Effects of Sb-filled on the Structural and Physical Properties of $CuCrO_2$ Delafossite Oxide

ผลของการเติม Sb ต่อโครงสร้างและสมบัติเชิงฟิสิกส์ของวัสดุออกไซด์เดลาฟอสไซท์ $CuCrO_2$

Chutarat Yonchai (จุฑารัตน์ ยนต์ชัย)* Dr.Teerasak Kamwanna (ดร.ธีรศักดิ์ คำวรรณะ)**

ABSTRACT

In this research, delafossite Sb_xCuCrO_2 ($0.0 \leq x \leq 0.15$) semiconductors were synthesized by a solid state reaction method. The effects of Sb concentration on microstructure, optical, magnetic and dielectric properties were investigated. The x-ray diffraction (XRD) results reveal the delafossite structure of all samples. The lattice spacing of the Sb_xCuCrO_2 is independent of the Sb content. The optical properties measured at room temperature by UV-visible spectroscopy showed a weak absorbability in the visible light and near IR regions. The corresponding direct optical band gap was about 3.46 eV, exhibiting the transparent in the visible region. The magnetic hysteresis loops measurements at room temperature show that the Sb-filled $CuCrO_2$ samples have the paramagnetic behavior. The dielectric measurements clearly revealed that the dielectric permittivity of $CuCrO_2$ ceramics was strongly inhibited by Sb filling.

บทคัดย่อ

งานวิจัยนี้ได้สังเคราะห์วัสดุออกไซด์เดลาฟอสไซท์ Sb_xCuCrO_2 ($0.0 \leq x \leq 0.15$) ด้วยวิธีปฏิกิริยาแบบสถานะของแข็ง โดยทำการศึกษาวิเคราะห์ผลของการเติม Sb ต่อลักษณะผลึก เฟสโครงสร้างของวัสดุ จากนั้นนำวัสดุที่ได้ไปทดสอบวัดสมบัติทางแสง สมบัติแม่เหล็กและสมบัติทางไดอิเล็กตริก รวมทั้งวิเคราะห์ถึงสาเหตุหรือแนวโน้มที่ทำให้สมบัติทางแสง สมบัติแม่เหล็กและสมบัติไดอิเล็กตริกที่เปลี่ยนไปเนื่องจากการเติมของ Sb จากผลการวิเคราะห์โดยเทคนิคการเลี้ยวเบนของรังสีเอกซ์แสดงให้เห็นว่าวัสดุออกไซด์ที่สังเคราะห์ได้มีโครงสร้างแบบเดลาฟอสไซท์ ค่าคงที่แลตทิตไม่มีการเปลี่ยนแปลงเมื่อปริมาณของ Sb ที่เติมเข้าไปในโครงสร้างเพิ่มขึ้น สเปคตรัมการดูดกลืนแสงมีค่าการดูดกลืนน้อยในย่านที่ตามองเห็น และมีค่าแถบพลังงานประมาณ 3.46 eV แสดงให้เห็นว่าวัสดุออกไซด์เดลาฟอสไซท์ที่สังเคราะห์ได้เป็นวัสดุโปรงแสง นอกจากนี้ จากการวัดสมบัติทางแม่เหล็กพบว่าวัสดุออกไซด์ Sb_xCuCrO_2 ที่อุณหภูมิห้องมีความเป็นแม่เหล็กแบบพาราแมกเนติก และจากการศึกษาสมบัติทางไดอิเล็กตริกพบว่า $CuCrO_2$ มีค่าคงที่ไดอิเล็กตริกลดลงเมื่อเติมด้วย Sb

Keywords: Delafossite oxide, Transparent conducting oxide, Magnetic properties

คำสำคัญ: วัสดุออกไซด์เดลาฟอสไซท์ วัสดุออกไซด์ตัวนำโปร่งแสง สมบัติทางแม่เหล็ก

* *Student, Master of Science Program in Physics, Department of Physics, Faculty of Science, Khon Kaen University*

** *Assistant Professor, Department of Physics, Faculty of Science, Khon Kaen University*

Introduction

In the past decade, delafossite oxides have attracted interest for transparent conducting oxides (TCOs) applications due to their unique combination of electrical conductivity and high transparency for visible light (Jlaiel et al., 2013; Marquardt et al., 2006). Moreover, the magnetic property of the delafossite oxide have also gained attention due to their great application potential for diluted magnetic semiconductors (DMSs). Oxide-based DMSs exhibit unique magnetic, magneto-electric effects, magneto-optical, and high transparency in the visible region (Lin et al., 2013). Therefore, delafossite oxides show potential application for DMSs. Among them, $CuCrO_2$ is widely studied due to its unique combination of electrical conductivity and optical transparency. Moreover, $CuCrO_2$ is reported to exhibit ferromagnetic properties in the case of Cr^{3+} substituted with nonmagnetic trivalent ions (Elkhouni et al., 2013). In our previous work, we observed weak ferromagnetism for Ge-doped $CuCrO_2$ (Rattanathrum et al., 2017) at 50 K and Fe-doped $CuCrO_2$ (Taddee et al., 2016) at room temperature. However, there are different ferromagnetic behavior available on both Cu-based delafossite oxides, which motivates further studies.

In this work, Sb-filled $CuCrO_2$ was synthesized by a conventional solid-state reaction. The ferromagnetism was considered. Moreover, no systematic studies of the magnetic properties of Sb-filled $CuCrO_2$ have been reported in the literature. Therefore, we systematically investigate the effects of Sb composition on the microstructural, optical, magnetic, and electrical properties of $CuCrO_2$. We also examine whether the partial Sb-filled would yield changes in the magnetic and electrical properties of $CuCrO_2$.

Objective of the study

The aim of this study was to assess the influence of Sb-filled on the structural and physical properties of $CuCrO_2$ delafossite oxide.

Materials and methods

Sample preparation

In this work, polycrystalline Sb_xCuCrO_2 (x = 0.01, 0.03, 0.05, 0.10 and 0.15) powders were synthesized by using a conventional solid-state reaction. High-purity powders of CuO (Aldrich, purity 99%), Cr2O3 (Aldrich, purity 99%), and Sb powder (Aldrich, purity 99.99%) were used as starting materials. The desired amounts of CuO, Cr_2O_3, and Sb powders were mixed to form a stoichiometric mixture. The obtained mixture of the starting materials was ball-milled for 24 h using ethanol as the medium. The resulting powder was dried at 413 K overnight. The obtained powder was calcined in N_2 atmosphere at 1,173 K for 6 h. The calcined powders were ground and pressed into pellets of 9.5 mm diameter and ~1 mm thickness by uniaxial compression under a pressure of 250 MPa and then sintered in N_2 atmosphere at 1,273 K for 9 h.

Characterizations

Phase and the crystal structure of the synthesized Sb_xCuCrO_2 powders were characterized by x-ray diffraction (XRD). This was carried out on a PANalytical, EMPYREAN diffractometer with Cu K_α radiation (λ = 0.15406 nm). Scanning electron microscope (SEM; SNE-4500M SEM, South Korea) images were recorded the microstructure of the Sb_xCuCrO_2 powders. The optical transmission spectra were recorded on powder sample by using a UV-VIS-NIR scanning spectrophotometer (UV-3101PC, Shimadzu) in the range of 200 to 800 nm at room temperature. The magnetization vs. magnetic field (M-H) curves was conducted using in Quantum Design VersaLab 3 Tesla Cryogen-free equipped with a vibrating sample magnetometer (VSM) at room temperature. The magnetization dependence on temperature was measured in the zero-field cooled (ZFC) and field cooled (FC) from 50 to 350 K at 0.15 T. For the dielectric measurement, surfaces of the sintered Sb_xCuCrO_2 ceramics were painted by silver past. The capacitance (C_p) and dissipation factor ($\tan\delta$) of the samples were measured using a KEYSIGHT E4990A Impedance Analyzer over the frequency range of 40 Hz – 10 MHz at room temperature with an oscillation voltage of 500 mV.

Results and Discussion

Structural characterization

Figure 1 shows the XRD patterns of Sb_xCuCrO_2 powders. The main phase of $CuCrO_2$ is detected and coincide well with standard peaks, proving that all Sb_xCuCrO_2 samples formed a pure polycrystalline phase having a delafossite structure. The XRD patterns of the sintered Sb_xCuCrO_2 ceramics are illustrated in figure 2. It is evident that XRD patterns display all peaks related to standard peaks. In addition, the relative strength of XRD peaks is different from the standard data and also the calcined Sb_xCuCrO_2 powders, especially, the strongest line (006) dominates over the (012). This behavior suggests that Sb_xCuCrO_2 ceramics grow preferentially parallel to the *c*-axis.

The extracted lattice parameters of the delafossite phase in Sb_xCuCrO_2 powders and ceramics are found that the lattice parameter *a* and *c* varied slightly from the standard JCPDS (*a* = 2.973 Å, *c* = 17.100 Å). This give further evidence of the lattice constant is independent of the Sb content. This behavior can be attributed to the Sb was partially filled for the delafossite structure. If the Sb was partially substituted for the sixfold coordination of Cr cite, the variations in lattice parameters *a* and *c* would be increased due to the larger size of Sb^{3+} than that of Cr^{3+} ($r_{Cr^{3+}}$ = 0.615 Å; $r_{Sb^{3+}}$ = 0.760 Å).

Figure 3 shows the SEM images of the Sb_xCuCrO_2 ceramics. The study revealed that the $Sb_xCuCrO2$ ceramics consisted of irregularly sized hexagonal-like structures. There is obvious dependence of particle size on Sb concentration.

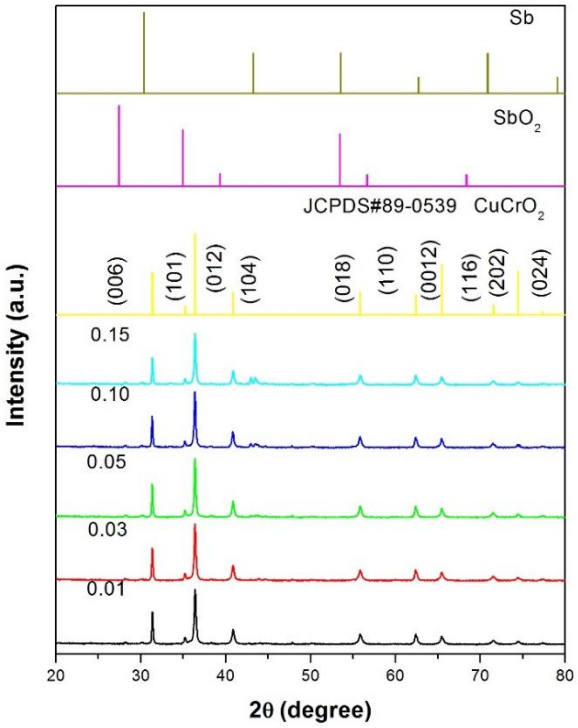

Figure 1 XRD patterns of calcined Sb_xCuCrO_2 powders with Sb contents of x = 0.01, 0.03, 0.05, 0.10 and 0.15.

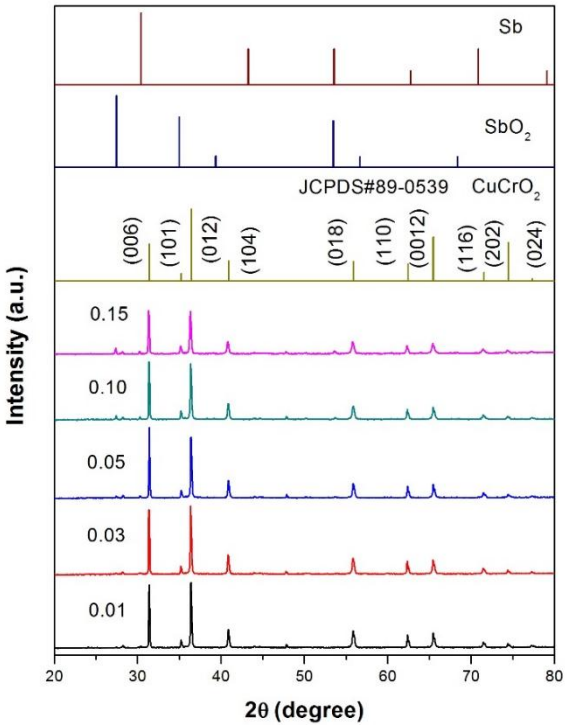

Figure 2 XRD patterns of sintereded Sb_xCuCrO_2 ceramics with Sb contents of $_x$ = 0.01, 0.03, 0.05, 0.10, and 0.15.

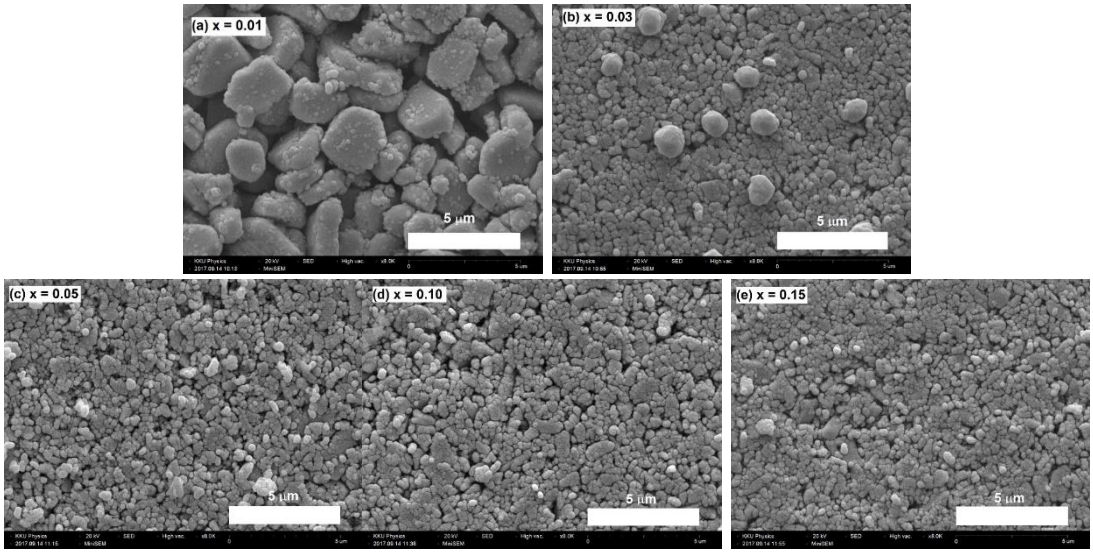

Figure 3 SEM image of sintered Sb_xCuCrO_2 ceramics where *x* are (a) 0.01, (b) 0.03, (c) 0.05, (d) 0.10, (e) 0.15, respectively.

Optical properties

The optical absorption spectra of Sb_xCuCrO_2 samples were measured in the region between 200 and 800 nm at room temperature, as showed in figure 4. Sb_xCuCrO_2 samples have a high absorption coefficient (α) in the UV light region (250-300 nm) and a low absorbability in the visible light and near-IR regions (300-800 nm). The corresponding direct optical band gaps (E_g) of the delafossite samples are 3.51, 3.49, 3.40, 3.42 and 3.46 eV for x = 0.01, 0.03, 0.05, 0.10 and 0.15, respectively. Obviously, the obtained direct energy gap for Sb_xCuCrO_2 is larger than 3.1 eV. This suggests that Sb_xCuCrO_2 delafossite can be used for the application of transparent conducting oxide materials.

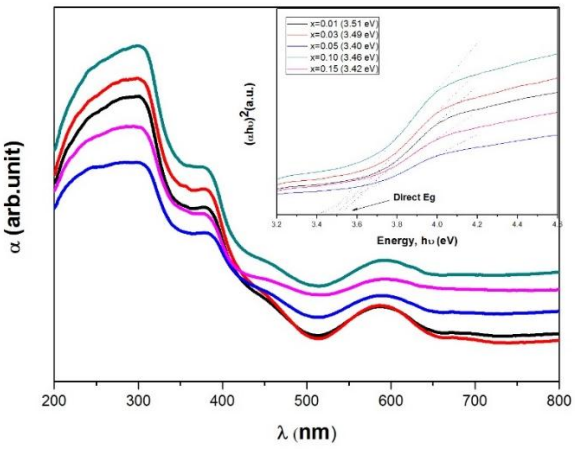

Figure 4 Absorption of calcined Sb_xCuCrO_2 powders at room temperature. The inset shows the extracted direct optical band gaps.

Magnetic properties

The magnetic properties of Sb_xCuCrO_2 powders were determined using a VSM with an applied magnetic field H ($-25 \leq H \leq 25$ kOe) at 300 K, as shown in figure 5. The *M-H* curves measured show a linear magnetization dependence on the applied magnetic field. The results are revealed a clear paramagnetic behavior for all samples at room temperature. This behavior indicated that the Sb-filled in the structure cannot be produces a mixed effect on the magnetic properties of this delafossite oxide.

In the delafossite structure, each Cu atom is linearly coordinated with two oxygen atoms, forming in O-Cu-O dumbbells parallel to the c-axis. This is form a layered triangular lattice anti-ferromagnetic. Actually, oxygens in the O-Cu-O dumbbells are each coordinated with three Cr atoms parallel to the ab plane. The interaction of the M cations with each other through M–O–M linkages of approximately 180^o was expected to be the dominant consideration, and that it would be anti-ferromagnetic in nature (Elkhouni et al., 2013). The combined influence of the number of the M–M pairs, and the M–M distances excludes the possibility of magnetic exchange interaction. Hence the primary effect of Cr^{3+} cite was to introduce a structural modulation in the triangular lattice. In this work, the Sb is not substitution for Cr^{3+} cite (no change in lattice parameters), which will not influence the M–M interaction. From this analysis, it is demonstrated that the magnetization has a high sensitivity to a change in lattice parameters, which correspond to literature (Gao et al., 2013; Rattanathrum et al., 2017).

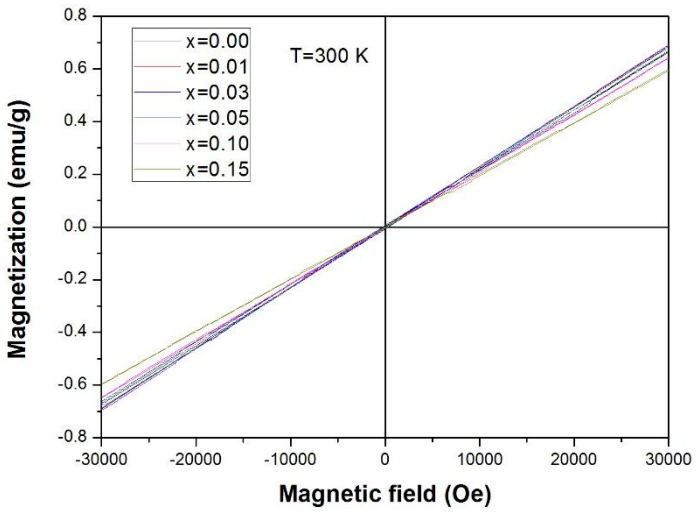

Figure 5 *M-H* curves of calcined Sb_xCuCrO_2 powders measured at 300 K

Dielectric properties

The dielectric properties at room temperature of the Sb_xCuCrO_2 ceramics were investigated in the frequency range of 40-10^6 Hz, as shown in figure 6. It is found that the dielectric permittivity (ε′) depends on the Sb content. Moreover, the ε′ of $Sb_{0.05}CuCrO_2$ ceramic in a low frequency range is about 300. It was nearly independent of frequency in the range of 10^2–10^4 Hz. When the frequency increased higher than 10^4 Hz, the steplike decrease in ε′ was observed. This may be attributed to the existence of dielectric relaxation. Figure 7 shows dielectric loss tangent

(tanδ) of the Sb_xCuCrO_2 ceramics. A significant decrease of tanδ values in a low frequency range was attributed to DC conduction, which is likely associated with the electrical properties of the grain boundaries (Xue, et al., 2016).

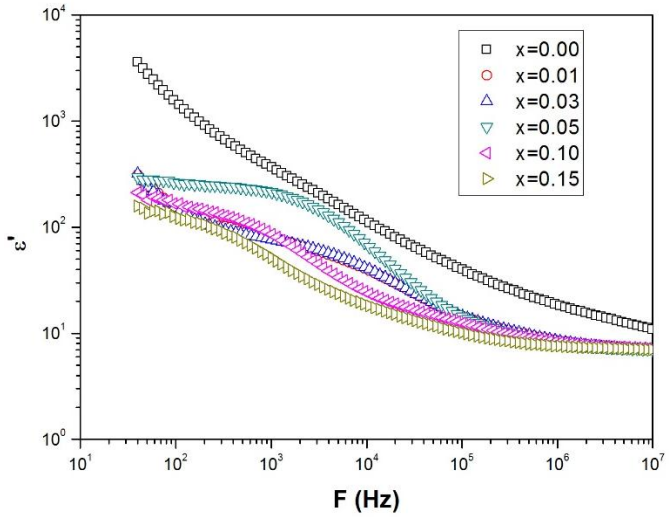

Figure 6 Frequency dependence of ε′ at room temperature of the Sb_xCuCrO_2 ceramics.

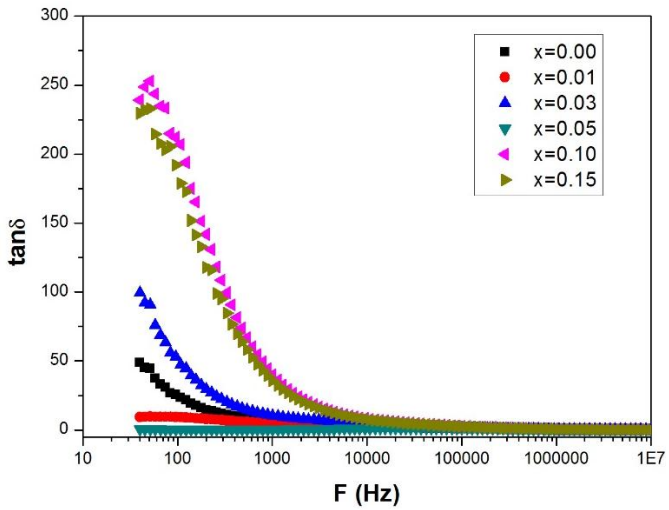

Figure 7 Frequency dependence of tanδ at room temperature of the Sb_xCuCrO_2 ceramics.

Conclusion

Sb_xCuCrO_2 semiconductors were successfully synthesized by using a solid-state reaction method. XRD analysis results revealed the formation of a delafossite structure. The optical band energy gap for the direct optical band transition was determined to be 3.40–3.51 eV, exhibiting transparency in the visible region. The magnetic measurements for Sb-filled CuCrO2 samples showed paramagnetism at 300 K, which was reinforced by the observation of a hysteresis loop. This behavior indicates that the Sb-filled cannot produced a mixed effect on the magnetic properties of this delafossite oxide. The dielectric measurements clearly revealed the dielectric permittivity of $CuCrO_2$ ceramics strongly inhibited by Sb filling.

Acknowledgement

This work was financially supported by the Integrated Nanotechnology Research Center (INRC), Khon Kaen University.

References

Jlaiel F, Elkhouni T, Amami M, Strobel P, Ben Salah A. Structural and physical properties of the (Ca, Mg)-doped delafossite powder $CuGaO_2$, Materials Research Bulletin 2013; 48: 1020–1026.

Marquardt MA, Ashmore NA, Cann DP. Crystal chemistry and electrical properties of the delafossite structure. Thin Solid Films 2006; 496: 146–156.

Lin F, Gao C, Zhou X, Shi W, Liu A. Magnetic, electrical and optical properties of p-type Fe-doped $CuCrO_2$ semiconductor thin films. Journal of Alloys and Compounds 2013; 581: 502–507.

Elkhouni T, Amami M, Colin CV, Strobel P, Ben Salah A. Synthesis, structural and magnetic studies of the $CuCr_{1-x}Co_xO_2$ delafossite oxide. Journal of Magnetism and Magnetic Materials 2013; 330: 101–105.

Rattanathrum P, Taddee C, Chanlek N, Thongbai P, Kamwanna T. Structural and physical properties of Ge-doped CuCrO2 delafossite oxide. Ceramics International 2017; 43: S417-S422.

Taddee C, Kamwanna T, Amornkitbamrung V. Characterization of transparent superconductivity Fe-doped $CuCrO_2$ delafossite oxide. Applied Surface Science 2016; 380: 237–242.

Gao C, Lin F, Zhou X, Shi W, Liu A. Fe concentration dependences of microstructure and magnetic properties for $Cu(Cr1_{-x}Fe_x)O_2$ ceramics. Journal of Alloys and Compounds 2013; 565: 154–158.

Xue R, Zhao G, Chen J, Chen Z, Liu D. Effect of doping ions on the structural defect and the electrical behavior of $CaCu_3Ti_4O_{12}$ ceramics. Materials Research Bulletin 2016; 76: 124–132.