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$CoMoO_4/CuMo_{0.9}W_{0.1}O_4$ Mixture as an Efficient Piezochromic Sensor to Detect Temperature/Pressure Shock Parameters

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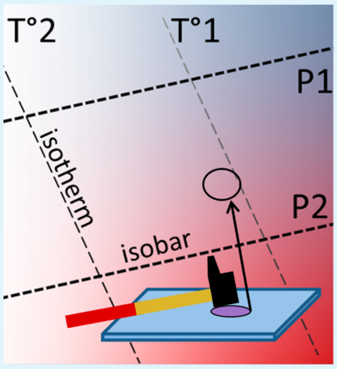
ABSTRACT: A mixture of two piezochromic compounds can be used as a universal shock detector, i.e., to determine the shock pressure without knowing a priori the temperature at which the shock occurred. For this purpose, both piezochromic compounds must exhibit different temperature influences in their transition-pressure values. This demonstration uses two piezochromic compounds ($CoMoO_4$ and $CuMoO_4$-type oxides) that exhibit a first-order phase transition between their two allotropic forms associated with a drastic color change. The colorimetric coordinates of the mixture indicate the pressure and temperature of a shock.



KEYWORDS: *oxides, chromogenic, piezochromic, shock detector*

1. INTRODUCTION

One of the most interesting properties of inorganic compounds is their capacity to change color under pressure. This phenomenon is exhibited by so-called piezochromic compounds. The most studied piezochromic compounds are metallo-organic complexes, which transition from high-spin to low-spin configurations in their metallic center under pressure.[1−5] Such sensors do not yet exist on the market, but an attractive class of iron(II) spin-crossover (SCO) molecular materials are potential candidates because they can be switched between two stable states via both temperature and pressure. Moreover, for some inorganic oxides, the piezochromic phenomenon can originate from a first order transition between two structural phases. In this field, the most studied piezochromic oxides are $AMoO_4$ (A = Co, Cu, etc.) molybdates, which are easily prepared via a solid-state route.[6−18] The first-order transition in these compounds was first mentioned by Sleight et al.,[6] and pressure-dependence phase diagrams were established for some $CuMoO_4$ compositions by Weitzel and co-workers.[7−9] Their chromogenic properties have been investigated by our team for approximately 10 years.[10−16] Indeed, a drastic color change with high optical contrast occurs for some $AMoO_4$ compositions associated with a phase transition. The two "ideal compositions", $CoMoO_4$ (a monoclinic molybdate) and $CuMo_{0.9}W_{0.1}O_4$ (a triclinic molybdate), exhibit phase transitions upon varying the temperature in an hysteresis loop with width of 500 and 100 °C, respectively. These transition loops frame the room temperature, i.e., when the transition temperatures are approximately 400 °C under heating and −100 °C under cooling for cobalt oxide and approximately 100 °C under heating and 0 °C under cooling for the copper one.[10−12] This fact makes the piezochromic compounds potential candidates as shock markers near room temperature because both allotropic forms are stable between 0 and 100 °C. Hence, the piezochromic phenomenon for both compositions can transit irreversibly from the high-temperature form (low-pressure form) to the low-temperature form (high-pressure form) when they experience an external pressure.

Piezochromic compounds can be described using two parameters, the transition pressure (P_{tr}), which is the pressure corresponding to a 50% phase transformation for the compound, and transition width (W), i.e., the pressure domain between the transition onset and ending, where complete phase transformation occurs. Some of the studies concerning these compounds demonstrated the possibility to tune the P_{tr} and W_{tr} values by modifying the particle size[13,14] and/or the dopant-ratio for $Co_{1-x}Mg_xMoO_4$[14,16] or $CuMo_{1-x}W_xO_4$.[10,11,17] The phase evolution with pressure can be followed by measuring the L^*, a^*, and b^* (or R, G, and B) color coordinates for the compound at each experimental point and representing the normalized value for these coordinates versus the pressure. Such a graph can provide the corresponding P_{tr} and W_{tr} parameters.

Here, we report that the temperature also influences the P_{tr} value. This feature, which may be considered a priori as a drawback for potential applications, allows a mixture of two piezochromic compounds to act as a shock detector capable of working at different temperatures. Measuring the color coordinates of an impacted piezochromic mixture under unknown temperature conditions can determine the pressure and temperature at which the shock occurred. To this end, the

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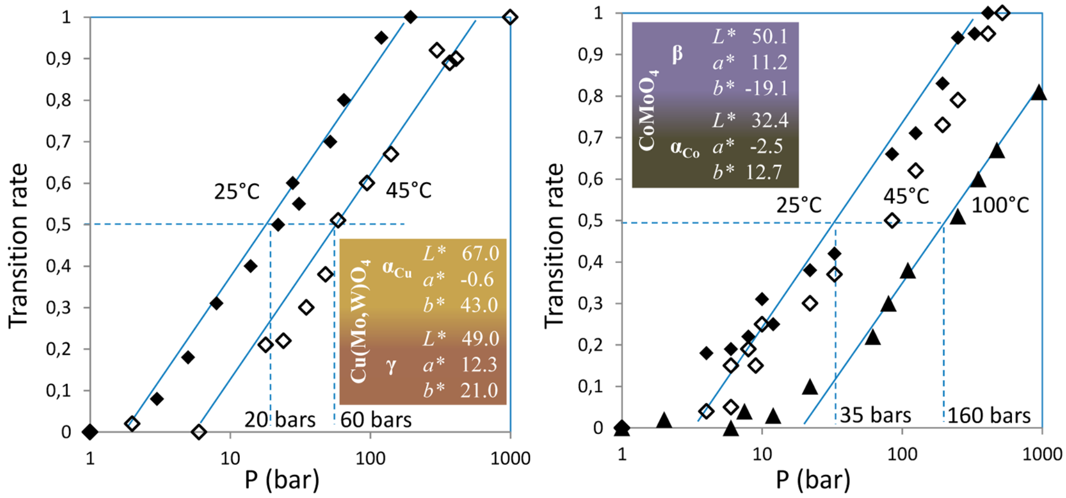

Figure 1. Transition rate versus pressure from low to high pressures for $CuMo_{0.9}W_{0.1}O_4$ (left) and $CoMoO_4$ (right) compounds at various temperatures (25, 45, and 100 °C).

experimental color coordinates must be compared to those collected in a standard grid graph composed by crossing isotherms and isobars.

2. RESULTS

2.1. Impact of Temperature on $CuMo_{0.9}W_{0.1}O_4$ and $CoMoO_4$ Piezochromic Properties. The first study used the first set of powder (100 g for each composition) prepared via the solid state process. Figure 1 shows the phase evolution versus pressure from a low-pressure (α-phase, transition rate = 0) to a high-pressure (γ-phase, transition rate = 1) form for $CuMo_{0.9}W_{0.1}O_4$ and a low-pressure (β-phase) to a high-pressure (α-phase) form for the $CoMoO_4$ piezochromic. The evolution for the copper compound has been plotted between both phases at temperatures of 298 K (25 °C) and 318 K (45 °C). The same transformation versus pressure has been plotted for the cobalt compound for three temperatures: 298, 318, and 373 K (100 °C). The colorimetric parameters associated with the pure allotropic forms (transition rate = 1 or 0) are also shown in the inset of Figure 1 for the two powders. Clearly, incrementing the temperature displaces the phase transformation to a higher pressure for both compositions. For $CuMo_{0.9}W_{0.1}O_4$, a P_{tr} value of 20 and 60 bar corresponds to 298 and 318 K, respectively. P_{tr} values of 35 and 162 bar were estimated for 298 and 373 K, respectively, for the $CoMoO_4$ composition. Furthermore, the W_{tr} parameter for both the compounds is approximately 2 orders of magnitude for the pressure regardless of the temperature. Measuring the two transformation rates versus the logarithm of the pressure can be roughly fitted using parallel lines whatever the experimental temperature. The linear dependency of the transition rate versus the applied pressure for such compounds has already been discussed in a previous study[13] based on the grain size distribution (as evidenced by the SEM measurements). The piezochromic pressure for one grain is impacted by the grain size, whereas the transition for each grain is extremely rapid (domino cascade transition).[16] Large grain size distributions are considered the main source behind the 100 °C transition width (W parameter). Moreover, the temperature effect on the transition pressures is more pronounced for the copper compound. Therefore, a larger phase transition displacement was observed when the experimental temperature increased. For example, curves obtained at 25 and 45 °C are largely separated for the $CuMo_{0.9}W_{0.1}O_4$ compound whereas they are nearly superimposed for the $CoMoO_4$ compound.

Using the phase evolution curves versus pressure at various temperatures for a single piezochromic pigment indicates the pressure at which a shock has occurred in a piezochromic compound by measuring the corresponding color coordinates after the shock; however, this capability requires knowing the temperature at which the shock occurred. However, as explained below, two piezochromic compounds with differing temperature effects for their P_{tr} form a mixture capable of indicating not only the pressure but also the temperature of a shock.

2.2. Modeling a *T* and *P* Shock Parameters Sensor. To confirm this idea, a model considering two hypothetical piezochromic compounds, A and B, with equivalent piezochromic properties to $CuMo_{0.9}W_{0.1}O_4$ and $CoMoO_4$ was made. The aim was to determine what concrete temperature−pressure information could be deduced from the color parameter evolution (in *RGB* or L^*, a^*, and b^*) for a mixture of compounds with differing temperature effects on their pressure-induced transformation. To focus only on this concept, two hypothetical compounds with drastically different colors and drastic color changes versus pressure were proposed. Although the experiment was developed in terms of L^*, a^*, and b^* (the parameters used by the color-measuring technique), the color-point graphs that support this theoretical study (Figure 2) are in *RGB* because this color spall is available via the software used to create the graphs. We suppose compound A transitions under pressure from black ($R = 0$, $G = 0$, $B = 0$) to white ($R = 250$, $G = 250$, $B = 250$) and B transitions from red ($R = 250$, $G = 0$, $B = 0$) to green ($R = 0$, $G = 250$, $B = 0$) (Figure 2a). The situation shown in Figure 2a corresponds to a certain temperature (T_0), if it is incremented based on this parameter, the phase transitions for both compounds would move to higher pressures as previously discussed (see Figure 1). This trend supposes each hypothetical compound has a different temperature influence for its P_{tr} with the same W_{tr} parameter, as characterized for $CuMo_{0.9}W_{0.1}O_4$ and $CoMoO_4$. Thus, Figure 2b,c shows the difference in pressure between the phase-transitions for compounds A and B is larger or smaller depending on the temperature. If A and B are mixed, we

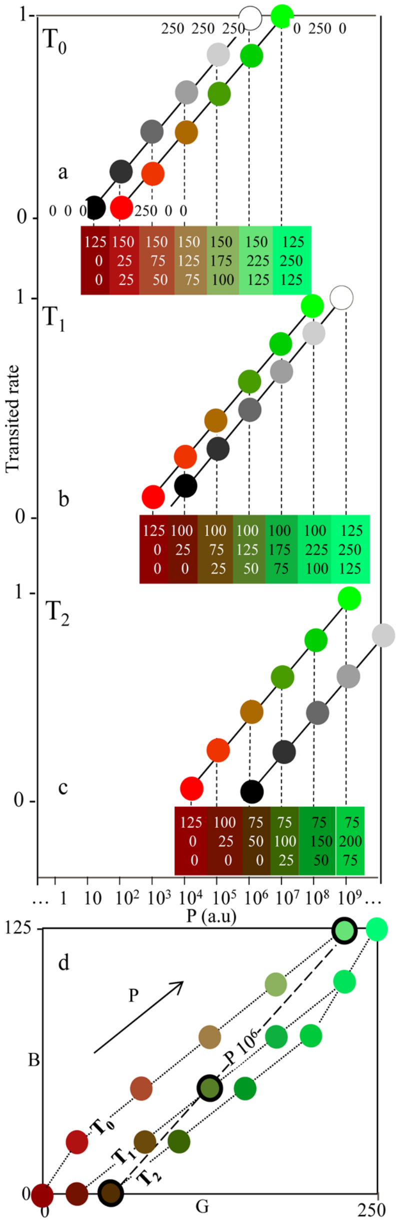

Figure 2. Phase transition with pressure for two hypothetical compounds at three temperatures, T_0, T_1, and T_2 (a, b, and c, respectively). d shows the isotherms (T_0, T_1, and T_2) and isobar ($P = 10^6$ a.u.) formed by the color-points (B−G values) for the mixture.

consider the resultant color parameters for the mixture (T and P) as an average of those corresponding to the compounds under the same conditions. The *RGB* values of the A−B mixture at different pressures have been indicated for each temperature (see values in color-squares). Figure 2d shows the B−G values (color-points) corresponding to the mixture under different (T and P) conditions. Because both compounds experience different temperature influences on their P_{tr}, a grid graph containing different color-points linked by isotherms and isobars can be obtained (Figure 2d). Therefore, when this piezochromic-mixture is subjected to an unknown pressure at an unknown temperature, measuring the B-G parameters and placing them on the corresponding grid graph can indicate the concrete pressure and temperature at which the shock occurred.

2.3. Experimental Section. To carry out this experimental study, a 50% weight mixture of $CoMoO_4$ and $CuMo_{0.9}W_{0.1}O_4$ was prepared using the first set of powders. These compounds were chosen because their high- and low-pressure polymorphs are stable at room temperature, and temperature exhibits differing influences over their P_{tr} value.

The color evolution was studied using the visible spectroscopy for temperatures and pressures corresponding to the molybdate compound and a mixture of both (Figure 3). The spectra corresponding to the low- and high-pressure forms of the $CoMoO_4$ and $CuMo_{0.9}W_{0.1}O_4$ piezochromic compounds are shown in Figure 3a,b, respectively. Spectra corresponding to the mixture at low and high pressures are also shown in Figure 3c,d, respectively, along with those corresponding to the low- and high-pressure form of each molybdate compound to facilitate comparison. The mixture spectrum always remained

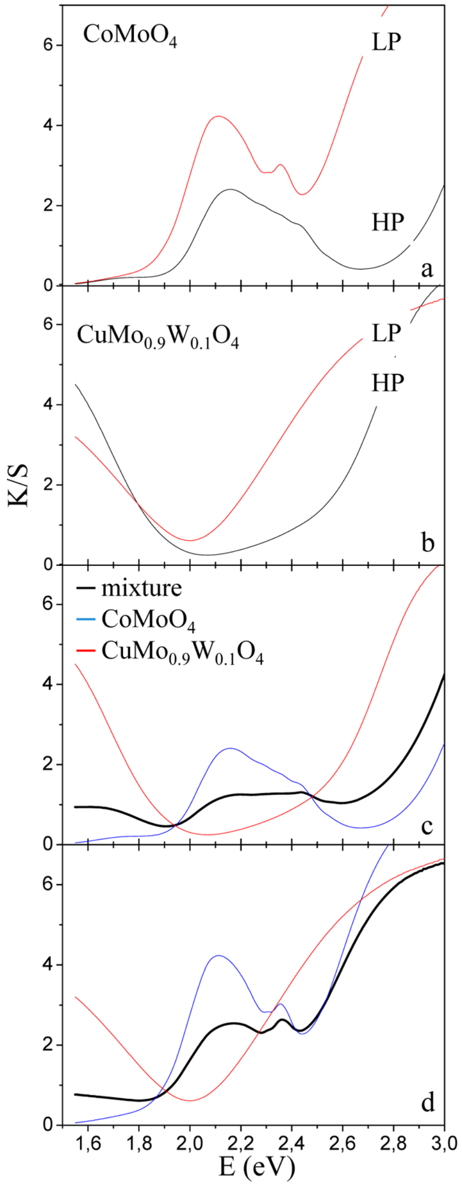

Figure 3. Visible spectra corresponding to the low-pressure (LP) and high-pressure (HP) for $CoMoO_4$ (a) and $CuMo_{0.9}W_{0.1}O_4$ (b). c and d show the spectrum corresponding to the mixture treated at low and high pressures, respectively.

between the spectra for the molybdate compounds, which agrees with the assumption that the mixture color parameters are an average of those for the corresponding molybdates (Figure 2).

The graph in Figure 4 shows the experimental L^*-a^* values obtained for a 50% weight mixture of $CoMoO_4$ and $CuMo_{0.9}W_{0.1}O_4$ subjected to several (*T* and *P*) values. A color evolution can be seen for the experimental points with the temperatures and pressures forming a grid graph of distinguishable isotherms and isobars. These color-points are depicted using the experimental color coordinates the mixture presents. The visualization of the L^*-a^* plane can provide concrete (*T* and *P*) information. Other visualization planes, such as L^*-b^* or b^*-a^*, exhibit crossing points between the different isotherms, which implies two (*T* and *P*) values for a certain L^*-a^* (or b^*-a^*) value. Actually, the b^* parameter is, in our case, a nondiscriminant colorimetric parameter.

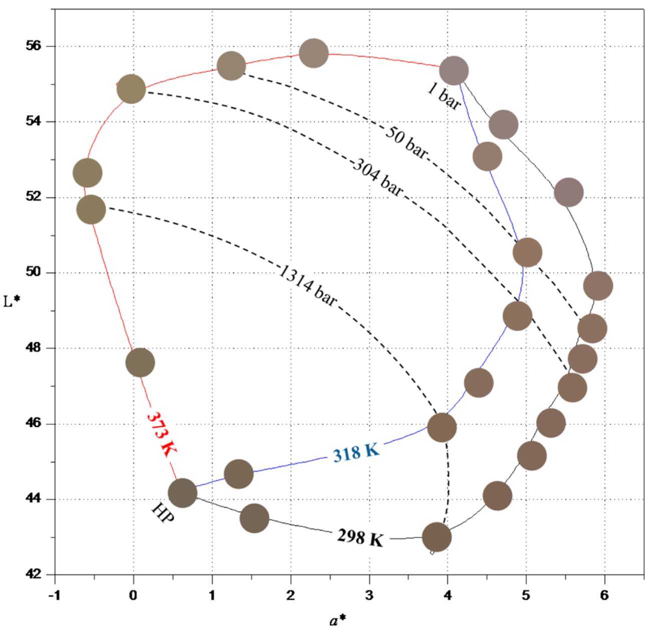

Figure 4. Colors for the 50% weight $CoMoO_4$ and $CuMo_{0.9}W_{0.1}O_4$ mixture (first-set) after shock (*T*° and P) in L^*-a^* graph (some isotherms and isobars are plotted).

At this stage, the reproducibility and accuracy of these experiments for the determined pressure−temperature shock parameters are questionable. A second set of powder was prepared. First, the colors of these new powders ($CoMoO_4$ and $CuMo_{0.9}W_{0.1}O_4$ compounds) are not identical to the first set. Some slight changes in the crystallite size distribution and/or cationic homogeneity probably caused these slight colorimetric changes. For comparison, a 50% weight mixture of the high temperature forms for $CoMoO_4$ and $CuMo_{0.9}W_{0.1}O_4$ subjected to several (*T* and *P*) values as shown in Figure 4 yielded initial parameters of $L^* = 55.5$ and $a^* = 4.05$; the new 50% weight $CoMoO_4$ and $CuMo_{0.9}W_{0.1}O_4$ mixture exhibited $L^* = 54.5$ and $a^* = 3.15$. Notably, the difficulty to exactly reproduce the colorimetric parameters between two sets of powders requires one measurement series to be tested per powder mixture. As for the study shown in Figure 4, the experimental L^*-a^* values obtained for the 50% weight $CoMoO_4$ and $CuMo_{0.9}W_{0.1}O_4$ mixture subjected to several (*T* and *P*) values was reported for this second powder set. Nevertheless, this new study focused only on four proximal (*T* and *P*) values, (40 °C, 500 bar), (60 °C, 500 bar), (40 °C, 750 bar), and (60 °C, 750 bar), with at least four repeated measurements for each pair to evaluate the associated error for all of the (*T* and *P*) pairs. The accuracy was limited by the grid graph positioning accuracy, which could be improved by increasing the number of measurements. The grid graph obtained is plotted in Figure 5 from the colorimetric values obtained and reported in Table 1.

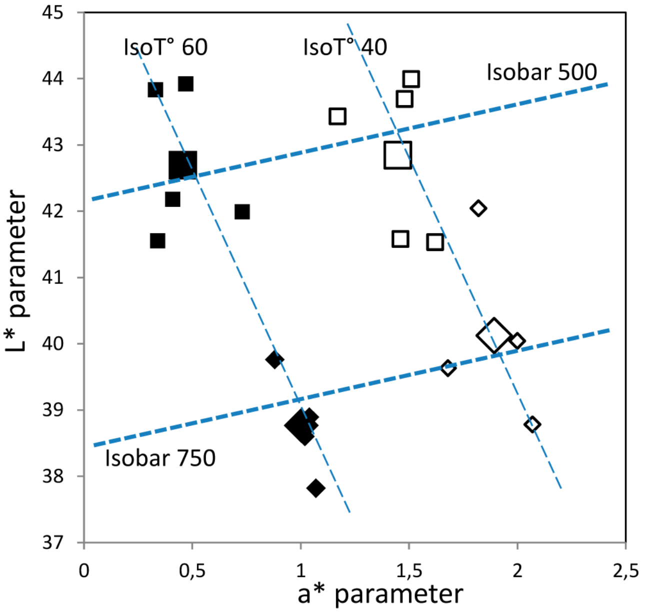

Figure 5. Colors for the 50% weight $CoMoO_4$ and $CuMo_{0.9}W_{0.1}O_4$ mixture (second-set) after shock (*T*° and P) in L^*-a^* graph. Each symbol corresponds to a point for the mixture submitted at the same (*T*, *P*) shock parameters: empty squares for (40 °C, 500 bar); full squares for (60 °C, 500 bar); empty rhombuses for (40 °C, 500 bar); full rhombuses for (60 °C, 500 bar). The largest symbols represent the average values.

This study confirmed that the isobars and isotherms can be well separated for the considered (*T* and *P*) values, i.e., our mixture distinguishes the four (*T* and *P*) shock parameters. The positioning accuracy for the grid graph was then extracted from the calculated error bars and is reported in Table 1 considering the standard deviations for each (*T* and *P*) couple parameters and using a τ student factor equal to 2.78 for four averaged points and 2.57 for five points. The error bar was approximately 0.2 for the a^* coefficient and 1.5 for the L^* parameter. The pseudosquare edges obtained from the four average points corresponding to the four studied (*T* and *P*) shock parameters were approximately three times these error bars. Hence, a shock yielding the colorimetric parameters in the center of the pseudosquare plotted in Figure 5 corresponds to a pressure between 500 and 750 bar and a temperature between 40 and 60 °C.

Finally, the grid graphs (Figures 4 and 5) can be explained using the scheme shown in Figure 6. The luminosity decreased with pressure for both molybdates in the mixture. However, while the a^* parameter decreases for $CoMoO_4$ from low- to high-pressure, it increased for $CuMo_{0.9}W_{0.1}O_4$. These two considerations mean the luminosity decreases regardless of the mixture temperature when subjected to pressure because both molybdates respond similarly. In contrast, if the mixture is at T_0 under a low pressure (upper-right side of the graph), its a^*

Table 1. L^*−a^*−b^* Colorimetric Parameters with Standard Deviations and Error Bars Corresponding to Four Different (T, P) Shock Parameters

(60 °C, 500 bar)	a^*	L^*	b^*	(60 °C, 750 bar)	a^*	L^*	b^*
	0.73	41.99	20.09				
	0.34	41.55	18.44		1.04	38.89	18.44
	0.47	43.92	19.12		1.07	37.82	19.12
	0.33	43.83	19.13		0.88	39.76	19.13
	0.41	42.18	18.86		1.02	38.6	18.86
average value standard	**0.46**	**42.69**	**19.13**	average value standard	**1.00**	**38.77**	**19.13**
deviation	0.16	1.10	0.61	deviation	0.08	0.80	0.61
error bar (95%)	**0.19**	**1.27**	**0.70**	error bar (95%)	**0.12**	**1.11**	**0.84**
(40 °C, 500 bar)	a^*	L^*	b^*	(40 °C, 750 bar)	a^*	L^*	b^*
	1.62	41.53	18.34				
	1.46	41.58	18		2	40.04	18.6
	1.48	43.69	19.13		1.68	39.63	18.36
	1.51	43.99	18.62		2.07	38.78	19.3
	1.17	43.43	19.23		1.82	42.04	19.53
average value standard	**1.45**	**42.84**	**18.66**	average value standard	**1.89**	**40.12**	**18.95**
deviation	0.17	1.19	0.52	deviation	0.18	1.38	0.56
error bar (95%)	**0.19**	**1.37**	**0.60**	error bar (95%)	**0.25**	**1.92**	**0.77**

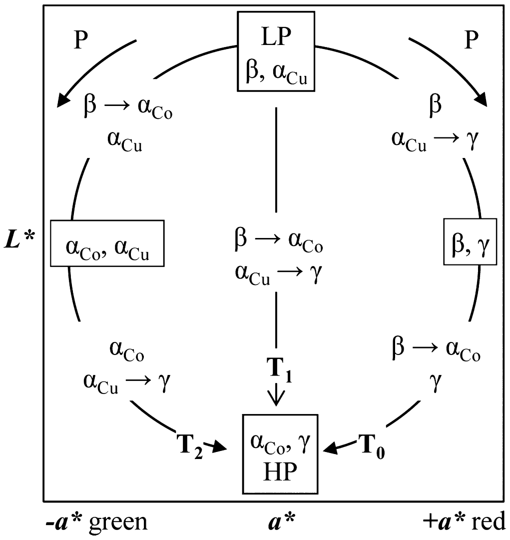

Figure 6. Scheme representing the L^* and a^* parameter evolution with temperature and pressure for the piezochromic mixture according to the $CoMoO_4$ and $CuMo_{0.9}W_{0.1}O_4$ phase transformations.

parameter increases due to a nonphase transition for $CoMoO_4$ and a gradual phase transformation for $CuMo_{0.9}W_{0.1}O_4$ (↑a^*). The maximum value for this parameter corresponds to an untransited Co-molybdate and a completely transited Cu-molybdate. If the pressure increases further at a low temperature (T_0), (lower-right side of the graph), the a^* value for the mixture decreases due to the gradual transformation of the Co-molybdate compound (↓a^*). Because the transformation for both phases is influenced by the temperature and this effect differs between the compounds, opposite phenomena were found with increasing pressure at a high temperature (T_2). At such a temperature under a low pressure (upper-left side of the graph), $CoMoO_4$ begins to transit (↓a^*), which reduces the a^* value of the mixture. This parameter reaches a minimum when $CoMoO_4$ has completely transformed and $CuMo_{0.9}W_{0.1}O_4$ has not begun to transit. Increasing the pressure (lower-left side of the graph) causes Cu-molybdate to transit (↑a^*), which increases the a^* value. Between the evolutions observed at T_0 and T_2, the situation at T_1 occurs where both compounds respond similarly to pressure with a gradual phase-transformation. Therefore, while the a^* value decreases in $CoMoO_4$, it increases in $CuMo_{0.9}W_{0.1}O_4$, which results in a negligible variation of the a^* parameter for the mixture.

3. CONCLUSIONS

The first part of this paper theoretically demonstrated that a mixture of two piezochromic compounds can be used as a universal shock detector at different temperatures. This use requires the piezochromic compounds to exhibit differing temperature influences for their P_{tr} value so the mixture color evolution depends on both the pressure and temperature. In a second experiment, a mixture of two different molybdate compounds exhibited to indicate the pressure and temperature of a shock. This transformation was measured using a visible spectra and experimental L^* and a^* values to determine a graph formed of isotherms and isobars. Determining exact error bars for each (T and P) shock parameter extracted from the color mixture after a shock is difficult. Indeed, the accuracy of the determined parameter is mainly linked to the accuracy of the grid graph positioning (isotherms/isobars) for the powder mixture. Furthermore, the accuracy differs depending on the (T and P) parameters. An obtained color with $L^* = 41$ and $a^* = 1.5$ for the second mixture was reasonably associated with a shock at a pressure of 625 bar (±125 bar) and temperature of 50 °C (±10 °C). This accuracy can be increased by optimizing the mixture formulation, modifying the piezochromic compound composition to increase optical contrast, etc. For example, our team is currently working on elaborating luminescent molybdates; luminescent spectra provide a more sensitive shock parameter characterization because the various changes, luminescence intensity, spectral distribution, and lifetimes, can all be used as complementary data.

The few shock detectors currently available on the market, for example, Fujifilm sensors (www.fujilfilm.eu), are only able to indicate the shock pressure when the exact temperature for the shock is known. In addition, the pressure parameter for such systems is significantly affected by humidity, i.e., one must know the atmospheric humidity/temperature at the moment

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the shock occurred to deduce the shock pressure. For these reasons, this work constitutes a break-through and represents a significant step in smart-paintings research for shock detection.

4. EXPERIMENTAL PROCEDURES

$CoMoO_4$ and $CuMo_{0.9}W_{0.1}O_4$ were synthesized via the ceramic method. Stoichiometric amounts of the corresponding oxides were mixed in an agate mortar and thermally treated in an alumina crucible at 700 °C for 20 h in air. Two different powder sets were prepared in sufficient quantity to perform these experiments. The first powder set was used for the first experiments, which included the work described in Figures 1, 3, and 4. The second powder set was synthesized 1 year later and used to evaluate the shock sensor performance robustness (work reported in Figure 5). The resulting solids were characterized by X-ray diffraction using a D8 Bruker diffractometer equipped with a Vantec position-sensitive detector in a Bragg−Brentano geometry. Pure CuK−L3 radiation was obtained using a germanium monochromator. The 5° to 120° 2 h range data collection with an acquisition time of 12 s per step was performed at room temperature using a sieved powder gently deposited into the cylindrical cavity of a Plexiglas plate. The piezochromic behavior was characterized up to 3000 bar by applying a uniaxial pressure with an as-scale pan balance system or pellet press depending on the desired P value.

CIE-Lab parameters were determined by mathematically treating the reflectivity curves obtained for powders with a Cary 17 spectrophotometer equipped with an integration sphere.

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Notes

The authors declare no competing financial interest.

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