Electrical studies on ceramic samples of $\text{Rb}_2\text{Ti}_4\text{O}_9$, $\text{Rb}_2\text{Ti}_5\text{O}_{11}$ and RbKTi_4O_9

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Abstract. Electrical conductivity studies have been reported on $\text{Rb}_2\text{Ti}_4\text{O}_9$, $\text{Rb}_2\text{Ti}_5\text{O}_{11}$ and RbKTi_4O_9 in the temperature range 373 K to 750 K. Three distinct regions have been identified in the $\log(\sigma T)$ versus $1000/T$ plots, the lowest temperature region being attributed to extrinsic defects, the intermediate one to exchange of alkali ions and the highest temperature region to thermally created defects. A phase transition is indicated for each of the three compounds. The plot of resistivity with temperature further indicates the occurrence of a positive temperature coefficient of resistivity in RbKTi_4O_9 .

Keywords. Phase transition; activation energy; PTCR.

1. Introduction

The alkali titanates are layered compounds (Anderson and Wadsley 1961; Verbaere and Tournouse 1973) and consist of layers of composition $(\text{Ti}_n\text{O}_{2n+1})$; $1 \leq n \leq 6$ held together by alkali ions. Ionic conductivity studies have recently been reported in polycrystalline samples of $\text{Na}_2\text{Ti}_3\text{O}_7$, $\text{K}_2\text{Ti}_4\text{O}_9$ and in some derivatives doped with niobium by Kikkawa *et al* (1985). Chen and Greenblatt (1985) have observed a remarkable enhancement in the conductivity of $\text{Li}_2\text{Ti}_3\text{O}_7$ by Li diffusion. Frequency and temperature dependence of loss tangent ($\tan \delta$) in $\text{Na}_2\text{Ti}_3\text{O}_7$ and NaKTi_3O_7 and d.c. conductivity studies in $\text{Na}_2\text{Ti}_3\text{O}_7$, NaKTi_3O_7 , $\text{K}_2\text{Ti}_4\text{O}_9$ and RbKTi_4O_9 have further been made in this laboratory by Shri Pal *et al* (1988) recently. In view of their current importance (Tareev 1979) a series of such compounds are being investigated for their use in industry. In our programme to explore such materials, it has been felt worthwhile to study some of the ceramic samples of alkali titanates. In the present communication we report our d.c. electrical conductivity investigations in polycrystalline samples of $\text{Rb}_2\text{Ti}_4\text{O}_9$, $\text{Rb}_2\text{Ti}_5\text{O}_{11}$ and RbKTi_4O_9 , and further the temperature dependence of the logarithm of resistivity in the temperature range 373 to 750 K for these samples.

2. Experimental

To prepare $\text{Rb}_2\text{Ti}_4\text{O}_9$ samples, Rb_2CO_3 powder (99.9%, AR, E Merck) and TiO_2 powder (99% pure, AR, Ferak) were mechanically mixed in the molar ratio 1:3:4 and the resulting mass was heated in a silica crucible in air at 900°C for 14 hr. The product obtained was compressed at 15 MPa to give pellets which were again heated at 1000°C for a day while wrapped in platinum foil. The pellets were then brought down to RT and the flat faces were coated with silver paint. The $\text{Rb}_2\text{Ti}_5\text{O}_{11}$ compound for this work was prepared as above by a sintering process after taking Rb_2CO_3 and TiO_2 powders in the molar ratio 1:4:5. The samples of mixed

RbKTi_4O_9 were prepared, similarly from a mixture of Rb_2CO_3 , K_2CO_3 and TiO_2 powders in the molar ratio 1:3:1:3:8.

The experimental set-up with a cell for measuring electrical conductivity/resistivity for the two samples together is shown in figure 1. The d.c. conductivity measurements have been performed in vacuum with a constant potential difference (3 V) applied across the samples, the through current being measured with an electrometer amplifier (Kiethley 614). The temperature of the samples was controlled with a temperature controller and was measured with the help of a calibrated chromel–alumel thermocouple. Using the measured current through a sample and its dimensions, the resistivity (ρ) and d.c. conductivity (σ) were then evaluated.

3. Results and discussion

The logarithm of the product of d.c. conductivity (σ) with absolute temperature (T) was plotted as a function of $1000/T$ in the temperature range 373 to 750 K for samples of $\text{Rb}_2\text{Ti}_4\text{O}_9$, $\text{Rb}_2\text{Ti}_5\text{O}_{11}$ and RbKTi_4O_9 . The curves thus obtained are shown in figure 2. Regions I, II and III obtained for each of the three compounds studied are shown in the figure. For all these, region I exists from near RT up to 450 K.

The limit of region I thus does not seem to change whether the sample is a tetra- or penta-titanate of rubidium. It is further seen that the limit of this region does not change even in RbKTi_4O_9 , obtained by replacing rubidium by potassium up to 50% in weight. Because of the positive temperature coefficient of resistivity (PTCR), the plot for RbKTi_4O_9 , however, is different from RT up to 415 K. Region II exists roughly up to 610 K for $\text{Rb}_2\text{Ti}_4\text{O}_9$ and $\text{Rb}_2\text{Ti}_5\text{O}_{11}$ but roughly up to 525 K for RbKTi_4O_9 . In the case of $\text{Rb}_2\text{Ti}_4\text{O}_9$ and $\text{Rb}_2\text{Ti}_5\text{O}_{11}$, region III exists above 640 K but for RbKTi_4O_9 , it starts above 550 K. The activation energies have been determined from different slopes of $\log(\sigma T)$ versus $1000/T$ plots and are given in table 1.

In figure 3 plots of logarithm of resistivity versus absolute temperature have been plotted for $\text{Rb}_2\text{Ti}_4\text{O}_9$, $\text{Rb}_2\text{Ti}_5\text{O}_{11}$ and RbKTi_4O_9 from 373 to 743 K.

For all the three compounds the values of activation energies are the least in region I. The lower values of activation energy in this region may be attributed to

Figure 1. Experimental set-up for measuring electrical conductivity/resistivity.

Figure 2. $\log(\sigma T)$ vs. $1000/T$ plots for $\text{Rb}_2\text{Ti}_4\text{O}_9$, $\text{Rb}_2\text{Ti}_5\text{O}_{11}$, and RbKTi_4O_9 samples.

Table 1. Values of activation energies estimated from the slope of $\log(\sigma T)$ vs. $1000/T$ plots.

Sample	Activation energies (eV)		
	Region I	Region II	Region III
$\text{Rb}_2\text{Ti}_4\text{O}_9$	0.33	0.66	0.66
$\text{Rb}_2\text{Ti}_5\text{O}_{11}$	0.37	0.73	0.73
RbKTi_4O_9	0.36	0.71	0.88

the presence of extrinsic defects. At higher temperatures in region II, the interlayer exchange of alkali ions begins and may be held attributable to higher value of activation energy necessary for conduction, which would be due to alkali ions. The $\log(\sigma T)$ vs $1000/T$ plots show a departure from straight line near the boundary where region II meets the next region III. This departure may be attributed to probable phase transitions in these lattices from 610 to 640 K for $\text{Rb}_2\text{Ti}_4\text{O}_9$ and $\text{Rb}_2\text{Ti}_5\text{O}_{11}$ and from 525 to 550 K for mixed RbKTi_4O_9 . At much higher temperatures in region III cation vacancies and subsequent interstitial ions are perhaps created. The corresponding activation energy is thus attributed to the energy necessary for creation of these new defects and their subsequent transfer leading to electrical conduction. The identical values of activation energies in regions II and III for $\text{Rb}_2\text{Ti}_4\text{O}_9$ and $\text{Rb}_2\text{Ti}_5\text{O}_{11}$ can be explained by assuming that the energy

Figure 3. Logarithm of resistivity vs. temperature plots for $\text{Rb}_2\text{Ti}_4\text{O}_9$, $\text{Rb}_2\text{Ti}_5\text{O}_{11}$ and RbKTi_4O_9 .

required for ionic conduction in region II due to ion exchange of rubidium ions and in region III via creation of new defects is the same. The region III has a higher slope for RbKTi_4O_9 . This may be explained by assuming that the defects in this case need greater value of energy for their creation and subsequent participation in electrical conduction.

As is also seen from figure 3 the variation of logarithm of resistivity with temperature for $\text{Rb}_2\text{Ti}_4\text{O}_9$ and $\text{Rb}_2\text{Ti}_5\text{O}_{11}$ exhibits the usual semiconductive nature all through but for RbKTi_4O_9 , this is seen only above 420 K. The preliminary investigations are thus indicative of possible positive temperature coefficient of resistivity (PTCR) in mixed RbKTi_4O_9 similar to that reported by Vijay Raghavan *et al* (1988) in the $\text{La}_{4-x}\text{Ba}_{1+x}\text{Cu}_5\text{O}_{13+\delta}$ system.

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