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Effect of copper on the electrical properties of $K_{1.6}(Mg_{1-y}Cu_y)_{0.8}Ti_{7.2}O_{16}$ ceramics

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The electrical conductivity of the $K_{1.6}(Mg_{1-y}Cu_y)_{0.8}Ti_{7.2}O_{16}$ ceramics has been investigated as a function of copper fraction ($0 \leqslant y \leqslant 1$). At the calcination temperature of 1000 °C, a tetragonal-single phase was obtained for the all compositions. In the specimens sintered at 1100 °C for 4 h, the electrical conductivity of the specimens increased with the increasing copper fraction, y. This result can be explained by the weakness of the K–O bonding and the increase of the bulk density and grain size. For the specimens with copper fraction ($0 \leqslant y < 0.8$), the electrical conduction was developed mainly by ionic conduction while electronic conduction abruptly occurred at copper fraction $y \geqslant 0.8$. This resulted from the valence transition of copper ions associated with the formation of oxygen vacancies.

1. Introduction

Recently, fast ionic conductors have been broadly investigated with a view to energy storage–production (such as batteries, fuel cell, magnetohydrodynamics) and the effective solutions of pollution problems [1]. Especially in batteries, a solid-state electrolyte can enlarge the capacity of energy storage and current density because a highly reactive alkali metal such as potassium, sodium and lithium can be used as electrode material. In general, a fast ionic conductor used as a solid state electrolyte should have a large ionic conductivity, small electronic transport number, high mechanical strength and large corrosion resistivity for alkali metals. Among the fast ionic conductors, K–Mg hollandite has been extensively studied as a one-dimensional ionic conductor. Hollandite-type materials with the general formula $A_2B_8O_{16}$ have a tunnel structure which has a host framework and conducting ions occupying some of the lattice sites within the tunnel structure. Each tunnel of hollandite-type structure has no intercommunication and consists of corner- and edge-sharing $[BO_6]$ octahedra [2–4]. Also, B sites can be easily replaced with magnesium, zinc, aluminium, iron, cobalt, chromium, etc. [5–7]. The conductivity achieved by the potassium ion in the hollandite single crystal is relatively high ($0.22\ \Omega^{-1}\,cm^{-1}$). But, defects (such as grain boundaries, impurities and intragrain misorientation) are the main obstacles to ionic conduction because of the one-dimensional conduction mechanism [4]. Thus it is thought that it is important to reduce them in application for the secondary battery.

The objectives of this study were to prepare polycrystalline and fast ionic conductor by substituting copper for magnesium in order to use the high ionic conductivity of hollandite-type structure materials. Therefore, in the case of a polycrystalline material, the $K_{1.6}(Mg_{1-y}Cu_y)_{0.8}Ti_{7.2}O_{16}$ specimens with different copper fractions, y, were prepared by conventional ceramic processing and the effects of compositional variation on the a.c. electrical conductivity were investigated in terms of bonding character, valence state of copper, density and microstructure analysis.

2. Experimental procedure

The $K_{1.6}(Mg_{1-y}Cu_y)_{0.8}Ti_{7.2}O_{16}$ specimens were prepared from reagent-grade K_2CO_3, MgO, CuO and TiO_2 powders. The composition of potassium was optimally selected, considering the number of vacancies within the tunnel structure, and the amounts of copper fraction were 0, 0.2, 0.5, 0.8 and 1, respectively. The fabrication of the $K_{1.6}(Mg_{1-y}Cu_y)_{0.8}Ti_{7.2}O_{16}$ ceramics was carried out by mixed oxide procedures. The $K_{1.6}(Mg_{1-y}Cu_y)_{0.8}Ti_{7.2}O_{16}$ mixtures milled with zirconia balls for 24 h were calcined at 1000 °C for 4 h. After post-milling and sieving, the calcined powders were cold-isostatically pressed into discs (diameter 12 mm and about 5 mm thick) at 20 000 psi (10^3 p.s.i. $= 6.89\ N\,mm^{-3}$) and then sintered at 1100 °C for 4 h with a heating rate of 300 °C h^{-1}. The pellets were buried in powders of the same composition to minimize material loss by evaporation of potassium during sintering. The phases present in the calcined powders and sintered specimens were analysed from X-ray diffraction patterns and the lattice constants were determined from the (5 2 1), (5 4 1), (6 0 0) and (4 1 1) reflections. Densities were obtained by the ASTM C373-72 method. The microstructures were observed by optical microscopy.

For electrical conductivity measurements, the flat surfaces of the pellets were ground parallel and electrical connections were made by applying gold electrodes as ion-blocking electrodes to both sides of the pellets. The measurements were carried out between 200 and 400 °C. The specimens in the furnace were heated/cooled to the measuring temperature at 2 °C min^{-1}. After thermal stabilization for 1 h at each temperature, the two-point technique was adopted to measure a.c. conductivity between 10^{-2} and 10^6 Hz using an impedance analyzer (Zhaner IM5d, Germany) controlled by a personal computer. The impedance spectra were analysed by using the "equivalent circuit" software devised by Boukamp [8]. For the evaluation of partial electronic conductivity [9], the voltage dependence of a steady-state (direct) current was measured by using a cell with a molten KNO_3 electrode and a gold-blocking one at 350 °C. The valence states of copper were analysed by X-ray photo electron spectroscopy (XPS) (Perkin–Elmer Co.).

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns of the $K_{1.6}(Mg_{1-y}Cu_y)_{0.8}Ti_{7.2}O_{16}$ powders calcined at 1000 °C for 4 h. The tetragonal-single phase of $K_{1.6}(Mg_{1-y}Cu_y)_{0.8}Ti_{7.2}O_{16}$ was achieved over the whole range of the copper fraction y. For $y = 0$ specimen, the lattice parameters of $K_{1.6}(Mg_{1-y}Cu_y)_{0.8}Ti_{7.2}O_{16}$ were $a = 1.0140$ nm and $c = 0.29691$ nm. These values slightly decreased with increasing y. The reduction of the cell volume of $K_{1.6}(Mg_{1-y}Cu_y)_{0.8}Ti_{7.2}O_{16}$ calculated from the results of XRD data are represented in Fig. 2. The cell volume decreased as the copper fraction y increased. The reduction of the cell volume is thought to be related to the decrease of the ionicity in the B site metal ions within oxygen octahedra of $K_{1.6}(Mg_{1-y}Cu_y)_{0.8}Ti_{7.2}O_{16}$ with increasing copper fraction y. As the electronegativities of magnesium (1.31) and titanium (1.54) atoms are slightly lower than that of the copper (1.90) atom, the ionicities of the metal–oxygen bonding, calculated by Pauling's formula [10], are 0.68, 0.59 and 0.45, respectively. The ionic sizes of Cu^{2+} and Mg^{2+} in oxygen octahedra are 0.073 and 0.072 nm, respectively [11]. Therefore, the bonding character with the oxygen atom is changed to covalent bonding with increasing copper fraction y.

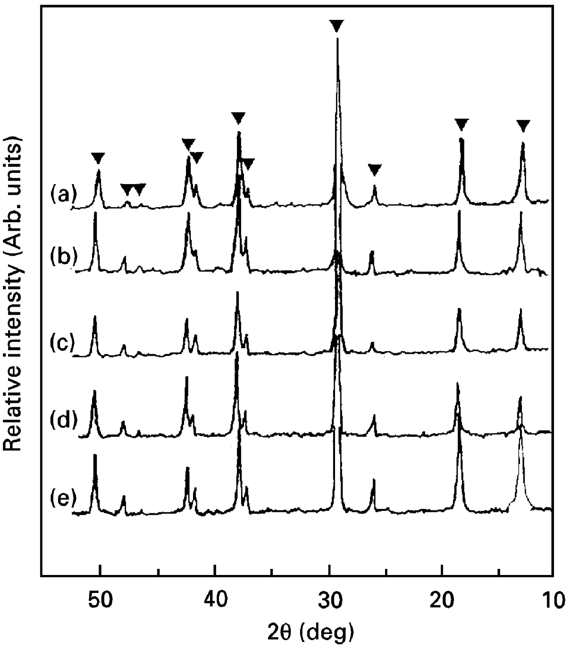


Figure 1 XRD patterns of $K_{1.6}(Mg_{1-y}Cu_y)_{0.8}Ti_{7.2}O_{16}$ ceramics powders calcined at 1000 °C for 4 h (▼ : hollandite phase) (a) $y = 0$, (b) $y = 0.2$, (c) $y = 0.5$, (d) $y = 0.8$, (e) $y = 1$.

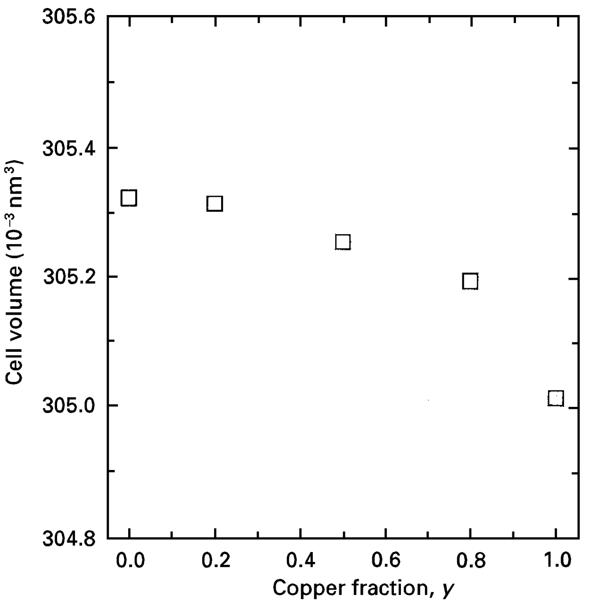


Figure 2 Cell volumes of $K_{1.6}(Mg_{1-y}Cu_y)_{0.8}Ti_{7.2}O_{16}$ ceramics with increasing copper fraction, y.

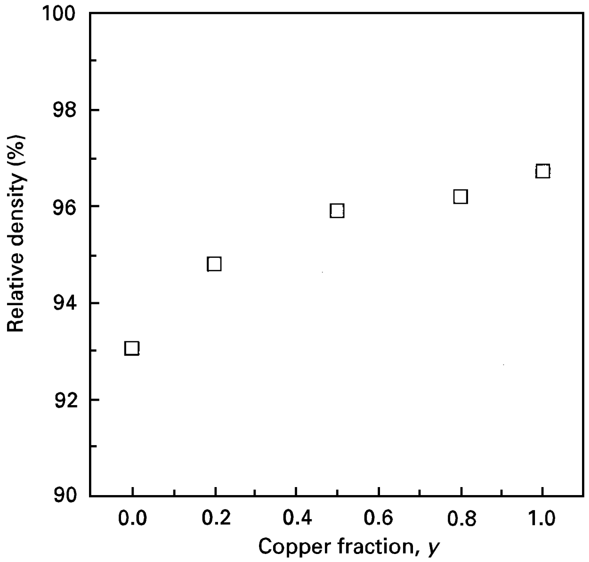
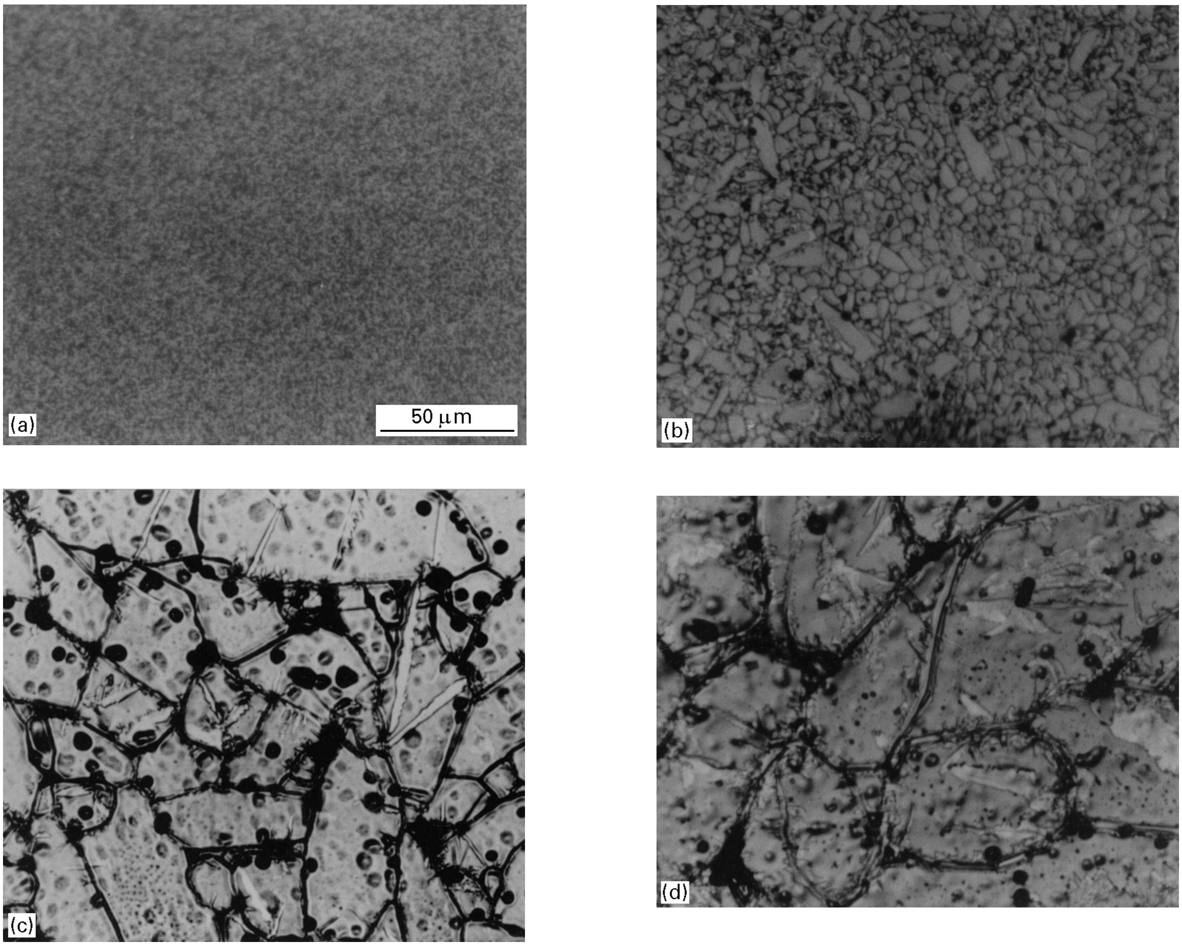


Figure 3 Relative density of $K_{1.6}(Mg_{1-y}Cu_y)_{0.8}Ti_{7.2}O_{16}$ ceramics as a function of copper fraction, y.

Fig. 3 shows the relative densities of the $K_{1.6}(Mg_{1-y}Cu_y)_{0.8}Ti_{7.2}O_{16}$ specimens sintered at



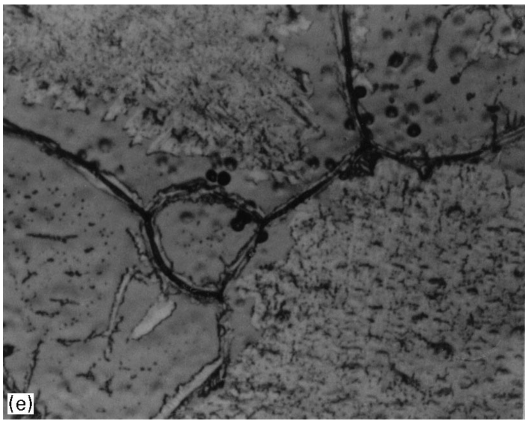


Figure 4 Optical micrographs of the $K_{1.6}(Mg_{1-y}Cu_y)_{0.8}Ti_{7.2}O_{16}$ ceramics with increasing copper fraction, y. (a) $y = 0$, (b) $y = 0.2$, (c) $y = 0.5$, (d) $y = 0.8$, (e) $y = 1$.

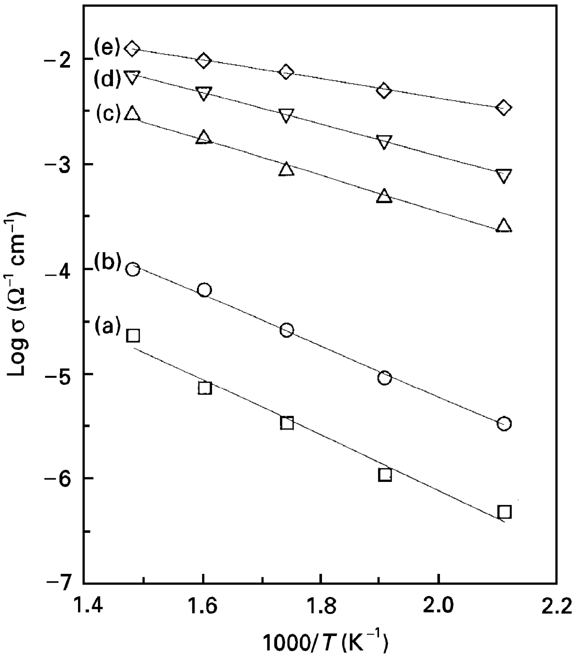


Figure 5 Electrical conductivity versus temperature in $K_{1.6}(Mg_{1-y}Cu_y)_{0.8}Ti_{7.2}O_{16}$ ceramics. (a) $y = 0$, (b) $y = 0.2$, (c) $y = 0.5$, (d) $y = 0.8$, (e) $y = 1$.

1100 °C for 4 h. It is reported that the density of ionic conductors is related to grain-boundary resistance [12]. As a result of the increase of copper fraction y, which replaced magnesium sites, the densities tended to increase, possibly due to the behaviour of copper as a sintering agent. The microstructures of the specimens sintered at 1100 °C for 4 h are shown as a function of the copper fraction y in Fig. 4. Abrupt grain growth has been observed with increasing copper fraction y, confirming the effect of copper on sinterability. For the $BaTiO_3$ system, a similar effect was also obtained by copper addition [13].

The effects of copper substitution on the a.c. electrical conductivity $K_{1.6}(Mg_{1-y}Cu_y)_{0.8}Ti_{7.2}O_{16}$ specimens were measured by using an impedance analyser as a function of temperature; the results are shown in Fig. 5. As the copper fraction y increased, the a.c. conductivity of the $K_{1.6}(Mg_{1-y}Cu_y)_{0.8}Ti_{7.2}O_{16}$ specimens monotonically increased while the activation energy decreased. Generally, for polycrystalline conductors, the electrical properties are known to be dependent not only on the size of ions, lattice defects and bonding type, but also on specimen density and microstructure due to the variations in composition and preparation conditions. Thus the improved conductivity with increasing copper fraction y can be explained first by the increase of the grain size that is equivalent to the decrease of the grain boundary. Furthermore, it is well known that the conduction properties of polycrystalline ceramics are susceptible to microstructural features such as grain size and grain-boundary morphology [14]. The deterioration in the electrical conductivity from the single crystal K–β-alumina to the polycrystal was reported to be clearly due to the presence of a grain-boundary effect [15]. The hollandite structure encourages a one-dimension conduction mechanism and so ionic conductivity strongly depends on the number of the grain–grain boundary–grain conduction paths. Abrupt grain growth occurred in the specimen with copper fraction $y = 0.5$ and the result has the same trend as the increase of the a.c. electrical conductivity with increase of the copper fraction y. Thus it is considered that the grain growth with increase of the copper fraction makes the number of the ionic conduction paths increase, due to a reduction of the grain boundaries. Therefore, the electrical conductivity increased with increasing grain growth.

Furthermore, it can be considered that the higher electrical conductivity with increasing copper fraction is due to the increase in bulk density, which means more interconnecting potassium conduction paths. The effect of densification on activation energy of the ionic conducting ceramics reported by Ho [12] is in good agreement with these results.

Finally, the increase in electrical conductivity can be explained by the strengthening covalent bonding in $[MO_6]$ (M = Ti, Mg and Cu) octahedra. In the ternary compounds of the formula $A_xB_yO_z$, weakening of the A–O bond may be a consequence of a strengthening in the competing B–O bond [16]. As mentioned previously, in this study, the substitution of copper on the magnesium site results in higher covalency in the framework of $[MO_6]$ octahedra, which induces weaker K–O bonds and reduces the activation energy of the potassium ion mobility in the tunnel of the framework. The interpretation is valid if the only electronic conduction portion is so small that it is negligible compared with the ionic conduction one. So the transport number of the $K_{1.6}(Mg_{1-y}Cu_y)_{0.8}Ti_{7.2}O_{16}$ specimens was measured by the modified Wagner's polarization method [9]. In the range of copper fraction $y = 0$–0.5, electronic contributions were less than 10^{-3} compared with ionic contributions, but electronic contributions abruptly increased in the specimens containing copper fraction $y \geqslant 0.8$. These results indicate that the increase in conductivity related to bond characterization, specimen density and reduction of grain boundaries, is considered effectively in the range of copper fraction $y = 0$–0.5. However, electronic conduction is predominant in the range of copper fraction $y = 0.8$–1. Because electrolyte/electrode interface reactions did not reach equilibrium, the transport numbers of the electrons are believed to be less than the value measured in this study. Similar results were reported for β-alumina [17]. Transport numbers of the specimens with copper fraction $y = 0.8$–1 are not meaningful, due to the relatively large error range and thus the only interpretation is that electronic conduction occurred in the specimens with copper fraction $y \geqslant 0.8$.

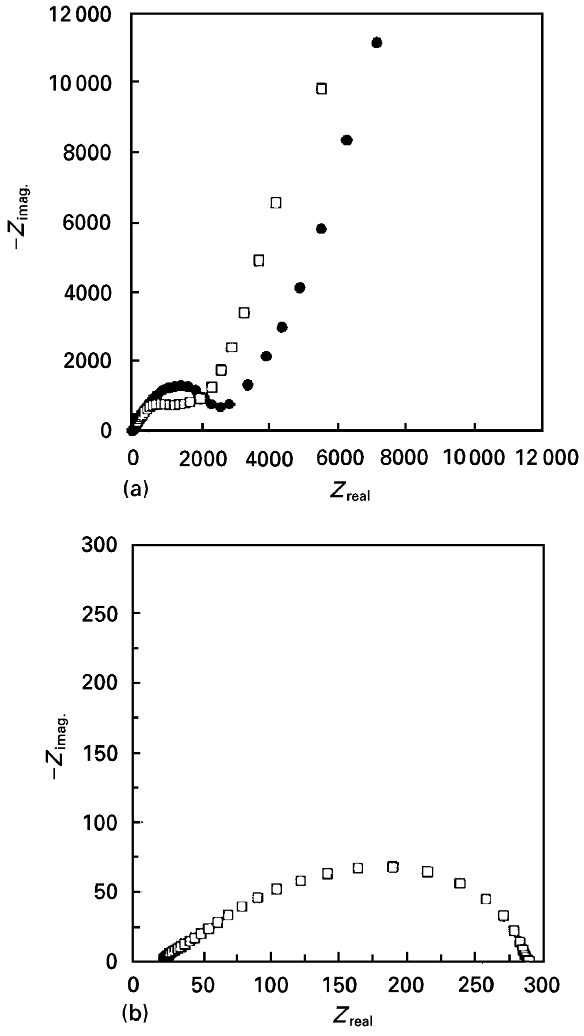


Figure 6 Impedance spectra of $K_{1.6}(Mg_{1-y}Cu_y)_{0.8}Ti_{7.2}O_{16}$. (a) (●) $y = 0.5$ and (□) 0.8, (b) □ $y = 1$.

Fig. 6 shows the impedance spectra of (a) specimens at $y = 0.5$, 0.8, and (b) $y = 1$ specimens. Spectra (a) appeared at electrolyte/electrode interface due to accumulation of potassium ions which indicated the presence of the potassium ion conduction. Spectrum (b), with no rising spectrum tale at low frequency, indicates only electronic conduction. The first arcs of the impedance spectra were the sum of the grain and grain-boundary resistances. The capacitance at each resonance frequency was about 4–8×10^{-8} μF cm^{-2}. The grain-boundary resistance was not extracted from the impedance spectra due to the dispersion of the relaxation time. It was reported that the intragrain resistance in the polycrystal was about ten times higher than that of the single crystal [18]. Therefore, the intragrain resistance is so small that it is negligible.

To elucidate any significant development of the electronic conduction, the valence states of the specimens with copper fractions of 0.5 and 0.8, were

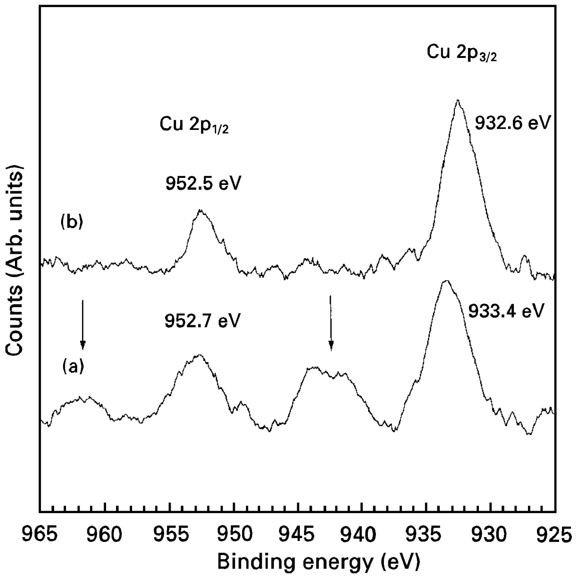


Figure 7 XPS spectra of (a) $K_{1.6}(Mg_{0.5}Cu_{0.5})_{0.8}Ti_{7.2}O_{16}$, and (b) $K_{1.6}(Mg_{0.2}Cu_{0.8})_{0.8}Ti_{7.2}O_{16}$ ceramics (↓ satellite line of Cu 2p).

analysed by XPS. In Fig. 7, the XPS spectra show that the Cu $2p_{3/2}$ main peak of the specimen with copper fraction $y = 0.8$ was shifted around 0.8 eV to lower binding energy of the metallic and/or 1+ valency state, compared with that of the specimen with copper fraction $y = 0.5$, and also that the Cu $2p_{3/2}$ satellite line of the copper fraction $y = 0.8$ apparently decreased compared with that of the specimen with copper fraction $y = 0.5$. The result suggested that the valence state of the copper changed from the 2+ state to the 1+ and/or metallic one during the sintering process. It could be considered that the generation of oxygen ion vacancies caused conduction electrons to be released, and they combined with the copper 2^+ ion, resulting in a change of the valence state of the copper in oxygen octahedra. So the conduction electrons in the specimen containing copper fraction $y \geqslant 0.8$ were majority charge carriers when an electric field was applied. These assumptions are represented in defect equations as follows

$$\mathrm{O_o} = \mathrm{V_o^{\cdot\cdot}} + 2\mathrm{e}' + \tfrac{1}{2}\mathrm{O_2} \qquad (1)$$

$$+\, 2\mathrm{Cu_{Cu}} + 2\mathrm{c}' = 2\mathrm{Cu'_{Cu}} \qquad (2)$$

$$2\mathrm{Cu_{Cu}} + \mathrm{O_o} = \mathrm{V_o^{\cdot\cdot}} + 2\mathrm{Cu'_{Cu}} + \tfrac{1}{2}\mathrm{O_2} \qquad (3)$$

Therefore, electronic conduction is thought to be affected by oxygen partial pressure. More systematic work on the dependence of the oxygen partial pressure is required.

4. Conclusion

At the calcination temperature of 1000 °C for 4 h, a tetragonal single phase was obtained for $K_{1.6}(Mg_{1-y}Cu_y)_{0.8}Ti_{7.2}O_{16}$ $(0 \leqslant y \leqslant 1)$ powders. As the copper fraction y increased, the increase in the covalency of bonds, the density and the grain size led to an increase of the electrical conductivity. The $K_{1.6}(Mg_{1-y}Cu_y)_{0.8}Ti_{7.2}O_{16}$ specimens containing copper fraction $y < 0.8$ showed ionic conduction while electronic conduction was observed for the specimens copper fraction $y \geqslant 0.8$ resulting from the valence transition of copper ions.

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