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X-ray photoelectron spectroscopy studies the cation valencies and distributions in crednerite-$Cu_{1.1}Mn_{0.9}O_2$ thin films

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ABSTRACT

In this study, the cation valencies and distributions in crednerite-$Cu_{1.1}Mn_{0.9}O_2$ thin films are studied. The lattice parameters of the sol–gel-derived crednerite-$Cu_{1.1}Mn_{0.9}O_2$ thin films were $a = 0.55759$ nm, $b = 0.28754$ nm, $c = 0.58847$ nm, and $\beta = 104.18°$. The binding energies of the Cu-2p spectrum were 932.3 ± 0.2 eV ($2p_{3/2}$) and 952.3 ± 0.2 eV ($2p_{1/2}$), which represent the Cu^+ in the thin films. Moreover, three binding energies at 639.8 ± 0.2 eV, 641.1 ± 0.2 eV, and 643.4 ± 0.2 eV were found in the Mn-2p spectrum. The binding energies of the Mn-3p spectrum were 47.3 ± 0.2 eV, 48.0 ± 0.2 eV, and 49.9 ± 0.2 eV for the crednerite-$Cu_{1.1}Mn_{0.9}O_2$ thin films, which reveal that the thin films have Mn^{2+}, Mn^{3+}, and Mn^{4+} cations. Additionally, the cation distributions in the thin films were $Cu^{+}_{1.1}[Mn^{2+}_{0.24-0.27}Mn^{3+}_{0.53-0.54}Mn^{4+}_{0.20-0.22}]_{0.9}O_2$ from the X-ray photoelectron spectroscopy.

1. Introduction

Recently, ternary Cu-based oxides have become attractive owing to their optoelectronic properties [1]. In particular, ternary Cu-based oxides are used to new transparent p-type conducting oxides for integration into transparent electronic devices, which has been reported [1]. $CuMnO_2$ is one of the members of ternary Cu-based oxides, and exhibits the delafossite structure at high temperature [2] and the monoclinic structure at room temperature [3]. $CuMnO_2$ at high temperature exhibits the delafossite structure (rhombohedral cell) because the lattice distortion due to the thermal expansion of the structure is larger than that due to the Jahn–Teller effect [2]. However, $CuMnO_2$ at room temperature is the monoclinic structure owing to the lattice distortion caused by the Jahn–Teller effect of Mn^{3+} ions. In order to accommodate these Jahn–Teller ions (Mn^{3+}) during cooling, the structure tends to elongate along the *c*-axis and decreases the cell symmetry. Consequently, the structure becomes the monoclinic structure at room temperature [2,3]. Moreover, crednerite-$CuMnO_2$ has catalytic properties [4–6], which leads to potential applications for a novel hydrogen photo-evolution catalyst [4], a three-way catalyst for the removal of air pollutants, i.e., carbon monoxide and nitrous oxides, from exhaust gas [5,6], respectively.

Nevertheless, the preparation of bulk or thin films for the crednerite-$CuMnO_2$ has not been reported extensively. The powder form was synthesized using solid-state reaction [3] and ion-exchange reaction [7]. Moreover, pulsed laser deposition was used to prepare the crednerite-$CuMnO_2$ thin films [8,9]. Additionally, Mn compounds frequently have multiple valencies of Mn cations [3,10–15]. Moreover, the studies concerning the cation valencies and distributions of Mn cations in crednerite-$CuMnO_2$ are documented. Trari et al. [3] reported cation distributions of crednerite-$Cu_{1+x}Mn_{1-x}O_2$ from the magnetic susceptibility measurement and Seebeck coefficient. Because crednerite-$Cu_{1+x}Mn_{1-x}O_2$ has excess Cu atoms, Cu cations occupying the octahedral site are divalent. In addition, Mn cations form Mn^{3+} and Mn^{4+} in crednerite-$Cu_{1+x}Mn_{1-x}O_2$ because the formation of Cu^{2+} and/or Mn^{4+} requires electrical neutrality. Töpfer et al. [14] pointed out the distribution of Cu and Mn cations in crendernite-$Cu_{1.04}Mn_{0.96}O_2$ using single crystal X-ray diffraction data and the total composition of the phase. A small numbers of Cu cations occupy the octahedral sites, which leads to the formation of Cu^{2+}. They conclude that the distribution of the cation is $Cu_{1.00}(Cu^{2+}_{0.04}Mn^{3+}_{0.92}Mn^{4+}_{0.04})O_2$.

So far, the cation valencies and distributions in crednerite-$CuMnO_2$ thin films have not been studied using X-ray photoelectron spectroscopy (XPS). Therefore, this study aims to investigate of cation valencies and distributions in crednerite-$CuMnO_2$ thin films using photoelectron spectra.

2. Experimental details

The pure crednerite-$CuMnO_2$ phase can be stabilized in $Cu_{1+x}Mn_{1-x}O_2$ with $0.1 \leqslant x \leqslant 0.13$ [3,16]. Therefore, the stoichiometry of Cu:Mn = 1.1:0.9 in this study leading to fall in the pure crednerite-$CuMnO_2$ phase, which corresponds to the chemical composition of $Cu_{1.1}Mn_{0.9}O_2$. Copper(II) acetate monohydrate ($Cu(CH_3COO)_2 \cdot H_2O$, purity 99%+, SHOWA, Japan) and manganese(III) acetate tetrahydrate

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($Mn(CH_3COO)_3{\cdot}4H_2O$, purity 98%+, SHOWA, Japan) were dissolved in 30 mL of ethanol and 5.0 g of triethanolamine (purity 95%+, Tedia, USA) was added to the solution. This precursor was then spin-coated onto quartz substrates at 2000 rpm for 15 s. Next, these specimens were annealed at 500 °C in air for 1 h at a ramp rate of 5 °C/min and the specimens were post-annealed at 650 °C in flowing nitrogen gas (99.995%) for 2 h at a ramp rate of 5 °C/min to obtain the pure crednerite-$CuMnO_2$ phase.

After annealing, the crystal structures of the films were examined using an X-ray diffractometer (Bruker D8 Discover) with a Cu Kα ($\lambda = 0.154$ nm) excitation source by the $\theta/2\theta$ couple scan. The operating voltage and current were 40 kV and 40 mA, respectively. The scan rate was 4 deg/min, and the collected interval was 0.01° (2θ). The lattice parameters of the thin films were refined using TOPAS (Total Pattern Analysis Software, Bruker). The morphology and thickness of the films were examined using an FE-SEM (JEOL JSM-6700F) operated at 3 kV. XPS was performed using a JEOL JAMP-9500F spectrometer with the Mg Kα ($h\nu = 1253.6$ eV) exciting X-ray source. The surface was sputter-cleaned using an Ar ion gun operated at 3 keV for 30 s before the measurement. The spectra of Cu-2p, Mn-2p, Mn-3p, and O-1s were obtained at an energy interval of 0.2 eV per step. All spectra were calibrated according to the C-1s peak at 284.8 eV. The XPS spectra were fitted using a nonlinear least squares fit with a Gaussian/Lorentzian peak shape (G/L mixing ratio = 0.3) and the background was subtracted before each fitting routine.

3. Results and discussion

3.1. X-ray diffraction analysis

Fig. 1 shows the X-ray diffraction pattern of the thin films in this study, where the diffraction peaks matched the $CuMnO_2$ phase (JCPDS #83-0034) with crednerite crystal structure (space group: C2/m). Additionally, the diffraction peaks had a narrow full width at half-maximum, which suggested good crystallinity of the films. The lattice parameters of the crednerite-$Cu_{1.1}Mn_{0.9}O_2$ phase were refined using TOPAS (Total Pattern Analysis Software). The lattice parameters of the crednerite-$Cu_{1.1}Mn_{0.9}O_2$ thin films were $a = 0.55759$ nm, $b = 0.28754$ nm, $c = 0.58847$ nm, and $\beta = 104.18°$. These obtained data are consistent with the reports of bulk and films [3,8,14,17].

The surface morphology of the crednerite-$Cu_{1.1}Mn_{0.9}O_2$ thin films was examined using an FE-SEM, which is displayed in the inset of Fig. 1. The crednerite-$Cu_{1.1}Mn_{0.9}O_2$ thin film shows a large granular surface morphology, which is consistent with the results of the narrow full width at half-maximum of the diffraction peaks.

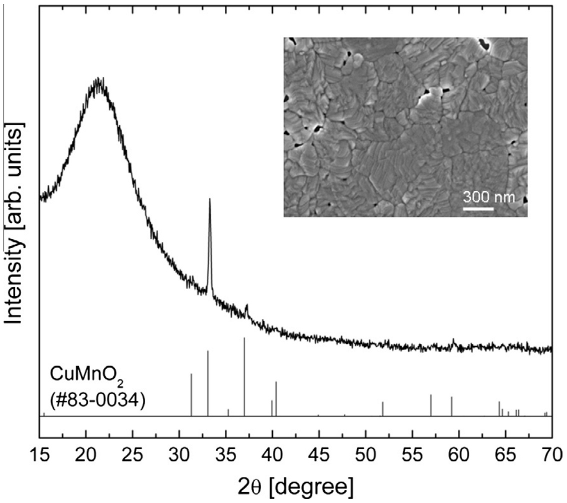

Fig. 1. X-ray diffraction pattern of the crednerite-$Cu_{1.1}Mn_{0.9}O_2$ films prepared using sol–gel processing. The inset shows the surface morphology of the thin films.

3.2. X-ray photoelectron spectroscopy analysis

3.2.1. Valence band spectrum

Fig. 2 shows the valence band spectrum of the crednerite-$Cu_{1.1}Mn_{0.9}O_2$ thin films. The main binding energy at approximately 3.0 eV with a shoulder at 2.0 eV was observed. Additionally, the minor binding energy at approximately 6.0 eV was also observed. This feature of binding energy for this valence band is correlated to the band structure of the crednerite-$CuMnO_2$ phase. The valence band of crednerite-$CuMnO_2$ is Cu-3d and O-2p orbitals [8,9,18], which contribute to the binding energy at 2.0 eV.

However, the binding energy at approximately 6.0 eV would be caused by the contribution of Mn-3d orbitals [8,18] because the Mn-3d orbitals exist at deeper energy levels, i.e., at high binding energy [8,9]. Additionally, a similar valence band feature was also observed in the $CuFeO_2$ phase [19]. However, it is worth noting that the photoionization cross section of the atoms mainly determines the shape of the valence band [19]. Hence, the photoionization cross section ratios by the Mg Kα excitation source were Cu-3d = 0.0148, Mn-3d = 0.002644, and O-2p = 0.0004842 [20], which leads to a relative ratio of 1:0.18:0.03 for the Cu-3d, Mn-3d, and O-2p. Therefore, this valence band feature mainly results from Cu-3d states.

3.2.2. Cu-2p spectrum

Fig. 3 shows the Cu-2p spectrum of the crednerite-$Cu_{1.1}Mn_{0.9}O_2$ thin films. As shown in the spectrum, two distinct and intense peaks with a binding energy of Cu-$2p_{3/2} = 932.5 \pm 0.2$ eV and Cu-$2p_{1/2} = 952.3 \pm 0.2$ eV were observed, which is similar to that of monovalent Cu cation in the Cu-based delafossites [21–23].

3.2.3. Mn-2p and Mn-3p spectra

Previous studies have pointed out that Mn cations in the credneritre-$CuMnO_2$ phase has multiple valence states [3,14]. Therefore, the Mn-2p and Mn-3p spectrum may be complex. Hence, we summarized the binding energies of the Mn-2p and Mn-3p region for different Mn cations from Mn^{2+} to Mn^{4+} from the literature data, which is given in Table 1. As given in the table, the binding energies of Mn-$2p_{3/2}$ are located at 640.3–641.0 eV for Mn^{2+}, 641.2–641.8 eV for Mn^{3+}, and 641.9–643.3 eV for Mn^{4+}, respectively. On the other hand, the binding energies of Mn-3p are located at 47.4–47.5 eV for Mn^{2+}, 48.3–49.1 eV for Mn^{3+}, and 49.6–50.4 eV for Mn^{4+}, respectively. It is worth noting that the Mn-$2p_{3/2}$ peaks are shifted by approximately 1 eV with the change of the formal oxidation state by one unit [13,15].

Fig. 4 displays the Mn-2p and Mn-3p spectrum in the crednerite-$Cu_{1.1}Mn_{0.9}O_2$ thin films. Initially, the Mn-$2p_{3/2}$ spectrum could be deconvoluted using two binding energies at 640.2 eV and 641.9 eV, which could be mainly attributed to Mn^{2+} and Mn^{3+}. Additionally, the Mn-3p spectrum could also be

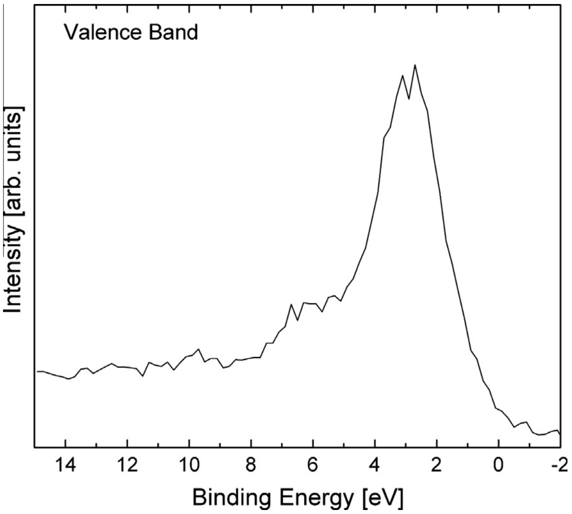

Fig. 2. The valence band spectrum of the crednerite-$Cu_{1.1}Mn_{0.9}O_2$ thin films.