Second- and third-harmonic generations in compositionally graded films

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We present a theoretical description of the effective nonlinear susceptibilities for second-harmonic generation (SHG) and third-harmonic generation (THG) of compositionally graded films, in which one of the components possesses nonvanishing second- and third-order nonlinear susceptibilities. We first resort to the nonlinear effective medium approximation to obtain the equivalent (local) second- and third-order nonlinear susceptibilities in a z slice. Then, the formulas for effective nonlinear SHG and THG susceptibilities of the graded film are directly established, if we regard the graded film as the limit of a multilayer one. Numerical results show that if the electric field is polarized perpendicular to the plane of layers, both effective SHG and THG susceptibilities for graded profiles are larger than those for nongraded ones. Furthermore, for a given total volume fraction p, the adjustment of compositional gradient results in a large enhancement of effective SHG and THG especially in the high-frequency region. Therefore, the compositionally graded films can be served as a noval candidate material for obtaining the optimal SHG and THG susceptibilities.

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There are practical needs for nonlinear optical composite materials that possess large nonlinear susceptibility [1,2]. A typical system is composed of nonlinear granular inclusions randomly embedded in the a linear (or nonlinear) host. By taking into account the local-field effect and the percolation effect, a large enhancement of the effective Kerr nonlinearity was found in multilayer structures [3], in uniaxial anisotropic composites [4], and in metal/dielectric composites with shape distribution [5]. In addition to the Kerr nonlinearity, there is much interest in the study of nonlinear optical susceptibilities for second-harmonic generation (SHG) and third-harmonic generation (THG) in composite media [6–9].

Graded composite materials have attracted much attention in various engineering applications [10] due to their novel physical properties. More recently, we proposed a nonlinear differential effective dipole approximation (NDEDA) and the first-principles approach [11] to investigate the effective nonlinear optical properties of graded composites. Interestingly, the dielectric gradient is found to be very useful for realizing the large enhancement of both the optical nonlinearity and figure of merit. Since the graded films can be fabricated more easily than graded particles, Huang and Yu carried out theoretical calculations on the optical nonlinearity enhancement in graded films [12]. Note that the gradation indicates the radial inhomogeneity of the local physical parameters such as the dielectric constant.

In contrast to graded composites with radial inhomogeneity, compositionally graded composites are a new generation of engineered materials in which the geometric parameters such as the composition or microstructure morphology (rather than the local physical parameters) are gradually varied in one or more dimensions [13]. In this Brief Report, we would like to address the problem of studying the effective SHG and THG susceptibilities of nonlinear spatially graded films, in which one of the components possesses both quadratic and third-order nonlinear susceptibilities. We shall show that the presence of compositional gradation can indeed lead to the enhancement of effective SHG and THG susceptibilities due to the nonuniform distribution of the local field.

Let us consider metallic/dielectric functionally graded films with the width L along the z axis. The local volume fraction $p(z)$ of the nonlinear metal component at the position z varies only in the z direction, which is common for spatially graded composites. The dielectric component is assumed to be linear with the isotropic dielectric constant ϵ_2^ω, while the metal component is nonlinear with the displacement $\mathbf{D}$ and the electric field $\mathbf{E}$ relation of the form $D_i = \epsilon_1 E_i + \sum_{jk} d_{ijk} E_j E_k + \sum_{jkl} \chi_{ijkl} E_j E_K E_l$, where $i=x,y,z$ represent the Cartesian components, while ϵ_1, d_{ijk}, and χ_{ijkl} are the linear dielectric function, SHG susceptibility, and THG susceptibility of the metal component, respectively.

It is known that the effective nonlinear susceptibility for general three-wave mixing $(\omega \equiv \omega_1 + \omega_2)$ is given by [9]

$$d_{e,ijk}^{(\omega_1,\omega_2)} = \langle K_{il}^{\omega_1+\omega_2} d_{lmn}^{(\omega_1,\omega_2)} K_{jm}^{\omega_1} K_{kn}^{\omega_2} \rangle, \tag{1}$$

where the local-field factor $K_{il}^\omega \equiv E_l(\omega)/E_{0,i}(\omega)$ gives the lth Cartesian component of the linear electric field inside the nonlinear metal component when the external field E_0 is applied along the ith direction at frequency ω. $\langle\cdots\rangle$ stands for the spatial average of $\cdots$. We mention that in the case of $\omega_1=\omega_2=\omega$, $d_{e,ijk}^{(\omega,\omega)}$ means effective SHG susceptibility. For effective THG susceptibility, one yields [9]

$$\chi_{e,ijkl}^{(\omega,\omega,\omega)} = \left\langle K_{im}^{3\omega} \left\{ 2 d_{mnp}^{(\omega,2\omega)} \left[\frac{(K_{rn}^{2\omega} - \mathbf{I}_{rn})}{\delta\epsilon^{(2\omega)}} \right] d_{rst}^{(\omega,\omega)} + \chi_{mstp}^{(\omega,\omega,\omega)} \right\} K_{js}^\omega K_{kt}^\omega K_{lp}^\omega \right\rangle, \tag{2}$$

where $\mathbf{I}$ is a unit matrix and $\delta\epsilon^{2\omega} \equiv \epsilon^{2\omega} - \epsilon_e^{2\omega}$, with $\epsilon_e^{2\omega}$ being the effective linear dielectric constant at the frequency 2ω. Equation (2) includes the contributions to the effective THG

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susceptibility in two aspects. The first part is due to the inducement of the second-harmonic susceptibility of the component, and the second results from the intrinsic third-harmonic susceptibility.

To investigate the effective SHG and THG susceptibilities of the graded films, we first obtain the equivalent (local) linear dielectric constant $\overline{\epsilon^{\omega}}(z)$ and nonlinear optical susceptibilities for SHG, general three-wave mixing, and THG for the z slice. For the equivalent linear dielectric constant $\overline{\epsilon^{\omega}}(z)$, we resort to the three-dimensional Bruggeman effective medium approximation (EMA) [14]

$$p(z)\frac{\epsilon_1^{\omega}-\overline{\epsilon^{\omega}}(z)}{\epsilon_1^{\omega}+2\overline{\epsilon^{\omega}}(z)}+[1-p(z)]\frac{\epsilon_2^{\omega}-\overline{\epsilon^{\omega}}(z)}{\epsilon_2^{\omega}+2\overline{\epsilon^{\omega}}(z)}=0. \tag{3}$$

With an appropriate decoupling treatment, the equivalent second-order nonlinear susceptibilities at each z slice are written as

$$\overline{d}_{lmn}^{(\omega,2\omega)} \approx p(z)d_{lmn}^{(\omega,2\omega)}\frac{3\overline{\epsilon^{3\omega}}(z)}{\epsilon_1^{3\omega}+2\overline{\epsilon^{3\omega}}(z)}\frac{3\overline{\epsilon^{2\omega}}(z)}{\epsilon_1^{2\omega}+2\overline{\epsilon^{2\omega}}(z)}\frac{3\overline{\epsilon^{\omega}}(z)}{\epsilon_1^{\omega}+2\overline{\epsilon^{\omega}}(z)}, \tag{4}$$

$$\overline{d}_{lmn}^{(\omega,\omega)} \approx d_{lmn}^{(\omega,\omega)}\frac{3\overline{\epsilon^{2\omega}}(z)}{\epsilon_1^{2\omega}+2\overline{\epsilon^{2\omega}}(z)}\frac{\partial\overline{\epsilon^{\omega}}(z)}{\partial\epsilon_1^{\omega}}. \tag{5}$$

For the equivalent THG susceptibility, we have

$$\overline{\chi}_{mstp}^{(\omega,\omega,\omega)}=\left[\frac{-2d_{mnp}^{(\omega,2\omega)}d_{nst}^{(\omega,\omega)}}{\epsilon_1^{2\omega}+2\overline{\epsilon^{2\omega}}(z)}+\chi_{mstp}^{(\omega,\omega,ga)}\right]\times\frac{\partial\overline{\epsilon^{\omega}}(z)}{\partial\epsilon_1^{\omega}}\frac{3\overline{\epsilon^{3\omega}}(z)}{\epsilon_1^{3\omega}+2\overline{\epsilon^{3\omega}}(z)}\frac{3\overline{\epsilon^{\omega}}(z)}{\epsilon_1^{\omega}+2\overline{\epsilon^{\omega}}(z)}. \tag{6}$$

Next, we investigate the effective linear dielectric constant tensor $\overleftrightarrow{\epsilon}_e$ and effective nonlinear susceptibilities tensors for SHG $\overleftrightarrow{d}_e^{\omega,\omega}$ and for THG $\overleftrightarrow{\chi}_e^{\omega,\omega,\omega}$. Actually, since the equivalent SHG and THG susceptibilities have been obtained, the problem reduces to one of multilayers [3]. In what follows, for simplicity, we only assume d_{iii} and χ_{iiii} ($l=x,y,z$) to be nonzero. For the compositionally graded film, the nondiagonal components of the second-rank tensor $\overleftrightarrow{\epsilon}_e$ are zero, while the diagonal components are given by

$$\frac{1}{\epsilon_{e,zz}^{\omega}}=\frac{1}{L}\int_0^L\frac{dz}{\overline{\epsilon^{\omega}}(z)}, \tag{7}$$

$$\epsilon_{e,xx}^{\omega}=\epsilon_{e,yy}^{\omega}=\frac{1}{L}\int_0^L\overline{\epsilon^{\omega}}(z)dz. \tag{8}$$

The effective nonlinear susceptibilities for SHG of the compositionally graded films are expressed as

$$d_{e,xxx}^{(\omega,\omega)}=\frac{1}{L}\int_0^L\overline{d}_{xxx}^{(\omega,\omega)}\,dz, \tag{9}$$

$$d_{e,zzz}^{(\omega,\omega)}=\frac{1}{L}\int_0^L\overline{d}_{zzz}^{(\omega,\omega)}\frac{\epsilon_{e,zz}^{2\omega}}{\overline{\epsilon^{2\omega}}(z)}\left(\frac{\epsilon_{e,zz}^{\omega}}{\overline{\epsilon^{\omega}}(z)}\right)^2 dz. \tag{10}$$

Similarly, the effective nonlinear susceptibilities for THG of the graded system have the form

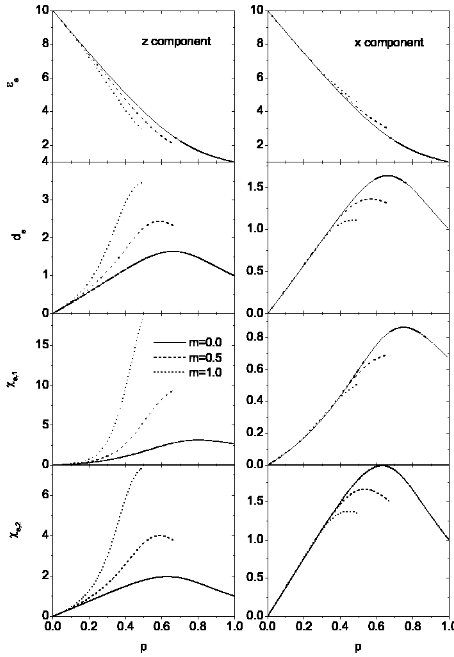

FIG. 1. The linear dielectric constant $\epsilon_e \equiv \epsilon_{e,ii}^{\omega}$; effective nonlinear susceptibility for SHG, $d_e \equiv d_{e,iii}^{(\omega,\omega)}/d_{iii}^{(\omega,\omega)}$; for induced THG, $\chi_{e,1}\equiv\chi_{e,iiii}^{(\omega,\omega,\omega)}/[d_{ii}^{(\omega,\omega)}d_{ii}^{(2\omega,\omega)}]$; and for THG due to the intrinsic nonlinear susceptibility $\chi_{e,2}\equiv\chi_{e,iiii}^{(\omega,\omega,\omega)}/\chi_{iiii}^{(\omega,\omega,\omega)}$ for $i=x$ and z components as a function of p with various compositional gradations m. Parameters are chosen to be $\epsilon_2^{\omega}/\epsilon_1^{\omega}=10$, $\epsilon_2^{2\omega}/\epsilon_1^{2\omega}=5$, and $\epsilon_2^{3\omega}/\epsilon_1^{3\omega}=3$.

$$\chi_{e,xxxx}^{(\omega,\omega,\omega)}=\frac{1}{L}\int_0^L\overline{\chi}_{xxxx}^{(\omega,\omega,\omega)}\,dz, \tag{11}$$

$$\chi_{e,zzzz}^{(\omega,\omega,\omega)}=\frac{1}{L}\int_0^L dz\left(\frac{\epsilon_{e,zz}^{3\omega}}{\overline{\epsilon^{3\omega}}(z)}\right)\left(\frac{\epsilon_{e,zz}^{\omega}}{\overline{\epsilon^{\omega}}(z)}\right)^3\times\left[\overline{\chi}_{zzzz}^{(\omega,\omega,\omega)}-\frac{2\overline{d}_{zzz}^{(\omega,2\omega)}\overline{d}_{zzz}^{(\omega,\omega)}}{\overline{\epsilon^{2\omega}}(z)}\right]. \tag{12}$$

In Fig. 1, we plot the effective linear dielectric constant, nonlinear susceptibilities for SHG $d_{e,iii}^{(\omega,\omega)}$, and THG $\chi_{e,iiii}^{(\omega,\omega,\omega)}$ ($i=x,z$) against the total volume fraction $p\equiv[\int_0^L p(z)dz]/L$ for power-law profile $p(z)=az^m$. For the nongraded compositional profile—i.e., $m=0$—the effective dielectric constant ϵ_e is independent of the directions of the polarized light, and hence we have $\epsilon_{e,zz}^{\omega}=\epsilon_{e,xx}^{\omega}$. However, for the graded profile, with increasing m, $\epsilon_{e,zz}^{\omega}$ becomes small, while $\epsilon_{e,xx}$ is increased. The reason is that for z- (or x-) polarized light, the effective dielectric constant $\epsilon_{e,zz}^{\omega}$ (or $\epsilon_{e,xx}^{\omega}$) is dominated by the slice possessing the smallest (largest) dielectric constant, similar to the case for capacitors in series (or in parallel). To one's interest, for z-polarized light, we predict that all of the effective nonlinear optical susceptibilities including the SHG and THG due to both the inducement of the second-order nonlinear susceptibility and the intrinsic third-order nonlinear susceptibility are enhanced largely in the presence of the compositional gradation. In addition, to enhance the effective THG susceptibility, the contribution of the inducement of

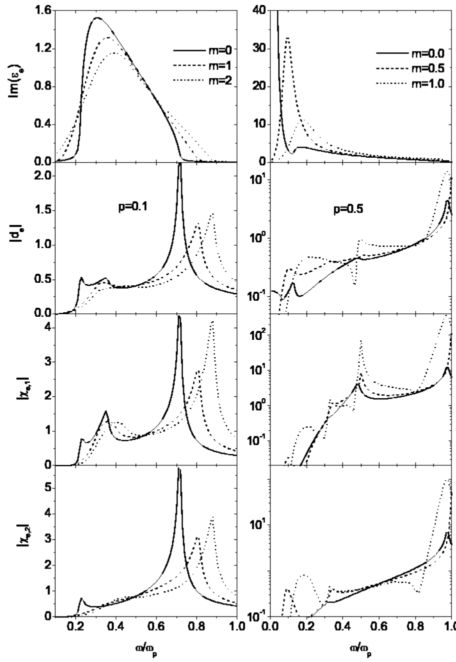

FIG. 2. $\mathrm{Im}(\epsilon_e) \equiv \mathrm{Im}[\epsilon_{e,zz}^{\omega}]$, $d_e \equiv d_{e,zzz}^{(\omega,\omega)}/d_{zzz}^{(\omega,\omega)}$, $\chi_{e,1} \equiv \chi_{e,zzzz}^{(\omega,\omega,\omega)}/[d_{zzz}^{(\omega,\omega)} d_{zzz}^{(2\omega,\omega)}]$, and $\chi_{e,2} \equiv \chi_{e,zzzz}^{(\omega,\omega,\omega)}/\chi_{zzzz}^{(\omega,\omega,\omega)}$ versus ω/ω_p for $p=0.1$ (the left column) and $p=0.5$ (the right column) but with various compositional gradations.

second-order nonlinear susceptibility is prominent over the intrinsic third-order nonlinear susceptibility. Therefore, one should take into account both contributions simultaneously when one aims at studying the effective THG susceptibility of the composites. In contrast, for x-polarized light, the magnitude of all effective nonlinear susceptibilities for compositional gradation is less than those of a random (nongraded) film. Such a difference can be easily understood. As we know the enhancement of effective nonlinear susceptibilities results from the local field effects. For z-polarized light, two factors such as the compositional gradation and the random mixing in each slice contribute to the local-field enhancement, while the effective nonlinear susceptibilities for the x component is determined only by the geometric average of the equivalent nonlinear susceptibility. Therefore, in what follows, we aim at the case where the electric field is polarized perpendicular to the plane of the layers.

Then, we consider nonlinear metal and dielectric compositionally graded films. The metal component is assumed to be a Drude like, whose linear dielectric constant admits the form $\epsilon_1^{\omega}=1-\omega_p^2/[\omega(\omega+i\gamma)]$ where γ is the relaxation rate, and ω_p represents the plasma frequency.

Figure 2 displays the imaginary part of the effective linear dielectric constant and the effective SHG and THG susceptibilities against the normalized frequency ω/ω_p for small and large total volume fractions $p=0.1$ and $p=0.5$.

For small volume fraction $p=0.1$ (see the left column), as the electromagnetic interactions among individual grains have been explicitly taken into account with the EMA for each slice, there exists a broad surface plasmon resonance band for $\mathrm{Im}(\epsilon_{e,zz}^{\omega})$. As m increases, the volume fraction of metal particles for slices with small z will be suppressed. Consequently, the center of the surface plasmon resonant band shifts to lower frequency with increasing m. Also, the broadband arises for effective SHG and THG susceptibilities. In addition, a sharp enhancement peak is observed near the band edge. It is believed that within the framework of the EMA, ϵ_e has a strong dispersion with a small imaginary part just beyond the band edge, resulting in a sharp peak. Furthermore, as is evident from the results, these nonlinear susceptibilities for the graded profile take on quite different behavior from those for the nongraded one. Interestingly, when the compositional gradation is considered, a large enhancement of the effective nonlinear susceptibilities for SHG and THG is evidently found in the high-frequency region near the plasma frequency ω_p as a result of the blueshift of resonant band with increasing m. Therefore, the introduction of a graded profile in the high-frequency region is helpful to achieve appreciable SHG and THG signals.

For large volume fraction $p=0.5$ (see the right column), since it is larger than the percolation threshold $p_c=1/3$ of metal components in random composite film without compositional gradient (i.e., $m=0$). As a result, a Drude peak appears in addition to the surface plasmon resonance bands. However, in the presence of gradation, the local volume fraction $p(z)$ in the small-z slices will be less than $1/3$, and thus these slices will be insulating. Consequently, the graded film will still be insulating, manifested by the absence of a Drude peak around zero frequency for $m=0.2$ and $m=0.4$. On the other hand, we again predict that near the plasma frequency ω_p, the enhancement of effective SHG and THG susceptibilities with compositional gradation is larger than the one without gradation. Therefore, for a given total volume fraction, we can choose a suitable compositonal gradation as an alternative freedom for realizing the possible enhancement of effective SHG and THG susceptibilities.

In this work, we have investigated the effective second-harmonic and third-harmonic nonlinear susceptibilities of compositionally graded films. It is found that the presence of compositional gradation is helpful to result in a large enhancement of the optical nonlinear susceptibilities especially when the applied field is polarized perpendicular to the plane of layers.

Our investigations are of interest because that in compositionally graded films, the local field in the nonlinear component can be largely enhanced due to two factors: one is the random mixing of metal component with the dielectric component, and the other is the compositional gradation effect, leading to the nonuniform-distributed local field in different slices. Therefore, we expect that our work can stimulate the experimentalists to check our theoretical predictions. On the other hand, numerical simulations are now being carried out to validate the present theoretical results.

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