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Introduction

Chemists and artists have long been interested in the preparation and properties of natural and synthetic pigments¹ and considerable attention is now being paid to their identification for forensic analysis and conservation purposes. An array of modern analytical instrumentation is available in most museum laboratories to help in the examination of artwork.²

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Effect of temperature and pressure on selected artists' pigments

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This brief review describes some recent research on the effect of varying temperatures (-150 to 600 °C) and external pressures (up to ~ 5 GPa) on the stability of various artists' pigments. These pigments, some of which have been known for centuries, are remarkably stable under such non-standard conditions.

For example, the decomposition temperatures of the Fe₂O₃based pigments, *red* and *yellow ochre*, have been determined by thermogravimetric (TG) analysis,³ while X-ray diffraction and TG analysis coupled with mass spectrometry (MS) have been used to report the stability of *cadmium yellow* (CdS) up to 800 °C.⁴ In our work, we focused on the stability of CdS up to 500 °C, with specific interest in the temperature-dependent vibrational modes rather than on decomposition or mass loss.⁴ Other spectroscopic techniques currently being used include FT-IR,⁵ photoacoustic IR,⁶ total reflection X-ray fluorescence⁷ and even synchrotron radiation spectroscopy.⁸ Rock paintings in South Africa have been dated with surprising accuracy by paper chromatography⁹ and indigoid dyes in natural organic pigments have been identified by high-performance liquid



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Prof. Ian S. Butler studied at the University of Bristol (1958–1964) and was then a Fulbright Postdoctoral Scholar at Indiana and Northwestern Universities in the U.S.A. prior to joining the Department of Chemistry at McGill University in Montreal, Canada in 1966. He is still continuing his teaching and research activities there and recently, he was a Visiting Professor at the University of Sydney in Australia, ChimieParisTech in France and

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chromatography coupled to electrospray ionization MS.¹⁰ The most popular method of pigment identification is undoubtedly Raman spectroscopy because of the minimal amount of sample required and the non-invasive nature of this technique.¹¹ A somewhat surprising aspect of the work on artists' pigments is that their stability with respect to temperature and pressure appears to have received relatively little attention. The Russian literature contains details of the high-temperature synthesis of various pigments, e.g., blue aluminium-cobalt,¹² aluminumnickel¹³ and black iron oxide pigments,¹⁴ but fails to comment on their stability. A variable-temperature synthetic study has been reported for lead stannate (lead-tin yellow, PbSnO₃) that involved heating intimate mixtures of red lead (Pb₃O₄, 3 parts) and tin oxide (SnO₂, 1 part) at 600-800 °C.¹⁵ Depending on the temperature employed, different coloured pigments were produced: orange (600 °C), canary yellow (725 °C) and lemon yellow (800 °C). One of the more famous uses of *lead-tin yellow* is in Rembrandt's 1636/1638 painting entitled "Belshazzar's Feast". The effect of the calcination temperature on the hues of red Fe₂O₃ pigments has also been investigated.¹⁶ Studies on the effect of pressure on artists' pigments are quite limited, but these measurements can provide diagnostic information on polymorphs. Some examples include our own recent work on high-pressure IR and/or Raman measurements on Prussian blue,¹⁷ ultramarine blue,¹⁸ Magnus' green salts¹⁹ and α - and β -copper phthalocyanine.²⁰ Experimentally, variable-temperature Raman measurements can readily be accomplished in the -196 to 600 °C range through the use of thermal stages designed to mount under the microscopes of Raman microprobe instruments.²¹ High-pressure IR and Raman measurements up to about 70 kbar (8 GPa) can be undertaken using commercial diamond-anvil cells and similar microscope arrangements.²²

Results and discussion

Cadmium chalcogenides

Cadmium yellow is a well-known pigment, especially in paintings by Monet, Van Gogh and Matisse.²⁵ The hexagonal wurtzite polymorph of CdS exists naturally as the mineral Greenockite²⁶ and became commercially available as a pigment in 1840. In its nanocrystalline form, CdS is also an efficient II-VI semiconductor.²⁷⁻²⁹ Its electrical, optical and photoconductive properties have led to its use in solar cells and thin film transistors.³⁰ Low-temperature Raman studies on CdS nanoparticles have been reported for the 4 to 45 $^\circ C^{27}$ and -258 $^\circ C$ to room temperature ranges.31 In our variable-temperature Raman study on bulk CdS, three peaks were observed at 301, 603 and 906 cm⁻¹, which are assigned to the main longitudinal optical phonon mode (1-LO) and its two overtones (2-LO and 3-LO) that are detectable because of resonance Raman effects. Upon increasing the temperature gradually from room temperature to 500 °C, all three peaks decreased in wavenumber and broadened (Fig. 1). The 1-LO, 2-LO and 3-LO modes shifted by a total of 8.1, 17.7 and 22.4 cm⁻¹, respectively.³² All the spectral changes were fully reversible and the original spectrum



Fig. 1 Variable-temperature micro-Raman spectra of CdS upon increasing temperature from 25 to 500 $^\circ\text{C}.$

was regenerated when CdS was brought back to room temperature.

Cadmium red (CdSe) became commercially available as an artists' pigment in 1919 and it can be prepared by heating a mixture of cadmium salt solutions with alkali and alkaline earth sulfides.³³ In its bulk form, CdSe is usually blended with varying amounts of CdS to obtain different shades of yellow and red. This material is also an important II–VI semiconductor because CdSe nanoparticles form quantum dots, which have a tunable band gap leading to bright luminescence in the visible range that can be adjusted according to nanoparticle size.³⁴

Room-temperature Raman spectroscopic studies have been reported for CdSe nanoparticles, ^{35,36} but the only temperature dependent work appears to be an analysis from -253 to $27 \,^{\circ}C.^{37}$ In our Raman study of bulk crystalline CdSe, three peaks were located at room temperature at 205, 413 and 618 cm⁻¹, which correspond to the longitudinal optical phonon mode (1-LO) and the two overtones 2-LO and 3-LO, respectively. Variable-temperature measurements were obtained in the -150 to 600 °C temperature



Fig. 2 Variable-temperature micro-Raman spectra of CdSe upon increasing temperature from 28 to 600 $^\circ\text{C}.$

range and the changes that were observed upon increasing and decreasing the temperature are shown in Fig. 2. Increasing the temperature from room temperature to 600 °C using 100 °C intervals displayed peak broadening and shifts to lower wavenumbers. Above 200 °C, the peaks disappeared and fluorescence dominated the spectrum. It is possible that this change could be the result of a crystalline to an amorphous phase transformation or a partial phase change from *zinc blende* to the wurtzite crystal structure.³⁸ Upon further analysis of the temperature range from room temperature to 200 °C, we observed that the 1-LO peak decreased in position by 2.2 cm⁻¹ and the 2-LO peak decreased by 3.2 cm⁻¹. The reversibility of the structural changes was established by regeneration of the original spectrum at room temperature. Decreasing the temperature from room temperature to -150 °C at 25 °C intervals resulted in disappearance of some peaks and blue shifts to higher wavenumbers of the 1-LO and 2-LO modes by 2.2 and 6.4 cm^{-1} , respectively.

Dark brown cadmium telluride (CdTe) is less used as an artists' pigment than are CdS and CdSe, chiefly because of its toxicity. However, it is also an important II-VI semiconductor, and colloidal CdTe nanomaterials can now be produced sonochemically,³⁹ which form quantum dots for use in gamma and X-ray detectors.⁴⁰ The effect of temperature on the Raman spectrum of bulk CdTe was studied in our laboratory using both 514 and 785 nm laser excitation. Previous Raman studies of CdTe have reported Raman spectra obtained at shorter wavelengths, namely 488 and 514 nm.^{41,42} We decided to use both 514 and 785 nm laser excitation with the hope of minimizing any problems with fluorescence at the shorter wavelength. When the 785 nm laser was used, five peaks were observed at 841.2, 664.9, 498.4, 330.2 and 165.7 cm⁻¹ (Fig. 3), which agrees quite well with the literature data obtained at -223 °C using 488 nm laser excitation, i.e., there is a 1-LO mode $\sim 170 \text{ cm}^{-1}$ with overtones at 340 (2-LO) and 510 (3-LO) cm^{-1} .⁴¹ The two additional peaks at 664.9 and 841.2 cm^{-1} have not been reported previously and correspond to the 4-LO and 5-LO overtones that are now detectable because of inappreciable resonance Raman effect. When the 514 nm laser excitation was used, however, a doublet with peaks at 139.0 and 119.1 cm^{-1} and a weak band at 744.0 cm⁻¹ were observed (Fig. 4). From the



Fig. 3 Baseline-corrected micro-Raman spectrum of CdTe at room temperature, 785 nm laser excitation.

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Fig. 4 Micro-Raman spectrum of CdTe at room temperature, 514 nm laser excitation.



Fig. 5 Variable-temperature micro-Raman spectra of CdTe upon increasing temperature from –150 to 250 °C.

literature, the sharp doublet peak is characteristic of elemental tellurium (Te) on the surface of the CdTe, which has characteristic Raman peaks at 120 and 139 cm $^{-1}$,⁴² while the remaining peak is probably an overtone from the bulk CdTe. Upon increasing the temperature from -150 to 250 °C at 50 °C intervals, changes in intensity, wavenumber and peak width at half maximum (PWHM) were observed (Fig. 5). At -150 °C, the 1-LO mode at 165.7 cm⁻¹ had the greatest intensity, but as the temperature was increased, its intensity decreased and the 2-LO overtone at 330.2 cm⁻¹ became the most intense. Additionally, all the peaks red-shifted to lower wavenumbers and broadened with increasing temperature. Above 250 °C, all the peaks disappeared, suggesting the possibility of a crystalline to amorphous phase change. When the temperature was decreased from 30 to -150 °C by 25 °C intervals, the 1-LO mode at 165.7 cm⁻¹ increased in intensity until it became the strongest peak, while the remaining four peaks decreased in intensity. Additionally, the 1-LO, 2-LO and 3-LO modes blue-shifted to higher wavenumbers. The changes that occurred throughout both the heating and cooling cycles were completely reversible.

Maya Blue

Since the discovery of the Maya Blue pigment by the Harvard archaeologist Raymond Merwin in the Temple of Warriors at

the ChitchénItzà site in the Yucatan, Mexico in 1931, scientists have been fascinated by the exceptional long-term stability of this pigment.^{43,44} The Maya Blue pigment has managed to withstand harsh conditions such as acid rain, and oxidizing and reducing agents since the 7-8th century A.D.⁴⁵⁻⁴⁷ The most primitive forms of Maya Blue were originally synthesized from indigo dye extracted from the Indigofera plant and encapsulated in palygorskite clay [(Mg,Al)₂Si₄O₁₀(OH)·4H₂O], but details of its synthesis still remain a mystery.⁴⁸ The stability of the Maya Blue pigment is thought to be due to strong hydrogen bonding interactions with the open tunnels of the clay.49 In our investigation, we employed a novel mechanochemical procedure to prepare the Maya Blue pigment by ball milling a mixture of 2% indigo and 98% sepiolite [Mg₄Si₆O₁₅(OH)₂⁻⁶H₂O] for 30 min.^{32a} Some previous Raman work on the interaction between indigo and sepiolite was performed at room temperature using 532 or 325 nm laser excitation.^{45,47} In our case, we undertook variable-temperature Raman measurements from 27 to 200 °C at 20 °C intervals using 514 nm laser excitation. No significant spectral changes were observed and above 200 °C the peaks vanished completely, possibly indicating the formation of an amorphous phase.

Lead molybdate

Lead molybdate, PbMoO₄, is one of the main components of orange molybdate, an important artists' pigment due to its brilliant colour, impressive covering ability and tinting strength.⁵⁰ In addition to its prevalence in art work, orange molybdate has also been a favoured pigment in plastics, protective coatings and printing inks. This unique pigment is actually a mixture of PbMoO₄ and PbCrO₄, and sometimes a little PbSO₄.⁵¹ Most of the literature on PbMoO₄ highlights its acousto-optical, photoconductive, luminescent, photocatalytic and thermoluminescent properties.^{52,53} However, there has been one Raman study in which the changes in its electrical conductivity with increasing temperature from room temperature to 700 °C at 100 °C intervals were examined.54 We have paralleled this Raman work up to 600 °C but using 785 nm laser excitation instead of 514.5 nm. Although both wavelengths yielded similar roomtemperature spectra, the 785 nm laser excitation was favoured for signal-to-noise purposes. No fluorescence was detected for either wavelength. We also investigated the Raman spectra upon decreasing the temperature from room temperature to -150 °C. Increasing the temperature from room temperature to 600 °C at 50 °C intervals indicated significant stability of the material with only slight wavenumber shifts and peak broadening being observed. The strong peak located near 315 cm⁻¹ decreased by 3.3 cm⁻¹ while the peak at \sim 868 cm⁻¹ decreased by 3.0 cm⁻¹. The two less intense peaks broadened and merged into one broad peak at high temperatures perhaps indicating the onset of a crystalline to amorphous phase transition \sim 600 °C. A high-pressure Raman study was also undertaken from ambient pressures to \sim 5 GPa and no significant changes were observed besides blue-shifts of the two strongest peaks around 868 and 315 cm⁻¹ to higher wavenumbers by 5.6 and 9.7 cm⁻¹, respectively. The pressure dependences $(d\nu/dP)$ for these two modes at 867.7 and 314.9 $\rm cm^{-1}$ were 1.1 and 2.0 $\rm cm^{-1}$

 GPa^{-1} , respectively, which correlates well to the literature recorded values of 1.0 and 2.0 cm⁻¹ GPa^{-1} .⁵⁵

Lead chromate

Lead chromate (PbCrO₄) is found naturally as the mineral *crocoite* and was first introduced as the *chrome yellow* pigment in 1818.⁵⁶ In addition to its presence in artwork by artists such as Van Gogh, it has been used to colour airplanes, cars, road paint and street signs.⁵⁷ We examined the temperature dependence of the Raman spectra of PbCrO₄ from -150 to 600 °C and observed peak broadening characteristic of the dominance of an amorphous phase at higher temperatures. Further analysis indicated some hysteresis upon cooling and the room temperature spectrum was regenerated. No phase changes were observed throughout the entire temperature range, but apparently there is an α - β transition at ~691 °C and a β - γ transition at ~795 °C from X-ray diffraction studies.⁵⁸

Copper phthalocyanine

Copper phthalocyanine (CuPc) (Fig. 6) has remained a popular blue pigment in artwork and industrially in such things as food packaging, greeting cards, paints and plastics.⁵⁹ Although CuPc has 11 known polymorphic forms, the most dominant are the α - and β -polymorphs.^{59,60} While α -CuPc is the metastable form commonly known as Phthalo Blue, β-CuPc is the thermodynamically stable polymorph known also as Phthalo Blue.61,62 Prior to our most recent work on the high-pressure micro-Raman spectra of CuPc,²⁰ variable-pressure measurements were only used to study the electrical properties of the β -polymorph.^{63,64} Our high-pressure analysis provided a non-destructive and effective method to monitor the transition between the α - and β -polymorphs and to determine the pigment's stability at high pressures. Pressure measurements up to ~ 5 GPa for both polymorphs were reported for the 200-1250 cm⁻¹ region for the most intense peaks found at 594 and 681 cm⁻¹. Both polymorphs experienced blue-shifts in wavenumber to higher values when the pressure was increased. Unlike the α -polymorph that displayed a constant linear slope in the pressure dependence plot (Fig. 7), the β -polymorph slope changed at ~2.0 GPa



Fig. 6 Copper phthalocyanine (CuPc).



Fig. 7 Pressure dependence of vibrational modes at 831, 847 and 870 cm⁻¹ for β -CuPc recorded at ambient temperature. Adapted from ref. 20.

indicating the possibility of a phase change. Upon releasing the pressure, the original spectrum was obtained. The data for this reversible phase change match those from the other pressure work quite well in which a phase transition ~ 3 GPa was recorded.^{63,64}

Prussian blue

Prussian blue $(Fe_4[Fe(CN)_6]_3)$, is considered to be the earliest modern synthetic pigment - it was discovered by the German artists' colour maker Diesbach in 1704.65 Its popularity and stability as a pigment is highlighted by its presence in historical artwork and other items, such as stamps. One previous article mentions the importance of Prussian blue in the determination of Hawaiian Missionary stamp forgeries because of its characteristic Raman spectrum.65 Many reports have been published on this pigment and its derivatives because of their unique negative thermal expansion (NTE) behaviour. For instance, when Fe[Co(CN)₆] was subjected to a high-pressure Raman analysis a phase change was detected at ~ 17.4 GPa.⁶⁶ A similar high-pressure study on Cs and Rb Prussian blue derivatives revealed phase changes attributable to rotational instability of the [Fe(CN)₆] units resulting from compression of the M-N bond distances.⁶⁷ Both articles highlighted the presence of NTEs, which result from increased amplitude and population of low-energy vibrational modes causing contraction of the M-C-N-M' bond distances with increasing temperature.^{17,65-67} Our publication on Prussian blue marked the first study where a high-pressure Raman analysis of the pigment was used to understand its NTE behaviour.17 The article included an analysis of the behaviour of Prussian blue from ambient pressure to ~ 5 GPa, where most of the peaks blue-shifted to higher wavenumbers with increasing pressure. No phase changes were observed as the slopes of the pressure dependence plots remained constant and linear. Interestingly, the slopes of the two modes associated with Fe(II)-C-N-Fe(III) bending modes were negative, whereas positive slopes are usually expected. These two modes located at 201 and 365 cm⁻¹ exhibited pressure dependences $(d\nu/dP)$ of -1.5 and -0.6 cm⁻¹ GPa⁻¹, respectively, while all the other vibrational modes had positive values.

These $d\nu/dP$ values were used to calculate the Grüneisen parameters, γ_1 , to better describe the NTE behaviour of *Prussian blue*. These parameters denote the volume dependences of the Raman shifts and are defined as $B_od(\ln\nu_i)/dP$, where B_o is the bulk modulus. Negative parameters were obtained for the two modes mentioned above, thus indicating that under increasing pressure conditions, compression occurs for these modes similar to the behaviour with increasing temperature. Evidently, the link between the high-pressure Raman study and the NTE behaviour provides additional information to help understand the NTE behaviour of *Prussian blue* and its derivatives.

Conclusions

In this brief review, we have described the variable-temperature micro-Raman spectra of CdS, CdSe, CdTe, Maya Blue, PbMoO₄ and PbCrO₄ and the high-pressure Raman spectra of PbMoO₄, the α - and β -CuPc polymorphs and *Prussian blue*. All of the pigments were relatively stable under extreme temperature conditions. The most significant changes were seen in the spectra of CdSe around 200 °C, Maya Blue above 200 °C and CdTe around 250 °C. Above these temperatures, the peaks disappeared, which suggests the possibility of crystalline to amorphous phase changes. Other minor spectral changes included changes to peak wavenumbers, intensities, and widths. Previous literature offers a plausible explanation for these spectral changes by emphasizing the dominance of anharmonicity at higher temperatures due to the collapse of a temperatureindependent force constant described by the harmonic oscillator model.⁶⁸ At higher temperatures, thermal expansion is understood to cause the shifts to lower wavenumbers of the various vibrational modes, while peak broadening is deemed to be a result of phonon decay.⁶⁸ High-pressure measurements up to ~ 5 GPa for PbMoO₄, α - and β -CuPc and *Prussian blue* were also described. The PbMoO₄ pigment only exhibited slight wavenumber shifts and peak broadening- no phase change was observed. The results for the two CuPc polymorphs afford a useful distinction between them since there is a phase change at ~ 2.0 GPa for only β -CuPc. No phase change was observed for Prussian blue, but the high-pressure measurements did provide further information on the interesting NTE behaviour of this pigment. Strikingly, all of the pigments thus far examined are remarkably stable to extreme changes in temperature and pressure. However, these non-standard conditions should now be followed by carefully examining the more modest and realistic changes in temperature, humidity and pressure that occur during the long-term storage of precious artwork in galleries, museums, attics, basements and even underground caves.^{69,70} We plan to move in this direction in the future and thus provide more direct information to the art conservationist community on the stability of certain pigments.

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