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Synthesis and electrical properties of ordered perovskite oxide $Cd_{3-x-y}Cu_xA_yTeO_6$ (A = Li, Na; $0.00 \leq x, y \leq 0.15$)

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Abstract

Polycrystalline $Cd_{3-x-y}Cu_xA_yTeO_6$ (A = Li, Na) samples were prepared by solid-state reaction, and their crystal structure and electrical properties were investigated. In $Cd_{3-x}Cu_xTeO_6$ and $Cd_{3-y}A_yTeO_6$ (A = Li, Na), the maxim solubility of x and y was 0.15 and 0.15 for A = Li, 0.05 for A = Na, respectively. For co-substituted samples $Cd_{2.9-y}Cu_{0.1}Li_yTeO_6$ and $Cd_{2.9-y}Cu_{0.1}Na_yTeO_6$, the maxim solubility of x was the same as single substitution above-mentioned. The alkali-metal substituted samples $Cd_{3-y}A_yTeO_6$ (A = Li, Na) showed a negative Seebeck coefficient, which indicates that the major conduction carriers are electron. On the other hand, the co-substituted samples $Cd_{2.9-y}Cu_{0.1}A_yTeO_6$ (A = Li, Na) represented a positive Seebeck coefficient, and major conduction carriers were hole through substitution by copper ions.

Keywords: A. Semiconductors; A. Oxides; C. X-ray diffraction; D. Electrical properties

1. Introduction

Tricadmium tellurium(VI) oxide (Cd_3TeO_6) has an ordered perovskite structure, in which B-sites are occupied by Cd^{2+} and Te^{6+} ions in the NaCl-type arrangement [1,2]. Cd_3TeO_6 is composed of the cations having the same outer electron configurations ($4d^{10}5s^0$) without unpaired electrons and expected to be insulating. However, it generally shows an n-type semiconducting property with a low electrical

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resistivity of ~0.1 Ω cm at room temperature, which indicates the oxygen vacancy. Furthermore, the resisitivity can be decreased remarkably by increasing the electron carrier concentration through the substitution of trivalent cation for Cd^{2+} ions. For example, the electrical resistivity of the In-substituted single crystal $Cd_{3-x}In_xTeO_6$ is of the order of 10^{-4} Ω cm [3]. Thus, the research of the electron doping has been successfully carried out, but the hole doping has not been attempted. If hole doping is also achieved for Cd_3TeO_6, the bipolar semiconductor like those based on silicon will be possible for useful various applications.

The electronic structures of the oxides of heavy metal cations with $(n-1)d^{10}ns^0$ configurations are very favorable for the n-type conduction, but not for the p-type conduction because of the low energy of the d bands [4–7]. For realizing p-type conduction in Cd_3TeO_6, we may have to add some valence state where electrons can be removed. Many p-type oxide semiconductors contain copper ions, which have 3d states strongly interacting with the O 2p, such as La_2CuO_4, $CuAlO_2$ and $SrCu_2O_2$ [8–11]. In the present work, we approached the problem of hole doping in Cd_3TeO_6 in two ways. The first approach was the replacement of the divalent cadmium cations with alkali-metal ions (Li^+ and Na^+). In the second approach, we examined the simultaneous substitution of alkali-metal ions and copper ions, which is abbreviated to “co-substitution” in the following.

2. Experimental

The polycrystalline samples of $Cd_{3-x-y}Cu_xA_yTeO_6$ (A = Li, Na) were prepared by the solid-state reaction. Starting materials, CdO (purity: 99.9%), TeO_2 (purity: 99.9%), CuO (purity: 99.9%), Li_2CO_3 (purity: 99.7%) and Na_2CO_3 (purity: 99.7%) were mixed in stoichiometry ratio. The mixed powder was calcined at 1023 K for 9 h in air, then ground, pressed into pellets and sintered at 1353 K for 2 h in oxygen atmosphere. The obtained samples were characterized by powder X-ray diffraction (XRD) (RINT-2000,

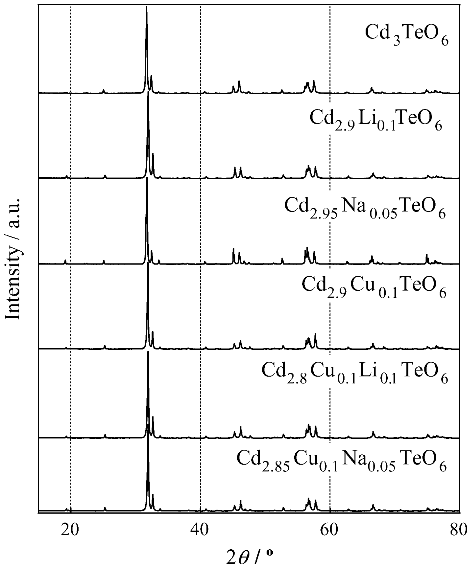

Fig. 1. XRD patterns of $Cd_{3-x-y}Cu_xA_yTeO_6$ (A = Li, Na).