

Research Article

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Keywords

Cadmium chalcogenide: a cadmium(II) compound of a group VI element in the Periodic Table having the general formula CdX (X = S, Se, Te)

Raman spectroscopy: an important light-scattering technique named in recognition of the work of the Indian physicist, Sir Chandrasekhara Venkata Raman (1888–1970), who was awarded the Nobel Prize in Physics in 1930

II–VI semiconductor: a material comprised of two elements, one from group II and one from group VI in the Periodic Table, which has an electrical conductivity between that of a conductor such as copper and an insulator such as glass

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# Cadmium(II) Chalcogenides Stable across Wide Temperature Range

## Abstract

**Background:** The three cadmium(II) chalcogenides CdX (X = S, Se, Te; Cadmium with either Sulphur, Selenium, or Tellurium), have important applications as artists' pigments and in the electronics industry. The purpose of this study is to assess the structural stabilities of bulk, microcrystalline samples of the three cadmium(II) chalcogenides over a wide temperature range by examining the changes that occur in their Raman spectra.

**Methods:** We recorded the Raman spectra of the three cadmium(II) chalcogenides from –196 °C to 500 °C on a commercial instrument equipped with a microscope and a variable-temperature stage.

**Results:** While the Raman spectra of all three cadmium(II) chalcogenides exhibited significant peak shifts and broadening with increasing temperature, these effects were completely reversible. There is no evidence of phase transitions, indicating structural stability.

**Conclusion:** Taken together, our results show that the three cadmium(II) chalcogenides are resistant to structural changes throughout the almost –700°C temperature range investigated, thereby reinforcing their continued use in artwork and in the electronics industry.

## Introduction

The three cadmium(II) chalcogenides, CdX (X = S, Se, Te), have wide ranging applications as artists' pigments (in the case of CdS and CdSe) and in the electronics industry (in the case of CdSe and CdTe). There are three polymorphs of cadmium sulfide, CdS. The hexagonal wurtzite polymorph of CdS is found in nature as the mineral Greenockite, which was named for the Englishman Lord Greenock, and is currently used as the artist's pigment cadmium yellow. (1) The industrial uses of the other two polymorphs of CdS are as photoresistors sensitive to visible and near-IR radiation and as thin films in the construction of solar cells. (2–4) Cadmium yellow has been commercially available since the 1840s and became fashionable as an artist's pigment because of its brilliant colour, light fastness and its prominence in artwork by such well-known artists as Monet, Van Gogh and Matisse. (5) Cadmium selenide, CdSe, became commercially available in 1919 as the artists' pigment cadmium red in the form of the stable wurtzite polymorph. It is nowadays usually blended with CdS to produce varying shades of yellow and red. (6) This material is also an important II–VI semiconductor in the electronics industry because it forms quantum dots with a tunable band gap in the visible region that depends on the nanoparticle size. (7) The third member of the chalcogenide series, cadmium telluride (CdTe), is a dark brown material that is not used at all as an artists' pigment due to its extreme toxicity when ingested, but it too is a well-established II–VI semiconductor. Colloidal CdTe nanoparticles form quantum dots used in gamma and X-ray detectors, while bulk CdTe is used to make photovoltaic arrays for thin solar panels that convert sunlight into DC electricity. (8, 9) When alloyed with mercury, CdTe is also used to manufacture HgCdTe (MCT) liquid N<sub>2</sub>-cooled infrared detectors. (10)

Although the effect of varying temperatures on artists' pigments plays an

instrumental role in art conservation, little work has been done on the structural dependence of artists' pigments on temperature using modern spectroscopic techniques. (11–13) Previously, Raman spectroscopy has been used to monitor the phase transformation of the less stable zinc blende form of CdS nanoparticles into their wurtzite counterpart, following annealing in an argon atmosphere at 200–500 °C for 2 h. (14) Raman spectroscopy has also been used to study the formation of CdS pellets in the production of thin films by pulsed laser deposition, the doping of nanocrystalline CdS thin films with cobalt ions by ion implantation at 300 °C, and the temperature dependence of CdS quantum dots from –258 °C to room temperature. (15–17) Additionally, some conventional and micro-Raman spectroscopic data have been published on CdS nanoparticles following their heat treatment at 150 °C for several hours. (18) In the case of cadmium red (CdSe), only a low-temperature (–253 to 27 °C) Raman spectroscopic study has been reported for CdSe nanocrystals. (19) Similarly, only a brief analysis of the Raman spectra of bulk CdTe at room temperature, using 488.0- and 514.5-nm laser excitation, has been reported. (20, 21) In view of the somewhat limited vibrational spectroscopic studies at higher temperatures of the CdX (X = S, Se, Te) compounds in the bulk form, we decided to investigate the Raman spectra of these materials over a wide temperature range (–196 to 500 °C). (22)

## Materials and Methods

Microcrystalline CdX (X = S, Se, Te) samples were purchased from Alfa Aesar (Ward Hill, MA, USA) and were used as received. Variable-temperature micro-Raman spectra (5 accumulations, 5s exposure time) were recorded on an inVia Renishaw (Wotton-under-Edge, Gloucestershire, UK) microscope using a 514.5-nm argon-ion laser (16 mW, maximum power) or a 785-nm near-IR diode laser (~15 mW; absolute power  $300 \pm 30$  mW; 0.05% power setting), a long working length 50X/0.75 objective and a Linkham (Tadworth, Surrey, UK) model THMS600 thermal stage fitted with a quartz window. Variable temperature measurements were performed chiefly in the -196 to 500 °C range at 50 °C intervals. The samples were allowed to equilibrate for 1 min at each temperature before recording the Raman spectra. Different gratings were used for the two lasers: 2400 grooves/mm (514.5 nm laser) and 1200 grooves/mm (785 nm laser). The spectral data were obtained and manipulated using the Renishaw wiRe2 proprietary software and the peak positions are considered to be accurate to at least  $\pm 1$  cm<sup>-1</sup>.

## Results and Discussion

The Raman spectrum of bulk, microcrystalline CdS exhibits two peaks at ambient temperature at 301 vs and 603s cm<sup>-1</sup>, together with a much weaker peak at 906 cm<sup>-1</sup>. The effect of increasing the temperature specifically on these two peaks from -160 to 500 °C is illustrated in Fig. 1.

The two main peaks have previously been attributed to the longitudinal

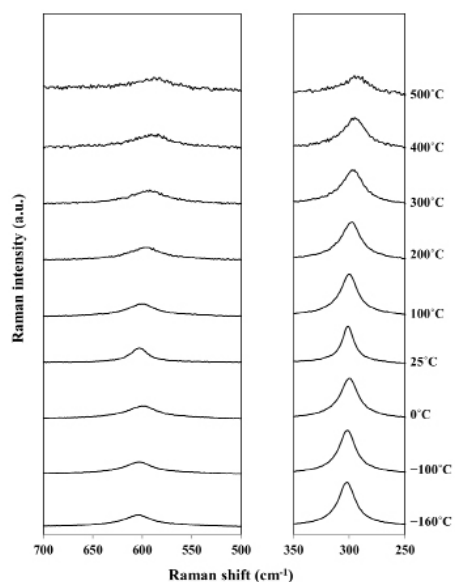


Figure 1. Variable-temperature (25 to 500 °C) spectra of bulk chrome yellow (CdS) pigment: changes observed for the 301 (1-LO) and 603 (2-LO) cm<sup>-1</sup> peaks.

optical 1-LO and 2-LO phonons, respectively (15, 18), while the 906 cm<sup>-1</sup> peak is presumably the 3-LO phonon or possibly a combination mode of the 1-LO and 2-LO phonons (calcd. 904 cm<sup>-1</sup>). Moreover, as observed in the earlier low-temperature Raman study on CdS quantum dots, all three Raman peaks gradually shift to lower wavenumbers with increasing temperature. (18) In addition, the three peaks broaden considerably with increasing temperature [cf. the peak-width at half-maximum (PWHM) plot in Fig. 2] and a shoulder begins to appear on the low-energy side of the 1-LO phonon. This asymmetry has been noted previously in the Raman spectra of CdS nanoparticles and has been discussed in terms of the phonon confinement model. (16) The shapes of bands in the Raman spectra of solid materials are considerably affected by structural defects and the presence of these defects results in a violation of the Raman selection rules that leads to band broadening and asymmetry, as observed in our study

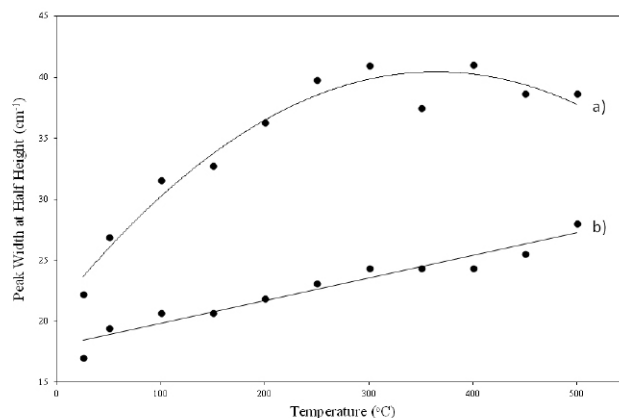


Figure 2. Temperature dependences of the peak widths at half maximum (PWHM) of the 301 (1-LO) and 603 (2-LO) cm<sup>-1</sup> modes of chrome yellow (CdS).

here. (23) The phonon confinement model is mathematical treatment of the shapes of Raman bands that takes into account these structural defects. A recent example of the use of this model is the analysis of the Raman band shapes associated with the LO phonons in III-V nanowires. (24) The quality of a material can be judged by a consideration of the so-called correlation length, which is the average size of the homogeneous regions of the material where there are no defects. The phonon confinement model has been almost exclusively applied to explain the asymmetry of LO Raman modes. The shift in the positions of the LO Raman bands is related to the size of the phonon confinement region in which a phonon can be restricted by such spatially limiting features as crystal twinning, stacking faults, vacancies, boundaries, and pores. (24) Considerable research has been reported on the analysis of defects in materials, including thin films, nanomaterials, and crystals using the phonon confinement model and there are now some excellent discussions on the topic. (25, 26) Upon cooling from 500 to -160 °C, the shifts and broadenings that were initially observed for the three phonons of CdS with increasing temperature are completely reversed.

Some similar Raman spectroscopic data were obtained in the variable-temperature (28-600 °C) Raman study of the bulk, microcrystalline cadmium red (CdSe) pigment. Three peaks are discernible at room temperature at 205, 413 and 618 cm<sup>-1</sup>, which can once again be attributed to the longitudinal optical 1-LO, 2-LO and 3-LO phonons, respectively. These three peaks also shift to lower energies and broaden with increasing temperature. Above 200 °C, fluorescence dominates the Raman spectra, possibly because of a zinc blende to wurtzite phase change, as has been suggested earlier (27), but there is no clear evidence of such a phase transition. The spectral changes observed with increasing temperature are fully reversible upon cooling to ambient temperature.

In the case of cadmium telluride (CdTe), both the 514.5- and 785-nm lasers were used to obtain the Raman spectra. The latter wavelength was chosen to reduce the fluorescence associated with the previously-employed shorter laser excitation wavelength (488.0 nm) (20, 21). At room temperature with 785-nm excitation, five peaks are observed at 165.7, 330.2, 498.4, 664.9, and 841.2 cm<sup>-1</sup>. The positions of the first three peaks agree quite well with those obtained at 223 °C using 488.0-nm laser excitation, and these peaks are assigned as the 1-LO, 2-LO and 3-LO phonons, respectively. (20,21) The two peaks located at 664.9 and 841.2 cm<sup>-1</sup> have not been observed previously and are attributed here to the 3-LO and 4-LO phonons, respectively, which may possibly have become active because of a resonance Raman effect. Interestingly, when the 514.5-nm laser is used, a completely different spectrum is obtained and a sharp doublet at 139.0 and 119.1 cm<sup>-1</sup> appears, together with a weaker broad peak at 744.0 cm<sup>-1</sup>. There is also a shoulder evident at ~169 cm<sup>-1</sup>, presumably the 1-LO phonon of CdTe. The sharp doublet at 139.0 and 119.1 cm<sup>-1</sup> is characteristic of optical modes of free elemental tellurium (Te), which may possibly have

been produced by laser irradiation of the CdTe surface. Elemental tellurium has been reported to exhibit Raman peaks at 139 and 120 cm<sup>-1</sup> and laser damage on the surface of thin CdTe films has been detected previously by Raman spectroscopy. (27, 28) The origin of the 744.0 cm<sup>-1</sup> peak is unclear, as it does not appear to be an overtone or a combination mode; it may, however, be associated with the formation of a cadmium or tellurium oxide species on the CdTe surface. (29-31)

## Conclusion

The common features of the Raman spectra of the three cadmium(II) chalcogenides, CdX (X = S, Se, Te), are the broadening and shifting of the phonon peaks with increasing temperature. Both of these effects have been investigated recently for a number of systems, e.g., zirconia (ZrO<sub>2</sub>) (29), the dye Nile Blue (33), the explosive hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) (34), amorphous silicon (35) and Al<sub>3</sub>BC<sub>3</sub> (36). Explanations have been put forward in the literature to rationalize these effects. One proposed explanation appeals to the dominance of anharmonicity at higher temperatures owing to the collapse of a temperature-independent force constant described by the harmonic oscillator model. Another, that photon decay causes the thermal expansion which results in shifts to lower wavenumbers of the vibrational modes and concomitant peak broadening. (37) All three compounds are quite resistant to structural changes throughout the wide temperature range investigated, which is an important characteristic that reinforces for their continued long-term use in artwork (CdS and CdSe) and in the electronics industry (CdSe and CdTe).

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