CHAPTER 15

THIRD-ORDER NONLINEAR OPTICAL RESPONSE
OF METAL NANOPARTICLES

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Abstract: We present a review of the main results reported in the literature regarding the third-order nonlinear optical response of nanocomposite media consisting of noble metal nanoparticles surrounded by a dielectric host. This phenomenon, known as optical Kerr effect, can be characterized by the intensity-dependent complex optical index of the material or, equivalently, its complex third-order susceptibility. The theoretical basis of the linear and nonlinear optical properties of metal nanoparticles and nanocomposite media are described first. The different third-order optical phenomena which have been observed in such materials are then examined. The dependence of the nonlinear properties on morphological parameters – nature of the dielectric host, metal concentration, particle size and shape – as well as on laser excitation characteristics – wavelength, intensity, pulsewidth – will be explained and illustrated by selected experimental results. The final part points out the important role played by thermal effects in the nonlinear optical response.

Keywords: Noble metals; nanoparticles; nanocomposite materials; surface plasmon resonance; local field enhancement; nonlinear optical response; optical Kerr effect; third-order susceptibility; saturation of absorption; optical limiting; self-focusing; metal concentration; size effects; spectral dispersion; interband transitions; hot electrons; thermal lensing

1. INTRODUCTION

The fascinating optical properties of metal nanoparticles have caught the attention of many researchers from the pioneering and almost parallel works of G. Mie and J.C. Maxwell-Garnett at the beginning of the twentieth century. These original properties, like many other phenomena specifically appearing in matter divided to the nanoscale, are linked with confinement effects, since quasi-free conduction...
electrons cannot spread beyond the limits of the metal nanoparticle. When particle size ranges from nanometer to a few tens of nanometers, confinement results in the possibility of resonantly exciting the electron gas collectively by coupling with an appropriate oscillating electromagnetic field. This phenomenon is known as the surface plasmon resonance (SPR). Whereas some of its detailed features may be explained by invoking quantum effects, its essential characteristics are understandable through very classical considerations. In the optical response of a material containing metal nanoparticles it manifests itself as an absorption band, which is located in the visible or near ultraviolet spectral domain for noble metal spheres.

As the local electric field in the particles is enhanced at the SPR, the metal nonlinear optical response can be amplified as compared to the bulk solid one. Moreover, the intrinsic nonlinear properties of metals may themselves be modified by effects linked with electronic confinement. These interesting features have led an increasing number of people to devote their research to the study of nonlinear optical properties of nanocomposite media for about two decades. The third-order nonlinear response known as optical Kerr effect have been particularly investigated, both theoretically and experimentally. It results in the linear variation of both the refraction index and the absorption coefficient as a function of light intensity. These effects are usually measured by techniques employing pulsed lasers.

In this chapter, we will present a large but non-exhaustive review of the main results which have been published about the third-order nonlinear optical properties of metal/dielectric nanocomposite materials. These properties depend significantly on many factors regarding both the materials themselves (metal and host medium kinds, metal concentration, particle size, shape and spatial arrangement) and the excitation laser (wavelength, intensity, pulsewidth). The comparison of different experimental results then appears to be a quite difficult task to perform if one aims at highlighting the role played by each of these factors independently. Nevertheless, several general features can be extracted from the abundant literature, as will be established in the different following sections.

In the first part, emphasis will be put on the linear optical properties of dielectric media doped with noble metal nanoparticles. Indeed, the study of the linear response is definitely needed to further explore the nonlinear one. We will then introduce the fundamentals of the theoretical tools required to understand why and how people inquire into the third-order nonlinear properties of nanocomposite materials. In the second part, experimental results will be presented by first examining the different nonlinear optical phenomena which have been observed in these media. We will then focus on the nanoparticle intrinsic nonlinear susceptibility before analysing the influence of the main morphological factors on the nonlinear optical response. The dependence of the latter on laser characteristics will finally be investigated, as well as the crucial role played by different thermal effects.