Electric Properties of a New Ferrite $K_4Cu_2Fe_7V_7O_{32}$ with a Hollandite-Type Structure

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Abstract. Results of investigation of electric transport properties of a new magnetically ordered hollandite compound with a composition $K_4Cu_2Fe_7V_7O_{32}$ will be reported. Resistance versus temperature measurements (78-350 K) on the ceramic samples were carried out by means of four-lead dc, pulse and ac techniques. The temperature coefficient of resistance determined from $R(T)$ measured by dc and pulse techniques has been found to be zero in 78-200 K range and it takes negative values in temperatures above 200 K. Additionally, hysteresis effect was observed in temperature range 200-310 K. Details of relationship between the resistance R and voltage U at different temperatures will be discussed. Surprisingly enough, the $R(T)$ dependence of studied compound bears a characteristic features for amorphous material although the crystallinity of our samples has been confirmed by XRD and Mössbauer spectroscopy.

1. INTRODUCTION

Electrically conducting oxides have always been an interesting subject of studies not only because of their electric and magnetic properties but also from the point of view of chemistry and electrochemistry. Such compounds are for example hollandites which are described by a general formula AB_8O_{16} [1], where A cation may be monovalent or divalent, and M cation may be a combination of two metals or one metal present at two different oxidation states. They are considered as possible solid electrolytes because of their characteristic structure. The unique feature of their structure is the presence of large tunnels of the B_8O_{16} framework in which univalent ions A such as Na^+ , K^+ , Rb^+ and Cs^+ can achieve high mobility. Hollandites form one-dimensional model-system for superionic conductors [2,3]. This paper reports results of the study of the bulk resistance of $K_4Cu_2Fe_7V_7O_{32}$ over the temperature range 78-350 K, made using three different techniques. It should be emphasized that the majority of hollandites studied so far did not show magnetic ordering. The compound $K_4Cu_2Fe_7V_7O_{32}$ belongs to the family of materials $K_4Me_2Fe_7V_7O_{32}$ where $Me=Ni, Co, Mn$ in which magnetic ordering (AF, FM or FIM) was observed [4].

2. EXPERIMENTAL

A new ferrite $K_4Cu_2Fe_7V_7O_{32}$ was prepared by standard ceramic technique starting with Cu, Fe and V oxides and potassium carbonate. The stoichiometric amounts of these substrates were ground together, pressed into pellets and then fired twice in air at about 1173 K. The pellets were characterized by conventional XRD technique. The XRD data have shown that the samples have the tetragonal hollandite-related structure ($c/a=1.07$) with a multiplication of the short-axis [1]. Electric transport measurements were performed using ac (at a frequency of 50 Hz), pulse and dc four-probe techniques. In addition, the relationship between the resistance R and voltage U at different temperatures (125 K and 295 K) has been studied.

3. RESULTS AND DISCUSSION.

In Fig. 1 the temperature dependences of the resistance of $K_4Cu_2Fe_7V_7O_{32}$ measured by three different techniques is plotted. The results can be described as follows: (i) In all cases the $R(T)$ curves can be divided into three distinct regions. In the first, from 78 to 200 K the resistance remains constant and practically independent of temperature. At about 200 K it begins to decrease significantly up till ~ 300 K. Above 320 K the effect of saturation is observed. (ii) Relaxations effects are observed in the $R(T)$ curves measured by the dc and pulse techniques. (iii) The temperature coefficient of resistance γ_{TCR} was determined on the basis of the data presented in Fig. 1 (I -) using the following equation:

$$\gamma_{TCR} = R^{-1}(dR/dT),$$

where R is the resistance of contacting grains consisting of contributions from both: materials composition and its geometrical features and resistance of contacts. In the region 200-350 K resistance of $K_4Cu_2Fe_7V_7O_{32}$ exhibits negative γ_{TCR} with minimum value -0.55 K^{-1} for $T=300 \text{ K}$ and $\gamma_{TCR}=0$ for $78 \text{ K} < T < 200 \text{ K}$.

Figure 1: Resistance vs temperature for $K_4Cu_2Fe_7V_7O_{32}$ for three techniques: ac(L), impulse (I_{imp}) and dc (L). Solid lines are to guide the reader's eye. Symbols the black triangles and empty circles used in the Figure indicate the data for heating and cooling cycle, respectively.

We also measured the resistance of $K_4Cu_2Fe_7V_7O_{32}$ as a function of voltage at fixed temperatures 125 K and 295 K by the dc and ac techniques. The dependence obtained by the dc method $R_-(U_-)$ shows entirely ohmic character ($R=\text{constant}$) while that obtained by the ac technique is linear with the slope $(dR/dU)_T=\text{constant}(U)$, where $(dR/dU)_{T=125 \text{ K}} = 0.084 \text{ M}\Omega/\text{V}$ and $(dR/dU)_{T=295 \text{ K}} = 0.037 \text{ M}\Omega/\text{V}$. The obtained results suggest the semiconducting - like behaviour of the compound studied. However, it should be noted that only the linear region between 200-300 K of the $\ln R$ vs T dependence indicates the activated behaviour of the resistance. As $K_4Cu_2Fe_7V_7O_{32}$ belongs to the family of low-dimensional hollandite-type compounds a large increase of electric conductivity observed for $T>200 \text{ K}$ can indicate increased mobility of K^+ ions in 1D type crystal structure. In conclusion, the obtained results are unexpected because the temperature dependence of resistance of the new ferrite $K_4Cu_2Fe_7V_7O_{32}$ has a character similar to that for amorphous samples although the crystallinity of our sample was confirmed by XRD and ^{57}Fe -Mössbauer spectroscopy [5]. To elucidate the observed effects further measurements like those of resistivity in higher temperatures ($T>350 \text{ K}$), Hall effect and termopower are required. Moreover, these measurements should be preferably performed on monocrystals.

References

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