

Ionic conductivity and crystal structure relationships in Ti/Cu substituted $\text{Bi}_4\text{V}_2\text{O}_{11}$

M. H. PAYDAR

Department of Metallurgy and Material Sciences Eng., School of Eng., Shiraz University, Shiraz, Iran

A. M. HADIAN

Department of Metallurgy and Material Sciences, Faculty of Eng., University of Tehran, Tehran, Iran

G. FAFILEK

Institute of Technical Electrochemistry and Solid State Chemistry, University of Technology of Vienna, Getreidemarkt 9/158, 1060 Vienna, Austria
E-mail: Fafilek@mail.zserv.tuwien.ac.at

Crystal structure and oxide ion conductivity of a series of Ti and Ti-Cu double substituted $\text{Bi}_4\text{V}_2\text{O}_{11}$ compounds, $\text{Bi}_2\text{V}_{(1-x)}\text{Ti}_x\text{O}_{(11-x)/2}$ ($0.085 \leq x \leq 0.15$), and $\text{Bi}_2\text{V}_{0.9}\text{Cu}_{(0.1-x)}\text{Ti}_x\text{O}_{5.35+x}$ ($0 \leq x \leq 0.1$), were investigated using X-ray powder diffraction and ac impedance spectroscopy in the temperature and frequency range of 100–700°C and 10^{-2} – 10^7 Hz, respectively.

Structural phase transitions, $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$, occur as a function of composition in Ti substituted compounds for which the γ is evidenced to be stable at room temperature when x exceeds 0.125. For all Ti-Cu double substituted compounds studied, the room temperature phase was identified to be γ phase.

The required amount of Ti for γ phase stabilization at room temperature was significantly reduced and the conductivity improved when Cu substituted a part of Ti. Therefore, for the $\text{Bi}_2\text{V}_{0.9}\text{Cu}_{(0.1-x)}\text{Ti}_x\text{O}_{5.35+x}$ ($0 \leq x \leq 0.075$) compounds the ionic conductivity increased and activation energy decreased with decreasing x . At low temperature, the highest ion conductivity was obtained for $\text{Bi}_2\text{V}_{0.9}\text{Cu}_{0.1}\text{O}_{5.35}$. At high temperature ($T > 500^\circ\text{C}$), a different behavior was observed. The total conductivity increased at first with decreasing x values down to $x = 0.05$ and then decreased. The maximum conductivity was obtained for $\text{Bi}_2\text{V}_{0.9}\text{Cu}_{0.05}\text{Ti}_{0.05}\text{O}_{5.4}$, and the activation energy decreased with decreasing x values, such as what happened at low temperature. © 2004 Kluwer Academic Publishers

1. Introduction

Since the introduction of $\text{Bi}_4\text{V}_2\text{O}_{11}$ as a solid electrolyte with high conductivity at moderate temperature [1], a great deal of research has been carried out to modify the composition and crystal structure to obtain the highest ionic conductivity at the lowest possible temperature. As a result, a new family of solid electrolyte, BIMEVOX, invented by stabilizing the high temperature phase of bismuth vanadate (tetragonal, γ , phase) at room temperature by replacing a part of vanadium with a metal element (e.g., Cu, Ni, Ti, Co, . . .) [2–7].

Generally, the room temperature crystal structure of BIMEVOX materials and their ionic conductivity depends on the nature and the amount of Me element, where substituted a part of vanadium [8]. Regarding this fact, BICUVOX [2, 3, 9], BITIVOX [4, 10], and BIZNVOX [11] systems are introduced as the best ones, among all the systems that investigated.

In the present paper we report a detailed study on the crystal structure and ionic conductivity of the BITIVOX

system, and also compare the ability of Ti, and Ti-Cu double substitution in stabilizing the γ crystal structure of the bismuth vanadate parent phase, and their effects on electrical properties of the new, BICUTIVOX, system.

2. Experimental procedure

Polycrystalline samples with nominal composition of $\text{Bi}_2\text{V}_{0.9}\text{Cu}_{(0.1-x)}\text{Ti}_x\text{O}_{5.35+x}$ ($0 \leq x \leq 0.1$), were prepared by solid state synthesis from analytical grade of Bi_2O_3 , V_2O_5 , CuO , and TiO_2 (Aldrich, 99.9% purity).

The reactants were thoroughly mixed using an attrition mill with zirconia balls and fired at 650°C for 15 h and then at 750°C for 5 h in air with an intermediate grinding. The crystal structure of the synthesized compounds was identified by means of X-ray diffraction using a $\text{Cu K}\alpha$ source. The lattice parameters were determined using a least squares cell refinement program [12]. Dense ceramic monoliths of 10 mm diameter and

approximately 1.4 mm thickness were formed by uniaxially cold pressing the mixed powders at 350 MPa and sintering in the temperature range of 730–750°C for 5 h. For $\text{Bi}_2\text{V}_{0.9}\text{Cu}_{(0.1-x)}\text{Ti}_x\text{O}_{5.35+x}$ ($0 \leq x \leq 0.1$) materials the optimum sintering temperature increased with increasing Ti content (x). The electrical properties of the samples were measured by means of ac impedance spectroscopy using a Solartron 1260. Pt electrodes were sputtered on both sides of the samples, which had been polished up to grade 1200, and annealed at 730°C for 3 h prior the measurements. Impedance spectra were measured in the frequency range of 0.01 Hz–10 MHz and from 100 to 700°C at 25°C intervals over two heating and cooling cycles in air. The experimental data was analyzed based on the equivalent circuits introduced, by Dygas *et al.* [13], which are a modification of Bauerles's model [14]. The circuit parameters were estimated by using a nonlinear least-square fitting program provided by Zplot software (Scribner Associate, Inc., USA).

3. Results and discussion

3.1. X-ray diffraction

The XRD patterns for the BITIVOX solid solutions are presented in Fig. 1. It indicates that for $x \geq 0.125$, the tetragonal γ phase of the parent material, $\text{Bi}_4\text{V}_2\text{O}_{11}$, has been stabilized at room temperature [1]. For $x = 0.115$ the diffraction pattern can be equally judged to be either the tetragonal or orthorhombic phase which is an indication of bordering between β and γ phase stability. Below $x = 0.115$, especially for $x = 0.1$, a clear splitting in the tetragonal 110 peak was observed which is evidence of the orthorhombic β type structure. For $x \leq 0.1$ the splitting of the tetragonal 110 peak developed and superstructure peaks were observed corresponding to the orthorhombic α phase. The variation of the unit cell parameters with composition is presented in Fig. 2. For $x < 0.125$, data were fitted to an orthorhombic mean cell and for $x \geq 0.125$, a tetragonal mean cell was selected to fit the X-ray patterns. In the range of $0.1 \leq x \leq 0.115$ a relatively large change in

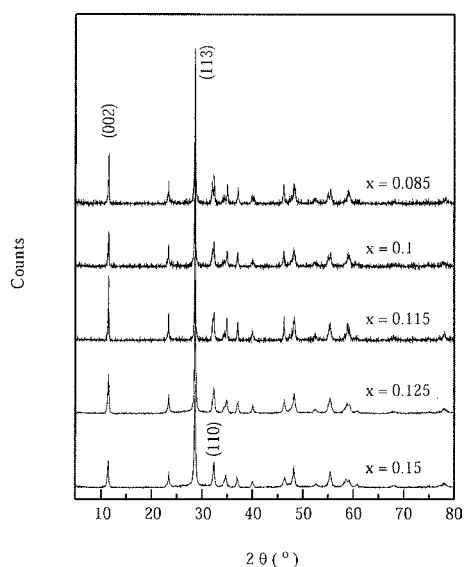


Figure 1 X-ray diffraction patterns for $\text{Bi}_2\text{V}_{(1-x)}\text{Ti}_x\text{O}_{(11-x)/2}$ ($0.085 \leq x \leq 0.15$) compounds.

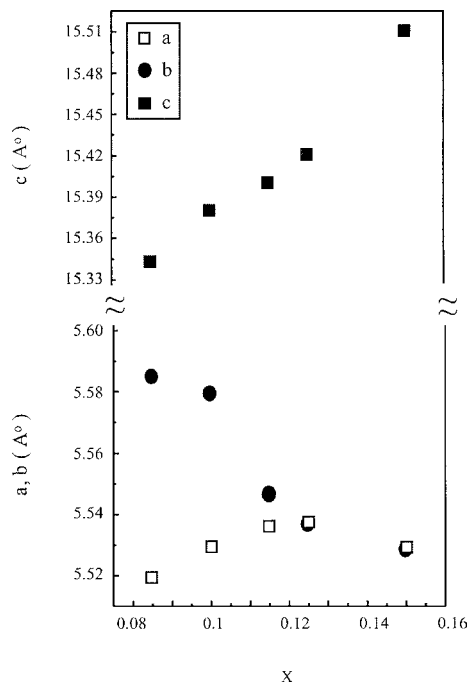


Figure 2 Variation of the unit cell parameter of BITIVOX system with X values (Ti content).

the b parameter was observed which is an indication of the $\alpha \rightarrow \beta$ phase transformation and the resulting small β phase is visible at $x = 0.115$. A tetragonal γ phase was identified to be stable in the range of $0.125 \leq x \leq 0.15$. These results are to some extent different from those obtained by Yan and Greenblatt [10] who suggested that the tetragonal phase is stable for $x \geq 0.1$, but in agreement with Lazure *et al.* [8] who identified $x \geq 0.125$ for the stability of the γ phase. The variation in basal a -parameter and axial c -parameter (decrease and increase with increasing the Ti substitution content, respectively) in the range of γ phase stability, where studied here, are consistent with those seen by Yan and Greenblatt [10]. If it is supposed that the oxygen vacancy ordering phenomena are restricted to the basal plane and there is not any axial vacancy in the defect structure [15], then the decrease in a -parameter can be considered as the result of oxygen loss in the basal plane. The increase in c -parameter could be expected in terms of the larger effective size of Ti^{4+} versus that of V^{5+} , although it is not completely clear because of the complexity of the $\text{Bi}_4\text{V}_2\text{O}_{11}$ crystal structure. In order to compare the ability of Cu and Ti for stabilizing the γ phase of the $\text{Bi}_4\text{V}_2\text{O}_{11}$ parent material, and to investigate the effect of Cu-Ti double substitution for V on stabilizing of the γ phase at room temperature and its ion conductivity, a series of BICUTIVOX compounds with nominal composition of $\text{Bi}_2\text{V}_{0.9}\text{Cu}_{(0.1-x)}\text{Ti}_x\text{O}_{5.35+x}$ ($0 \leq x \leq 0.1$) was synthesized. The X-ray patterns of these compounds are presented in Fig. 3. For all these compositions the crystal structures were identified to be γ phase and no significant change could be detected. Only for $x = 0.075$, a few superstructure peaks were observed so that the X-ray pattern could also be equally fitted with tetragonal or an orthorhombic mean cell. These results definitely confirm the ability of Cu with regards to Ti

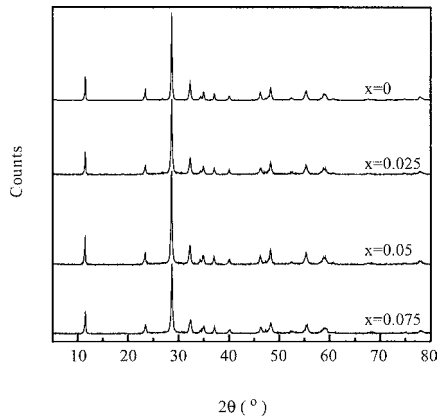


Figure 3 X-ray diffraction patterns for $\text{Bi}_2\text{V}_{0.9}\text{Cu}_{(0.1-x)}\text{Ti}_x\text{O}_{5.35+x}$ ($0 \leq x \leq 0.075$) compounds.

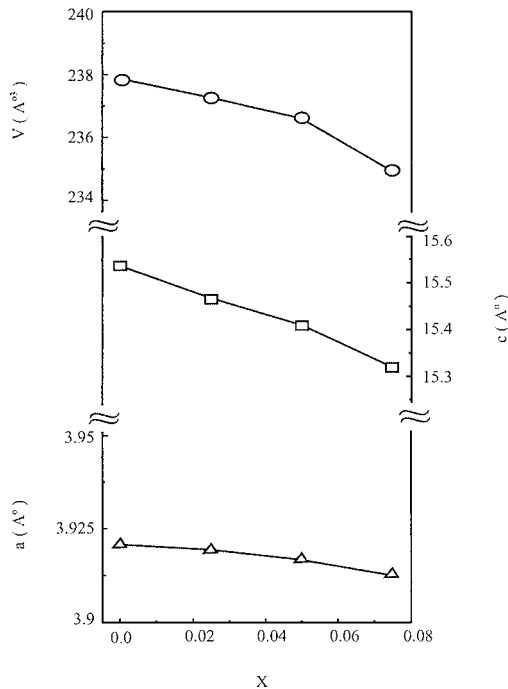


Figure 4 Unit cell parameter and cell volume variation of BITICUVOX system with X values (Ti and Cu content).

in affecting the long range ordering of the parent compound and stabilizing the high temperature γ phase at room temperature. The change in cell parameters with composition is shown in Fig. 4. With increasing Ti content (x), a and c parameters and also the cell volume concurrently decreased. As shown in Fig. 2, by increasing the Ti substitution amount within the range of the γ phase stability, the a -parameter decreased and the c -parameter increased in contrast to the BICUVOX system. There, it was observed [16] that both a and c parameters increased, which reflects the substitution of V (V) by the larger Cu (II), (0.59 \AA versus 0.73 \AA). Concerning these facts, it can be supposed that in the BICUTIVOX system the decrease in the a -parameter with increasing Ti content is dominated by increasing the amount of oxygen loss. It also reflects the substitution of Cu (II) by the smaller Ti (IV) ions, which is considered to have minor effect. For the decrease of the c -parameter this factor can be considered to have major effect. The volume decrease of the crystal by increasing

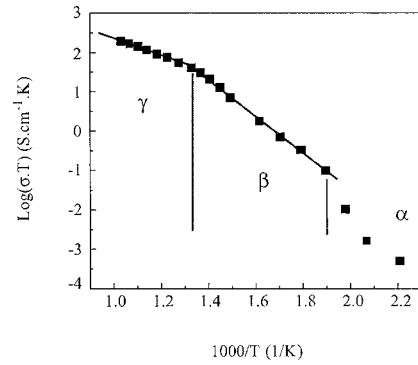


Figure 5 Temperature dependence of the total conductivity of the polycrystalline sample of BITIVOX $x = 0.085$.

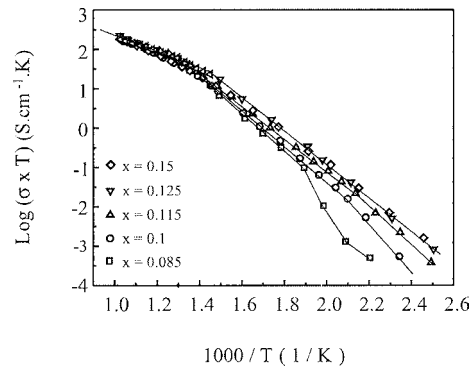


Figure 6 Comparison of total conductivities of the polycrystalline samples of BITIVOX system ($0.085 \leq x \leq 0.15$) at different temperature.

the Ti content is natural when both a and c -parameters decrease.

3.2. Ionic conductivity

The temperature dependence of total ionic conductivity of BITIVOX ($0.085 \leq x \leq 0.15$) compounds is illustrated in Figs 5 and 6. The variations of the conductivity with composition follow the same trend reported for all other materials of the BIMEVOX family [2–10] and confirm the phase transitions detected by X-ray diffraction. At $x = 0.085$ the variation of $\text{Log}(\sigma T)$ versus $1000/T$ (Fig. 5) can be definitely separated into three different temperature regions, where the slope of the total conductivity line (activation energy, E_a) changes. The variation in conductivity corresponds to the change in the crystal structure with temperature. At $x = 0.085$ the low temperature phase had α crystal structure as shown in Fig. 1. By increasing the temperature it undergoes two phase transformations, $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$, at 525 and 735 K, respectively.

Fig. 6 compares the Arrhenius plots for the samples with $0.085 \leq x \leq 0.15$. The corresponding activation energy for each linear part was estimated by assuming the following Arrhenius equation:

$$\sigma = (\sigma_0/T) \exp(-E_a/KT) \quad (1)$$

These values are summarized in Table I. By increasing the Ti content in the range of $0.085 \leq x \leq 0.125$, the α phase region disappears and the slope of the line corresponds to the β region which also gradually vanishes

TABLE I Crystal structure and ionic conductivity's activation energy for $\text{Bi}_2\text{V}_{(1-x)}\text{Ti}_x\text{O}_{(11-x)/2}$ ($0.085 \leq x \leq 0.15$) and $\text{Bi}_2\text{V}_{0.9}\text{Cu}_{(0.1-x)}\text{Ti}_x\text{O}_{5.35+x}$ ($0 \leq x \leq 0.075$) compounds

Sample	Structure type	Activation energy (eV)	
		At room temperature	$T < 400^\circ\text{C}$ $T > 500^\circ\text{C}$
$\text{Bi}_2\text{V}_{(1-x)}\text{Ti}_x\text{O}_{(11-x)/2}$			
$X = 0.085$	α	0.926	0.47
$X = 0.1$	α	0.86	0.5
$X = 0.115$	β	0.82	0.454
$X = 0.125$	γ	0.78	0.455
$X = 0.15$	γ	0.8	0.467
$\text{Bi}_2\text{V}_{0.9}\text{Cu}_{(0.1-x)}\text{Ti}_x\text{O}_{5.35+x}$			
$X = 0$	γ	0.66	0.4
$X = 0.025$	γ	0.695	0.416
$X = 0.05$	γ	0.7422	0.42
$X = 0.075$	γ	0.78	0.44

so that for $x = 0.125$ the structure relates to the γ phase. As the XRD results also indicated for this composition, the stable phase had the γ crystal structure at room temperature. In the range of the γ phase stability, $x \geq 0.125$, the low and high temperature activation energies, $E_{a(\text{LT})}$ and $E_{a(\text{HT})}$ increased with composition which is a common feature of BIMEVOX materials [8, 17]. The high temperature activation energy of other compositions studied was nearly the same.

The low temperature ionic conductivity ($T < 500^\circ\text{C}$) increased with compositions up to $x = 0.125$ while in the range of the γ phase stability it decreased with increasing Ti substitution. The variations of ionic conductivity with composition at 300°C (σ_{300}) are compared in Fig. 7. The data shows a clear maximum in ionic conductivity at $x = 0.125$ which is $2.6 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$. These results are in agreement with Lazure *et al.* [8], who introduced $x = 0.125$ as the optimum composition in the BITIVOX system, but it is different from the data found by Yan and Greenblatt [10], who suggested $x = 0.15$ as the optimum composition. The high temperature ionic conductivity for the samples with $x \leq 0.125$ did not follow a clear trend, and changed in narrow range. It decreased with increasing x in the range of $0.125 \leq x \leq 0.15$, therefore at $T = 600^\circ\text{C}$ the lowest ionic conductivity, $0.109 \text{ S}\cdot\text{cm}^{-1}$, was obtained at $x = 0.15$. Arrhenius plots for $\text{Bi}_2\text{V}_{0.9}\text{Cu}_{(0.1-x)}\text{Ti}_x\text{O}_{5.35+x}$ ($0 \leq x \leq 0.075$) compounds are shown in Fig. 8. The activation energies

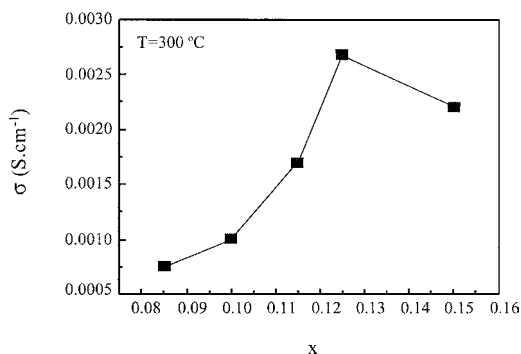


Figure 7 Variation of the ionic conductivity of BITIVOX with X values (Ti content) at 300°C .

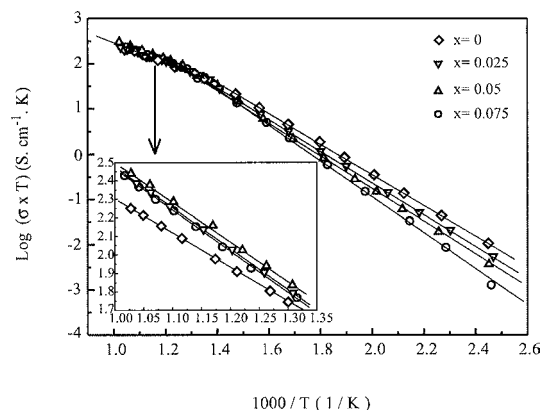


Figure 8 Comparison of total conductivities of the polycrystalline samples of $\text{Bi}_2\text{V}_{0.9}\text{Cu}_{(0.1-x)}\text{Ti}_x\text{O}_{5.35+x}$ system ($0 \leq x \leq 0.075$) at different temperature.

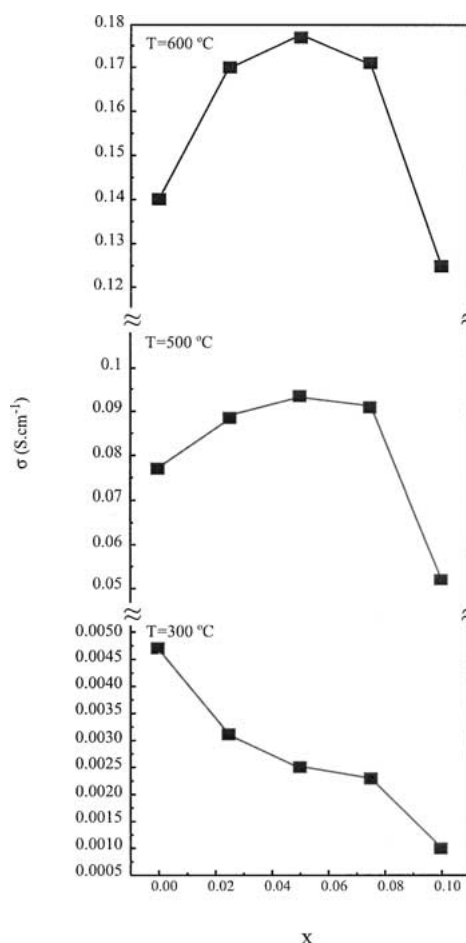


Figure 9 Variation of the ionic conductivity of BITICUVOX with X values (Ti and Cu content) at 300, 500 and 600°C .

for low and high temperature are presented in Table I. The activation energies ($E_{a(\text{LT})}$ and $E_{a(\text{HT})}$) clearly increased by increasing the Ti substitution rate, and became closer to the value obtained for BITIVOX system. Fig. 9 shows the variation of ionic conductivity with composition at $T = 300, 500$ and 600°C . The ionic conductivity at low temperature is in agreement with the change in activation energy and also as expected from the change in the cell parameters (Fig. 4), a and c decreasing with increasing x values. At high temperature ($T \geq 500^\circ\text{C}$), a different behavior was observed. The conductivity increased with x values up to $x = 0.05$

and then decreased, so that the maximum conductivity was obtained for $\text{Bi}_2\text{V}_{0.9}\text{Cu}_{0.05}\text{Ti}_{0.05}\text{O}_{5.4}$. Probably, the contribution of the electronic conductivity to the total conductivity is relatively high for BITICUVOX system at high temperature. Further research in this regard is in progress.

4. Conclusion

In this study, crystal structure and its relation to the ionic conductivity of the BITIVOX and BITICUVOX systems was investigated. The lowest limit of Ti substitution for the $\text{Bi}_2\text{V}_{(1-x)}\text{Ti}_x\text{O}_{(11-x)/2}$ system required to stabilize the γ -phase of $\text{Bi}_4\text{V}_2\text{O}_{11}$ at room temperature, which corresponds to the maximum σ values at low and high temperature, was determined at $x = 0.125$. It was found that the lowest limit of the required Ti content for stabilization of the γ -phase at room temperature could be decreased by partial substitution of Ti with Cu. The ionic conductivity at low temperature decreased and its corresponding activation energy increased by increasing the Ti content in the $\text{Bi}_2\text{V}_{0.9}\text{Cu}_{(0.1-x)}\text{Ti}_x\text{O}_{5.35+x}$ ($0 \leq x \leq 0.1$) system. At high temperature the variation of the activation energy with composition followed the same trend as in the low temperature region but the total conductivity increased with Ti substitution level up to $x = 0.05$ and then decreased. This effect was more pronounced at higher temperature and probably indicates that the electronic contribution to the total conductivity at high temperature is higher for Ti-Cu double substituted compounds.

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