

Electrical conductivity and electron paramagnetic resonance investigations in manganese-doped polycrystalline $\text{Na}_2\text{Ti}_3\text{O}_7$

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D.c. electrical conductivity studies have been reported in $\text{Na}_2\text{Ti}_3\text{O}_7$ in the temperature range 370–750 K. Three distinct regions have been identified in the $\log(\sigma T)$ versus $1000/T$ plots, the lowest temperature region being proposed to be due to electronic hopping conduction involving loose electrons of $\text{Ti}_3\text{O}_7^{2-}$ groups, the intermediate region to associated extrinsic ionic conduction through dilated interlayer space and the highest temperature region to modified interlayer ionic conduction, the modification being affected by loose oxygens from $\text{Ti}_3\text{O}_7^{2-}$ groups. The room-temperature electron paramagnetic resonance (EPR) investigations have been interpreted in terms of manganese substitution in the lattice. For a lower percentage of doping the substitution of manganese ions occur as Mn^{3+} at Ti^{4+} sites, whereas for a higher percentage of doping, Mn^{2+} ions predominantly occupy the interlayer Na^+ sites. The dilation of interlayer space has further been proposed to occur due to a Ti^{4+} substitution of manganese ions.

1. Introduction

In recent years there has been much progress in the field of layered inorganic materials [1]. Much attention has very recently been given to layered $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{H}_2\text{Ti}_3\text{O}_7$. Because of their excellent properties for cation exchange, these compounds are also under consideration for applications in treating high-level radioactive liquid waste [2]. However, in layered materials the knowledge of the relationship between properties such as selectivity and capacity for cation exchange and layered structure is insufficient [2]. The electrical conductivity studies in such compounds could be useful and corresponding studies have been reported in some layered alkali titanates recently [3, 4].

Kikkawa *et al.* [5] have reported the results of electrical conductivity on Nb^{5+} -doped $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{K}_2\text{Ti}_4\text{O}_9$. Very recently the electrical conductivity and EPR investigations in iron-doped polycrystalline $\text{Na}_2\text{Ti}_3\text{O}_7$ were made by Shri Pal [6]. These results have been interpreted by proposing that Fe^{4+} ions substitute for Ti^{4+} sites up to a very low molar percentage of Fe_2O_3 doping. On increasing the doping, the substitution of Fe^{3+} ions was proposed to occur at interlayered Na^+ sites. Furthermore, these doped ions probably shift to interstitial positions in the interlayer space and simultaneously form bonding with nearby oxygens of TiO_6 octahedra.

There is no published work in the literature on $\text{Na}_2\text{Ti}_3\text{O}_7$ doped with manganese impurity. However, when a paramagnetic manganese ion is doped in a sample of $\text{Na}_2\text{Ti}_3\text{O}_7$, it may occupy either an inter-

layer Na^+ site (the case of $\text{Na}_2\text{Ti}_3\text{O}_7$ doped with iron ions [6]) or a Ti^{4+} site (the case of iron-doped $\text{Na}_2\text{Ti}_3\text{O}_7$ [6]). In both cases cation–anion vacancies will have to be created for charge neutrality. The other possibility of impurity ions inclusion is at an interstitial site, leading to many more vacancies.

It is known that a Mn^{2+} ion ($3d^5$ paramagnetic) furnishes a well-resolved discernible EPR spectrum even at room temperature [7]. The EPR study of manganese ions could provide information about the $I-V$ pairs, if any, existing in the system and the nature of the ionic state of manganese impurity (Mn^{2+} , Mn^{3+} or Mn^{4+}) entering into the lattice of $\text{Na}_2\text{Ti}_3\text{O}_7$. Accordingly, it was found interesting to dope $\text{Na}_2\text{Ti}_3\text{O}_7$ with manganese and make d.c. electrical conductivity and EPR studies in the system.

2. Experimental

The polycrystalline samples of $\text{Na}_2\text{Ti}_3\text{O}_7$ were prepared by heating a mixture of Na_2CO_3 (99.9% pure, AR grade) and TiO_2 powder (99.6% pure, AR grade) in the molar ratio 1.1:3 at 1173 K for 12 h. The heated product was cooled to room temperature and mixed in acetone for grinding to achieve fine powder, then compressed at 15 MPa to get a pellet of $\text{Na}_2\text{Ti}_3\text{O}_7$, 1.2 cm in diameter and 0.07 cm thick. The pellet obtained was wrapped in platinum foil then heated at 1273 K for 10 h. The product was cooled to room temperature at a rate of 3.0 K min^{-1} . The flat faces of the pellet were coated with silver for electrical measurements. The manganese-doped samples of

$\text{Na}_2\text{Ti}_3\text{O}_7$ were obtained by additional mixing of appropriate molar percentages of MnO_2 powder (99.8% pure, AR grade) in the base mixture. The nomenclature of the samples used in conductivity studies is given in Table I.

The d.c. conductivity measurements were performed in vacuum with a constant potential difference (3 V) applied across the sample, the through current being measured with an electrometer amplifier (Kiethly 614). The temperature of the furnace was controlled with a temperature controller and was measured with the help of a calibrated chromel–alumel thermocouple. Using the measured current through the sample and its dimensions, the d.c. conductivity ($\sigma_{\text{d.c.}}$) was evaluated. However, all the measurements were made by stabilizing the temperature of the sample for about 20 min at each desired value.

The EPR spectra were recorded on a Varian E-line Century Series spectrophotometer E-109, which operates at X-band frequencies (about 9.3 GHz). All of the spectra were recorded with a 100 kHz field modulation. The magnetic field was measured accurately with a Varian E-500 digital nuclear magnetic resonance gaussmeter. A small speck of diphenyl picryl hydrazyl (DPPH) ($g = 2.0036$) was used as a standard g -marker for frequency measurement. The temperature variation of EPR spectra was studied by using a Varian temperature controller (V-4540). The temperature of the sample was measured with the help of a copper–constantan thermocouple in contact with the sample.

3. Results

The values of d.c. conductivity ($\sigma_{\text{d.c.}}$) for pure $\text{Na}_2\text{Ti}_3\text{O}_7$ and its light blackish manganese-doped products were determined in the temperature range 370–750 K. The corresponding $\log(\sigma_{\text{d.c.}} T)$ versus $1000/T$ plots are shown in Fig. 1. For all samples the three regions I, II and III have been identified over the entire temperature range of study.

Region I exists roughly up to 415 K for samples PST, MST1 and MST2. This region, however, extends only up to 395 K for samples MST3 and MST4. Thus, the limit of region I does not change appreciably whether the sample is in the pure form or doped with manganese impurity. Region II exists up to 700 K for pure $\text{Na}_2\text{Ti}_3\text{O}_7$, up to 675 K for sample MST1 and roughly up to 650 K for samples MST2, MST3 and MST4. Thus, the upper limit of region II slightly lowers for a small amount of manganese doping and

TABLE I Nomenclature for $\text{Na}_2\text{Ti}_3\text{O}_7$ doped with different concentrations of manganese ions

Sample	Molar percentage of doped ions
PST ^a	0.00
MST ^b 1	0.01
MST2	0.10
MST3	1.00
MST4	5.00

^a Pure sodium trititanate.

^b Manganese-doped sodium trititanate.

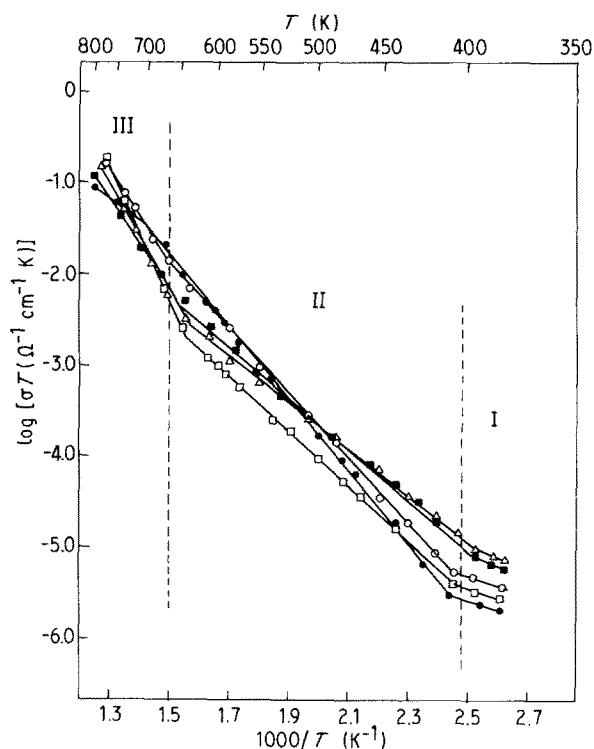


Figure 1 $\log(\sigma T)$ versus $1000/T$ plots of pure and different manganese-doped samples of $\text{Na}_2\text{Ti}_3\text{O}_7$. (●) PST, (○) MST1, (□) MST2, (△) MST3 and (■) MST4.

TABLE II Values of activation energy (eV), determined from the slopes of $\log(\sigma T)$ versus $1000/T$ plots for pure and manganese-doped $\text{Na}_2\text{Ti}_3\text{O}_7$

Sample	Region I	Region II	Region III
PST	0.27	0.73	0.44
MST1	0.27	0.64	0.99
MST2	0.24	0.60	1.49
MST3	0.35	0.51	1.16
MST4	0.37	0.56	0.95

there is no further change in the upper limit of this region with a further increase in doping. The activation energies, determined from the slopes of the $\log(\sigma_{\text{d.c.}} T)$ versus $1000/T$ plots are summarized in Table II.

For all of the samples the values of activation energies are the least in region I. Furthermore, for manganese-doped samples the activation energies in region II are intermediate to those in regions I and III.

The EPR spectra recorded at room temperature for samples MST1, MST2, MST3, MST4 and that containing 0.50 mole percentage of manganese are shown in Fig. 2. Sample MST1 gives a two-peak spectrum, one composite peak “A” with $g \approx 4.4$ and the other weak line “B” with $g \approx 2$. The broadening of the composite peak “A” with the increase of manganese concentration is seen and perhaps it is too broad to be unseen in sample MST4. Furthermore, we get a five group EPR spectrum containing six hyperfine lines with $g \approx 2$ in all of the manganese-doped samples.

So far as the temperature variation of EPR spectrum for sample MST4 is concerned, no pronounced effect is seen over the entire temperature range of study, as is shown in Fig. 3.

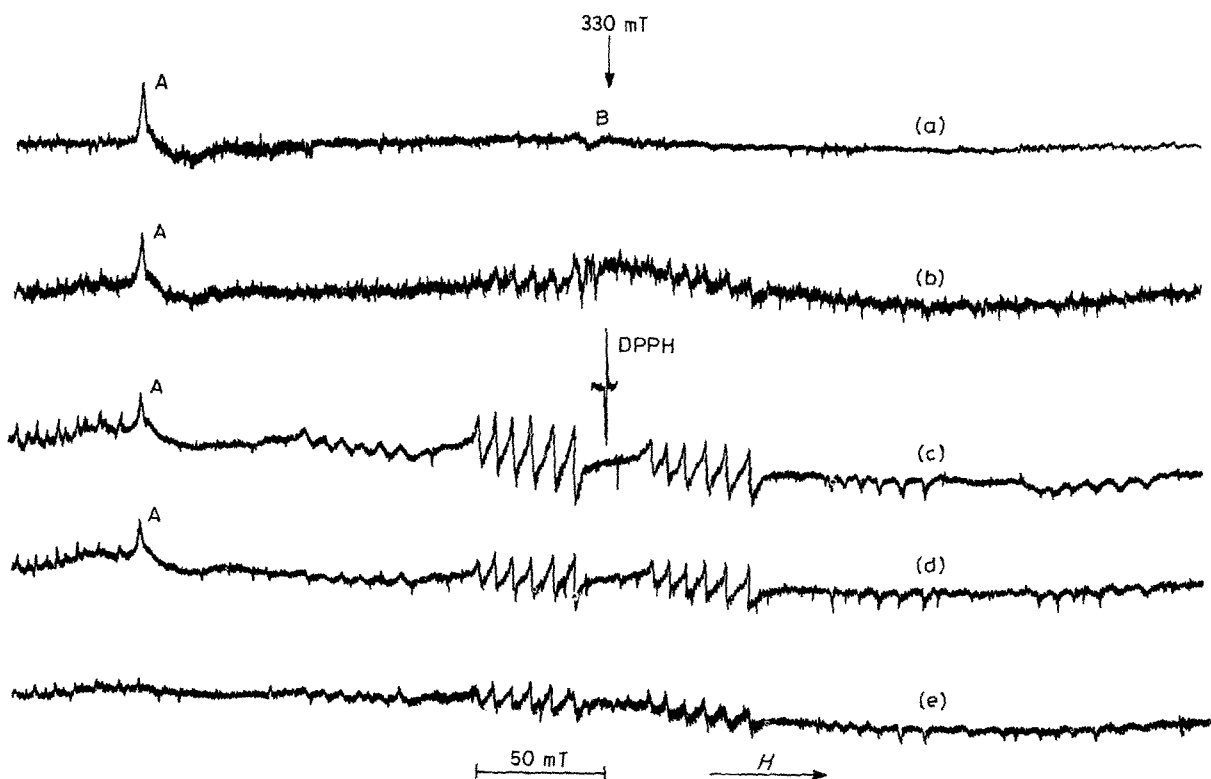


Figure 2 EPR spectra of different manganese-doped polycrystalline samples of $\text{Na}_2\text{Ti}_3\text{O}_7$ at room temperature: (a) sample MST1, (b) sample MST2, (c) sample with 0.50 mole percentage of manganese, (d) sample MST3 and (e) sample MST4.

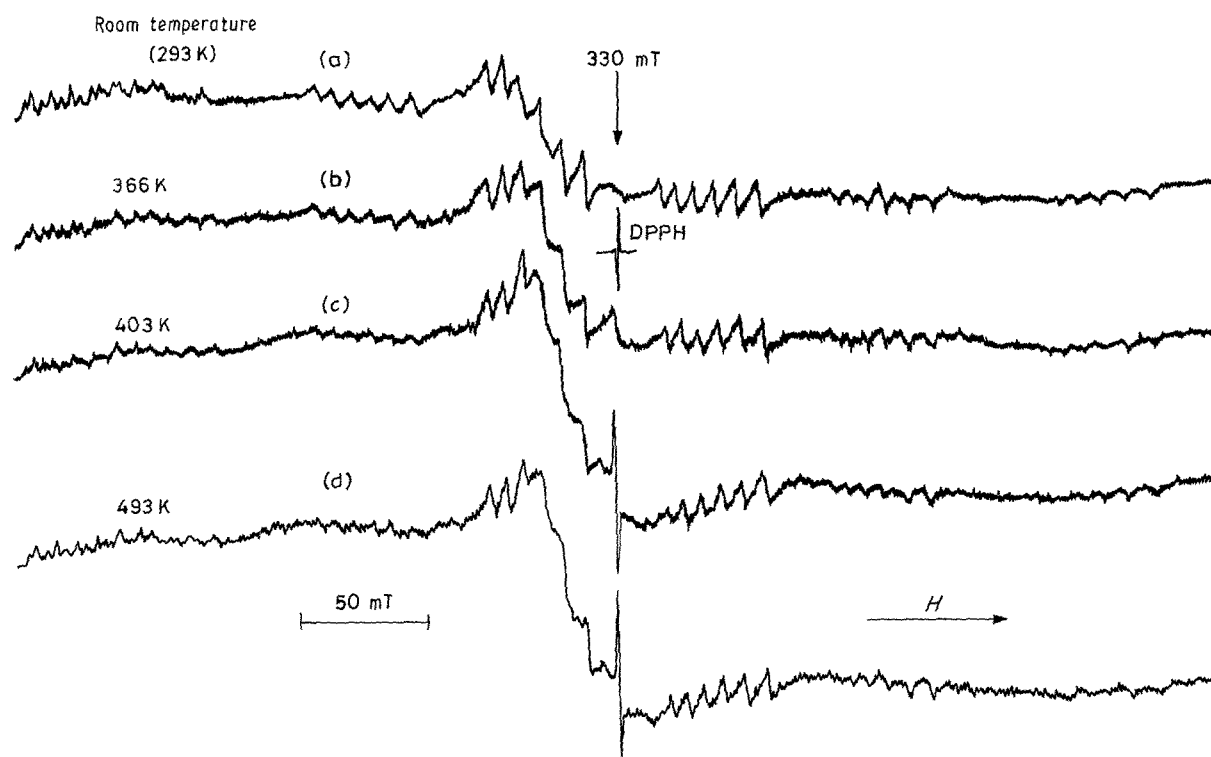


Figure 3 Temperature variation of EPR spectra of sample MST4 in the temperature range from room temperature to 493 K.

4. Discussion

In the EPR spectrum of sample MST1, the observed very weak line "B" with $g \approx 2$ can be represented to aggregated Mn^{2+} ions in the interlayer space. The composite peak "A" in the EPR spectrum with a large g -value cannot be attributed to the $3d^5$ configuration of the manganese ions. It seems that manganese ion substitutes as Mn^{3+} ($3d^4$ configuration) and the sur-

rounding oxygens rearrange to yield a tetrahedral field at the ion site, when an abnormal g -value may be possible [7].

Furthermore, the absence of composite peak "A" with $g \approx 4.4$ in sample MST4 indicates that the Mn^{3+} ions probably preferentially replace adjacent TiO_6 octahedra with increased manganese doping. Due to the exchange interaction among such neighbouring

Mn³⁺ ions, the EPR line could broaden and be absent in sample MST4.

The fine-structure spectrum consists of five prominent groups of six hyperfine lines each. This is similar to that observed for manganese doped in alkali halide crystals [8, 9], where such impurities are associated with cation vacancies. In Na₂Ti₃O₇ only Na ions exist in the interlayer region. The Mn²⁺ ions entering into this space could substitute for Na⁺ ions and simultaneously create the necessary vacancy at the nearby Na⁺ sites. The *I-V* pairs so obtained would furnish an EPR spectrum consisting of five groups of six lines each. Furthermore, as the present system is polycrystalline, the observed EPR spectrum would be an averaged one corresponding to all possible orientations of *I-V* pairs, with respect to the magnetic field. A close resemblance of this spectrum "C" to that reported by Chand and Upreti [10] for a powdered sample of NH₄I:Mn²⁺ is evident.

With this knowledge about the occupancy of manganese ions in Na₂Ti₃O₇ lattice, it has been easy to discuss the results of conductivity studies in samples with different manganese concentrations. A broad categorization of conductivity plots into three regions is quite evident and corresponding results are accordingly discussed region by region, as in the following.

4.1. Region I

The slopes for this region are about the same in the conductivity plots of all of the manganese-doped Na₂Ti₃O₇ samples. Accordingly, the impurities do not seem to play a major role for conduction in this region. This conduction is thus characteristic of the host and is attributed to the hopping process involving loose electrons of Ti₃O₇²⁻ groups, which probably jump from one Ti-Ti chain to an adjacent one. Such a process would involve a low activation energy [11, 12] and our investigations do support this.

As manganese ions that substitute at Ti⁴⁺ sites are in the tripositive valance state (Mn³⁺), their substitution would naturally cause the number of loose (trapped) electrons to increase appreciably. The observed continuous increase in conductivity in region I with the increase of impurity content in the samples from MST1 to MST3 seems to support the above conclusion. However, the observed decrease in conductivity in sample MST4 compared with sample MST3 does not follow the above behaviour. This suggests that the manganese entry into the Ti⁴⁺ sites becomes saturated for sample MST3 and further addition of impurity leads to their occupying the interlayer space.

Thus, the electronic hopping, conduction in this region may be intrinsic or otherwise, depending on the doping.

4.2. Region II

As the starting materials used for preparing the Na₂Ti₃O₇ samples were not very pure, some defects (e.g. impurities, interstitials and vacancies) are likely to be present in the interlayer space of the polycrystalline

compound prepared. At moderately low temperatures (intermediate to those for regions I and III) the cation vacancies present will always form impurity vacancy as well as interstitial vacancy pairs. The large activation energy in this region is thus naturally attributed to ionic conduction in the presence of such extrinsic defects through sodium interlayers.

In manganese-doped compounds the ions occupying Ti⁴⁺ sites with the configuration 3d⁴, similar to Fe⁴⁺ ions, reflect themselves in the composite peak "A" of the EPR spectrum. These substituting Mn³⁺ ions are expected to have smaller ionic radii than Ti⁴⁺ ions. This would naturally cause the distance between opposite Ti-Ti layers to dilate. That for a higher doping concentration the manganese definitely enters as Mn²⁺ in the interlayer space is evidenced by the observation of a five-group EPR spectrum with each group containing six hyperfine lines. Such Mn²⁺ ions are naturally expected to occupy interlayer Na⁺ sites. Now, as the ionic radius of a substituting Mn²⁺ ion is smaller than that of Na⁺ ion, the opposite Ti-Ti layers would become somewhat closer.

The change in the interlayer space as above with the increase in the impurity concentration would cause a corresponding change in the activation energy. This is reflected well in the continuous decrease of activation energy from sample PST to sample MST3 and in an increase from sample MST3 to sample MST4.

Finally, the ionic conduction in this region may easily be called "associated extrinsic ionic conduction through interlayer space".

4.3. Region III

Impurity vacancy pairs-interstitial vacancy pairs that were present in the interlayer space of pure Na₂Ti₃O₇, probably break completely up to the lower limit of region III. Thus, the ionic conduction in region III of pure sample would not be affected by *I-V* pairs. It may be attributed to free migration of sodium ions within the interlayer space, with a lower value of activation energy than that for region II. The conduction in region III for iron-doped Na₂Ti₃O₇ samples has been proposed by Shri Pal [6]. For these iron-doped samples the slope of region III was lower than that of region II. This lowering was explained on the pre-assumption that *I-V* pairs become dissociated at high temperatures and thus do not affect the conduction.

In the present manganese-doped samples the slope of region III is greater than that of region II. This cannot be explained with the usual viewpoint as above. It seems that in such samples the Mn³⁺ substitution at the Ti⁴⁺ site loosen oxygens from the Ti₃O₇²⁻ groups and then participate in large number for conduction in this region III, resulting in the apparent increase in the slope of the conductivity plot (Fig. 1). Such a behaviour is expected as long as Mn³⁺ substitutes at the Ti⁴⁺ sites, as is the case for the samples PST, MST1 and MST2.

Furthermore, doping of manganese as in samples MST3 and MST4 occurs as Mn²⁺ occupying interlayer Na⁺ sites, as reflected by the room-temperature

EPR spectrum with $g \approx 2$ and possessing five fine structure groups each of six hyperfine lines. Such substituting Mn^{2+} ions would, in general, be associated with cation vacancies. However, these would be detached from the influence of associated vacancies up to the upper limit of region II and would then perhaps pull some of the loose oxygens obtained due to substitution of Mn^{3+} at the Ti^{4+} sites. This process reduces the number of participating loose oxygens in the conduction of this region. The decreased values of activation energies from 1.49 to 0.95 eV in going from sample MST2 to sample MST4 can thus be understood.

Thus, the conduction in this region III for a manganese-doped $\text{Na}_2\text{Ti}_3\text{O}_7$ sample may easily be called "modified interlayer ionic conduction", the modification being affected by loose oxygens from $\text{Ti}_3\text{O}_7^{2-}$ groups.

5. Conclusions

The outcome of present investigations can be summarized as in the following. For the first time manganese-doped samples of $\text{Na}_2\text{Ti}_3\text{O}_7$ have been prepared and characterized through d.c. conductivity studies coupled with EPR measurements. The EPR studies help greatly in understanding the conduction process in manganese-doped $\text{Na}_2\text{Ti}_3\text{O}_7$ prepared by a ceramic method. Two types of manganese impurity substitutions are identified. A portion of manganese ions enter at the Ti^{4+} sites and acquire the $3d^4$ configuration (as for Mn^{3+}) with surrounding oxygens leading to a tetrahedral MnO_4 arrangement. Some of the manganese ions (Mn^{2+}) substitute for interlayer Na^+ ions, creating vacancies in the interlayer space for charge neutrality and thus forming $I-V$ pairs within the interlayer space.

The dilation of interlayer space for Mn^{3+} substitution at the Ti^{4+} sites has been identified through conductivity studies in manganese-doped samples of $\text{Na}_2\text{Ti}_3\text{O}_7$ and appears to affect the interlayer ionic conduction in the compound. However, the contraction of interlayer space for Mn^{2+} substitution at the Na^+ sites has also been observed through studies as above in the compound.

In doped samples (MST1, MST2, MST3 and MST4) the conduction at higher temperature is

strongly affected through participation of loose oxygens from Ti_3O_7 groups (due to the transformation of TiO_6 octahedral into MnO_4 tetrahedral arrangement for Mn^{3+} substitution at the Ti^{4+} sites). This leads to a region of modified interlayer ionic conduction.

Finally, it is seen that the $\text{Na}_2\text{Ti}_3\text{O}_7$ comes up as a compound in which electronic hopping and ionic conduction coexist at moderate temperatures, the latter gaining prominence at higher temperatures.

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