Investigation of Local Electronic, Dielectric and Optical Properties of Individual Composite Tabular AgX Emulsion Microcrystals by Cryo-EELS and LMTO-ASA Techniques

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AgX (X=Br, I, Cl) microcrystals are well known as quantum detectors. The unique character of optical absorption, considerable complexity in the valence-band structure, and remarkable quantum-size effects make them attractive for solid-state research. Here we report local electronic, dielectric and optical properties of composite AgBr core-Ag(Br,I) shells tabular AgX microcrystals studied by cryo-EELS and the *ab initio* linear muffin-tin orbital method (LMTO) in its atomic sphere approximation (ASA) [1]. Cryo-EELS (T= -193°C) within areas of 100 nm in size of the AgBr core was performed on a ZEISS CEM902 computerized electron microscope at U= 80 kV using an integrated energy filter connected to a Kontron IBAS-2000 image analysis system. Fig. 1a compares ε_1, ε_2, and Im(-1/ε) computed using Kramers-Kronig relations and self-consistent LMTO-ASA. For E$\leq\hbar\omega_p = [(\hbar\omega_p^f)^2 + E_g^{i\,2}]^{0.5} = 21.6$ eV, Im(-1/ε) describes interband transitions at 4, 7-8, 15-17 and the volume plasmon at 22 eV. The LMTO-ASA calculations of dielectric parameters have been performed from first principles taking into account only direct transitions. Assuming all the transition matrix elements to be equal, independent of the k-point and the band number of the initial and final electron states, the following expressions for ε_1 and ε_2 were derived [2]:

$$\varepsilon_1 = 1 + V_1 \sum P \int_{BZ} \frac{1}{[E_{j'}(\vec{k}) - E_j(\vec{k})]^2 [E_{j'}(\vec{k}) - E_j(\vec{k}) - \hbar\omega]} d^3k \tag{1}$$

$$\varepsilon_2 = \frac{V_2}{\omega^2} \sum_{jj'} \int_{BZ} \delta(E_{j'}(\vec{k}) - E_j(\vec{k}) - \hbar\omega) d^3k \tag{2}$$

Here fitting parameters $V_1 = \frac{2h^4 e^2}{\pi^2 m^2} |M|^2 = 1/25$ and $V_2 = \frac{2h^2 e^2}{\pi m^2} |M|^2 = 1/95$, respectively, with M being

the constant transition matrix element. The needed energies have been taken from the self-consistent LMTO-ASA energy band calculations (Fig. 1b). Although ε_2 and Im(-1/ε) fall to zero at 4.3 eV (the direct band gap of AgBr) due to limitations of the model, the maxima of ε_2 at 9 eV, 11 eV and 13 eV satisfactorily fit to the intensive composite band at 7-14 eV (with maxima at 8 eV and 10 eV) assigned to the proposed exciton transitions at X point. The computed minimum of ε_1 at 14 eV fits well to the experimental minimum of ε_1, similar to the minimum of Re(1/ε) at 13 eV. Moreover, the crossings of Re(1/ε) and Im(-1/ε) at 8 eV coincide as well as of Re(1/ε) and ε_2 at 22 eV, where Im(-1/ε) has its maximum and ε_1 has a local minimum. Furthermore, there is the shoulder of ε_2 at 15-16 eV superimposed with the previous band and the corresponding maximum of Im (-1/ε). For E>25 eV, both computed and experimental curves closely agree. Again, the features at 4-5 eV cannot be computed due to having no direct transitions at this energy. Fig. 1c presents an overview plot of the projected density of states (DOS) splitted into s-, p- and d-orbital momentums of the projected Ag and Br atoms. One can see the Br s-state at − 15 eV and the Br p-states and Ag d-states mixing between −5–0 eV. Strong mixing of the Ag s-, p- and valence d-states and the Br valence p- and d-states occur above the Fermi

level (Fig. 1c). The first conduction band at 3-7 eV seems to be mainly a mixture of the Ag s-states and the Br p-states, while the second and the third ones are due to complicated mixing of the Br d- and p-states with the Ag p- and d-states. Fig. 1d shows the local complex refractive index, $N = \varepsilon^{1/2} = n+ik$, derived from EELS data and from LMTO-ASA calculations. Here the index of refraction, $n = \{0.5[(\varepsilon_1^2 + \varepsilon_2^2)^{0.5}+\varepsilon_1]\}^{0.5}$, and the extinction coefficient, $k = \{0.5[(\varepsilon_1^2 + \varepsilon_2^2)^{0.5}-\varepsilon_1]\}^{0.5}$ are given. The values of n closely approach 1.0 above 50 eV. The local absorption coefficient, $\mu(E) = E/(\hbar c)[2(\varepsilon_1^2+ \varepsilon_2^2) -2\varepsilon_1]^{0.5}$ is

shown in Fig.1e. Maxima of the real part of the optical joint DOS (OJDOS), $Re\{J_1(E)\} = \dfrac{E\varepsilon_2}{0.5\pi E_p^2}$, E_p

= 21.4 eV at about 5 eV, 10-11 eV and at 18 eV (Fig. 1f) satisfactorily fit to the corresponding maxima of the calculated DOS in Fig. 1c.
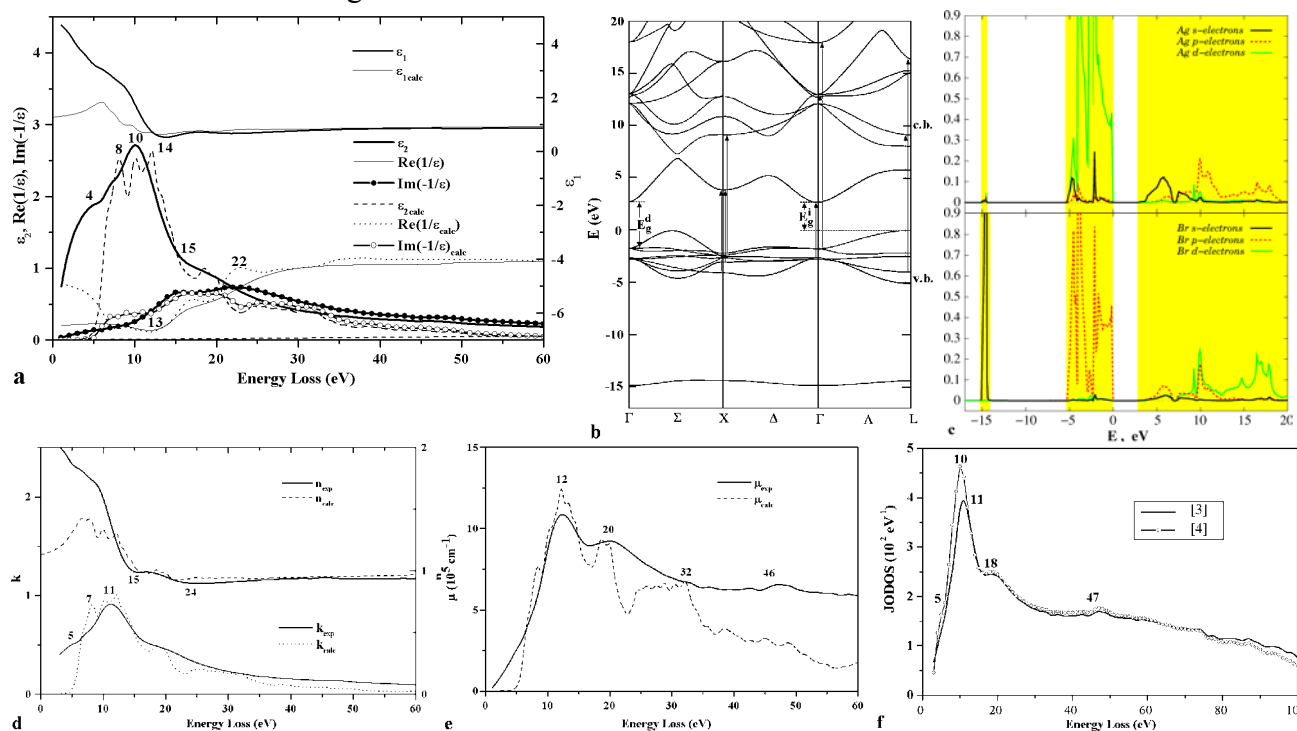

Fig. 1. (a) Dielectric permittivity, $\varepsilon=\varepsilon_1+i\varepsilon_2$, and energy-loss function, $Im(-1/\varepsilon)$, for an AgBr core of a composite tabular microcrystal vs. LMTO-ASA calculations. (b) Electronic band structure of AgBr calculated by the LMTO-ASA method with a proposed assignment of experimentally observed exciton assisted interband transitions at Γ, L and X points. E^d_g and E^i_g denote energies of the lowest direct and indirect gap, respectively, v.b. is the valence band, c.b. is the conductive band. (c) Projected DOS calculated within the LMTO-ASA approach, splitted into s-, p- and d-orbital momentums of the projected Ag and Br atoms. (d) Refractive index, $N=\varepsilon^{1/2}=n+ik$. (e) Absorption coefficient, $\mu(E)$. (f) The real part of OJDOS, $Re\{J_1(E)\}$, calculated from experimental data using computing programs [3] and [4], respectively.

References

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