LEAD NANOCRYSTALS IN KCl MATRIX

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Silver nanocrystals embedded into alkali halide crystals obtained by starting with negative metal ions, show an unusual arrangement and take a configuration "corals"-like [1,2,3,4], while in the case of indium nanocrystals they are distributed as separated and almost spherical particles [5]. These features have been carefully studied through Transmission Electron Microscopy (TEM) and by optical analysis using the Mie theory [6] of absorption and scattering of light on these structures. Kleeman obtained similar configuration of silver and other heavy metals, not in alkali halide crystals, but in the glass [7, 8].

All the previous authors studied the metallic nanoparticles especially in solutions, but not in crystals. In solutions, the Mie theory applies very satisfactorily, because the basic conditions of this theory are satisfied, especially the spherical shape of the particles. In the crystals, where the possibilities of motion are very limited, the form and spatial arrangement of the nanoparticles are different.

There are two ways to produce nanocrystals in alkali halide crystals: a) starting with crystals doped with heavy metal ions in concentrations of ppm, growth by Kyropoulos method, electrolytically colored and thermally treated, or b) starting with probes with tens of ppm and electrolytically colored, when we obtain, directly, metallic nanocrystals. The form and the spatial arrangement in these two cases are different.

Alkali halide crystals, especially KCl crystals, were grown by Kyropoulos method, using purified raw salts by chemical and/or fusion zone method. Salts of lead metal, especially $PbCl_2$ salt, were used for doping. The electrolytical coloring was performed into a simple device, described in [1], by injection of electrons in probe, between two electrodes, a plane electrode and a narrow and sharp one, at high temperatures. Metal ions and successive thermal treatments were used in preparations.

Using a Carry 17D spectrophotometer performed optical measurements and the TEM measurements were performed with a PHILIPS CM 30 transmission electron microscope. In all experiments we used an accelerating voltage of 200 kV.

For the crystals thermally treated at high temperature, step by step, a shift of the absorption peak was observed, this shift being less than in the case of silver nanocrystals (Fig. 1).
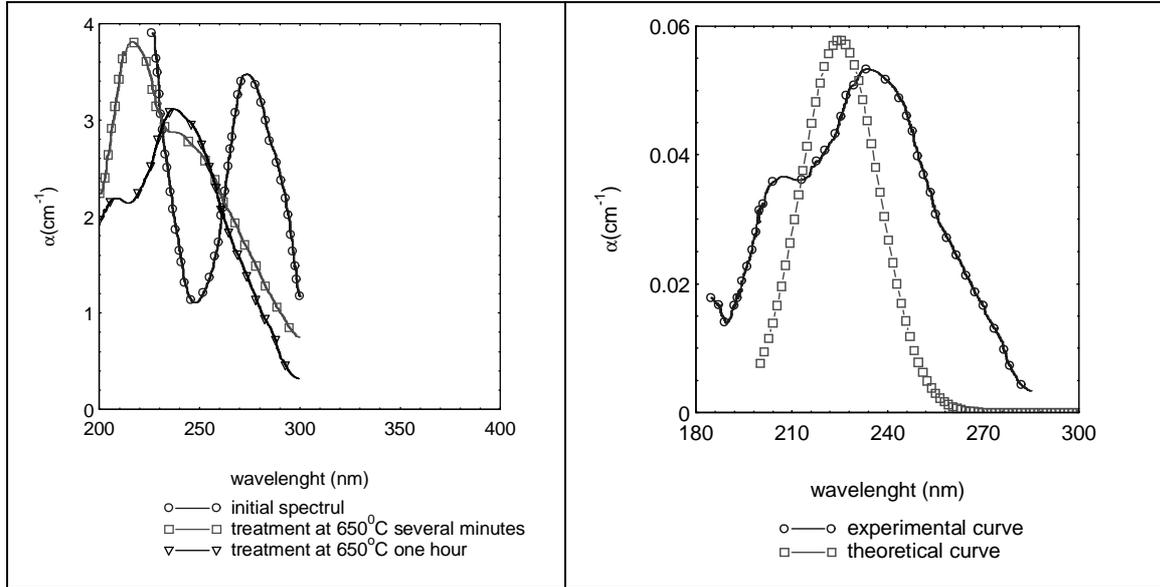
Fig. 1. The absorption curves during thermal treatments (left) and comparison with theoretical calculations (right).

This fact can be explained by the ratio between optical constants of lead, which depend on the wavelength of light. It is known, and confirmed by Raman spectroscopy, that the collective excitation of free electrons in metals are strongest in the cases characterized by:

$$|\varepsilon_2| > |\varepsilon_1| \tag{1}$$

where $\varepsilon_1, \varepsilon_2$ -are the real and imaginary part of the dielectric constant of metal. For the determination of nanocrystal size, it was used the Mie theory, which relates the absorption constant of metal to the dielectric constants by the relation:

$$k(mm^{-1}) = \frac{18\pi C \varepsilon_m^{\frac{3}{2}}}{\lambda} \cdot \frac{\varepsilon_2}{(\varepsilon_1 + 2\varepsilon_m)^2 + \varepsilon_2^{\,2}} \tag{2}$$

where ε_m -is the dielectric constant of matrix and C is the molar nanocrystal concentration. The relation between dielectric constants (imaginary part) and the mean size (R) of the nanocrystals is:

$$\varepsilon_2(R) \propto 1 + \frac{l_\infty}{R} \tag{3}$$

where l_∞ -is the mean free path of electrons in metal and R -the radius of particles, considering spherical form [5]. The peak of lead colloid absorption is situated at 235 nm and the shift is very weak towards short wavelength, like in the case of silver nanocrystals in the final stage of the thermal treatment. If the theoretical curve is compared with the experimental one, the size obtained from the shift of the absorption band is around 120 nm.
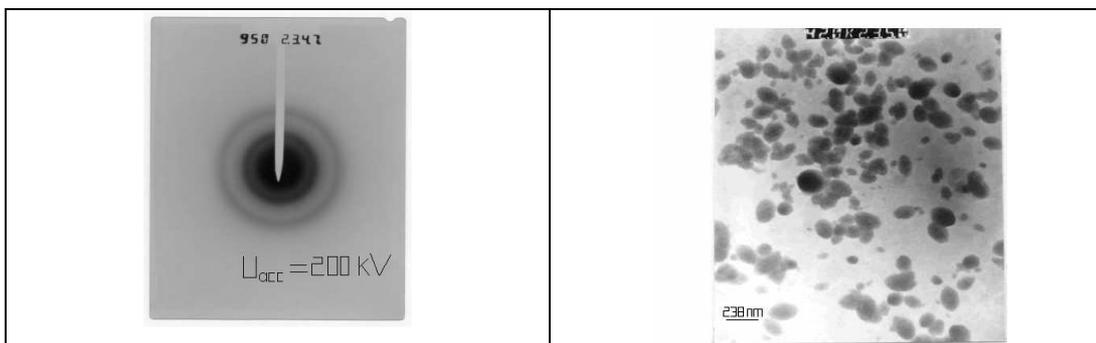
Fig. 2. SAED and TEM of lead nanocrystals.

TEM measurements (Fig. 2) reveal thin metallic structures with ellipsoidal form with the average size around 125 nm. The nanoparticles are separated, and the Mie theory is applied because the general condition is fulfilled:

$$v = a \cdot r^b$$

where v - is the volume of the colloid and *r*-is its radius.

A typical electron diffraction paltern (SAED) for these mettalic structures is shown also in Fig. 2 (left).
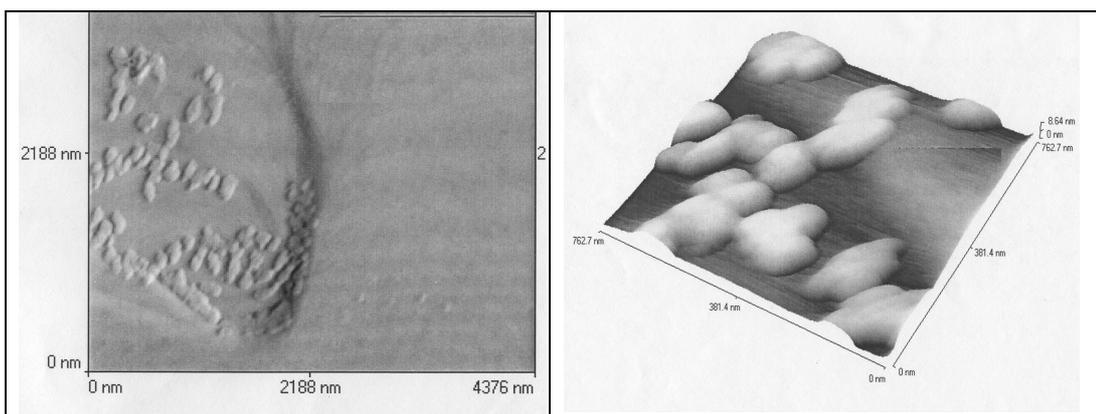

Fig. 3. AFM two-dimensional and three-dimensional images.

AFM measurements show another interesting feature (Fig. 3). The metallic particles are concentrated around some type of dislocations and the images confirm the ellipsoidal, plate like form of these particles.

Two major characteristics determine the applicability of Mie theory [9]:
a) spherical particles
b) well separated particles, with no interactions

In fact, the difference between nanocrystals of silver and lead is connected with the melting point of these metals. In the case of silver nanocrystals, the melting point is around 980 ^{o}C, the thermal treatment do not exceed 600 ^{o}C and the process of coagulation is produced in solid phase of the metal. In the case of lead nanoparticles, the melting point of lead is around 326 ^{o}C but the thermal treatment was conducted also at high temperature. Therefore, the coalescence process takes place in the liquid phase of metal. This is called liquid-like coalescence process.

The shift of the absorption peak to the short wavelengths could be simply explained. During thermal treatments, the (return) point of the critical dimension was extended. As was explained in [1], the shift of the absorption peak in the case of silver nanocrystals towards long wavelength takes place until the size of nanocrystals reaches a critical value. Later, successive thermal treatments lead to some dispersion of the atoms from the nanocrystals.

From AFM measurements, it is possible to conclude that the distribution of the Pb^{2+} ions in the KCl matrix during the crystal growth is not uniform, and the impurity ions are concentrated along

some defects of the matrix, probably dislocations. During electrolytical coloring, the change of ion valence passes from zero for neutral atoms, to value corresponding to negative metal ions, after a short migration under high temperature, through the matrix. The process of electrolytical coloring, compared with that of thermal treatment, is a very short one and the process of nanocrystal formation is avoided during the change of valence. Long thermal treatments determine an other short migration of the neutral particles and produce a process called coagulation in different phases.

The optical, AFM and TEM data allowed to investigate the particular features related to the spatial configuration of metal nanocrystals. The process of coagulation, in the case of lead nanoparticles, takes place into liquid phase, also called liquid-like coalescence. All the results for nanocrystals can be explained in the frame of Mie theory.

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