Cu halide nanoparticle formation by diffusion of copper in alkali halide crystals

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Copper atoms have been introduced by diffusion in NaCl, KCl and KBr crystals at 500°C. The crystals have been optically analyzed with photoluminescence measurements and by scanning electron microscopy. The emission and excitation spectra measured at low temperatures show the exciton confinement effect, indicating the formation of CuX (X=Cl, Br) nanoparticles, which has been confirmed by electron microscopy images. This is proposed as an alternative method to obtain CuX nanoparticles in alkali halides crystals.

Keywords: Nanoparticles; photoluminescence; alkali halides; defects.

Atomos de cobre han sido introducidos por difusión en cristales de NaCl, KCl y KBr a 500°C. Los cristales han sido analizados ópticamente con medidas de fotoluminiscencia y por microscopía electrónica de barrido. Los espectros de emisión y excitación, medidos a baja temperatura muestran el efecto de confinamiento de exciton, indicando la formación de nanopartículas de CuX (X=Cl, Br), lo cual ha sido confirmado por imágenes de microscopía electrónica. Este método es propuesto como un método alternativo para obtener nanopartículas de CuX en cristales halogenuros alcalinos.

Descriptores: Nanopartículas; fotoluminiscencia; halogenuros alcalinos; defectos.

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1. Introduction

Research into the physical properties of nanoparticles (NP's) is one of the fields given most attention nowadays because of their multiple applications in diverse technological areas such as optoelectronics, white light diodes, optical shutters, etc. The NP's, as a set of a few ions, have physical properties very different from those observed in the bulk of the corresponding material. In particular, NP's of CuX (X= Cl, Br, I) embedded in glasses or in other materials such as the alkali halide crystals, have been utilized to study non-linear optical properties [1], changes in thermal properties [2], and size induced quantum effects as the exciton confinement [3-6].

In CuX crystals, the exciton transition is splitted by the spin-orbit interaction into the $Z_{1,2}$ and Z_3 absorption levels [7]. As in the bulk, CuX nanoparticles present the $Z_{1,2}$ and Z_3 exciton levels but they are shifted to higher energy than in the CuX bulk as an effect of the exciton confinement, which is called the NP size effect. The energy shift for a nanoparticle of radius a has been given as

$$\Delta E = \frac{\hbar^2}{Ma^{*2}}, \qquad (1)$$

where $M = 3m_0$, m_0 is the mass of the electron at rest, and a^* is the difference between a and the Bohr radius of the exciton [3].

Based on the optical absorption induced by the exciton confinement, and also on the direct observation of electron microscopy (SEM, TEM) images, different methods have been utilized to obtain CuX nanoparticles. In glasses and crystals, CuX has been added to the melt, then, after cooling and adequate annealing treatments, the growth of nanoparticles is observed through the exciton optical absorption [8].

Takahiro *et al.* [9] have found another method to produce CuCl NP's consisting in a sequential Cl$^-$ and Cu$^+$ ion implantation in Al$_2$O$_3$ substrates. The NP's formation was revelead by the exciton confinement determined in the optical absorption spectrum. A method for preparing the CuCl nanoparticles in NaCl crystals has been reported by Samah *et al.* [10]. In this case, the crystal was grown by the Czochralsky technique after adding fine copper powder to the melt.

In this work, we report on a different method to produce NP's of CuX in alkali halide crystals based on the diffusion of copper in crystals during annealing at 500°C. This has been confirmed by scanning electron microscopy (SEM) images, and the confinement effect present in the photoluminescence spectra measured at low temperatures.

2. Experimental

The crystals were grown by the Czochralski technique in an argon atmosphere. Copper has been added to the crystals by a diffusion method very similar to that used to color this type of crystal additively. Crystals of a size of approximated to $0.6 \times 0.6 \times 1$ mm^3 and short wires of copper were enclosed in glass ampoules sealed at low pressure. The ampoules were annealed at 500°C for 24 hrs. Then the crystals were removed from the ampoule and cooled on a metallic plate at room temperature. These crystals were analyzed by optical absorption, photoluminescence, and scanning electron microscopy. Optical absorption was obtained from samples at room temperature with a Perkin Elmer spectrophotometer λ19. Photoluminescence was measured with a Fluorolog-3 spectrofluorometer from samples fixed to the coldfinger of a helium closed cycle APD-DE202 cryostat. Images were taken and samples

TABLE I. Excitation and emission wavelengths attributed to the $3d^{10} - 3d^9 4s$ transitions of the Cu+ ions.

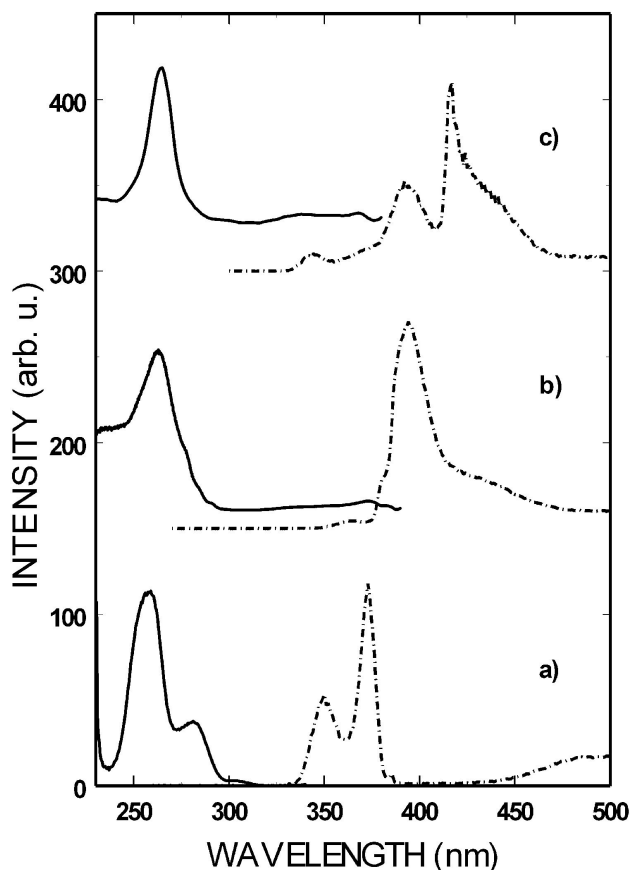| Host Material	Ex WL(nm)	Em WL (nm)
NaCl	258	350
KCl	262	393
KBr	265	395

FIGURE 1. Excitation and emission spectra of copper-doped a) NaCl, b) KCl and c) KBr crystals, obtained at 18K.

studied by analytical X-ray with a XL30 ESEM Phillips scanning electron microscope (SEM).

3.   Results and discussion

The characteristical excitation and emission spectra of freshly copper doped NaCl, KCl, and KBr samples are shown in Figs. 1a, 1b, and 1c, respectively. For each material, the excitation spectrum (left side of the graph) presents a broad band around 260 nm. An excitation light of wavelength around 260 nm on each crystal produces an emission spectrum consisting of several bands in the region from 330 to 600 nm. In all cases, the emission spectrum shows a broad band located at wavelengths in the range of 330- 400 nm. The spectral positions of the excitation and emission bands for

each material are listed in Table I. For each crystal, this emission band and the excitation band around 260 nm are identified with the electronic transition between the $3d^{10}$-$3d^9 4s$ levels of Cu$^+$ions. These previous results suggest that, during the diffusion process, the copper is incorporated into the alkali halide crystal sustitutionally as Cu$^+$-ion. The lower energy bands of the emission spectra produced with light of 260 nm and the low energy region of the excitation spectra (300-400 nm) in which bands of smaller intensity were found, were analyzed extensively and correspond to different types of aggregates of Cu$^+$ ions which will be discussed below.

Figures 2, 3 and 4 all show excitation (left side) and emission (rigth side) spectra for copper doped crystals, measured at 18 K, corresponding to the low energy regions. As can be seen in Figs. 2 and 3, the composition of the emission spectrum depends on the excitation wavelength. For NaCl:Cu (Fig. 2) emission, spectra 1 and 2 were obtained under excitation light of 350 and 370 nm. The excitation spectra A and B correspond to fixed emission lines of 400 and 377 nm, respectively. Excitation spectrum A contains intense bands located at 366, 377 and 385 nm, while B shows bands located at 358
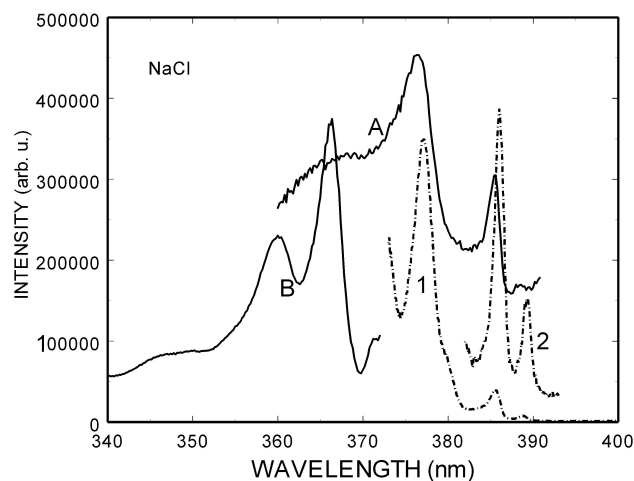

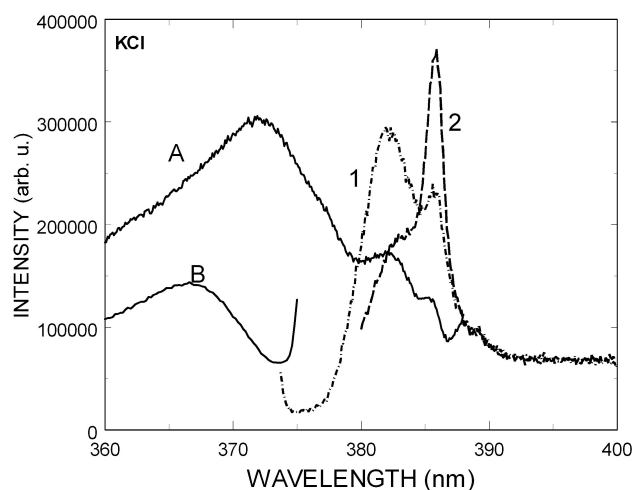FIGURE 2. Excitation and emission spectra of NaCl:Cu at 18K.

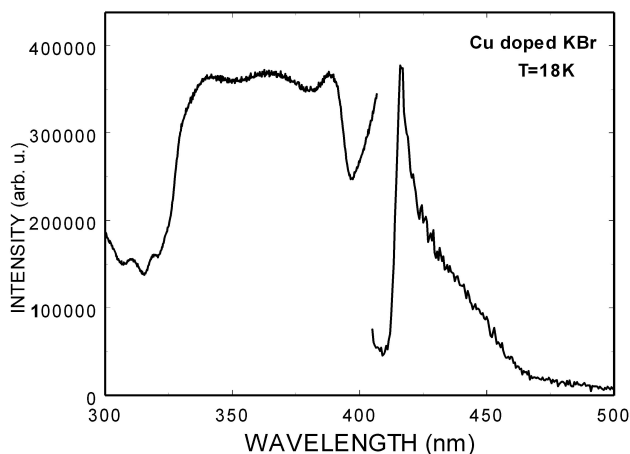FIGURE 3. Excitation and emission spectra of KCl:Cu at 18K.

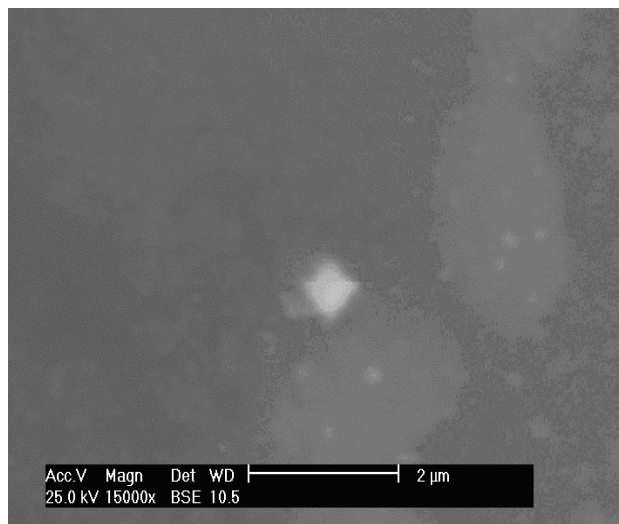FIGURE 4. Excitation and emission spectra of KBr:Cu at 18K.

FIGURE 5. SEM image taken with backscattered electrons from the surface of NaCl:Cu after a copper diffusion, showing a non-uniform surface related to the copper distribution.

and 366 nm. The bands located at 377 (3.289 eV) nm and 385 nm (3.220 eV) could be ascribed to the Z_3 exciton of NP's having different sizes. These energies are higher than the energies reported by Nakayama *et al.* [11] for the exciton Z_3 in CuCl films, which is very similar to the energy of the Z_3 exciton in the CuCl bulk. (3.204 eV). Exciton bands of higher energy than in the bulk are also observed in the optical response of the KCl:Cu and KBr:Cu crystals at low temperatures.

Using the energy shift of the exciton band from the excitation spectra of the NaCl:Cu crystals and the equation (1) with an effective Bohr radius of 0.68nm [based on the data of Ref. 3], a particle radius of about 5 nm is obtained. We have seen before that the energy of the exciton band in an excitation spectrum depends on the wavelength emission, which suggests that the crystal must contain particles of different sizes that could have grown during the diffusion process, achieving different sizes, from a few to several hundreds of nanometers. This has been verified by images of Cu^+-doped crystals taken by scanning electronic microscopy. Figure 5 shows a SEM image of a face of a Cu-doped NaCl crystal. The image shows white regions of different sizes, one of which has been analyzed by analytical x-rays, finding that it is composed mainly of Cu and Cl atoms, although a very low concentration of Na atoms has been detected. The Na atoms detected may be found in the CuCl particles or in the bulk NaCl due to the fact that the electron beam has gone beyond the limits of the CuCl particle, partially reaching the host. In any case, these results verify that the white regions appearing in the image represent particles of CuCl.

A mechanism to form NP's by the method employed could be the following. The copper atoms reaching the surface of the MX crystal (M = alkali metal) are trapped by halogen ions and diffused into the crystal, where they act as nucleation centers to form CuX aggregates. However, the depth achieved by the copper ions is not known. The method for obtaining NP's is relatively simpler than those pointed out above.

4. Conclusions

The measurements of the excitation and emission spectra of the NaCl, KCl, and KBr crystals containing copper ions present the characteristical absorption and emission of the exciton in the confinement state. The shift in the excitation energy of the exciton show that in these crystals there are nanoparticles of different sizes, which has been verified by the SEM images. Thus, we have found a useful method for producing CuX nanoparticles, which can be combined with adequate thermal treatments to modify the size of the NP's.

Acknowledgements

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