Dielectric and a.c. conductivity studies in pure and manganese doped layered K$_2$Ti$_4$O$_9$ ceramics

SHRIPAL$^1$, S. BADHWAR$^1$, DEEPA MAURYA$^1$, JITENDRA KUMAR$^2$
$^1$Department of Physics, P.P.N. College Kanpur-208001, India
E-mail: shripalsharmappn@yahoo.co.in
$^2$Materials Science Programme, I.I.T. Kanpur-208016, India

The results of a.c. electrical conductivity studies have been reported on pure K$_2$Ti$_4$O$_9$ (named PT) and its 1.0 molar percentage of MnO$_2$ doped derivative (named MPT) ceramics in the temperature range 373–898 K. Four regions have been identified in the log($\sigma_{a.c.}$ T) versus 1000/T plots. Conduction in the lowest temperature region I is attributed to the mixed exchangeable interlayer ionic and electronic hopping (polaron) conduction. A dielectric loss peak with distribution of relaxation times perturbs the conduction in next regions II and III. However, in region III for both the samples non-relaxor ferroelectric property may be proposed. The modified interlayer ionic conduction has been proposed towards the higher temperature region IV. Loss tangent (tan $\delta$) versus frequency and dielectric constant ($\varepsilon$) versus frequency plots at different temperatures have also been given for both the samples. The results of tan $\delta$ versus temperature and $\varepsilon$ versus temperature at different frequencies have further been reported for both of the above compounds in this paper. © 2005 Springer Science + Business Media, Inc.

1. Introduction

Different types of alkali titane possessing unique layered and tunnel structure have been synthesized by some research groups [1]. Their physico-chemical properties, such as optical properties, ionic and electronic conductivities [2–9] have been investigated on account of their applicability in the industry as ion exchangers, electrodes for secondary batteries, filters, reinforcement, heat insulators, catalysts and so on. Yaohua et al. [10] have reported hydrothermal intercalation reaction of nickel hydroxide into layered manganese oxides. Alkali titanates have also been synthesized by hydrothermal reaction at a relatively low temperature of around 100 °C. A nano size titania powder, with particles 7 nm in diameter, was supplied as the starting material to allow the hydrothermal synthesis of layered titanates, Na$_2$Ti$_3$O$_7$ and K$_2$Ti$_4$O$_9$ with a pentagonal prism tunnel and K$_2$Ti$_4$O$_9$ with a zigzag layered structure have been studied by Machida et al. [21]. Effects of RuO$_2$ dispersion on photocatalytic activity of water decomposition of BaTi$_4$O$_9$ with a pentagonal prism tunnel and K$_2$Ti$_4$O$_9$ with a zigzag layered structure have been reported by Ogura et al. [22]. Shripal et al. [23–25] investigated K$_2$Ti$_4$O$_9$ and other similar compounds through EPR and d.c. conductivity studies. Very recently, Na$_2$Ti$_3$O$_7$ and its manganese doped derivatives have been studied through dielectric-spectroscopic and a.c. conductivity investigations by Shripal et al. [26]. Dawar et al. [27] have also reported the results of d.c. electrical conductivity studies on ceramic samples of Rb$_2$Ti$_3$O$_7$, Rb$_2$Ti$_5$O$_{11}$ and RbKTi$_4$O$_9$.

As far as PT and MPT are concerned; no attempt has been made to characterize these compounds.

*Author to whom all correspondence should be addressed.
through a.c. conductivity and dielectric-spectroscopic measurements. It was thus found interesting to synthesize and characterize pure and 1.0 molar parentage of MnO₂ doped derivatives of K₂Ti₄O₉. The corresponding results have been reported in this manuscript.

2. Experimental

The polycrystalline samples of pure K₂Ti₄O₉ (named PT) were prepared by heating a mixture of K₂CO₃ powder (99.9% pure, AR grade) and TiO₂ powder (99% pure, AR grade) in the molar ratio 1.3:4 at 1100 K for 16 h. The heated product was cooled to room temperature (RT) and mixed in acetone for grinding to achieve fine powder, then compressed to 15 MPa to get a pallet of K₂Ti₄O₉ (10.25 mm in diameter and 1.2 mm in thickness). The resulting pellets are covered with the powder of the same composition to prevent reaction with the wall of the crucible and also to diminish soda loss then sintered at 1100 K for 14 h and cooled to room temperature (RT) at a rate of 3.0 K per min. Flat faces of pellets were coated with silver for electrical measurements. Doped derivative of K₂Ti₄O₉ with 1.0 molar percentage of MnO₂ (named MPT) was prepared as above by mixing the appropriate molar percentages of MnO₂ powder (99.8% pure, AR grade) in the base matrix. X-ray diffraction patterns of the synthesized compounds have been recorded with Rich-Seifert ISO-Debyeflex 2002 powder diffractometer using Cu Kα radiations at a scanning speed of 3°/min and time constant of 10 s. The details of a.c conductivity and dielectric-spectroscopic measurements have been reported elsewhere [26].

3. Results and discussion

XRD-patterns obtained at RT for both PT and MPT samples are shown in Fig. 1 which are also in agreement to that reported in the literature [6, 12]. This confirms the formation of these titanates. The reflection peaks have been indexed.

The polycrystalline samples of pure K₂Ti₄O₉ (named PT) were prepared by heating a mixture of K₂CO₃ powder (99.9% pure, AR grade) and TiO₂ powder (99% pure, AR grade) in the molar ratio 1.3:4 at 1100 K for 16 h. The heated product was cooled to room temperature (RT) and mixed in acetone for grinding to achieve fine powder, then compressed to 15 MPa to get a pallet of K₂Ti₄O₉ (10.25 mm in diameter and 1.2 mm in thickness). The resulting pellets are covered with the powder of the same composition to prevent reaction with the wall of the crucible and also to diminish soda loss then sintered at 1100 K for 14 h and cooled to room temperature (RT) at a rate of 3.0 K per min. Flat faces of pellets were coated with silver for electrical measurements. Doped derivative of K₂Ti₄O₉ with 1.0 molar percentage of MnO₂ (named MPT) was prepared as above by mixing the appropriate molar percentages of MnO₂ powder (99.8% pure, AR grade) in the base matrix. X-ray diffraction patterns of the synthesized compounds have been recorded with Rich-Seifert ISO-Debyeflex 2002 powder diffractometer using Cu Kα radiations at a scanning speed of 3°/min and time constant of 10 s. The details of a.c conductivity and dielectric-spectroscopic measurements have been reported elsewhere [26].

3. Results and discussion

XRD-patterns obtained at RT for both PT and MPT samples are shown in Fig. 1 which are also in agreement to that reported in the literature [6, 12]. This confirms the formation of these titanates. The reflection peaks have been indexed.

A monoclinic crystal system with a cell configuration is selected on the basis of a good agreement in d{sub}obs and d{sub}cal.

The values for a.c. conductivity (σ{sub}a.c.) for PT and MPT have been calculated with Rich-Seifert ISO-Debyeflex 2002 powder diffractometer using Cu Kα radiations at a scanning speed of 3°/min and time constant of 10 s. The details of a.c conductivity and dielectric-spectroscopic measurements have been reported elsewhere [26].

The values for a.c. conductivity (σ{sub}a.c.) for PT and MPT have been calculated with Rich-Seifert ISO-Debyeflex 2002 powder diffractometer using Cu Kα radiations at a scanning speed of 3°/min and time constant of 10 s. The details of a.c conductivity and dielectric-spectroscopic measurements have been reported elsewhere [26].

Region I: This lowest temperature region exists from 373–498 K for PT and is not clear due to the presence of superimposed dielectric loss peak for MPT. The strong frequency dependence of measured a.c. conductivity (more in MPT) is observed in this lower temperature region for both the samples. It can easily be explained by proposing that the substitution of Mn{sup+} at Ti{sup+} sites [24] increases the number of loose electrons involved in hopping process by jumping through Ti-Ti chains. It is therefore attributed to the electronic hopping (polaron) conduction as already been proposed for PT in the lower temperature region by Shripal et al. [24]. Furthermore, a number of research groups [28, 29] interpreted such results by proposing that a.c. conductivity due to hopping conduction increases with increasing frequency (ω) and is proportional to ω{sup s}, where s is a parameter having value less than unity. Such a frequency dependence, which has been attributed to a wide distribution of relaxation times due to distribution of jump distances [30] and barrier heights [31].

It is very interesting to propose that exchangeable interlayer ionic conduction (which require very low activation energy) co-exist with electronic hopping conduction in this region for both the samples as well reflected from the higher values of a.c. conductivity.

Region II: This region exists in the temperature range 498–573 K for PT and 423–573 K for MPT. It can be seen from Fig. 2(a) and (b) that in this region, conductivity is less frequency dependent as compared to region I and temperature dependent for PT, while still strong frequency dependent and almost temperature independent for MPT. The decrease in conductivity in this region has also been observed for MPT, which may be due to hindrance produced in conduction through interlayer space by contracted interlayer space due to Mn{sup+} substitution at Ti{sup+} sites [24]. Also, different shape of these conductivity plot from the d.c. conductivity plot [24] can be explained by taking into consideration [32] that there are two mechanisms responsible for the a.c.