Section 6: Nano-structured materials

PROPERTIES OF METAL CLUSTERS EMBEDDED IN KCl MATRIX

S. Polosan, E. Apostol, V. Topa

National Institute for Materials Physics, Bucharest-Magurele, 76900, PO Box MG 7

The characterization of nanocrystals embedded in alkali halide crystals concerning shape and size distribution has been performed. Optical absorption, transmission electron microscopy (TEM), x-ray diffraction (XRD) and electron spin resonance (RES) methods has been used. The experimental results are in good agreement with the theoretical considerations concerning absorption and scattering of light by the metal clusters.

Keywords: Nanocrystals, Colloids, Optical absorption, TEM, ESR, XRD

1. Introduction

In many cases, the shape of the colloidal particles is assumed to be spheres, but in the real cases, they are irregular configuration like corals or spatial aggregates with unusual shapes. Jain [1], using TEM, observed patterns of silver colloids almost spherical and usually, isolated. Nistor et al. [2], using the same techniques, have found various spatial arrangements of silver aggregates, without separated particles, as a function of the experimental conditions used for obtaining nanoparticles.

Starting with the cationic state of metals in alkali halide crystals, there are two ways for obtaining such structures: additive coloring and electrolytic coloring.

In practice, it is important to know the size of the colloidal particles because the macroscopic properties of colloids strongly depend on their linear dimensions, for example static polarizability, or coagulation processes.

This paper aims to investigate the optical properties of the colloidal particles, especially those embedded in KCl matrix by using TEM, ESR and XRD techniques.

2. Experimental

The metallic colloids were prepared starting from negative heavy ions in alkali halide crystals, using the electrolytic coloring [3]. The procedures for obtaining colloidal structure, starting with dissociation of negative metal centers, consist in step-by-step thermal treatments at different temperatures [4].

Single crystals of KCl:Ag^+ or In^+ were grown in air or in nitrogen atmosphere by the Kyropoulos method in quartz or platinum crucible. Ultrapure and p.a. salts were used. Metallic salts were added to the melt in order to obtain various concentrations of metallic cations. Several crystals of KCl with different concentrations of negative metal ions, between 5.10^{15}-10^{17} ions/cm^3, were grown. The concentrations were determined using Smakula formula, with the f value reported by Fukuda [5].

Electrolytic colorings were performed in air at various temperatures (350-600°C) and for different electric fields (200-4000 V/cm), using devices already described in [3]. The reversal of the electric field polarity led to the removal of the F-centers for the samples and thus only Ag^- centers were obtained. The measurements of optical absorption and TEM were already described in [4].

Theoretical investigations were based on the Mie theory [6] of the turbidity, which connects the absorption coefficient with the dielectric constants of metal clusters. The analytical expression of these connections is:

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

where C is the volume concentration of the colloids and ε_m the dielectric constant of matrix.

Obviously, the theory implies two major conditions:
- spherical colloidal particles
- separated non-interacting particles.

3. Results

The absorption spectra reveal several interesting features. For instance, in the case of silver dopant, a marked absorption maximum due to the colloidal absorption between 400-420 nm (Fig.1), was observed. In the case on indium, the spectra are completely different before and after electrolytic coloring. The thermal treatments were made step by step, in order to obtain various colloidal dimensions (Fig 2). At 650°C, annealing of the KCl:Ag⁻ samples leads progressively to the decreases of the negative ions amount and in the same time to increasing of the numbers of colloidal particles. Thermal annealing of indium doped crystals produces two bands, which are attributed to cationic ions of indium and colloidal structures of In°.
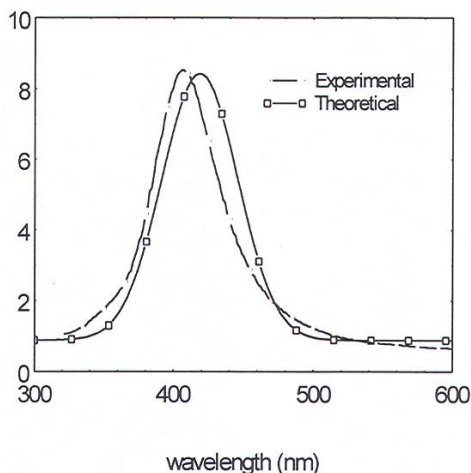

Fig. 1. Experimental and theoretical curve of the optical absorption of KCl:Ag crystals.
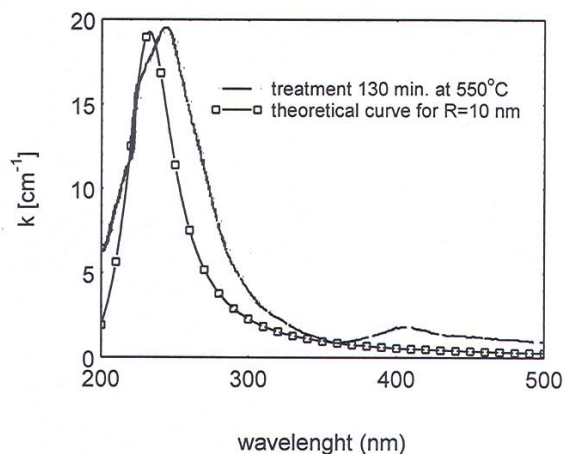
Fig.2. Experimental and theoretical curve of the optical absorption of KCl:In crystals.

Obviously, the sizes of the colloidal particles tend to increase with the increasing of annealing time. The absorption maxima shifts progressively towards longer wavelength in the first case, but when all negative centers are destroyed and converted into silver colloids, this absorption is shifted into opposite direction. This features proves that, during the annealing process, the size of the colloidal particles increases and, when the source of negative ions is out of stock, the colloid size decreases and the number of particles, increases. In the second case, almost all the colloidal centers are converted into the initial cationic structures. This is a proof for a reversible process In⁻→In⁺.

TEM measurements evidenced two different types of structures. In the case of silver, the images reveal coral-like structures formed by the coalescence of spherical particles (Fig.4), while in the case of indium the particles are almost spherical and separated (Fig. 3).
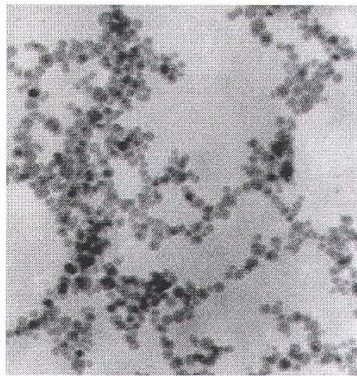
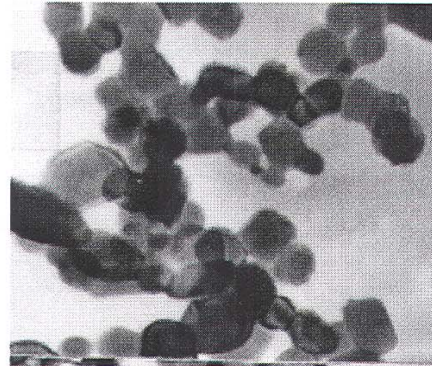Fig. 3. TEM image of KCl:In crystal
(1 cm = 144 nm).

Fig. 4. TEM image of KCl:Ag crystal
(1 cm = 83 nm).

From the XRD and ESR measurements it was concluded that the colloidal particles have metallic crystalline nanostructures (Fig. 5,6).
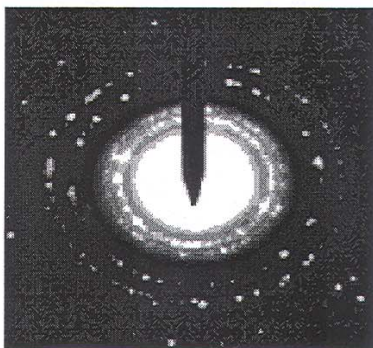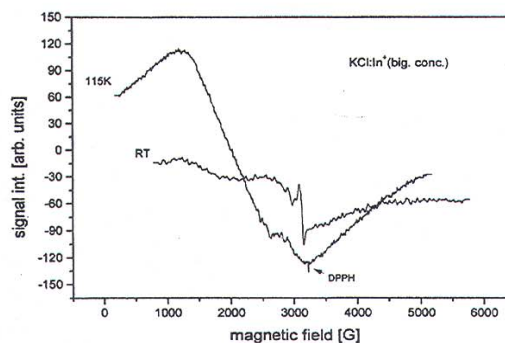

Fig. 5. XRD image of KCl:Ag crystal.

Fig.6. ESR spectrum of KCl:In crystal.

4. Discussion

The difference between the two above described colloids is explained by the difference between the melting points of metals. In the case of silver, the melting point is around 1000 °C, above the temperatures of alkali halide growing. Electrolytic coloring or thermal annealing and the process of aggregation is made in the solid phase by coalescence process. In the case of indium, the melting point is 156 °C, much below the temperatures used during the transformation process $In^+ \rightarrow In^-$.

Differences appear even in the absorption spectra where, for example in the case of silver, all negative ions are irreversibly transformed in colloids. During thermal annealing, the shift of the absorption band is changed when the source of negative ions is out of stocks or when the colloids reach critical dimensions. The shifts are large because of the large difference between real and imaginary part of dielectric constants. In the case of indium, the absorption spectra prove that, varying the concentration of In^+-ions into the samples, we obtain both types of defects, In^- and colloids. In the case of silver, when starting with a certain concentration of cations, only the absorption band of colloids was observed. After relative long thermal annealing, there was observed an increase of the band (230 nm) of the In^+-ions, which proves that part of nanocrystals of metallic indium are reversibly transformed into the initial cationic configuration.

Because in the case of indium we have almost spherical particles almost separated, the fit between theoretical and experimental curve is very good, unlike the case of silver, where the

difference between the curves is a little larger. This fact could be explained by the completely different mechanism of aggregation.

In the previous work [4], we concluded that the shift towards short wavelength after long annealing is probably due to the dispersion of colloids, connected with the increase in the number of aggregates. Another explanation would be related to the increase of the aggregate size, which modifies the surface of the clusters, and the "radius" of the aggregate will be difficult to define. Probably, it is necessary to take into account another dependence of the geometrical shape of clusters and to estimate exactly the collision time of the conduction electrons with that surface. This seems to be the reason for the difference between the peaks position of the experimental curve and the theoretical curve one.

5. Conclusions

The mechanisms of coagulation are different for silver and indium metals embedded into KCl crystals due to the different melting points of these metals, and therefore, the coalescence mechanisms are completely different. In the case of silver, the relative high melting point results into a mechanism of coalescence in the solid phase, and this fact is proved by the spatial arrangement coral-like structures. In the case of indium, its relative low melting point results into coalescence in the liquid phase of metal, the so-called liquid-like coalescence. This fact is proved by the almost spherical particles of metal observed through TEM measurements and by the good agreement between theoretical and experimental curve of optical absorption spectra.

References

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