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Hydrothermal growth and characterisation of $Na_2Ti_3O_7$ crystals

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Abstract : The hydrothermal growth of $Na_2Ti_3O_7$ has been carried out at T = 500°C and P = 1 Kb The crystals obtained were subjected to a systematic characterization by various techniques like X-ray diffraction, Infrared and Impedance spectroscopy. $Na_2Ti_3O_7$ shows very interesting impedance spectroscopic characteristics.

Keywords : $Na_2Ti_3O_7$, hydrothermal growth, X-ray diffraction

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1. Introduction

Alkali titanates are technologically very important owing to their channel or skeleton structures, which make them good superionic materials. A number of titanates have been synthesised and characterized by various authors [1–3].

In the early 19th century, titanates were obtained by Rose [4] by fusing titanium dioxide with surplus potassium carbonate. Similarly, sodium metatitanate, Nd_2TiO_3, sodium orthotitanate Na_4TiO_4, sodium paratitanate $Na_2Ti_3O_7$, sodium mesodititanate, $Na_2Ti_2O_5$, and $Na_2Ti_7O_{15}$, $Na_2Ti_8O_{17}$ and so on, were obtained by various authors [5–7].

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In the present work, the authors report the hydrothermal growth of $Na_2Ti_3O_7$ crystals obtained under slightly elevated PT conditions.

2. Crystal growth

Alkalititanates can be easily obtained by solid-state reaction method at elevated temperatures in an inert atmosphere. Though a large variety of alkali titanates have been obtained in the series $A_2O.nTiO_2$ ($1 \leq n \leq 6$), where A = Li, Na, K, Rb, Cs, Tl, Ag, by solid state reactions method, the member (n = 5) has not been obtained [6,8,9]. Keeping this in mind, we have made an effort to obtain this member (n = 5) of the series by hydrothermal technique. The experiments were carried out using Tuttle cold-cone sealed autoclaves provided with platinum liners. The starting materials such as TiO_2 and NaOH (GR Loba Chemie, India), were taken in desired molar proportions and placed inside the platinum liner. The suitable mineralizer solution with a definite molarity was added into the platinum liner which was sealed later. The platinum liner was later placed inside an autoclave which was kept at T = 500°C, and P = 1 Kb for a period of 3 days. At the end of the experimental run, the platinum liner was taken out form the Tuttle autoclave and it was cut open. The resultant product was washed thoroughly in distilled water to remove the excess solvent. Long needle like crystals of $Na_2Ti_3O_7$ were obtained. The crystals were about 5 to 8 mm long, colourless and transparent. Such good quality crystals of $Na_2Ti_3O_7$ have not been obtained by solid state reactions method, wherein the resultant product was mostly a crystalline powder. The experimental conditions of the growth of $Na_2Ti_3O_7$ crystals are given in Table 1.

Table 1. Experimental conditions of the growth of $Na_2Ti_3O_7$ crystals.

Sl No	Nutrient composition		*T* (°C)	*P* (Kb)	Duration (days)	Results	Crystal size (mm)	Remarks
1	NaOH	= 5.0 g	500	1	3	$Na_2Ti_3O_7$	10	long rod like crystals
	TiO_2	= 2.5 g						
	3 *M* HCOOH	= 6 ml						
2	NaOH	= 4.0 g						
	TiO_2	= 2.5 g	500	1	3	$Na_2Ti_3O_7$	4	rod like crystals
	3 *M* HCOOH	= 6 ml						
3	NaOH	= 5.0 g						
	TiO_2	= 2.5 g	500	1	3	$Na_2Ti_3O_7$	2	small needles
	2 *M* HCOOH	= 6 ml						
4	NaOH	= 6.0 g						
	TiO_2	= 2.5 g	650	1.5	3	$Na_2Ti_3O_7$	1	fine crystals
	3 *M* HCOOH	= 6 ml						
5	NaOH	= 4.5 g						
	TiO_2	= 2.5 g	650	1	2	$Na_2Ti_3O_7$ +	< 1	fine crystals
	3 *M* HCOOH	= 6 ml				$Na_2Ti_6O_{13}$		
6	NaOH	= 5.0 g						
	TiO_2	= 2.5 g	500	1	3	$Na_2Ti_3O_7$	< 1	fine crystals
	8 *M* HCOOH	= 6 ml						
7	NaOH	= 5.0 g						
	TiO_2	= 2.5 g	500	1	3	–	–	No crystals
	11 *M* HCOOH	= 6 ml						
8	NaOH	= 6 5 g						
	TiO_2	= 2.5 g	550	1	3	$TiOSO_4$	0.2 –	fine grained
	4 *M* H_2SO_4	= 6 ml				+ Rutile	0.4	
9	NaOH	= 4.0 g						
	TiO_2	= 2.5 g	500	1.5	2	$Na_2Ti_3O_7$	0.3	fine grained
	2 *M* HNO_3	= 6 ml				+ Rutile		
10	NaOH	= 6.0 g	300	1	3 1/2	$Na_2Ti_3O_7$	< 0 2	fine grained
	TiO_2	= 2.0 g				+ $Na_2Ti_2O_5$		
	3 *M* HCOOH	= 6 ml				+ Rutile		
11	NaOH	= 6.0 g						
	TiO_2	= 2.5 g	400	1	3	$Na_2Ti_3O_7$	< 0 2	fine grained
	3 *M* HCOOH	= 6 ml				+ $Na_2Ti_2O_5$		
12	NaOH	= 6.0 g						
	TiO_2	= 2.5 g	450	1	4	$Na_2Ti_3O_7$	0.3 –	well developed
	3 *M* HCOOH	= 6 ml					0.5	needles
13	NaOH	= 4.0 g						
	TiO_2	= 2.0 g	400	1	3	Rutile	0.1 –	fine grained
	H_2O	= 6 ml					0.2	
14	NaOH	= 5.0 g						
	TiO_2	= 2.0 g	450	1.5	3	Rutile	0.1	fine grained
	H_2O	= 6 ml						

An ideal experimental condition in the growth of $Na_2Ti_3O_7$ crystals are given below :

NaOH	–	5.0 gms,
TiO_2	–	2.5 gms,
HCOOH	–	6 ml [3 molar],
Temperature	–	600°C,
Pressure	–	1 Kb,
Duration	–	4 days.

In experiments with high molarity of HCOOH, the crystal quality was poor, and beyond 10 *M* HCOOH, the $Na_2Ti_3O_7$ did not crystallize. In the present work, the other mineralizers like HCl, HNO_3, H_2SO_4 and H_2O were tried, but these experiments did not yield good

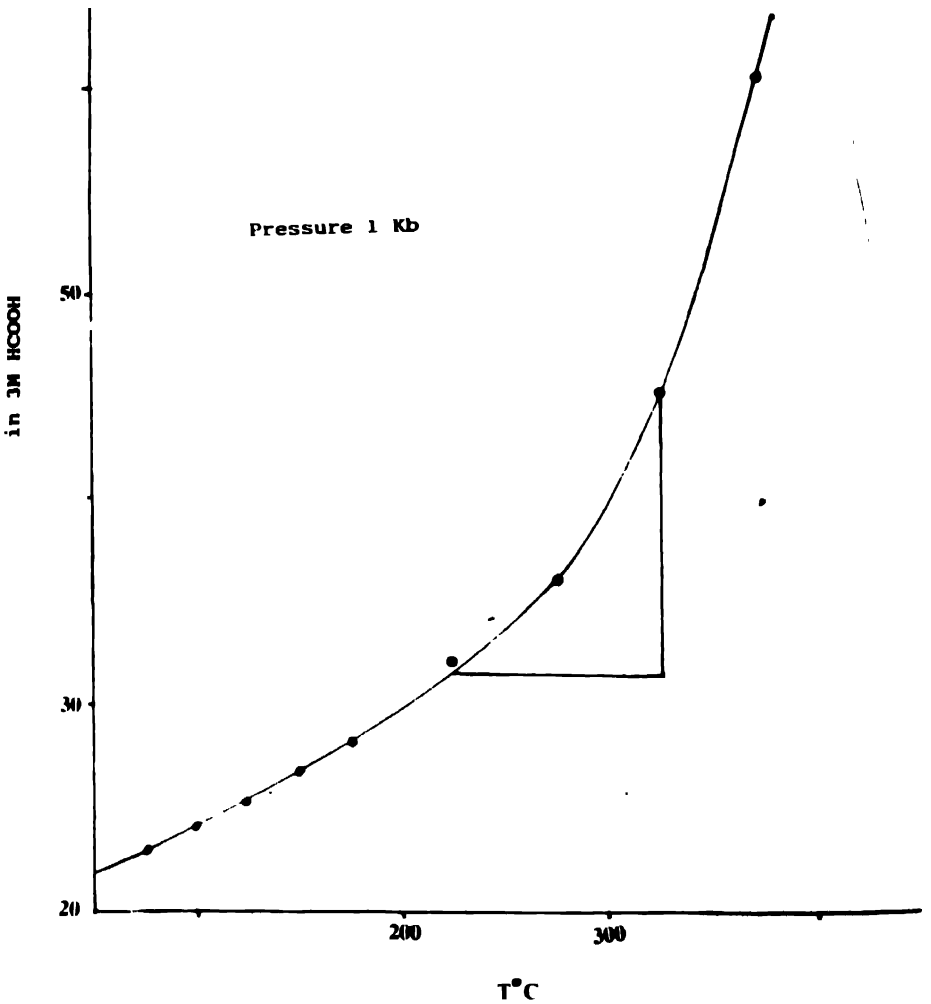

Figure 1. Solubility curve for $Na_2Ti_3O_7$ at 1 Kb pressure in 3M HCOOH with a varying temperature.

results and instead, produced either mixed or other phases. The crystallization of $Na_2Ti_3O_7$ probably takes place through the following reactions :

$$NaOH + HCOOH \longrightarrow NaHCOOH + H_2O,$$

$$5\ NaHCOO + TiO_2 \longrightarrow NaTi(OH)_5 + 2\ Na_2O + 5\ CO,$$

$$Na_2O + HCOOH \longrightarrow NaHCOOH + NaOH,$$

$$5\ NaOH + TiO_2 \longrightarrow NaTi(OH)_5 + 2\ Na_2O,$$

$$2\ NaTi(OH)_5 + TiO_2 \longrightarrow Na_2Ti_3O_7 + 5H_2O$$

The solubility of $Na_2Ti_3O_7$ was determined under hydrothermal conditions in the HCOOH media with a varying temperature and at a constant pressure of 1 Kb. The solubility curve is shown in Figure 1. It is evident from Figure 1 that the hydrothermal synthesis of $Na_2Ti_3O_7$ can be carried out within the temperature range 350 to 600°C.

An attempt to obtain a member (n = 5) by hydrothermal technique was successfull. The probable reason might be the high stabilities of $Na_2Ti_3O_7$, $Na_2Ti_6O_{13}$ and $K_2Ti_4O_7$ and they may not allow the formation of other stable phases, although such members might be present during the course of crystallization reactions.

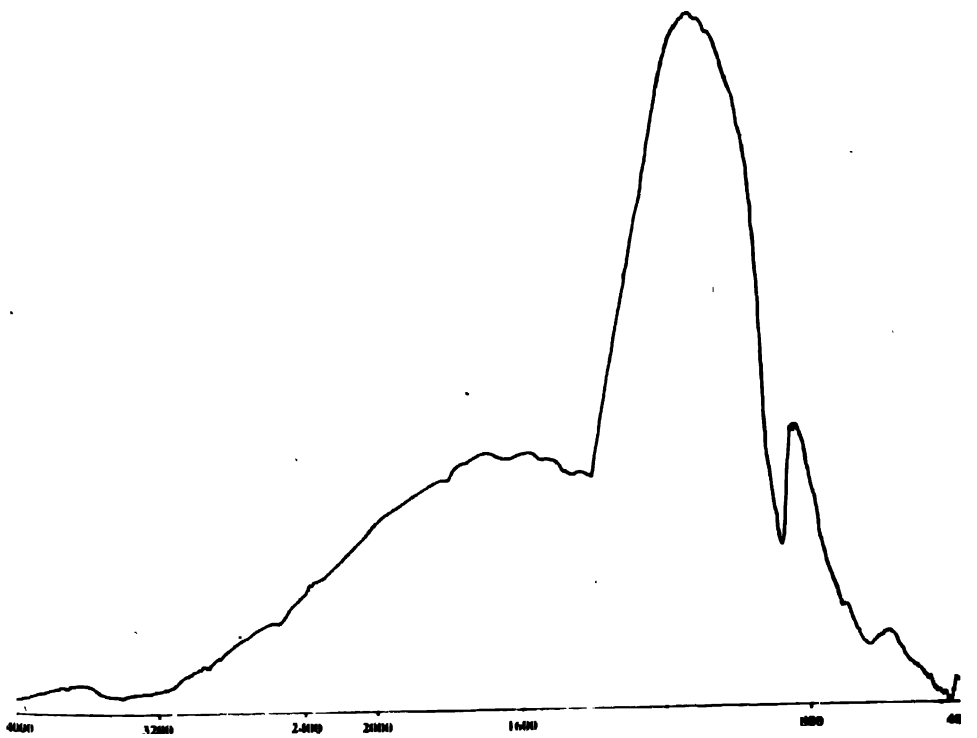

Figure 2. FTIR spectrum for $Na_2Ti_3O_7$.

3. Characterization

The $Na_2Ti_3O_7$ crystals obtained by hydrothermal technique have been subjected to a systematic characterization through various techniques like X-ray powder diffraction, infrared and impedance spectroscopic studies. The X-ray powder diffraction pattern studies were carried out using Siemens D500, Germany. X-ray diffractometer with a monochromatic radiation, CuK_α (λ = 0.15406 nm). The powder diffraction pattern matches well with that of $Na_2Ti_3O_7$. The cell parameters calculated for this compound are as follows : a = 8.58, b = 3.801, c = 9.129 Å, β = 101.59°.

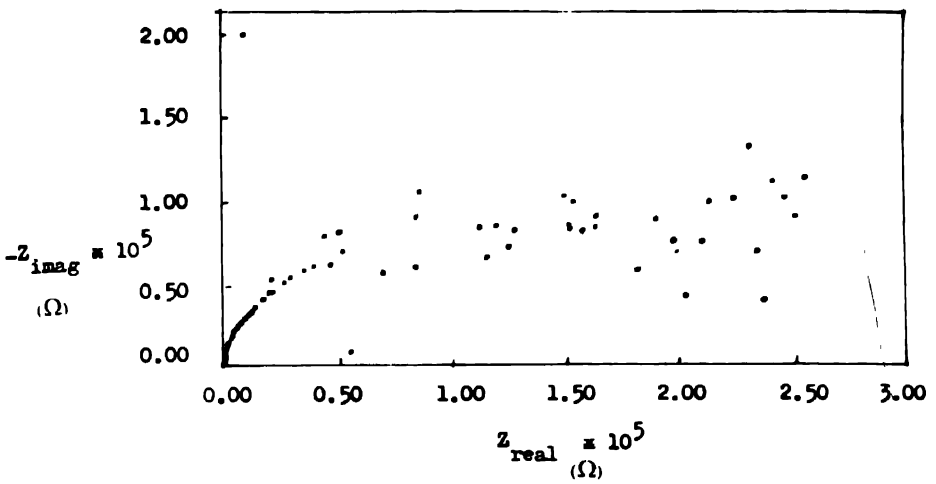

Figure 3(a). Complex impedance spectroscopic plots for $Na_2Ti_3O_7$ crystals at 299 K

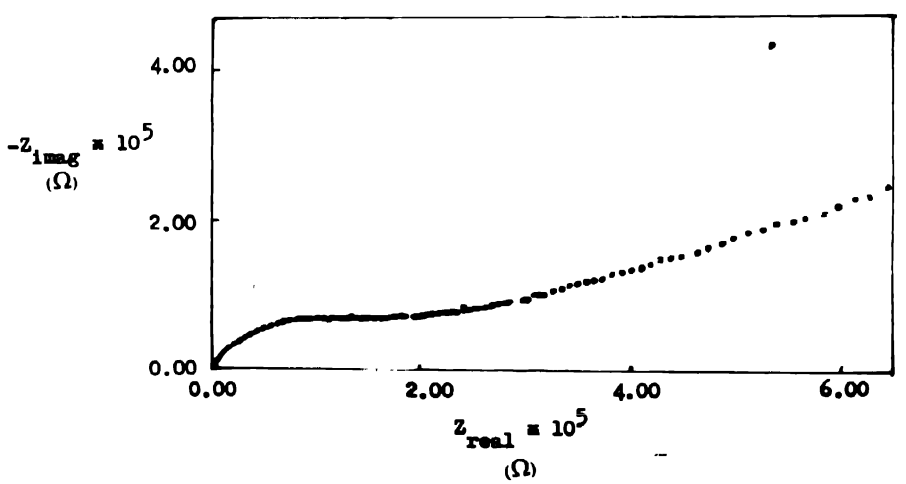

Figure 3(b). Complex impedance spectroscopic plots for $Na_2Ti_3O_7$ crystals at 323 K.

The FTIR spectrum has been recorded for the $Na_2Ti_3O_7$ crystals using KBr windows and the spectrum is shown in Figure 2.

The complex impedance spectroscopic (CIS) measurements were done using Solatron impedance/gain-phase analyser system (Model 1260) from 1 Hz to 32 MHz. The sample was taken in the form of a pellet (10 mm dia, 2 mm thick). The temperature was varied from 293 K to 493 K. The impedance analyser system was interfaced

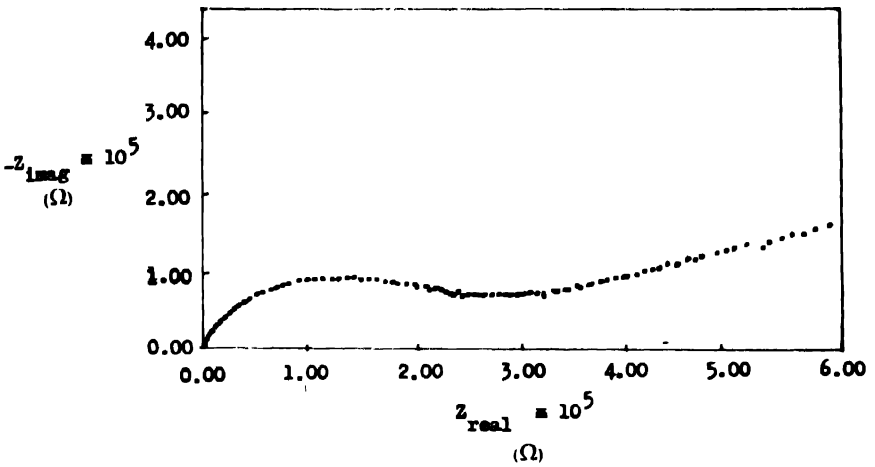

Figure 3(c). Complex impedance spectroscopic plots for $Na_2Ti_3O_7$ crystals at 373 K

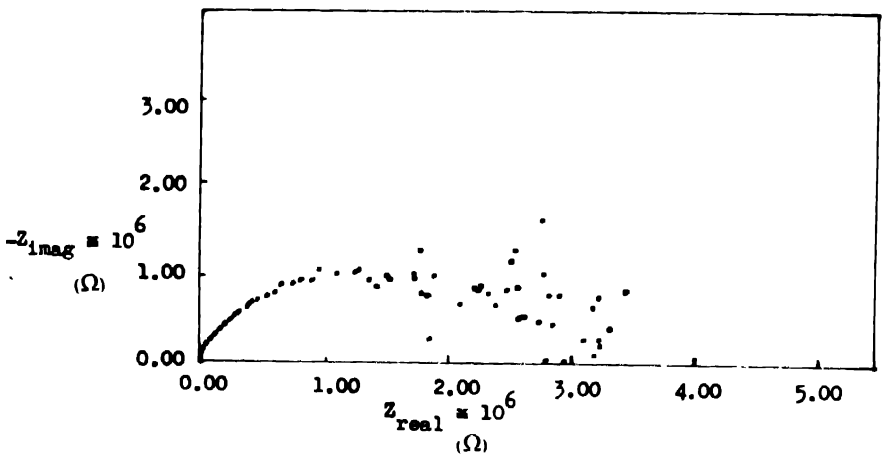

Figure 3(d). Complex impedance spectroscopic plots for $Na_2Ti_3O_7$ crystals at 423 K

to a PC/AT 486 through a general purpose interface bus (GPIB) for automated data acquisition.

The pellets were prepared by pressing the material at pressure 5 ton/cm^2. Two screw loaded silver electrodes were provided on either side of the pellet. The compactness of the pellet was 85%. The pellets were prepared 60 days after the synthesis. The CIS measurements were carried 20 days after the pelletization.

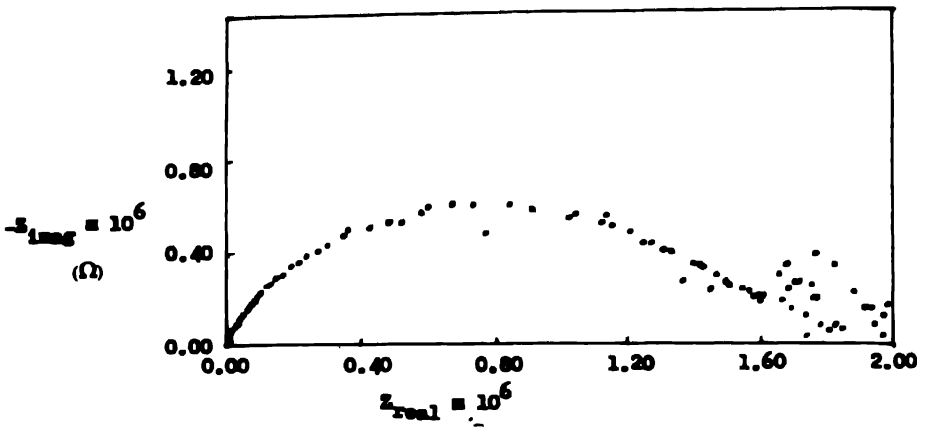

Figure 3(e). Complex impedance spectroscopic plots for $Na_2Ti_3O_7$ crystals at 473 K.

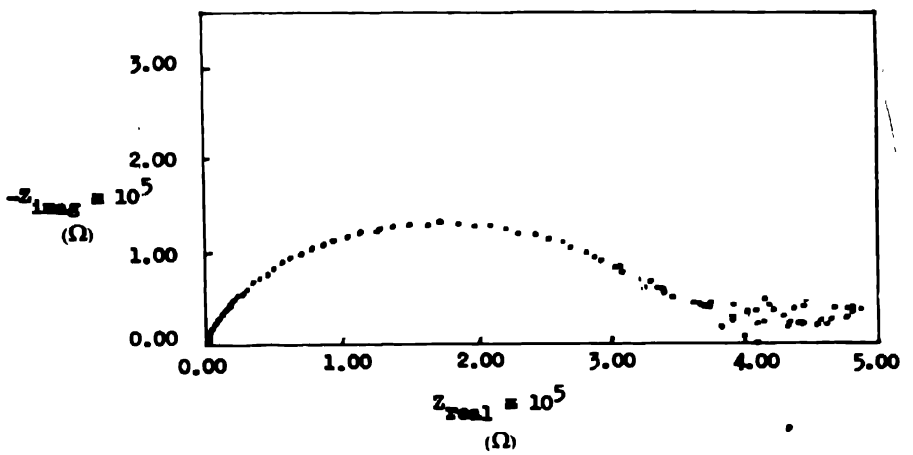

Figure 3(f). Complex impedance spectroscopic plots for $Na_2Ti_3O_7$ crystals at 523 K.

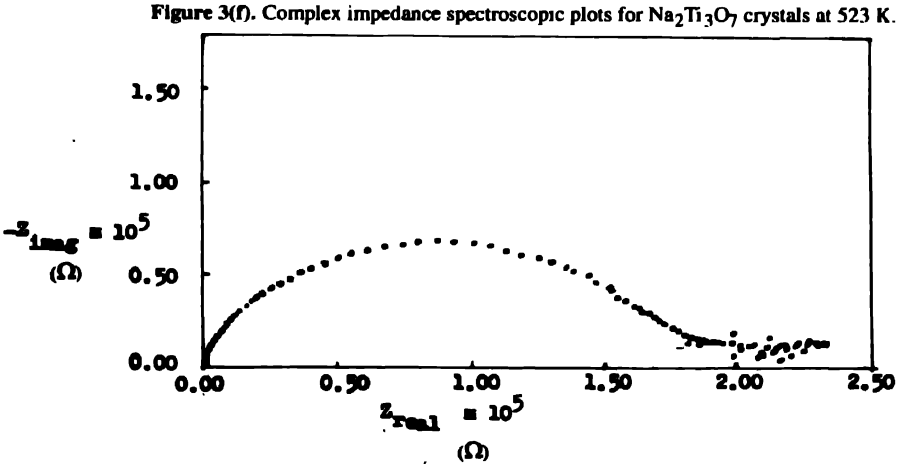

Figure 3(g). Complex impedance spectroscopic plots for $Na_2Ti_3O_7$ crystals at 548 K.

The data was analyzed using Equivalent Circuit (EQU CRT PAS) Program [11]. The frequencies mentioned in the impedance plots are in Hz. K stands for KHz and M stands for MHz.

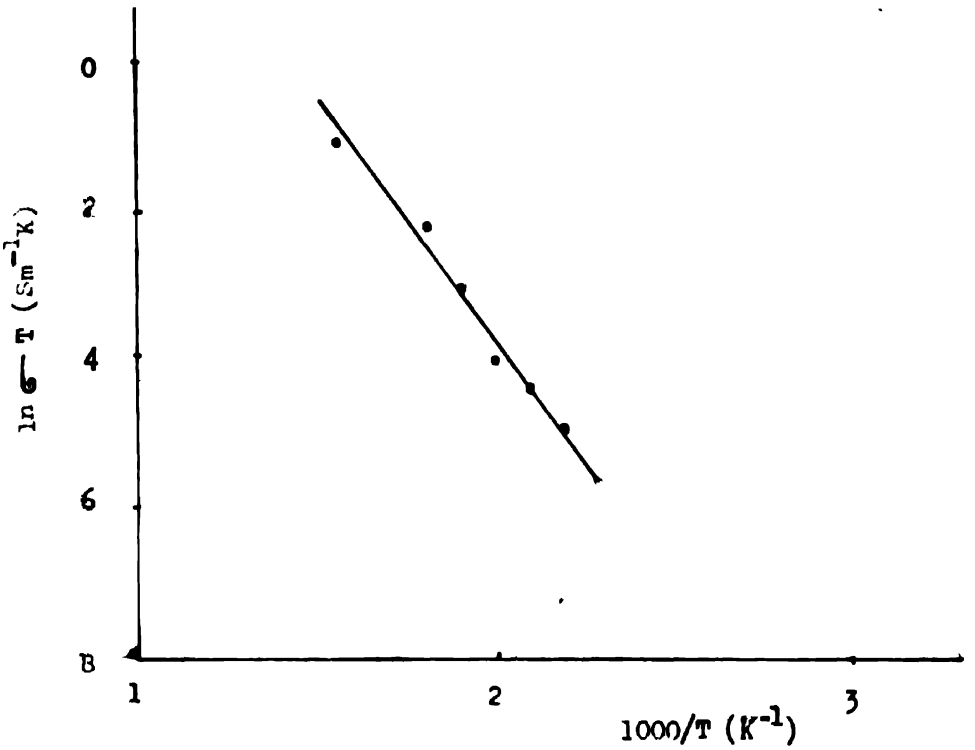

Figure 4. Arrhenius plot for $Na_2Ti_3O_7$ crystals.

The CIS plots are shown in Figures 3(a–g) respectively for temperatures 360 K to 548 K. The CIS circles to obtain equivalent electronic circuits with a resistance (R_1) in series with a parallel combination of resistance (R_2) and a constant phase element.

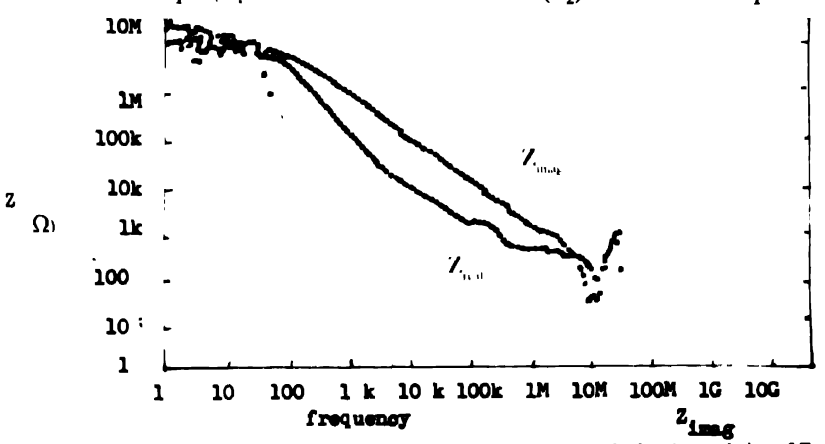

Figure 5(a). Representative Bode plots for $Na_2Ti_3O_7$ crystals showing variation of Z and Z'' as a function of frequencies at 299 K.

The semicircles are depressed below the real axis indicating the distribution of relaxation times. At higher temperatures (125–275°C), the grain boundary effects are present but are not clearly discernible.

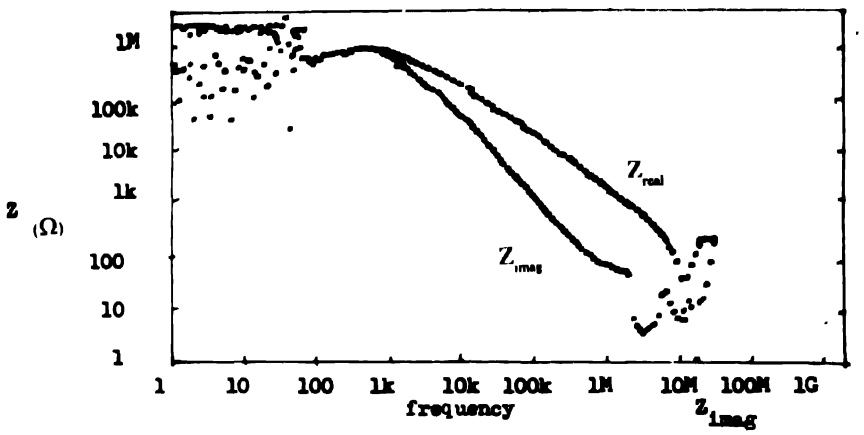

Figure 5(b). Representative Bode plots for $Na_2Ti_3O_7$ crystals showing variation of Z' and Z'' as a function of frequencies at 398 K.

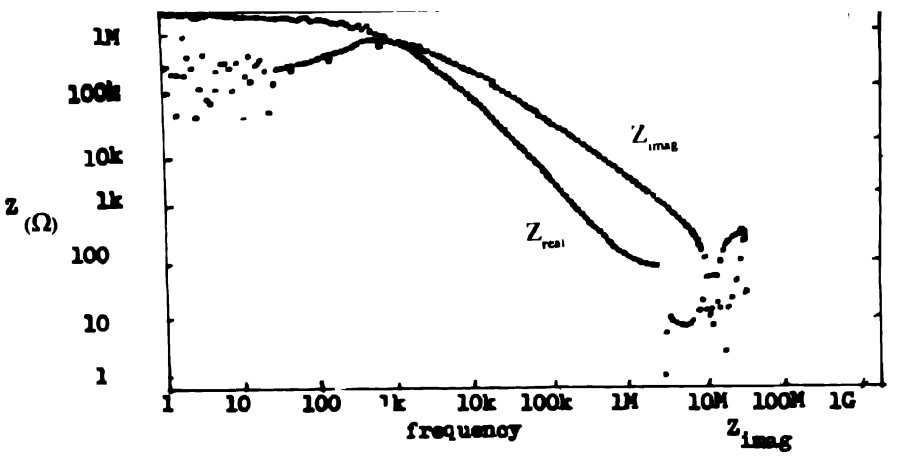

Figure 5(c). Representative Bode plots for $Na_2Ti_3O_7$ crystals showing variation of Z' and Z'' as a function of frequencies at 473 K.

A careful observation of the CIS plots reveals that noise appears at lower frequency limits. This noise is due to electrodic phenomenon and it reduces as temperature increases from 473 K to 550 K and the variation in the noise effect is not systematic with temperature. It also reveals that this noise is not the thermal noise, but may be Flicker noise. Further, the noise decreases as the frequency is increased and it may be the function of $1/f^{\delta}$, where δ is a constant. However, the $1/f$ noise has not been understood clearly. This kind of noise can be explained by considering fluctuations of the lattice scattering, occurring in the

bulk material which are not yet understood for most of the solid electrolytes, in general. The authors have given separately, plausible explanation for noise in this compound [12].

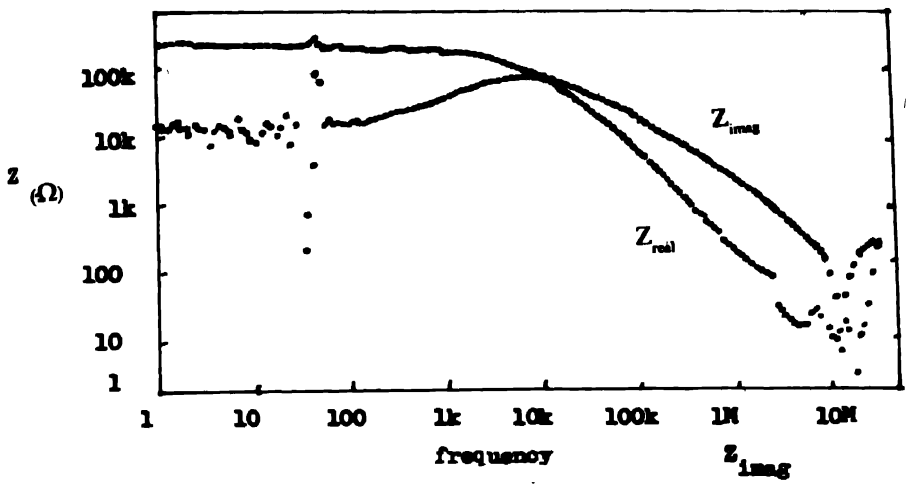

Figure 5(d). Representative Bode plots for $Na_2Ti_3O_7$ crystals showing variation of Z and Z'' as a function of frequencies at 548 K.

The CIS data has been used to obtain bulk resistance from the electronic equivalent circuit. The bulk resistance R_b in turn, is used to obtain bulk conductance (σ_b). The Arrhenius plot ($\ln \sigma T$ *vs* $1000/T$) is shown in Figure 4. The activation energy from the Arrhenius plot is 1.3 eV. The Bode plots (log Z'*vs* log frequency and log Z'' *vs* log frequency are shown in Figures 5(a–d). The Bode plots indicate least values for Z and Z'' at about 10 MHz. This indicates that the material represents resonance at about 10 MHz. With a possible modification of the material, it could be used as a dielectric resonator at 10 Hz.

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