Effect of W doping on phase transition behavior and dielectric relaxation of CuMoO₄ obtained by a modified sol-gel method

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Abstract

Tungsten (W)-doped copper molybdate (CuMo₁₋ₓWXO₄, x = 0~0.12) compounds were prepared by the sol-gel method. The effects of doping content on the phase transition behavior and dielectric properties of CuMo₁₋ₓWXO₄ (x = 0~0.12) were investigated. X-ray diffraction and UV–vis diffuse reflectance spectroscopy clarified that W doping facilitated the transition of green α-phase to brown γ-phase. The chemical composition and structure of the CuMo₁₋ₓWXO₄ (x = 0~0.12) were investigated by Fourier transform infrared (FT-IR) spectroscopy and Raman spectra. The dielectric spectra of CuMo₁₋ₓWXO₄ at −130 °C~150 °C and the color change of CuMo₀.₉₄W₀.₀₆O₄ at 20 °C~50 °C illustrated that the phase-transition temperature moves toward high temperature with increasing W. The functional relationship between the electrical modulus M’ and the frequency (1 Hz~10 MHz) indicated that there are two dielectric relaxation mechanisms for CuMo₁₋ₓWXO₄, which correspond to the polarization relaxation caused by hopping motion of polaron at low-temperature region (R₁) and the relaxation dominated by oxygen vacancies at high temperatures (R₂). It has also been confirmed that the phase transition of relaxation type exists in CuMo₁₋ₓWXO₄ at α-phase and R₂ occurs in γ-phase, and that R₁ occurs in γ-phase and R₂ occurs in α-phase. It is of great significance to establish the dielectric relationship between phase transition and relaxation. With the content of W, the intensity of relaxation peak and activation energy of R₁ did not change too much, but the relaxation behavior of R₂ was inhibited and the activation energy increased gradually. The above results show that dielectric spectra are an important discovery as a new method to study the phase transition of materials, and is conducive to exploring the motion state of micro-particles. The control of phase-transition temperature is of great significance for this thermochromic material as a temperature sensor.

1. Introduction

AMoO₄ (A refers to transition-metal ions) compounds have attracted wide attention because of their thermochromic properties, and have great potential applications in temperature sensors. Among them, CuMoO₄ was most widely studied [1–5]. It was believed that the thermochromic properties of CuMoO₄ originate from the reversible first-order phase transition of α-CuMoO₄ (green) and γ-CuMoO₄ (red-brown) during temperature and pressure change [6–8]. Therefore, the material can also be used as pressure indicators [2]. The phase-transition temperature of CuMoO₄ is generally within the range of 200 to 250 K [9, 10]. Whether as a pressure sensor or a temperature sensor, precise control of its phase-transition temperature is the key to the practical application. Chemical doping is often an important means to control the phase-transition temperature. At present, it has been reported that the phase transition temperature can be controlled by doping at A site or B site. Ikuo Yanase et al [11] found that the phase-transition temperature gradually shifted to high temperature with the increase of doping content by replacing Mo with W in CuMoO₄, while Robertson et al [12]...
found that the phase-transition temperature shifted to low temperature with the increase of doping content by replacing Co with Mg in CoMoO₄. Ikuo Yanase et al. further studied the effect of Zn-doped CuMoO₉₋ₓWₓO₄ on the phase transition and thermochromism properties. The results showed that Zn-doped CuMoO₉₋ₓWₓO₄ promoted the transition of the α-phase into the γₐ-phase, and made the color change more remarkable. Therefore, it is of great significance to provide more information on the phase transition of CuMoO₄ system for the development of CuMoO₄ as a sensor. At present, there are many methods for the preparation of molybdate. The common ones are sol-gel method and traditional solid-state reaction method. Here is a summary of the preparation methods of molybdate as shown in table 1.

Dielectric spectra are usually used to evaluate the dielectric properties (dielectric constant, dielectric loss) of materials. However, very few attentions have been focused on studying the dielectric properties of CuMoO₄ system. Our assumption is whether the phase-transition characteristics during the heating process can be better reflected in the dielectric spectra. In the current work, the dielectric properties of CuMo₁₋ₓWₓO₄ (x = 0–0.12) compounds were studied from −130 to 150 °C and 1 Hz to 10 MHz. As expected, the dielectric spectra of CuMo₁₋ₓWₓO₄ (x = 0–0.12) exhibited the phase-transition characteristics. And, an interesting phenomenon that the position of phase-transition peak moves to high temperature with increasing the content of W was also be found. The discovery of this work paves a new way for the study of structural phase transition in materials by dielectric spectra.

Dielectric spectra can not only reflect the phase transition process of materials, but also play an important role in studying the relaxation behavior of micro-particles. According to the current work, CuMo₁₋ₓWₓO₄ system mainly consists of two relaxation mechanisms, relaxations are located in the low-temperature and high-temperature regions. It is worth noting that the temperature where the two relaxations are disconnected corresponds to the measured phase transition temperature, so the first-order phase transition in CuMo₁₋ₓWₓO₄ system is also called phase transition of relaxation type. This is of great significance to the establishment of dielectric relationship between phase transition and relaxation.

2. Experimental

The CuMo₁₋ₓWₓO₄ (x = 0–0.12) (hereafter, CMW) sample was prepared by a modified sol-gel method using high purity (>99.9%) Cu(NO₃)₂, ammonium tungstate, citric acid (C₆H₈O₇·2H₂O), ammonium molybdate ((NH₄)₆MoO₂⁴·4H₂O), concentrated nitric acid and ammonia water. The analytically pure copper nitrate, ammonium molybdate and ammonium tungstate were separately dissolved in deionized water and mixed in proportion, then citric acid was added to the mixed solution in a molar ratio of citric acid to the metal cation of 2:1, and the pH of the solution was adjusted to 1. The mixed solution was heated (40 °C) and stirred for 5 h and then evaporated rapidly at 100 °C until a sol was formed on a magnetic stirrer. The sol was calcined in air and then annealed in a muffle furnace (500 °C) to obtain the desired powder. The required CMW ceramics can be obtained by compacting the powder into a cylindrical billet with a diameter of 12 mm and a thickness of about 2 mm under 8 MPa, and finally sintered at 750 °C for 5 h.

The structural phase of the CMW powder was characterized by x-ray diffractometry (XRD, Rigaku SmartLab). Thermal analysis was performed using a differential scanning calorimeter (DSC, TA Q20). To clarify the relationship between color change caused by structural transition and optical properties in CMW ceramics, the diffuse reflectance spectra of CMW powders were measured by UV–vis–NIR spectrophotometer (SolidSpec-3700). Fourier transform infrared spectroscopy (FTIR) spectra were gained using a Nicolet 6700.

| Table 1. The summary on the preparation methods of molybdate. |
|----------------------|------------------------|
| Methods              | Process |
| Solid-state reaction | The constituent oxides Cu₂O, MoO₃, and WO₃ were intimately mixed in the prerequisite proportions, in an agate mortar. Then, the mixture was ball-milled in an agate container partially filled with acetone. The blend was calcined at 750 °C for 24 h and cooled down to RT [6]. |
| Sol-gel              | A citric acid (CA) solution was added to an equimolar solution of ammonium molybdate and copper salt in a proportion such that CA/cation≤1/3; the pH was close to pH1. The evaporation of the solution at 80 °C led to the formation of gels named G (i is the source of copper; i=1 nitrate, i=2 chloride, and i=3 acetate). The gels were dried at 120 °C for 24 h, then pre-calcined at 300 °C for 12 h [14]. |
| Sonochemical         | Appropriate amounts of Cu(NO₃)₂·6H₂O and (NH₄)₆MoO₂⁴·4H₂O were used as the Cu and Mo sources. In a typical synthesis (NH₄)₆MoO₂⁴·4H₂O and Cu(NO₃)₂·6H₂O were dissolved in 30 ml distilled water, respectively. Then Cu(NO₃)₂·6H₂O was heated at 50 °C for 10 min and finally the (NH₄)₆MoO₂⁴·4H₂O solution was added drop wise to this solution and solution was heated at 45 °C and finally treated with ultrasonic irradiation with power 50 W. The white product was filtered, washed with distilled water and ethanol several times. The final product obtained was dried at 60 °C for 60 min [15]. |
spectrophotometer (3300 to 400 cm$^{-1}$). Raman spectra were surveyed with a Renishaw in Via Raman spectrometer with a holographic notch filter and a CCD detector. The silver paste was applied to both sides of the samples and then calcined in a furnace to obtain silver electrode. The dielectric properties of the ceramic samples were measured by wide temperature broadband dielectric analyzer (Novocontrol Concept50) in the temperature range of $-130$ °C$\sim 150$ °C and the frequency range of 1 Hz$\sim 10$ MHz. X-ray photoelectron spectroscopy (XPS, ESCALAB 250) was used for valence analysis of elements.

3. Results and discussion

Figure 1 shows the room-temperature XRD pattern of CMW powder sintered at 750 °C. Comparing with the standard JCPDS cards of $\alpha$-CuMoO$_4$ (73–0488) and $\gamma$-CuMoO$_4$ (85–1529), it was confirmed that all the prepared powders were W-substituted single-phase ($\alpha$-phase) CuMoO$_4$ compounds, and a new $\gamma$-phase was formed. The ratio of $\gamma/\alpha$ increases with increasing the content of W in CMW. It is worth mentioning that the fundamental reason for the phase transition is that the crystal structure of the $\gamma$-phase consists of octahedral CuO$_6$ and MoO$_6$. When the $\gamma$-phase is transformed into the $\alpha$-phase, one-third of the octahedral CuO$_6$ becomes a square pyramid CuO$_5$, and all the octahedral MoO$_6$ become tetrahedral MoO$_4$ and vice versa [11].

Figure 2(a) shows the room-temperature color change of CMW powders sintered at 750 °C. It can be observed that CMW powders have obvious differences in color, and each color is stable at room temperature. The color shifts from green to brown with the increase of W. This is consistent with the color change caused by structural phase transition for CuMoO$_4$ system as reported previously [3, 16, 17]. When CMW powders were heated from 20 to 50 °C, the color changed from light brown to yellowish green as shown in figure 2(b), which indicated that the $\gamma$-phase CMW also undergoes phase transition after heating. According to the fact that the ratio of $\gamma/\alpha$ increases with increasing W, the effect of W doping on the phase transition and thermochromism of CMW compounds was explained. The phase-transition behavior of CMW ceramics will be further studied by dielectric measurements in the later section.

Figure 3(a) shows the temperature dependence of dielectric loss tan $\delta$ of CMW ($x = 0\sim0.12$) at the same frequency. It is an intriguing and valuable discovery that there is an upward dielectric-anomaly peak in the curve for all the samples, and the position of the peak moved towards high temperature with increasing the doping content of W. Many studies have demonstrated that CuMoO$_4$ undergoes a first-order phase transition ($\gamma \rightarrow \alpha$) from low temperature to high temperature [9, 18–20], and the phase-transition temperature ranges from 200 to 250 K under the environmental pressure [9, 10]. Therefore, it is reasonable to believe that CuMoO$_4$ has a phase-transition peak of relaxation type with dielectric properties. And the phase-transition peak moved towards high temperature with increasing the content of W. In other words, the phase-transition temperature from $\gamma$-phase to $\alpha$-phase increased gradually in CMW. It is worth noting that the concept of ‘phase transition of relaxation type’ is shown in figure 3(b). The left side of the dielectric peak changed obviously with increasing the frequency, while the right side was combined. In addition, the temperature of phase transition is a temperature region rather than a temperature point. The dielectric-anomaly peak corresponding to phase transition in the dielectric spectrum become wider, and thus it can be inferred that this is a diffusive phase transition. Therefore, both
phase-transition process of adjustable-temperature and dielectric relaxation behavior exist in CMW, and the relationship between the two modes will be elaborated in the following work.

The characteristic of structural transition caused by heating or cooling for CMW was thoroughly embodied in DSC. Figure 4 shows the DSC patterns of CMW powders during heating process. A group of downward endothermic peaks indicated that phase transition exists in CMW, and the position of phase-transition peak moved toward high temperature with increasing the doping content of W. The impact of W doping on the structural behavior of CMW ceramics is very similar to the dielectric behavior shown in figure 3(a). Therefore, it can be concluded that there was a structural phase-transition process in CMW, and the phase-transition peak moved towards high temperature with increasing W content.

The result can be attributed to the phase-structure change of W-doped CuMoO₄. In the polymorph α-CuMoO₄, stable at high temperature, the Cu²⁺ ions are located both in octahedral (CuO₆) and in pyramidal (CuO₅) sites. The Mo⁶⁺ cations are in tetrahedral environment (MoO₄) [2, 18]. In the polymorph γ-CuMoO₄, stable at low temperature, both metallic cations are in octahedral environment [2, 18]. In the polycrystalline γ-CuMoO₄ stable at low temperature, both metal ions are in octahedral environment [2, 18]. With the increase of x value, the shift of transition temperature can be understood as the transformation of γ-phase to α-phase of CMW due to heating, that is, one third of octahedral CuO₆ is transformed into square cone CuO₅, and octahedral MoO₆ is transformed into tetrahedral MoO₄. The above statement is in accordance with the report that in tungsten doped copper molybdate CuMo₁₋ₓWₓO₄ (x = 0.06, 0.12), the transition temperature is dependent upon the tungsten content [11].

The optical properties of CMW powders were studied by UV–vis-NIR diffuse reflectance spectra as shown in figure 5(a). It can be seen that the wavelength corresponding to the diffuse reflectance peak increased gradually with increasing W content, which was closely related to the existence of the ratio of γ/α in the system. There are two reflection bands in CMW powders. The reflection band with wavelength less than 600 nm corresponding to x = 0~0.03 was mainly attributed to the charge transition of O²⁻ → Cu²⁺ and O²⁻ → Mo⁶⁺ [6, 16, 21]. The reflection band with wavelength higher than 600 nm corresponding to x = 0.06~0.12 was mainly attributed to the d-d transition of Cu²⁺ [16, 21]. It should be noted that with the increase of x value, the diffuse reflection peaks showed a red-shift trend. It is reported that the red shift of reflection peaks may be caused by the smaller lattice constant. Therefore, the red shift could be attributed to the volume reduction, which was caused by a part of the CuO₆ octahedron gradually became CuO₅ hexahedron [22]. To further elaborate the influence of W doping on the optical properties of CMW, the optical band gaps were calculated by equation (1).

$$\alpha h\nu = A(h\nu - E_g)^{1/2}$$

where, α, h, ν, A and Eg represent the absorption coefficient, Plank constant, incident light frequency, proportionality constant, and band energy, respectively. The relationship between ($\alpha h\nu$)$^2$ and energy (hν) was finally obtained by calculating and processing complex data, as shown in figure 5(b). The band gap energies of
the samples (2.62 eV, 2.55 eV, 2.48 eV, 2.37 eV, 2.20 eV) were calculated according to the intercept of the tangent lines. The above results show that the color change was caused by the difference of optical band gap of CMW powders, and the band gap energy decreased with the increase of W content in CMW.

The FTIR is used to check for changes of the structural units for CMW (figure 6(a)). The spectra exhibited the typical absorption bands for CuMO₄ at 965, 955, 900, 875, 820, 800, 750, 725, and 495 cm⁻¹, and partial absorption bands for CuWO₄ at 900, 750, 720, 615, 560, 470, 420 cm⁻¹. The band at 965 cm⁻¹ corresponds to stretching modes of Mo=O double bonds. As the value of x increases, the position of the peak moves to the right. It was considered that the part of Mo was replaced by w to form a new W–O bond [15]. And the bands at 875 and 820 cm⁻¹ are assigned to stretching vibrations of Mo–O–Mo bridging bonds. The band 750 cm⁻¹ is due to the vibrations of WO₂ entity present in the W₂O₈ groups. The bands at 720 and 615 cm⁻¹ are typical of a two-oxygen bridge species (W₂O₄), and they are due to the asymmetric stretching vibrations of the same units. The vibrations of the CuO₆ polyhedra are in the absorption range below 600 cm⁻¹ [23–25].

As Raman spectra is more sensitive in characterizing the change of crystal structure than XRD, it was studied that the variation of Raman spectrum of CMW with different doping amount as shown in figure 6(b). The MoO₄ tetrahedra molecular groups with strong covalent bond are peculiar to the molybdates and exhibit active modes. It has a weak coupling with Cu²⁺ cations and hence the vibrational modes obtained are low [4]. The difference of
Figure 4. DSC pattern of CMW (x = 0–0.12) powders.

Figure 5. (a) shows the UV–vis diffuse reflectance spectra of CMW (x = 0–0.12) powders, (b) shows the relationship between (αhv)² and energy (hv) in CMW (x = 0–0.12).
Raman spectra among the entire series CMW ceramics is obscure, but the Raman peaks of 800 and 950 cm\(^{-1}\) changed obviously with the increase of x value. It is only one Raman vibration peak in CMW (X = 0, 0.03) ceramics, when two Raman vibration peaks are detected in CMW (X = 0.06, 0.09, 0.12) ceramics. Obviously, the result of Raman spectra of the whole series CMW ceramics is consistent with XRD [26].

Generally, the main method of studying dielectric relaxation is to establish the functional relationship between dielectric parameters (dielectric constant (\(\varepsilon\)), dielectric loss (tan \(\delta\)), electrical modulus (M), etc) and frequency, and this functional relationship can reflect the relaxation phenomena intuitively. However, it is often impossible to observe the complete relaxation signal due to the strong background. To effectively eliminate the complex background and better present the useful relaxation phenomenon, the dielectric relaxation mechanism was studied directly by using the electrical modulus M' (M is the imaginary part of the electrical modulus M) as a function of frequency [10, 27]. The M' was calculate according to the following equation.

\[
M = 1/\varepsilon
\]  \hspace{1cm} (2)

\[
M = M' + jM''
\]  \hspace{1cm} (3)

where \(j\) is an imaginary unit, and \(M'\) and \(M''\) represent the real part and the imaginary part of the electric modulus, respectively.

Figure 7(a) shows the frequency dependence of the electrical modulus M' of CuMoO\(_4\) at different temperatures. It can be clearly seen that there are two groups of characteristic peaks, and the positions of each group of peaks moved towards high frequency with increasing temperature. This phenomenon is called relaxation behavior. These two relaxations correspond to the relaxation 1 of the low-temperature segments (\(-130^\circ\text{C} \sim 50^\circ\text{C}\)) and the relaxation 2 of the high-temperature segments (\(-30^\circ\text{C} \sim 150^\circ\text{C}\)), respectively, and they were named as R1 and R2. It should be noted that the temperature change from R1 to R2 (\(-50^\circ\text{C} \sim 30^\circ\text{C}\)) was exactly similar to the phase-transition temperature mentioned earlier in CoMoO\(_4\), which confirmed that the
phase transition belongs to phase transition of relaxation type in CMW. Therefore, it can also be concluded that R1 occurred in the $\gamma$-phase and R2 occurred in the $\alpha$-phase. Since these two kinds of relaxations are related to the temperature, it indicates that there is a thermally activated relaxation process in CMW. The activation energy is helpful to better understand the relaxation mechanism, therefore, through taking the logarithm ($\ln f$) of the frequency corresponding to all peaks in R1 and Figure 7.

Figure 7. (a) The functional relationship between the $M''$ and frequency for CMW ($x = 0$) at different temperatures, in which the illustration shows the relationship between $\ln f$ and $1000/T$ in Arrhenius equation; (b) the functional relationship between the $M'$ and frequency for CMW ($x = 0$) at low-temperature segments, in which the illustration shows the XPS results of powder; (c) the functional relationship between the $M'$ and frequency for CMW ($x = 0$) at high-temperature segments, in which the illustration shows the frequency dependence of $M'$ for CMW ($x = 0$) after annealing in different atmosphere.
R2, a functional relationship between the logarithm (lnf) and reciprocal of the temperature (1/T) can be established. The fitted straight line can pass through each data point well as shown in figure 7(a), which indicated that the R1 mechanism is perfectly following the Arrhenius equation:

\[ f = f_0 \exp\left(-\frac{E_a}{k_B T}\right) \]  

Where \( f_0 \) represents the pre-exponential factor, \( E_a \) is the activation energy, \( k_B \) is the Boltzmann constant. According to the fitted results as shown in figure 7(a), the activation energies of R1 and R2 were deduced to be 0.33 and 0.66 eV, respectively.

Figure 7(b) shows the functional relationship between the electrical modulus \( M' \) and frequency for CuMoO4 at low-temperature segments, and the details of R1 can be observed here. The activation energy (0.33 eV) of R1 is similar to the reported value (about 0.24–0.36 eV) of activation energy for polarization relaxation [28–30]. Therefore, it should be considered this relaxation at low temperatures may be related to the polarization relaxation caused by the hopping motion of electrons between Cu\(^{2+}\) and Cu\(^{3+}\) ions due to the presence of Cu. For example, the effect of valence-change behavior for Cu on relaxation has been described in CaCu3Ti4O12 and Cu3TeO6 systems [31–34]. When an electron carrying a negative charge is captured by Cu\(^{2+}\) ions carrying two positive charges, the Cu\(^{2+}\) ions will be generated accordingly in CMW. The XPS results of CMW powders were shown in figure 7(b). The fitting results with two characteristic peaks were obtained after fitting the measured data. The binding energies of the two peaks are 934.8 and 932.7 eV, respectively, which is consistent with the results reported in the literature [35], and the results proved that there is a mixed-valence state of Cu\(^{2+}/Cu^{3+}\) in CMW. Moreover, it was demonstrated that R1 is a small polaron relaxation through combining with the activation energy.

With regard to the R2 at high-temperature segments, the functional relationship between the electrical modulus \( M' \) and frequency for CuMoO4 at high-temperature segments was shown in figure 7(c). It is a widespread thing for the intrinsic point defects caused by the existence of oxygen vacancies for most oxides. In general, vacancies are used as donors which are capable of generating conductive electrons, and they play an important role in the valence transition between cations [30]. Therefore, it can be considered that the relaxation behavior of oxides at high temperatures is mainly dominated by oxygen vacancies. In addition, the activation energy (0.66 eV) of R2 is within the activation energy range of 0.3–1.2 eV in the relaxation caused by oxygen vacancies [36, 37]. Therefore, it is reasonable to believe that R2 at high-temperature segments is related to oxygen vacancies. To further investigate the deep relationship between R2 and oxygen vacancies, CuMoO4 samples were annealed in N2 and O2 for comparison. As can be seen from figure 7(c), the dielectric-peak intensity and the corresponding activation energies at 50 °C for different atmospheres are compared. The peaks of the samples annealed in N2 and O2 were higher and lower than the untreated CuMoO4 sample, respectively. And the calculated activation energies are 0.44 eV (N2) and 1.15 eV (O2). The concentration of oxygen vacancy in CuMoO4 increases (decreases) at high temperatures when annealing in N2 (O2).

Generally, the intensity of dielectric-relaxation peak caused by point defect is proportional to the defect concentration [27, 36, 38]. In other words, the peak value is higher (lower) with increasing (decreasing) the oxygen-vacancy concentration. The relationship between oxygen-vacancy concentration and activation energy has been studied previously, and it was reported that the concentration of oxygen vacancy (in the absence of oxygen-vacancy clusters) is inversely proportional to activation energy [27, 39]. That is to say, when the oxygen-vacancy concentration increases (decreases), the activation energy decreases (increases). In summary, R2 is related to oxygen vacancies.

The mechanisms of dielectric relaxation have been analyzed for CuMoO4 in detail, and the impact of W doping on the relaxation behavior of CMW was also investigated. To briefly highlight the relaxation phenomenon in CMW, the functional relationship between \( M' \) and frequency for CuMo0.97W0.03O4 and CuMo0.94W0.06O4 at different temperatures was given in figure 8(a) and (b). Obviously, the two different relaxation processes (R1, R2) were still shown in the \( M' \) curve corresponding to each doping content. It should be noted that R1 and R2 appear again in the \( \gamma \)-phase and \( \alpha \)-phase respectively for CMW during the heating process. For example, when \( x = 0.03 \) and \( x = 0.06 \), the temperature range (\(-10^\circ C\) to \(10^\circ C\)) from R1 to R2 is in accordance with the DSC results (figure 4). Therefore, there is a phase transition of relaxation type in CMW regardless of the doping of W during the heating process.

The effect of W doping on the relaxation behavior of CMW was studied by observing the change of relaxation-peak position and calculating activation energy. Figure 9(a) shows the \( M' \) curves of CMW at −90 °C. It can be seen that the relaxation peak shifted slightly to the low frequency when \( x = 0 \), but the intensity of all peaks remained basically unchanged, and the value fluctuated very slightly around \( M'' = 0.02 \).

Considering the proportional relationship between vacancy concentration and relaxation-peak intensity, it can be inferred that increasing W doping did not change the vacancy concentration and the number of partial carriers. Because most vacancies and carriers are frozen at very low temperatures, they lack the ability to gain and lose electrons, which naturally does not have a great impact on the relaxation process [10]. Therefore, the W
doping variation has little effect on $R_1$ at the low-temperature segments for CMW. However, the influence of W doping on the relaxation behavior of $R_2$ is more obvious at high temperatures, as shown in figure 9(b). The relaxation peak shifted to low frequency and the intensity of the peak decreased significantly with varying the doping content at high temperature (taking 150°C as an example). The results suggest that the relaxation of $R_2$ is inhibited by decreasing the vacancy concentration.

In order to further analyze the effect of W doping on the relaxation in CMW, effective activation energies were calculated to quantitatively explain the variation law. The comparison of the activation energies of $R_1$ was shown in figure 9(a). And it is clear to observe that the activation energy did not change two much and basically maintained the value of 0.33 eV, which is close to the activation energy required for small polarization relaxation, and it was similar to the results deduced from the intensity of relaxation peaks for different samples. Therefore, it can be concluded that there is still a polaron-related relaxation mechanism for CMW oxides and there is no obvious impact on the relaxation ($R_1$) process at low-temperature segments.

The activation energies corresponding to different doping contents for $R_2$ are presented in figure 9(b). Obviously, the activation energy has an obvious upward trend with the increase of $x$ value. There may be two reasons for the increase of activation energy. Firstly, when the concentration of oxygen vacancy is not very large (no oxygen-vacancy clusters are formed), its concentration is proportional to the activation energy. Secondly, the structure of CMW is distorted due to the doping of W, and more obstacles need to be overcome to increase the activation energy. Thus, $R_2$ was inhibited. This was consistent with the aforementioned discussion on the change of relaxation-peak intensity caused by doping content. Therefore, the relaxation mechanism dominated by oxygen vacancies still exists for CMW. With the increase of $x$ value, the intensity of relaxation peak decreased and the activation energy increased gradually, and, besides, the relaxation ($R_2$) was inhibited at high-temperature segments.
4. Conclusions

W doping caused the structure and color change from green $\alpha$-phase to brown $\gamma$-phase for CuMo$_{1-x}$W$_x$O$_4$ (CMW, $x = 0 \sim 0.12$). UV–vis diffuse reflectance spectra reveal the mechanism of color change in CMW. The color change of CMW ($x = 0.06$) from 20 to 50 $^\circ$C was consistent with the dielectric spectra and DSC results, and the phase-transition temperature moved towards high temperature with the increase of x value. The frequency dependence of $M''$ indicated the existence of small polaron relaxation ($R_1$) and oxygen-vacancy related relaxation ($R_2$) in CMW. It is worth noting that the phase transition of relaxation type has been confirmed in CMW as well, and $R_1$ occurred in the $\gamma$-phase and $R_2$ occurred in the $\alpha$-phase. With the increase of W doping, the intensity of relaxation peak and activation energy for $R_1$ did not change significantly, and the relaxation of $R_2$ was inhibited because the activation energy increased gradually.

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