Science in China Series G: Physics, Mechanics & Astronomy

© 2008 SCIENCE IN CHINA PRESS
Springer-Verlag

www.scichina.com
phys.scichina.com
www.springerlink.com

Segregation during crystal growth from melt and absorption cross section determination by optical absorption method

ZHANG QingLi†, YIN ShaoTang, SUN DunLu & WAN SongMing

Crystal Laboratory, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei 230031, China

Segregation during crystal growth from melt under two conditions is studied by using crystal mass, which can be measured easily, as an independent variable, and a method to determine the effective segregation coefficient and absorption cross section of optical dopant is given. When the segregated solute disperses into the whole or just a part of melt homogenously, the concentration C_S in solid interface will change by different formulas. If the crystal growth interface is conical and segregated solute disperses into melt in total or part, the solute concentration at $r = 2/3R$, where r is the distance from the growth cross section center and R the crystal radius, is independent on the shape of the crystal growth interface, and its variation at $r = 2/3R$ can be regarded as the result from crystal growth in flat interface. With C_S variation formula in solid and absorption cross section σ for optical dopant, the absorption coefficients along the crystal growth direction can be calculated, and the corresponding experimental value can be obtained through the crystal optical absorption spectra. By minimizing the half sum, whose independent variables are k, ΔW or σ, of the difference square between the calculated and experimental absorption coefficients from one or more absorption peaks along the crystal growth direction, k and σ, or k and ΔW, can be determined at the same time through the Levenberg-Marquardt iteration method. Finally, the effective segregation coefficient k, ΔW and absorption cross sections of Nd:GGG were determined, the results fitted by two formula gave more closed effective segregation coefficient, and the value ΔW also indicates that the segregated dopant had nearly dispersed into the whole melt. Experimental results show that the method to determine effective segregation coefficient k, ΔW and absorption cross sections σ is convenient and reliable, and the two segregation formulas can describe the segregation during the crystal growth from melt relatively commendably.

effective segregation coefficient, absorption cross section, absorption spectrum, crystal growth, Nd:GGG

Received February 4, 2007; accepted January 25, 2008
doi: 10.1007/s11433-008-0064-z

† Corresponding author (email: zql@aiofm.ac.cn)

Supported by the National Natural Science Foundation of China (Grant No. 50772112)

1 Introduction

Segregation is a very popular phenomenon during crystal growth from melt, especially in laser crystal growth, whose dopant acted as laser active ion is indispensable. Segregation effect results in the dopant concentration variation in the as-grown crystal. The important parameter to characterize segregation is segregation coefficient k, which is defined as $k = C_S/C_L$, where C_S and C_L are solute concentration in crystal and melt, respectively. Here the solute boundary will be omitted, and melt fluid or crystal seed may not be static, so the segregation coefficient in this paper is a factual effective segregation one. For convenience, it is still named segregation coefficient. If k is less than 1, the dopant concentration will increase with the grown crystal mass increasing. If k is more than 1, the dopant concentration will decrease with the growth crystal mass increasing. This will affect the crystal optical uniformity seriously and output laser quality if no suitable growth technology is adopted. It can be seen that the segregation coefficient k is a key parameter to describe the solute concentration variation during crystal growth.

Ref. [1] has discussed the establishment of solute concentration equilibrium state in melt with a sophisticated mode in one-dimension condition, in which C_S depends on C_L, and other melt property parameters by a complex nonlinear relation. This mode can describe the solute concentration variation in melt, but it is very difficult to determine C_L during the experiment. On the other hand, its independent variable is position coordinate z, which will encounter so complex three or two-dimension growth interface that cannot be applied. Thus the mode is not so convenient from an experimental and practical view. This work will use grown crystal mass W_S as an independent variable to discuss solute effective segregation, which is convenient due to easiness for crystal mass measurement. On the other hand, a phenomenological parameter ΔW is introduced to characterize the solute dispersion condition in melts and a segregation mode is given.

It is necessary to determine the solute segregation coefficient k in order to obtain a dopant concentration variation rule and take a suitable technical measure to improve crystal optical uniformity. The widely used method to determine the segregation coefficient k is such chemical methods as inductively coupled plasma atomic emission spectroscopy (ICP-AES)[2−7] and fluorescent X-ray analysis[8,9], which are obviously not so convenient. For example, in order to obtain a gasoloid sample for ICP-AES, crystal should be dissolved firstly. It is often difficult to find good dissolvant for crystals such as gadolinium gallium garnet (GGG), yttrium aluminium garnet (YAG) and many other oxide crystals. As far as the fluorescent X-ray analysis is concerned, the necessary work to determine the dopant concentration is to prepare a standard sample firstly, which will also consume a long time.

On the other hand, the absorption cross section σ is an important parameter to characterize the laser performance of a laser crystal. In general, σ is obtained by measuring their concentration C_N and absorption coefficient α in host with the formula $\sigma = \alpha/C_N$. If the concentration is determined by a chemical analysis method, there existed the same before-mentioned difficulty.

Recently ref. [10] has used optical absorption of crystal to determine the segregation k, which is based on linear extrapolation, however, by which the absorption cross section cannot be determined and multi-peaks absorption cannot be processed at the same time, which is of no advantage to decreasing a statistic error.

This work studies the segregation behavior under two different growth conditions, in which segregated solute dispersed into the whole growing melt homogeneously and just into a certain volume melt homogeneously, respectively. A simple optical method is proposed to determine the segregation coefficient and absorption cross section for optical dopant, by which segregation coefficient k and σ can be determined at the same time with the absorption spectrum of crystal. As far as we know, the method has not been reported elsewhere. Meanwhile, the influence of crystal growth interface on determination precision is discussed. It will be shown that this influence can be avoided if optical absorption spectra were measured at a certain position of crystal.

Gadolinium gallium garnet doped by Nd^{3+}, namely Nd:GGG, has attracted great attention[10−13] recently due to available core-free and good optical homogenous boule with large-diameter used in the high average power solid state laser pumped by laser diode. Kuwano[8] had reported the effective segregation coefficient determined by the optical absorption method, which is different from our method, and that work uses crystal absorption spectra to determine Nd concentration with known “absorption coefficient” (it seems that the “absorption coefficient” should be absorption cross section). On the other hand, if that sample used to measure optical absorption is not coated by high-transmission film for 481.3 nm light, the cited formula by that work $I = I_0 R\exp(-kCt)$ is not so precise, at least with 10% error. Therefore the segregation coefficient and absorption cross section of Nd:GGG crystal are determined by our proposed method and model.

2 Dopant segregation in crystal

2.1 The case that segregated dopant disperses into melt homogenously

This is an ideal condition where there does not exist segregated solute concentration gradient in melt, and the segregated solute ions will spread into melt with relatively quick speed compared with the crystal growth rate, which is a good approximation during many crystal growth processes by Czochralski method due to stirring effect of the seed crystal and the free convection of the melt. Although many references[14,15] have studied segregation behavior in this condition with many other assumptions during the zone melting crystal growth, we will discuss solute segregation just with the homogeneously dispersion assumption by using crystal growth mass W_S as an independent variable, which is an easily measured parameter. So it is convenient for the practical use.

At a certain time, the volume of the melt and crystal are V_L and V_S, the solute concentrations in crystal and melt C_L and C_S. At the next instantaneous time, these quantities are changed by $-dV_L$, dV_S, dC_L and dC_S, and the segregated solute mass is

$$dW_{S,d} = -C_L\rho_L dV_L - C_S\rho_S dV_S, \tag{1}$$

where ρ_S and ρ_L are the crystal and melt density, respectively.

At the same time, the added solute mass in the melt is

$$dW_{L,d} = \rho_L dC_L(V_L + dV_L) = \rho_L(dC_L V_L + dC_L dV_L). \tag{2}$$

Omitting the second order item $dC_L dV_L$ in the above equation yields

$$dW_{L,d} = \rho_L dC_L V_L. \tag{3}$$

Considering the relations $dW_{S,d} = -dW_{L,d}$, $-\rho_L dV_L = \rho_S dV_S$, $C_S = kC_L$ and $V_L = V_0 - \frac{\rho_S V_S}{\rho_L}$ (V_0 is the initial melt volume), we can obtain the following formula:

$$(1-k)\frac{\rho_S}{\rho_L}\frac{dV_S}{V_0 - \frac{\rho_S V_S}{\rho_L}} = \frac{dC_L}{C_L}, \tag{4}$$

where $V_0 = W_T/\rho_S$, and W_T is the total mass of raw material.

Integrating the left of the equation from 0 to V_S, and the right from C_0 to C_L, where 0 and V_S are the initial and current crystal volume, C_0 and C_L the initial and current solute concentration, eventually the solute concentration in the melt is expressed by

$$C_L = C_0\left(1-\frac{\rho_S V_S}{V_0\rho_L}\right)^{(k-1)} = C_0\left(1-\frac{W_S}{W_T}\right)^{(k-1)}. \tag{5}$$

Correspondingly, the solute concentration in the crystal on the growth interface is

$$C_S = kC_0\left(1-\frac{W_S}{W_T}\right)^{(k-1)}. \tag{6}$$

No interface shape and detailed crystallized procedure were considered in formula (5) and (6), and they can be used in any crystal growth process if only the segregated dopant homogeneous dispersion condition is satisfied. The solute concentration in the melt and crystal growth interface is just relative to the grown crystal mass, not dependent on the crystal growth procedure. This is very useful for us to compute the solute concentration in growth residual material and determine the solute amount to be added for the next crystal growth in order to obtain the crystal with desired dopant concentration.

If the growth residual material is pW_T (p is less than 1), namely $W_T - W_S = pW_T$, eq. (6) is changed into

$$C_S = kC_0(pW_T)^{(k-1)}. \tag{7}$$

If k is 1, $C_S = kC_0$, which is a constant and means that the solute concentration in the whole crystal has no variation. If k is less than 1 greatly, C_S will increase greatly when p decreases. On the contrary, if k is more than 1, C_S will decrease greatly. So p should be as small as possible in order to grow crystal with relatively good uniformity if the solute segregation coefficient is not 1.

2.2 The case that segregated dopant disperses into melt with mass ΔW

Under this condition, the transport state of the segregated solute ions is not so good that they only disperse into the part of grown melt with mass ΔW. Generally, ΔW may be changed during the whole crystal growth. Within a short enough time, the variation amount of ΔW can be omitted. As a simplified case, the assumption that ΔW is a constant during crystal growth will be taken here.

Similar to the above derivation, the following equations for this condition can be obtained:

$$C_L\rho_L \mathrm{d}V_L + C_S\rho_S\mathrm{d}V_S = -\rho_L \mathrm{d}C_L\Delta V_L, \tag{8}$$

$$\frac{(1-k)\rho_S\mathrm{d}V_S}{\Delta W} = \frac{\mathrm{d}C_L}{C_L}. \tag{9}$$

Integrating eq. (9), we will obtain the formula finally:

$$C_L = C_0\mathrm{e}^{(k-1)\frac{W_S}{\Delta W}}. \tag{10}$$

Correspondingly, the solute concentration in crystal on the growth interface is

$$C_S = kC_0\mathrm{e}^{(1-k)\frac{W_S}{\Delta W}}. \tag{11}$$

The comparison of eq. (11) with (6) shows that solute segregation has different rules under homogenously dispersion into the whole melt and just into a part melt.

The following discussion will be based on the assumption that the segregated solute disperses into melt in part or total.

2.3 Crystal growth interface effect on dopant segregation

During the crystal growth process, the growth interface shape between the solid and melt is changed continuously. In many actual crystal growth cases such as by Czochralski method, the growth interface can be approximated by a cone with angle θ, which is not a constant during the whole crystal growth. At any crystal position (z, r) with interface cone angle θ, the grown crystal mass

$$W_{\mathrm{S}} = \frac{1}{3}\rho_{\mathrm{S}}\pi R^3 \mathrm{ctg}\theta + W_0, \tag{12}$$

where R is the crystal boule radius and W_0 the mass of the conical interface part of crystal dipping in the melt, shown in Figure 1.

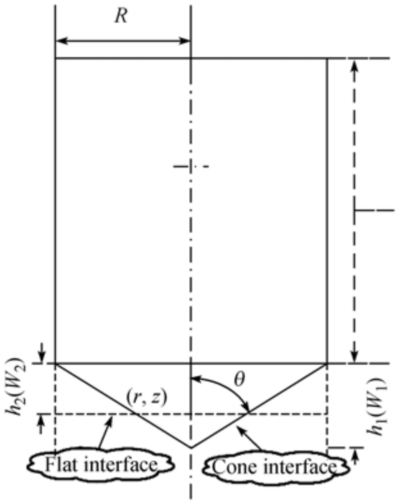

Figure 1 Crystal grows with cone and flat interface. h_0 and h_2 are the height of cylinder, h_1 is the height of cone, and the corresponding mass is W_0, W_1 and W_2, respectively.

It is not so easy to obtain the general quantitative equation of interface cone θ, which depends on many growth conditions such as heating, crucible position and geometry, thermal retardation, seed pull and rotation rates, and so on.

If the growth interface at position (z, r) is flat, the grown crystal mass with flat interface is

$$W'_{\mathrm{S}} = W_0 + \rho_{\mathrm{S}}\pi R^2 (R - r)\mathrm{ctg}\theta. \tag{13}$$

The growth mass difference with the two interfaces is

$$\Delta W_{\mathrm{S}} = W_{\mathrm{S}} - W'_{\mathrm{S}} = \pi R^2 \mathrm{ctg}\theta \left(r - \frac{2}{3}R \right). \tag{14}$$

From eq. (14) we can see that the weight difference value ΔW_{S} will be 0 if only the position (r, z) meets the following condition:

$$r = \frac{2}{3}R. \tag{15}$$

So at position $r = 2R/3$, the crystal can be regarded as growing in the flat interface, which will result in C_{S} independence on the interface angle θ.

In summary, it can be concluded that the solute concentration at position (z, $2R/3$) is independent on the crystal growth interface angle and can be treated as the flat growth interface when the crystal growth interface is conical, and the measure error resulting from interface variation will be very little when the absorption spectra of optical dopant are measured at position (z, $2R/3$).

On the other hand, the following formula can be gotten from eq. (6):

$$\frac{\mathrm{d}C_{\mathrm{S}}}{C_{\mathrm{S}}} = \frac{(k-1)}{p}\frac{\mathrm{d}W_{\mathrm{S}}}{W_{\mathrm{T}}}. \tag{16}$$

If $r <> 2R/3$, the cone interface approximation by flat interface results in crystal mass difference $\mathrm{d}W_{\mathrm{S}}$, then concentration difference $\mathrm{d}C_{\mathrm{S}}$. When W_{T} is larger than $\mathrm{d}W_{\mathrm{S}}$, which can usually be met in the actual crystal growth, the variation $\mathrm{d}C_{\mathrm{S}}/C_{\mathrm{S}}$ is very little, which is of advantage to measure the absorption spectra of optical dopant precisely.

3 Determination method of effective segregation coefficient and absorption cross section through the optical absorption method

For optical dopant ions, its absorption coefficient α_c is given by

$$\alpha^{\exp} = N\sigma = \frac{AC_S\rho}{M_d} N_A \sigma, \tag{17}$$

where N is the dopant ion number per volume, σ the absorption cross section, A the dopant ion number per molecular of doped compound, M_d the doped compound molecular weight, ρ the host density, N_A Avogadro constant, and C_S is given by eq. (6) or (11). The value σ is usually of the order of magnitude of 10^{-20} cm^2; k, 0—1; ΔW, 10—10^3 g. In order to improve the iteration convergence rate and stability, eq. (17) can be expressed as

$$\alpha^{\exp} = N\sigma = \frac{AC_S\rho}{M_d} N_A \times 10^{-20}\sigma. \tag{17a}$$

Then all fitted values are of the same order, and the unit of fitted σ would be of 10^{-20} cm^2.

For a series of transmissivities $T_{i,j}$, where i and j stand for the ith absorption peak and jth measure point along the crystal growth direction at $r = 2R/3$, according to ref. [16] the absorption coefficient can be calculated by

$$\alpha_{ij}^{\exp} = -\frac{1}{d}\ln\frac{-(1-R_i)^2 + \sqrt{(1-R_i)^2 + 4R_i^2T_{ij}^2}}{2R_i^2T_{ij}}, \tag{18}$$

where d is the sample thickness, $R_i = \left(\frac{n_i - 1}{n_i + 1}\right)^2$, and n_i the refractive index at absorption peak i. Meanwhile, a series of corresponding absorption coefficients α_{ij}^{c} can be calculated by formula (18). Half of total difference square of n absorption peaks with m points between calculated and experimental absorption coefficients is given by

$$\varphi = \frac{1}{2}\boldsymbol{f}(\boldsymbol{x})^{\mathrm{T}}\boldsymbol{f}(\boldsymbol{x}) = \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{m}(\alpha_{ij}^{\exp} - \alpha_{ij}^{c})^2, \tag{19}$$

where $\boldsymbol{x}^{\mathrm{T}} = (k, \sigma_1, ..., \sigma_m)$ when fitted by eq. (6), $\boldsymbol{x}^{\mathrm{T}} = (k, \Delta W)$ when fitted by eq. (11), and $f_{ij} = \alpha_{ij}^{\exp} - \alpha_{ij}^{c}$. φ is a function of k and absorption cross sections σ_i, which can be obtained by minimizing φ. This is a nonlinear iteration procedure. It is found that Levenbery-Marquardt method[17] is a fast convergent and stable algorithm to obtain k and σ_i, whose iteration formula is

$$\boldsymbol{x}^{k+1} = \boldsymbol{x}^k - \hat{\boldsymbol{G}}(\boldsymbol{x}^k)\boldsymbol{g}(\boldsymbol{x}^k), \tag{20}$$

$$\hat{\boldsymbol{G}}(\boldsymbol{x}^k) = \boldsymbol{Df}(\boldsymbol{x})^{\mathrm{T}}\boldsymbol{Df}(\boldsymbol{x}) + \mu_k\boldsymbol{I}, \tag{21}$$

$$\boldsymbol{Df}(\boldsymbol{x})^{\mathrm{T}} = \begin{bmatrix} \frac{\partial f_{1,1}}{\partial k}\cdots\frac{\partial f_{1,m}}{\partial k}\cdots\frac{\partial f_{n,m}}{\partial k} \\ \frac{\partial f_{1,1}}{\partial \sigma_1}\cdots\frac{\partial f_{1,m}}{\partial \sigma_1}\cdots\frac{\partial f_{n,m}}{\partial \sigma_1} \\ \vdots \qquad \vdots \qquad \vdots \\ \frac{\partial f_{1,1}}{\partial \sigma_n}\cdots\frac{\partial f_{1,m}}{\partial \sigma_n}\cdots\frac{\partial f_{n,m}}{\partial \sigma_n} \end{bmatrix}. \tag{22}$$

μ_k is a damping factor and its value is more than zero, which can be adjusted during the iteration process so that the suitable convergence rate and convergence domain can be found, and ***I*** unit matrix of $(n+1)\times(n+1)$. Matrix element express (22) is suitable to using formula (6) to fit absorption coefficients. If formula (11) is used to fit, the matrix elements of $\boldsymbol{Df}(\boldsymbol{x})^{\mathrm{T}}$ should be

$$\begin{bmatrix} \frac{\partial f_{1,1}}{\partial k}\cdots\frac{\partial f_{1,m}}{\partial k}\cdots\frac{\partial f_{n,m}}{\partial k} \\ \frac{\partial f_{1,1}}{\partial \Delta W}\cdots\frac{\partial f_{1,m}}{\partial \Delta W}\cdots\frac{\partial f_{n,m}}{\partial \Delta W} \end{bmatrix}. \tag{22a}$$

Fitting relative residual can be defined as

$$R_{\mathrm{S}} = \sqrt{\frac{\sum_{i=1}^{n}\sum_{j=1}^{m}(\alpha_{ij}^{\exp}-\alpha_{ij}^{\mathrm{c}})^2}{\sum_{i=1}^{n}\sum_{j=1}^{m}(\alpha_{ij}^{\exp})^2}}. \tag{23}$$

According to this principle, a program FitKSigma has been developed to deal with absorption spectra and get k, ΔW and σ.

It was found that k, ΔW and σ in formula (11) cannot be fitted at the same time, which will result in the unreasonable and uncertain k and ΔW. Although the computed absorption coefficients are very close to experimental values, namely, fitting relative residual R_{S} is very little, different initial values of k, ΔW and σ can result in fitted results with great differences, contrary to the case that the final k, ΔW and σ should be stable values for the given segregation rule even if they have different iteration initial values when no physical procedure changes. On the other hand, the absorption cross section of optical ion is a constant in a certain host, and changes little with dopant concentration variation, so when fitting absorption coefficients by eq. (11), we can use known absorption cross sections σ to obtain k and ΔW through the Levenberg-Marquardt iteration method.

4 Segregation coefficient and absorption cross section determination of Nd:GGG

Now we use the before-proposed method and model to determine the efficient segregation coefficient k, ΔW and σ.

Nd:GGG crystal in size Φ30×43 mm was grown in direction [111] by Czochralski with SJ78-3 furnace, made by Xi'an University of Technology. The raw material of 708.85 g is doped by 1.1wt% Nd_2O_3, the Iridium crucible Φ 60 mm, and the pulling and rotating rates are 2—3 mm and 10—15 rpm, respectively. The as-grown crystal is crack-free and scattering-free observed by ~1 W 532 nm laser. After annealing, a slab sample along [111] direction was cut in a size of 40 mm × 30 mm × 5 mm, shown in Figure 2. The incident optical is perpendicular to the 40 mm × 30 mm slab plane. All measured positions far from the outside by 5 mm are shown in Figure 2. The absorption spectra were measured with a wavelength step of 0.5 nm by using Lamda 900 of Perkin Elmer, Inc. at room temperature. After

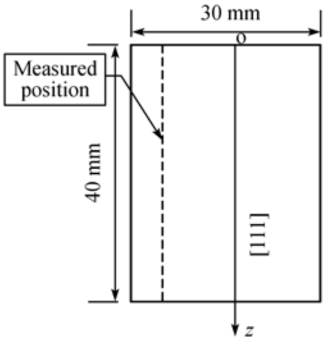

Figure 2 Nd:GGG slab sample.

obtaining transmissivities T, the experimental absorption coefficients are calculated with formula (18), and the refractive indices of Nd:GGG are computed with the following formula[18]:

$$n^2 = A + \frac{B}{\lambda^2 - C} - D\lambda^2, \tag{24}$$

where the unit of wavelength λ is nm, $A = 3.74931$, $B = 44080\ \text{nm}^2$, $C = 22390\ \text{nm}^2$, and $D = 0.00976\times10^{-6}\ \text{nm}^{-2}$. The experimental absorption coefficients are shown in Figure 3 and Table 1.

With initial values iteration precision $\varepsilon = 10^{-5}$, $\mu_0 = 0.02$, scale factor $v = 5$, the maximum search number for suitable damping factor CLA = 1000, the maximum iteration number CLB = 1000 and $x^{0\,\mathrm{T}} = (k, \sigma_1,.., \sigma_{17}) = (0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17)$, formula (6) was used to fit the absorption coefficients of seventeen peaks of (1.1wt%) Nd:GGG in the range of 700—1100 nm. The fitted relative residual R_S is 1.00%, fitted effective segregation coefficient k 0.5448, and fitted σ_S are shown in Table 2. The fitted σ at 807.5 nm is $3.1577\times10^{-20}\ \text{cm}^2$, which is close to that in ref. [10]. The effective segregation coefficient is more than 0.4 in refs. [8,10]. Our fitting procedure is reasonable, so the value should be reliable. The calculated absorption coefficients are also listed in Table 1. The curves of calculated and experimental values versus grown crystal weight W_S are shown in Figure 4. It can be seen that their consistent degree is good.

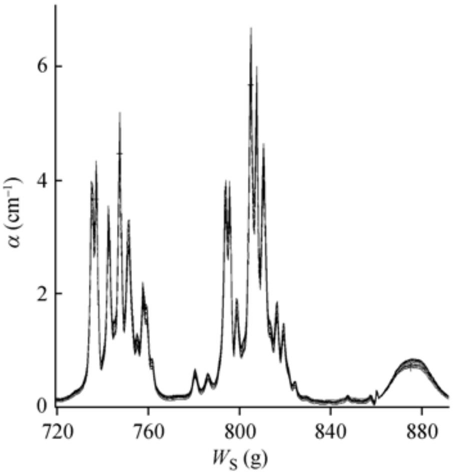

Figure 3 The absorption spectra of Nd:GGG slab at different positions along [111] direction.

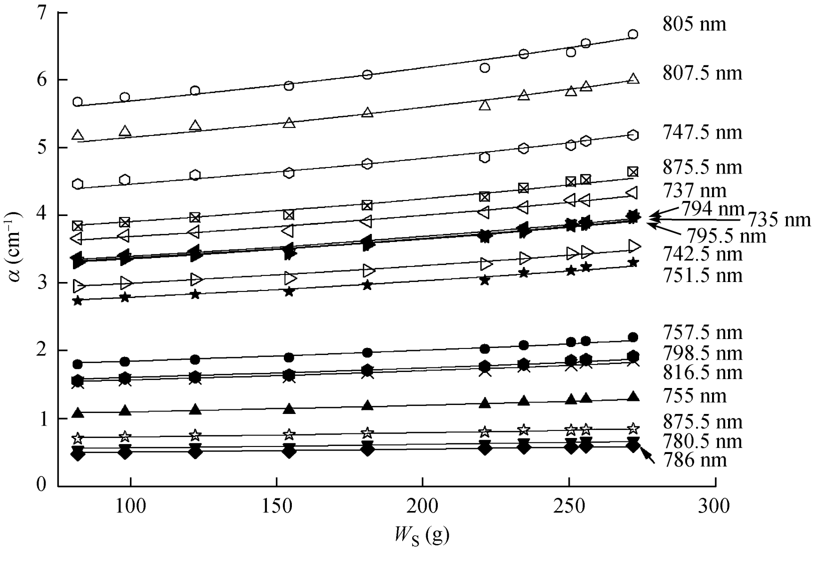

Figure 4 Experimental and calculated absorption coefficients by formula (7) of Nd:GGG.

Now we use segregation formula (11) to fit these absorption coefficients to obtain k and ΔW. The values of σ are from before-fitted results by formula (6), the iteration initial values are $\varepsilon = 10^{-5}$, $\mu_0 = 0.02$, scale factor $v = 5$, the maximum search number for suitable damping factor CLA = 1000,

Table 1 Experimental and calculated absorption coefficients with formula (6) and (11) with fitted parameters, marked by I and II, respectively

z (mm)	W_S (g)	735 nm, cm^{-1}			737 nm, cm^{-1}			742.5 nm, cm^{-1}		
		α^{exp}	α^c(I)	α^c(II)	α^{exp}	α^c(I)	α^c(II)	α^{exp}	α^c(I)	α^c(II)
3.5	81.8	3.3329	3.3295	3.3179	3.6605	3.6379	3.6252	2.9551	2.9617	2.9514
6.5	97.9	3.386	3.3691	3.3643	3.7015	3.6812	3.6759	3.0042	2.9969	2.9926
11	122	3.4343	3.4314	3.4349	3.7585	3.7493	3.7531	3.0534	3.0523	3.0555
17	154.2	3.4474	3.5207	3.5316	3.7751	3.8468	3.8588	3.0754	3.1318	3.1415
22	181	3.5819	3.601	3.6142	3.9098	3.9345	3.949	3.1842	3.2032	3.2149
27	221.2	3.6994	3.7332	3.7417	4.0451	4.079	4.0883	3.2809	3.3208	3.3283
32	234.6	3.7657	3.7808	3.7852	4.1203	4.131	4.1358	3.3687	3.3632	3.367
35	250.7	3.8835	3.8407	3.8381	4.23	4.1965	4.1936	3.4393	3.4165	3.4141
36	255.9	3.8737	3.8607	3.8553	4.2253	4.2184	4.2125	3.4569	3.4343	3.4294
39	272.1	3.9806	3.9253	3.9096	4.3342	4.2889	4.2717	3.546	3.4917	3.4777

z (mm)	W_S (g)	757.5 nm, cm^{-1}			780.5 nm, cm^{-1}			786 nm, cm^{-1}		
		α^{exp}	α^c(I)	α^c(II)	α^{exp}	α^c(I)	α^c(II)	α^{exp}	α^c(I)	α^c(II)
3.5	81.8	1.8016	1.8271	1.8207	0.538	0.5643	0.5623	0.4742	0.5011	0.4994
6.5	97.9	1.8409	1.8489	1.8462	0.5658	0.571	0.5702	0.5036	0.5071	0.5064
11	122	1.8717	1.8831	1.8849	0.5769	0.5816	0.5822	0.5109	0.5165	0.5171
17	154.2	1.8988	1.9321	1.938	0.5828	0.5967	0.5986	0.516	0.5299	0.5316
22	181	1.9692	1.9761	1.9833	0.6167	0.6103	0.6126	0.5481	0.542	0.544
27	221.2	2.0268	2.0487	2.0533	0.6269	0.6327	0.6342	0.5604	0.5619	0.5632
32	234.6	2.0808	2.0748	2.0771	0.6516	0.6408	0.6415	0.5789	0.5691	0.5698
35	250.7	2.1268	2.1077	2.1062	0.6555	0.6509	0.6505	0.5819	0.5781	0.5777
36	255.9	2.1468	2.1187	2.1156	0.6703	0.6543	0.6534	0.5942	0.5811	0.5803
39	272.1	2.1975	2.1541	2.1454	0.6775	0.6653	0.6626	0.6038	0.5908	0.5885

z (mm)	W_S (g)	794 nm, cm^{-1}			795 nm, cm^{-1}			798.5 nm, cm^{-1}		
		α^{exp}	α^c(I)	α^c(II)	α^{exp}	α^c(I)	α^c(II)	α^{exp}	α^c(I)	α^c(II)
3.5	81.8	3.3767	3.353	3.3413	3.3063	3.3178	3.3062	1.5566	1.5886	1.583
6.5	97.9	3.4104	3.3929	3.388	3.3544	3.3573	3.3524	1.5946	1.6075	1.6052
11	122	3.4763	3.4556	3.4592	3.4058	3.4194	3.4228	1.6164	1.6372	1.6389
17	154.2	3.5055	3.5456	3.5566	3.4409	3.5084	3.5192	1.6411	1.6798	1.685
22	181	3.6253	3.6264	3.6397	3.5656	3.5883	3.6015	1.7163	1.7181	1.7244
27	221.2	3.6919	3.7595	3.7681	3.6986	3.7201	3.7285	1.7707	1.7812	1.7852
32	234.6	3.8154	3.8075	3.8119	3.7638	3.7676	3.7718	1.8056	1.8039	1.806
35	250.7	3.8485	3.8679	3.8652	3.8654	3.8273	3.8245	1.8558	1.8325	1.8312
36	255.9	3.908	3.888	3.8826	3.874	3.8472	3.8417	1.8763	1.8421	1.8395
39	272.1	3.9927	3.953	3.9372	3.9775	3.9115	3.8958	1.9177	1.8729	1.8653

z (mm)	W_S (g)	805 nm, cm^{-1}			807.5 nm, cm^{-1}			810.5 nm, cm^{-1}		
		α^{exp}	α^c(I)	α^c(II)	α^{exp}	α^c(I)	α^c(II)	α^{exp}	α^c(I)	α^c(II)
3.5	81.8	5.6735	5.6183	5.5987	5.1702	5.0855	5.0677	3.8392	3.8605	3.847
6.5	97.9	5.7479	5.6852	5.677	5.2282	5.1461	5.1385	3.8962	3.9065	3.9008
11	122	5.8348	5.7903	5.7962	5.3083	5.2412	5.2464	3.9646	3.9787	3.9827
17	154.2	5.9115	5.941	5.9594	5.3467	5.3776	5.3942	4.004	4.0822	4.0949
22	181	6.0775	6.0764	6.0987	5.4981	5.5002	5.5203	4.1454	4.1753	4.1906
27	221.2	6.1757	6.2995	6.3139	5.6049	5.7021	5.715	4.2728	4.3286	4.3384
32	234.6	6.38	6.3799	6.3872	5.7541	5.7749	5.7814	4.3985	4.3839	4.3888
35	250.7	6.4081	6.481	6.4765	5.8131	5.8664	5.8622	4.4929	4.4533	4.4502
36	255.9	6.5388	6.5148	6.5056	5.8874	5.897	5.8886	4.524	4.4765	4.4702
39	272.1	6.6751	6.6237	6.5972	5.9983	5.9956	5.9714	4.6417	4.5514	4.5331

z (mm)	W_S (g)	816.5 nm, cm^{-1}			875.5 nm, cm^{-1}		
		α^{exp}	α^c(I)	α^c(II)	α^{exp}	α^c(I)	α^c(II)
3.5	81.8	1.5294	1.5519	1.5465	0.7024	0.7215	0.719
6.5	97.9	1.5695	1.5704	1.5681	0.7322	0.7301	0.729
11	122	1.5942	1.5994	1.601	0.7524	0.7436	0.7443
17	154.2	1.6138	1.641	1.6461	0.761	0.7629	0.7653
22	181	1.6805	1.6784	1.6846	0.787	0.7803	0.7832
27	221.2	1.7142	1.7401	1.744	0.8011	0.809	0.8108
32	234.6	1.7748	1.7623	1.7642	0.8322	0.8193	0.8202
35	250.7	1.79	1.7902	1.7889	0.8288	0.8323	0.8317
36	255.9	1.8268	1.7995	1.7969	0.8387	0.8366	0.8354
39	272.1	1.8623	1.8296	1.8222	0.8493	0.8506	0.8472

Table 2 Absorption cross section of Nd:GGG fitted by formula (6)

λ (nm)	σ (10^{-20} cm^2)	λ (nm)	σ (10^{-20} cm^2)
735	2.0674	794	2.082
737	2.2589	795.5	2.0601
742.5	1.839	798.5	0.9864
747.5	2.7344	805	3.4886
751.5	1.7123	807.5	3.1577
755	0.6763	810.5	2.3971
757.5	1.1345	816.5	0.9636
780.5	0.3504	875.5	0.448
786	0.3112		

Fitted $k = 0.5448$.

the maximum iteration number CLB = 1000 and $x^{0\,\mathrm{T}} = (k, \Delta W) = (0.1, 10)$. The fitting relative residual R_{S} is 1.17%, $k = 0.535$, $\Delta W = 539.29$ g, and the fitted absorption coefficients are shown in Table 1. $k = 0.535$ is very close to $k = 0.5448$ before fitting. Meanwhile, ΔW should be understood as an average segregation boundary layer mass, which characterizes diffuse degree of the segregated ions in grown melt. Here $\Delta W/W_{\mathrm{T}}$ is 76%, which indicates that the segregated dopant ions had nearly dispersed into the whole melts, and also that the assumption of the segregated dopant ions in the whole melt homogenously is reasonable. Again we can see that the consistent degree between calculated and experimental values is good.

5 Conclusions

During crystal growth from melt, dopant concentration on the solid growth interface under two different conditions, in which the segregated dopant ions disperse into the whole melt and just into a part melt with mass ΔW homogenously, will change by $C_{\mathrm{S}} = kC_0\left(1-\frac{W_{\mathrm{S}}}{W_{\mathrm{T}}}\right)^{(k-1)}$ and $C_{\mathrm{S}} = kC_0\mathrm{e}^{(1-k)\frac{W_{\mathrm{S}}}{\Delta W}}$, respectively. From the two formulas it can be seen that the dopant concentration in solid at the interface depends on the crystallized mass W_{S} in two formulas. When the grown crystal interface is conical and segregated solute disperses into melt in part or total, the solute concentration C_{S} at $r = 2/3R$ is independent on the crystal growth cone interface angle, and its variation can be regarded as the result from crystal growth in flat interface. For optical dopant, by minimizing the half sum of the difference square between the calculated and experimental absorption coefficients from one or more absorption peaks along the crystal growth direction, k and σ, or k and ΔW, can be determined at the same time with Levenbery-Marquardt iteration method, by which the effective segregation coefficient $k = 0.535 - 0.5448$, $\Delta W = 539.29$ g and $\sigma = 3.1577 \times 10^{-20}$ cm^2 at 807.5 nm and other absorption cross sections of Nd:GGG were given. Fitted results with two formulas gave very closed k, and the value of ΔW also indicates that the segregated dopant ions had nearly dispersed into the whole melt. All of the results show that the method to determine k, ΔW, and σ for optical dopant ions is convenient and reliable, and the two segregation formulas can describe the solute segregation during crystal growth from melt commendably.

1 Min N B. Physical Fundamentals of Crystal Growth. Shanghai: Shanghai Press of Science and Technology, 1982. 56—67

2 Lifshin E. Characterization of Materials, translated by Ye H Q. Beijing: Science Press, 1998. 398—400

3 Zhao Z W, Jiang Y D. Valence compensation and segregation coefficient of (Yb^{3+}, Nd^{3+}): $Ca_3(VO_4)_2$ crystals. J Synth Cryst, 2000, 29(2): 143—146

4 Zeng X H, Zhang L H, Zhao G J, et al. Crystal growth and optical properties of $LaAlO_3$ and Ce-doped $LaAlO_3$ single crystals. J Cryst Growth, 2004, 271: 319—324[DOI]

5 Xia H P, Wang J H, Zeng X L, et al. Determination of distribution and effective distribution coefficient of Cr^{3+} in $LiNbO_3$ single crystals using UV/Visible absorption spectra and ICP. Spectrosc Spectral Anal, 2005, 25(6): 960—963

6 Benayad A, Sebald G, Lebrun L, et al. Segregation study and segregation modeling of Ti in $Pb[(Mg_{1/3}Nb_{2/3})_{0.60}Ti_{0.40}]O_3$ single crystal grown by Bridgman method. Mats Res Bull, 2006, 41: 1069—1076[DOI]

7 Namujilatu, Yuan B, Ruan Y F, et al. Effective segregation coefficient of rare earth ions in $LiYF_4$ crystals. J Chin Ceram Soc, 2001, 29(6): 584—586

8 Kuwano Y. Effective distribution coefficient of neodymium in $Nd:Gd_3Ga_5O_{12}$ crystals grown by the Czochralski Method. J Cryst Growth, 1982, 57: 353—361[DOI]

9 Cheng Y, Zhang H J, Yu Y G, et al. Growth and thermal properties of Nd^{3+}: $YbVO^4$ crystal. Phys B, 2006, 383: 213—218 [DOI]

10 Sun D L, Zhang Q L, Wang Z B, et al. Concentration distribution of Nd^{3+} in $Nd:Gd_3Ga_5O_{12}$ crystals studied by optical absorption method. Cryst Res Technol, 2005, 40(7): 698—702[DOI]

11 Sun D L, Zhang Q L, Wang Z B. Co-precipitation synthesis and sintering of nanoscaled $Nd:Gd_3Ga_5O_{12}$ polycrystalline material. Mater Sci Engin A, 2005, 392: 278—281[DOI]

12 Bi G J, Tang X J, Yan W S, et al. Research of transient temperature distribution of Nd:GGG gain medium in solid-state head capacity laser. Chin J Lasers, 2006, 33(Suppl.): 30—33

13 Wang Y G, Mo X G, Xu X Z, et al. Growth of large-sized Nd:GGG crystal with automatic control of diameter and flat interface. Chin J Lasers, 2006, 33(Suppl.): 313—315

14 Hartman P. Crystal Growth: An Introduction. Amsterdam London: North-Holland Publishing Company, 1973. 225

15 Pfann W G. Zone Melting, 2nd printing. New York, London: John Wiley & Sons, Inc., 1958, 10

16 Fang R C. Solid State Spectroscopy. Hefei: Press of University of Science and Technology of China, 2001. 31

17 Li Q Y, Guan Z, Bai F S. The Numerical Computation Principle. Beijing: Tsinghua University Press, 2000. 293

18 Wang Z B. Study on physical properties and defects of heat capacity laser crystal $Nd^{3+}:Gd_3Ga_5O_{12}$. Dissertation for the Doctoral Degree of Chinese Academy of Sciences. Hefei: Anhui Institute of Optics and Fine Mechanics, CAS, 2006. 65