OPTICAL AND RELATED PROPERTIES OF METAL-HALIDE CHAIN COMPOUNDS: BULK AND SMALL PARTICLES

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ABSTRACT. Reflectance-, absorption-, resonance Raman-, luminescence-spectra and resonance Raman excitation profiles of some complexes of the type -M-X---M---X (where M=Pt, Pd, Ni, Rh; X=Cl, Br, I), experimentally observed at room temperature, are briefly reviewed and some recent results are described. Experimental spectra are compared to those calculated on the basis of Lorentzian, vibronic and excitonic models. Also, the results are compared to those obtained from other organic or inorganic semiconductors.

1. Introduction

In our previous papers, the preparation and optical properties of a number of metal-halide chain compounds have been described [1-16]. In this paper, the optical and related properties of these compounds at room temperature are briefly reviewed and some recent results are described.

2. Experimental

Metal-halide chain compounds were prepared by methods reported in [1-18]. Precursors $Z_2Rh(dmit)_2$ (:Z= Bu_4N, Et_4N, Me_4N; dmit= 1,3-dithiole-2-thione-4,5-dithiolate) were prepared by treating $RhCl_3.3H_2O$ with $Na_2(dmit)$ in methanol in the presence of ZBr under an argon atmosphere. $(Bu_4N)_2Rh(dmit)_2$ is a brown solid, mp=137°C [17]. The absorption spectrum of this compound showed solvent effects (:554 nm in acetone, 518 nm in methanol) similar to those observed in other $Z_2M(dmit)_2$ compounds [19]. Treatment of $Z_2Rh(dmit)_2$ with Br_2 in acetonitrile yielded $Z_xRh(dmit)_2Br_y$ [17,18] in a powder or microcrystalline form.

Reflectance-, absorption-, resonance Raman- and luminescence-spectra were recorded by instrumentation reported in [4,6,10,11].

3. Results

The metal-halide mixed valence compounds have quasi-1-dimensional structures (see for example [20]) and show quasi-1-dimensional semiconducting behaviour [21].

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It was found that the single crystal reflectance spectra of these compounds vary from crystal to crystal [1,4,13, 22, 23]. Reflectance spectrum of a greenish single crystal of $\mathrm{Pt(en)_2\ Pt(en)_2Cl_2(ClO_4)_4}$ (where en=ethylenediamine), for example, showed a maximum at 465 nm, a shoulder at 730 and a maximum at 1492 nm [4], while that of a red-yellow crystal showed a maximum at 435 nm and some weak bands at longer wavelengths [13]. Figure 1 shows the reflectance spectra of a red single crystal of $\mathrm{Pt(en)_2\ Pt(en)_2\ Cl_2(ClO_4)_4}$ with the polarization parallel ($E \parallel$) and perpendicular ($E \perp$) to the chain axis(Z). One can see that, except the main mixed-valence (MV) band, some other weak bands or shoulders (S, A, B, P) appear in the low frequency spectral region for $E \parallel Z$. The S-band appears also in the spectrum observed with perpendicular polarization ($E \perp Z$). There is no other band, except a shoulder (Q) at ca 420 nm and an upward slope from 400 nm to shorter wavelengths, in the spectrum with $E \perp Z$. Values of real (ε_1) and imaginary (ε_2) parts of the dielectric constant (ε) were obtained by a Kramers-Krönig analysis of the reflectance spectra with $E \parallel Z$ [1,4,6]. ε_1 and ε_2 values of red $\mathrm{Pt(en)_2\ Pt(en)_2\ Cl_2\ (ClO_4)_4}$ are listed in Table 1. The frequency dependence of ε_2/λ is shown in the insert of Figure 1 (λ is the wavelength).

The single crystal absorption spectra [23-26] showed the MV-, A-, B- bands for

Table 1. ε_1 and ε_2 values of red $\mathrm{Pt(en)_2\ Pt(en)_2\ Cl_2(ClO_4)_4}$ for $E \parallel Z$.

ω/kcm^{-1}	ε_1	ε_2	ω	ε_1	ε_2	ω	ε_1	ε_2
8.6	6.64	0.01	14.6	6.25	0.74	20.6	10.61	2.56
8.8	6.58	0.12	14.8	6.12	0.84	20.8	10.88	3.23
9.0	6.60	0.23	15.0	5.94	0.80	21.0	11.11	4.00
9.2	6.54	0.34	15.2	5.93	0.74	21.2	11.41	5.51
9.4	6.50	0.44	15.4	5.97	0.71	21.4	10.43	6.27
9.6	6.46	0.55	15.6	5.97	0.67	21.6	9.70	6.41
9.8	6.35	0.63	15.8	6.04	0.66	21.8	9.51	7.09
10.0	6.30	0.71	16.0	6.06	0.68	22.0	8.99	7.80
10.2	6.15	0.75	16.2	6.02	0.67	22.2	8.18	8.51
10.4	6.10	0.78	16.4	5.97	0.60	22.4	7.30	8.31
10.6	5.98	0.78	16.6	6.01	0.51	22.6	6.65	8.86
10.8	5.90	0.77	16.8	6.07	0.42	22.8	5.76	8.82
11.0	5.85	0.75	17.0	6.21	0.37	23.0	5.02	8.69
11.2	5.78	0.72	17.2	6.27	0.32	23.2	4.20	8.70
11.4	5.73	0.68	17.4	6.41	0.26	23.4	3.49	8.21
11.6	5.72	0.64	17.6	6.52	0.22	23.6	2.90	7.81
11.8	5.71	0.59	17.8	6.64	0.16	23.8	2.43	7.29
12.0	5.73	0.56	18.0	6.90	0.13	24.0	2.21	6.67
12.2	5.75	0.53	18.2	7.10	0.17	24.2	1.95	6.31
12.4	5.78	0.51	18.4	7.21	0.20	24.4	1.75	5.83
12.6	5.80	0.50	18.6	7.36	0.17	24.6	1.70	5.32
12.8	5.84	0.49	18.8	7.66	0.16	24.8	1.63	4.96
13.0	5.87	0.48	19.0	7.98	0.21	25.0	1.62	4.55
13.2	5.89	0.47	19..2	8.32	0.34	25.2	1.69	4.13
13.4	5.98	0.49	19.4	8.65	0.55	25.4	1.85	3.75
13.6	6.01	0.51	19.6	8.77	0.71	25.6	1.98	3.53
13.8	6.08	0.57	19.8	9.12	0.84	25.8	2.11	3.32
14.0	6.03	0.59	20.0	9.59	1.08	26.0	2.27	3.08
14.2	6.08	0.61	20.2	10.17	1.62	26.2	2.42	3.04
14.4	6.08	0.62	20.4	10.18	2.04	26.4	2.52	2.94

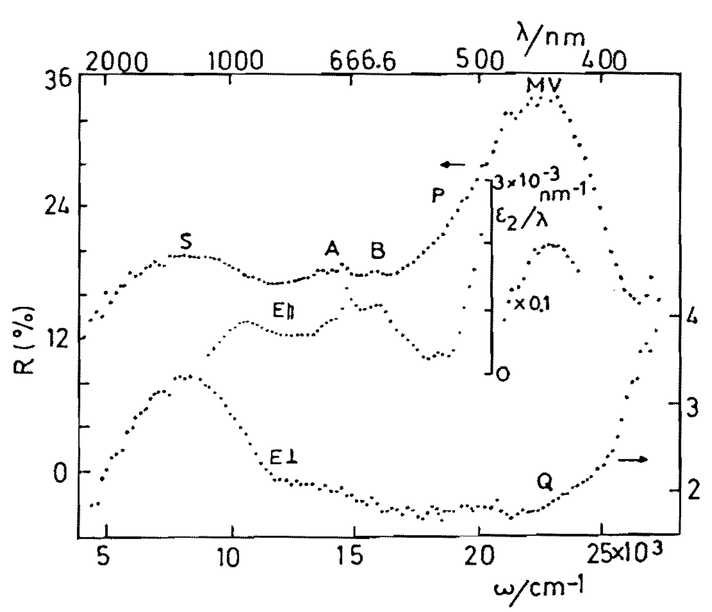

Figure 1. Reflectance spectra (R) of a red crystal of Pt(en)$_2$Pt(en)$_2$Cl$_2$(ClO$_4$)$_4$ with E∥Z and E⊥Z. The frequency dependence of ε$_2$/λ for E∥Z is shown in the insert.

E∥Z. The MV band in the absorption spectra of powdered materials (suspensions or thin deposits) showed particle size effects [1-7, 9,11,15]. The S-, A-, B- bands appear as shoulders in the absorption spectra of particles. Similar results have been obtained from MTCNQ (M=K, Cu etc) [27].

Polarized Raman spectra of single crystals of metal-halide chain complexes showed a strong enhancement of the X-M-X---M--- symmetric streching vibration in the chain (LO), when E∥Z and the laser excitation wavelengths reach the MV- band. Normal Raman spectra of the lateral to the chain bonds (: M-N etc) were observed with E⊥Z [2-4, 6-10, 13]. The Raman spectra of powders showed only the resonance enhancement, because of lower intensity of the normal lines (the intensity, I, of a fundamental line, LO, in some cases is 500 times higher than that of v_{M-N}) [10]. The resonance Raman lines of small particles showed a small shift to higher Raman frequencies [1]. Also, they showed a decrease of the ratio I_{2LO}/I_{1LO} on decreasing the particle size. Similar results have been obtained from the spectra of CdS [28], ZnTe [29] and (CH=CH)$_x$ [30]. Figure 2 shows the resonance Raman (and luminescence) spectra of large (≥ 250 nm) particles and small (ca 15 nm) particles of Pt(en)$_2$ Pt(en)$_2$ Cl$_2$(ClO$_4$)$_4$ observed with the 454.5 nm argon-laser excitation line. Figure 3 shows the particle size dependence of the ratio I_{2LO}/I_{1LO} of Pt(en)$_2$ Pt(en)$_2$ Cl$_2$(ClO$_4$) as well as that of CdS, for comparison. Laser line with frequency close to that of the gap frequency of the material has been used for these observations (514.5 and 488 nm, respectively). Similar resonance Raman spectra were observed from powders of Z$_x$Rh(dmit)$_2$Br$_2$ and iodide analogs [17,18].

Metal halide chain complexes showed strong luminescence bands which occur in the visible [2,4, 31] or in the near infrared region (see [4, 31, 32] and refs. therein). Figure 2 shows the luminescence spectra of large (≥ 250 nm) and small (ca 15 nm) particles of Pt(en)$_2$ Pt(en)$_2$ Cl$_2$(ClO$_4$)$_4$. The luminescence spectra of a single crystal of Pt(en)$_2$Pt(en)$_2$Cl$_2$(ClO$_4$)$_4$ [4, 32] showed a strong band at 1000 nm, which occurs close to the S-absorption band, a shoulder at ca 750 nm, which occurs close to A, B-absorp-

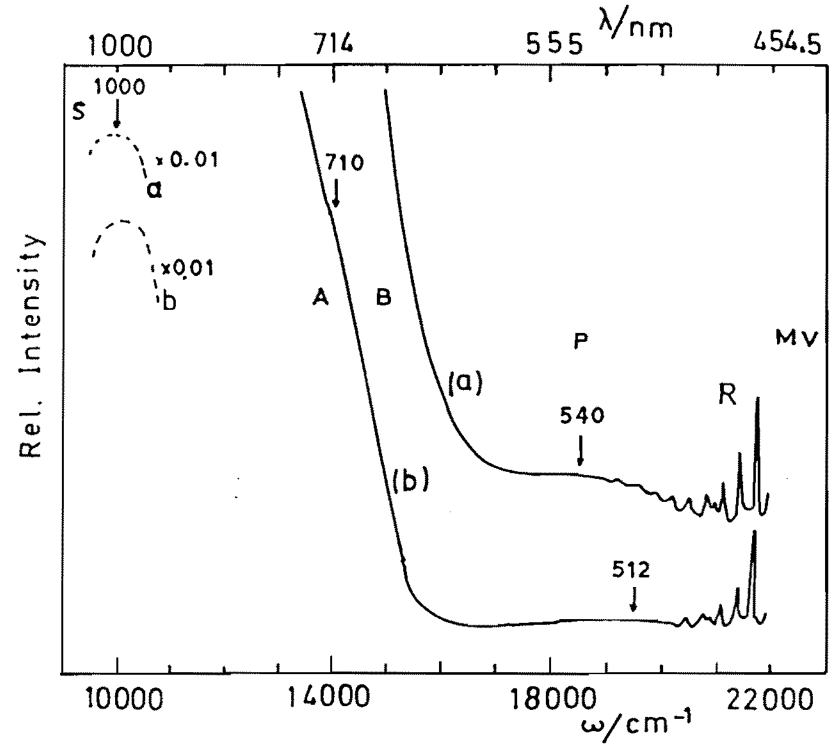

Figure 2. Resonance Raman and luminescence spectra of $Pt(en)_2Pt(en)_2Cl_2(ClO_4)_4$ large (a) and small (b) particles.

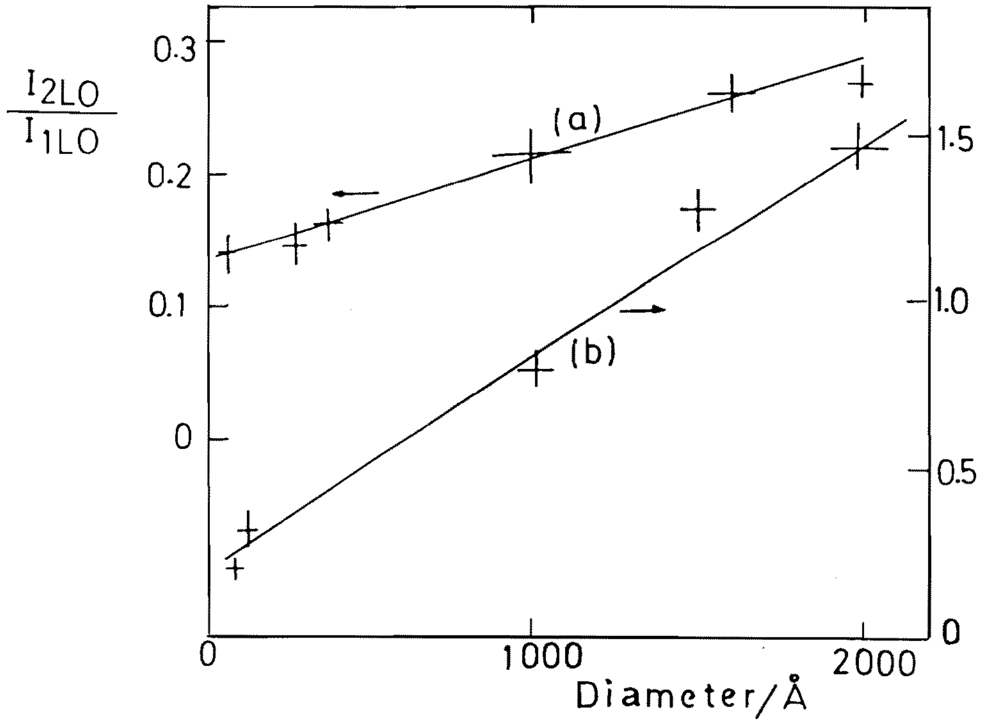

Figure 3. Particle size dependence of the ratio I_{2LO}/I_{1LO} for $Pt(en)_2Pt(en)_2Cl_2(ClO_4)_4$ (a) and CdS(b) small particles.

tion region and a weak band at 540 nm, which occurs close to the gap frequency of the compound. This last band shifts to higher frequencies by decreasing the size of the particles (Figure 2). Similar results have been observed from CdS [28] and $(CD{=}CD)_x$ [33].

The resonance Raman excitation profiles of the metal-halide chain compounds showed maxima which occur at the gap frequencies [1,6]. It was observed that the maxima-potitions shift to the higher frequencies by decreasing the size of the particles, as in the case of CdS [28].

4. Calculations and Discussion

Experimental data indicate that the variety in the appearence of single crystals of metal-halide chain compounds is due to the strand (or segments) lengths as in the case of $(CH{=}CH)_x$ (see for example [30]).Taking into account the equations resulting from the Lorentzian [6], PKS [34], Pinczuk-Burnstein [6] and broken-strand [35] models, we can calculate the reflectance and absorption spectra (MV-band) as well as the resonance Raman excitation profiles of different samples, if we suppose that only the gap frequency varies from sample to sample and it becomes higher in the samples consisting of small particles (strands or segments). In most cases, calculated spectra were found to be in agreement with the experimental ones (see [1,6]). These models explain also the fine structures of the Raman lines observed at low temperatures [36]. From ε_2 values it was found that the gap-frequency is 20.3 and 22.7 kcm^{-1} for a greenish and red crystal, respectively,while that obtained from electrical measurements [21] is 22.2 kcm^{-1}. These values are close to those calculated by using an angular overlap model [37].In the gap-region a treatment similar to that reported in [38] is necessary to calculate the spectrum near the P-spectral region. If we consider that the resonance Raman spectra is a consequence of exciton-LO interaction, as in the case of CdS [28] and ZnTe [29], the following equation [29] gives the excitonic frequency of small metal-halide chain particles

$$\omega_{ex} = \omega_L - 2\omega_{LO} + (C/A)^{1/2},$$

where ω_L is the frequency of incident light, A is the ratio of the 2LO to the 1LO intensity and C is a constant. From this equation one can calculate ω_{ex} using the experimental data of Figure 3. The results indicate that quantum size effects, close to the gap frequency (P-region), are observable in the Raman spectra of this kind of materials .

The A- and B-bands have been attributed to polarons, bipolarons or solitons (see [22-26] and refs. therein).Structural transformations effect on the shape of these bands [24].

The S-absorption band coincides with the strong luminescence band. The last band has been attributed to self-trapped excitons [31]. The S-band occurs in the mid-gap and appears in both polarizations. These observations indicate that there are interchain interactions. If there are strong interactions, as it is possible in halogen-rich [7,9, 39] or dmit containing [17, 18] complexes, superconductivity could be observed [40] in this kind of materials.

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