}	4.4×10^{-3}	5.1×10^{-3}	2.6×10^{-4}	1.0
Middle portion, first run	8.7×10^{-4}	1.6×10^{-3}	2.8×10^{-3}	2.9×10^{-3}	2.5×10^{-4}	1.0
Lower portion, first run	ND	5.0×10^{-3}	1.4×10^{-2}	1.5×10^{-2}	ND	1.0
Middle portion, second run	3.1×10^{-4}	1.2×10^{-3}	4.8×10^{-3}	7.9×10^{-3}	6.0×10^{-4}	1.0

ND means "not detected".

Fig. 4. Photograph of a typical ZnS_xSe_{1-x} ($x = 0.04$) single crystal grown in an ampule. Marker represents 10 mm.

shown in fig. 5. The sharp maximum and minimum of the reflection spectrum are observed near 2.802 eV. This shape is very similar to that reported by Hite et al. [13]. The prominent emission peak at 2.8021 eV, labelled as Ex, is considered to be due to the radiative annihilation of free excitons, because this peak is located near the maximum of the reflection spectrum, and this energy is in good agreement with a previous report [14]. The peaks at 2.8164 and 2.8175 eV are considered to arise from the recombination luminescence of free excitons at the excited states of $n = 2$ and $n = 3$ from a comparison with the reflection spectrum.

Emission near 2.797 eV resolved into five lines is regarded as due to the recombination emission of excitons bound to neutral donors. These donors are considered to be F, In, Ga, Cl and Al impurities remaining in the ZnSe single crystals from the comparison with data reported previously [15]. These shallow donor levels (E_d) can be estimated from the empirical expression [16]

$$E_d = \frac{\mathrm{Ex}(n = 1) - E_{I_2}^{\mathrm{imp}}}{0.20}, \qquad (1)$$

where $\mathrm{Ex}(n = 1) - E_{I_2}^{\mathrm{imp}}$ is the binding energy of an exciton bound to a neutral donor, that is, the energy difference between the free exciton peak ($\mathrm{Ex}(n = 1)$) and I_2^{imp} lines of the various donor impurities ($E_{I_2}^{\mathrm{imp}}$). The energies of these peaks and

Table 2
Energies of bound exciton spectral lines and neutral donor levels in ZnSe

Spectral line and donor level	Energy (eV)				
	Al	Cl	Ga	In	F
I_2	2.7977_6	2.7976_6	2.7973_9	2.7971_7	2.7969_4
I_3		2.7964_9	2.7953_1		
		2.7959_2	2.7949_6	2.7940_7	
$I_{2\beta^*}$	2.7982_8				
	2.7999_8			2.8010_1	
E_d	0.0217	0.0222	0.0236	0.0247	0.0258

$\beta^* =$ a, b, c, d.

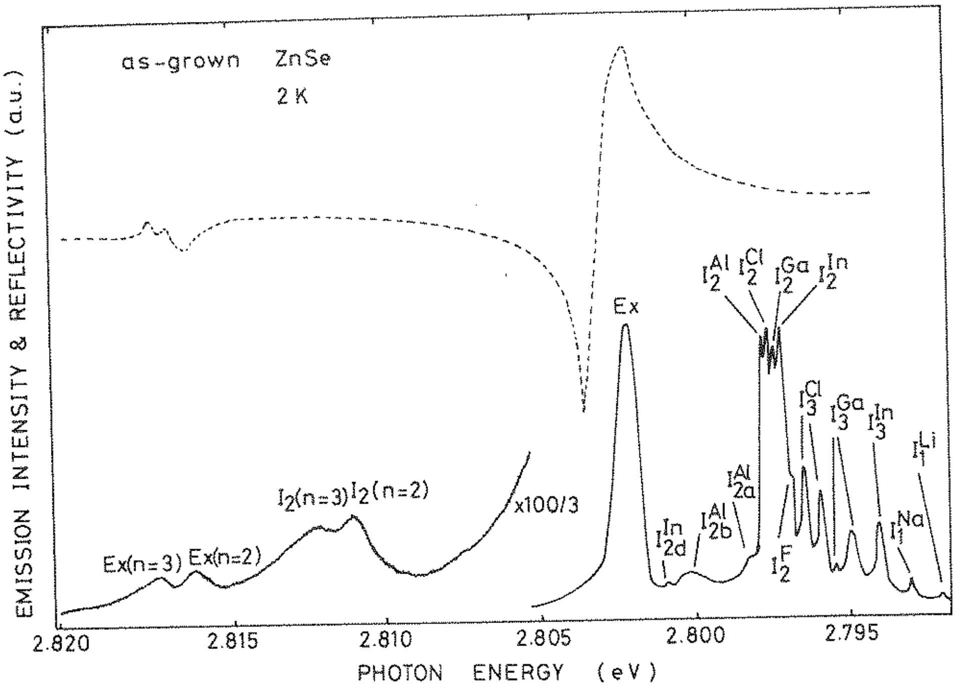

Fig. 5. Free-exciton and bound-exciton emission spectra (solid line) and reflection spectrum (dashed line) of an as-grown undoped ZnSe at 2 K.

donor levels are shown in table 2. The energy difference between the I_2^{Al} and I_2^{Cl} lines is less than 0.1 meV, but these lines are very sharp and clearly split, which means that the crystals are of very high quality. These donor levels are very shallow, since these impurities are believed to be simple substitutional defects. The peaks at 2.811 and 2.812 eV are supposed to originate from the recombination luminescence of excitons in the excited state of $n = 2$ and $n = 3$ bound to neutral donors, respectively, by reference to the peak positions of the free exciton luminescences. There are three weak peaks between the EX and I_2 lines, which oroginate from excited states of the bound exciton complex [15]. These are labelled I_{2a}^{Al}, I_{2b}^{Al} and I_{2d}^{In}. The I_3^{Cl}, I_3^{Ga} and I_3^{In} doublet lines are considered to be due to the recombination of excitons bound to the ionized donors [15].

The intensity of the free exciton luminescence (Ex) is very strong and nearly equal to that of the I_2 line as seen in fig. 5. The increased probability of the radiative annihilation of free excitons is considered to be caused by the increased lifetime of the free exciton through the decreased concentration of trap centers in the high quality single crystals. The sharp lines of bound exciton emission and the sharp maximum and minimum on the reflection spectrum reflect the high quality of the crystals and also of the specimen surface.

3.4. Exciton emission spectra of ZnSe doped with Al

The exciton emission spectra of the undoped and Al-doped ZnSe single crystals at 2 K are shown in fig. 6. Fig. 6a is the undoped specimen already described in the preceding section, fig. 6b is Al-doped ZnSe, and fig. 6c is the specimen doped with Al after the prior heat-treatment under Se saturation vapor pressure. On doping with Al, the intensity of Ex decreases, and the intensities of the I_2^{Al}, I_{2a}^{Al} and I_{2b}^{Al} lines increase. The equilibrium between the vapor and the ZnSe solid during the heat-treatment is controlled by the Se

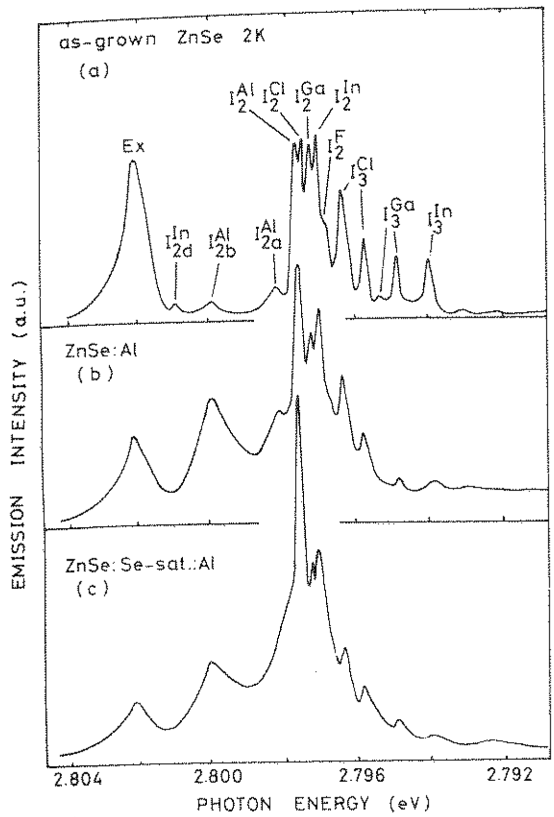

Fig. 6. Free-exciton and bound-exciton emission spectra of ZnSe at 2 K: (a) as-grown, undoped and nearly stoichiometric; (b) Al-doped to specimen (a); (c) Al-doped to the specimen previously heat-treated under Se saturation pressure.

partial pressure. Consider the following reaction:

$$\tfrac{1}{2}Se_2(g) = Se_{Se} + V_{Zn}, \qquad (2)$$

where V_{Zn} is a Zn vacancy and Se_{Se} is a Se atom occupying a normal Se site. Then the concentration of V_{Zn} is known to increase with the increasing Se pressure. The probable sites of Al in ZnSe crystals are the substitutional site (Al_{Zn}) and/or the interstitial site (Al_I). Al was diffused under the same condition, so that the increased parts of the intensity of the I_2^{Al}, I_{2a}^{Al} and I_{2b}^{al} lines in the case of fig. 6c in comparison with the case of fig. 6b are considered to be due to the increased amount of Al_{Zn} (Al occupying Zn sites). The Zn sites were left vacant in the prior heat-treatment under Se saturation pressure. A doped Al atom reacts with a zinc vacancy:

$$Al + V_{Zn} = Al_{Zn}. \qquad (3)$$

In the case of fig. 6c, the concentration of Al on the Zn sublattice (Al_{Zn}) is highly increased through the increased concentration of zinc vacancies (V_{Zn}) by the prior heat-treatment. These results give definitive evidence for the fact that the lines at 2.7977_6 eV (I_2^{Al}), 2.7982_8 eV (I_{2a}^{Al}) and 2.7999_8 eV (I_{2b}^{Al}) originate from the recombination luminescence of excitons bound to simple shallow donors (Al_{Zn}), in agreement with the result of the previous work [15].

4. Conclusion

The IMA results of the refined S and Se show that the refining method used in this study is very effective. The concentrations of some impurities in the refined samples are 5–10 times lower than that of the residue.

Pale yellowish-green transparent single crystals in the shape of a hexagonal column were obtained using the novel growth chamber. The very sharp spectral lines of the bound exciton and the sharp maximum and minimum of the reflection spectrum show that the crystals grown are of high purity and perfection.

Some bound exciton spectral lines were related to Al_{Zn} shallow donors using a back-doping method at low temperature.

Acknowledgments

We would like to thank Dr. Y. Nozue of the Department of Physics of Tohoku University for his measurements and for helpful discussions, and Professor M. Ueta for his kind support throughout this study.

References

[1] E. Kaldis, J. Phys. Chem. Solids 26 (1965) 1701.
[2] A. Catano and Z.K. Kun, J. Crystal Growth 33 (1976) 324.

[3] M.E. Özan and J. Woods, J. Phys. D (Appl. Phys.) 10 (1977) 1335.

[4] Y. Tsujimoto, Y. Onodera and M. Fukai, Japan. J. Appl. Phys. 5 (1966) 636.

[5] T. Kiyosawa, K. Igaki and N. Onashi, Trans. Japan Inst. Metals 13 (1972) 248.

[6] K. Mochizuki and K. Igaki, J. Crystal Growth 45 (1978) 218.

[7] K.F. Burr and J. Woods, J. Crystal Growth 9 (1971) 183.

[8] P.J. Dean, D.C. Herbert, C.J. Werkhoven, B.J. Fitzpatrick and R.N. Bhargava, Phys. Rev. B 23 (1981) 4888.

[9] S.M. Huang, Y. Nozue and K. Igaki, Japan. J. Appl. Phys. 22 (1983) L420.

[10] S.M. Huang, S. Satoh, K. Mochizuki and K. Igaki, Japan. J. Appl. Phys. 22 (1983) 674.

[11] S. Satoh and K. Igaki, Japan. J. Appl. Phys. 22 (1983) 68.

[12] J.L. Merz, K. Nassau and J.W. Shiever, Phys. Rev. B8 (1973) 1444.

[13] G.E. Hite, D.T.F. Marple, M. Aven and B. Segall, Phys. Rev. 156 (1967) 850.

[14] P.J. Dean and J.L. Merz, Phys. Rev. 178 (1969) 1310.

[15] J.L. Merz, H. Kukimoto, K. Nassau and J.W. Shiever, Phys. Rev. B6 (1972) 545.

[16] R.E. Halsted and M. Aven, Phys. Rev. Letters 14 (1965) 64.

Journal of Cryst
North-Holland,

GROWTH
BY TEMPE

ZHOU Yong
Shanghai Institu

Received 1 Octo

The phase
aluminium in
that of the und
modified and
density and hig

1. Introducti

In 1965,
commercial
time, this m
solid state la
are obtained
the Czochral
vex interfac
growth, the
inhomogene
only be cut
it is not pos
laser amplifi

In 1979,
a modificati
the growth
solid–liquid
the growth
and the res
However, it
0.8 at% Nd
supercoolin
tions.

The auth
high quality
ture gradie
crystal gro

0022-0248/
(North-Hol