

Spectroscopic and electrical studies of sodium tetraborate glasses containing nickel oxide

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The infrared spectra, X-ray diffraction and electrical conductivity of sodium tetraborate glasses containing nickel have been studied as a function of nickel oxide content. It was found that addition of nickel oxide does not seem to introduce any new absorption band as compared with the infrared spectrum of pure sodium tetraborate glass. The electrical conductivity measurements revealed that the activation energy for conductivity increases with nickel oxide content. This could be explained on the basis of the concept of Hubbard bands, and possibly by a block effect of the nickel ion on the overall mobility of the sodium ion. Measurements were made on unannealed samples and some samples annealed at different temperatures. Annealing the samples at temperatures in the range 460 to 480°C causes the appearance of a crystalline phase, resulting in an increase of electronic conductivity.

1. Introduction

Transition metal glasses consist of inorganic oxides containing significant amounts of transition metal ions, which enter the glass structure in at least two different valency states. Nickel produces different colours when introduced into different base glasses, and the colours produced depend on the equilibrium between the Ni²⁺ ions in the six-fold and the four-fold coordinations. Juza and Schultz [1] attributed the colour changes in the different glasses to a change in the equilibrium between NiO₆ and NiO₄ with changing the glass composition. Berkes and White [2] assigned all absorption bands in the glasses containing nickel on the basis of NiO₆ with a small amount of NiO₄.

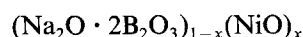
Paul and Douglas [3] explained that nickel usually occurs in glass as nickel(II) in octahedral, square planar and tetrahedral symmetry depending on the glass composition. The equilibrium between the octahedral and the tetrahedral coordinations of the nickel ion in some mixed alkali borate glasses has been investigated [4].

Recently Mott [5] has given a full account of the role of nickel ions, as to how these ions in the crystal make the material an insulator or a metal.

In this work, we have carried out measurements of infrared absorption spectra in order to study (i) the effect of NiO addition on sodium tetraborate glasses, (ii) the effect of heat treatment on the course of crystallization, and (iii) the effect of NiO addition on the electrical conductivity of pure sodium tetraborate glasses.

2. Experimental work

All glasses, containing various amounts of NiCO₃ (as a source of NiO), had the formula



where $x = 0.01, 0.03$ and 0.05 , and were prepared from analytical grade material melted in alumina crucibles at about 1050°C. The melts were stirred occasionally using an alumina rod and were finally poured on to a clean stainless steel plate and cast into the shape of a disc of 20 mm diameter and 2 to 3 mm thickness. Two discs of each composition were cast, one on a stainless steel plate which was at room temperature (unannealed sample) and the other cast on a steel plate maintained at a temperature of 500°C and introduced into a furnace which was already at this temperature. The furnace was maintained at this temperature for 2 h and was then switched off to cool down to room temperature. The glass samples were polished using diamond paste down to a minimum grit size of 0.1 μm. Thin glassy samples of specific compositions for infrared measurements were prepared by blowing in air using an alumina tube. Specimens in the thickness range from 5 to 12 μm were obtained as measured by sigma comparators.

The as-blown thin glass film was mounted on a specially designed machinable glass-ceramic specimen holder. The holder was directly placed into an annealing furnace as well as the sample compartment of the infrared spectrophotometer. Also, for comparison, infrared samples of the listed compositions were ground in a clean mortar to a fine powder. A few milligrams of glass powder were mixed and ground with a relatively large quantity of KBr. KBr pellets transparent to light were formed by pressing the mixture at 10 to 15 tons (9.8 to 14.8 tonne) for a few minutes under vacuum. The infrared absorption spectra of these samples were determined by using an SP2000 recording infrared spectrometer (Unicam, Cambridge, UK) in the range 200 to 4000 cm⁻¹.

For electrical measurements silver paste electrodes were used on thick glass discs. One side had a silver

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circular electrode of 1 cm diameter while the other side had a slightly smaller electrode surrounded by an annular guard-ring electrode.

Electrical measurements were made by standard techniques in the temperature range 300 to 773 K. Measurements of d.c. conductivity were carried out using the device described by Khan *et al.* [6] which could employ five samples at a time. This ensured the accurate comparison of five samples under similar conditions. A stabilized power supply was used to provide the voltage source and the circulating currents were measured with the aid of a Keithley 610C electrometer.

The temperature of the samples was monitored using a chromel–alumel thermocouple attached to the sample.

3. Results and discussion

Infrared absorption spectra for the pure $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ system and glasses containing various amounts of NiO are shown in Fig. 1. The assignment of each absorption band can be found in published papers [7–10]. The various energies which are involved in the bonding of a solid may be determined by infrared absorption.

In general the energy of a molecule can be separated into three parts: (i) the rotation of the molecule as a whole, (ii) the vibration of the constituent atoms, and (iii) the motion of the electrons in the molecule. Because the rotational levels of molecules are relatively close to each other, the transitions between these levels occur at low frequency (long wavelength) and pure rotational spectra normally appear in the range between 10^2 and $10^4 \mu\text{m}$ (1 to 100 cm^{-1}). The separation of vibrational energy levels is greater, and the transitions occur at higher frequencies (shorter wavelengths); therefore pure vibrational spectra are usually observed in the range between 1 and $100 \mu\text{m}$ (10^4 to 10^2 cm^{-1}).

Finally the electronic energy levels are usually well separated and electronic spectra are observed in the range between 1 and $0.1 \mu\text{m}$ (10^4 to 10^5 cm^{-1}). Thus as a general rule, pure rotational spectra are observed in the microwave and far infrared regions, pure vibrational spectra are observed in the infrared region and pure electronic spectra are observed in the visible and ultraviolet regions.

The vibrational absorption peaks at 790 and 1190 cm^{-1} in $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ glasses could be due to a number of causes such as bridging and non-bridging oxygen ions which are doubly or singly bonded, to high-state BO_4 groups and low-state BO_3 groups, to sodium ions, and possibly to some combinations of these. The infrared spectra for various nickel-doped glasses containing 3 and 5 mol % of NiO are quite similar in shape to the spectrum of undoped sodium tetraborate glass without the appearance of any new peaks. Fig. 1b shows the spectra of thin blown films. Comparing the spectra of thin blown films with KBr pellets of the same composition, it appears that all the glasses show a great similarity in the general shape of the absorption spectra, with the exception that in the blown thin films the peaks become sharper and better

defined. The absorption peak at 1190 cm^{-1} is assigned to the antisymmetric stretching mode involving bridged oxygen, whereas the peak at 790 cm^{-1} is attributed to the stretching mode of non-bridging oxygens. Actually the sodium can readily give the oxygen required for the formation of BO_4 groups; hence the maximum BO_4/BO_3 ratio will depend on the amount and the nature of Na_2O [11].

The observed vibration modes in pure $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ glasses as well as nickel-doped glasses can be explained using the model of Lam *et al.* [12], which is based on the random network concept of Warren and Brisco [13]. Actually two types of oxygen can be assumed to exist in the $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ system: (i) the bridging oxygen linking BO_4 groups, and (ii) the non-bridging oxygens bonded to BO_3 groups. The percentage of new nickel bonding resulting from the addition of NiO is very small. Since the ratio of bridging and non-bridging oxygens remains unchanged, no new peaks are expected to appear in nickel containing sodium tetraborate glasses. Following Sigal [14] we suggest that non-bridging oxygens were involved with this absorption mechanism. The non-bridging oxygen is well known in soda glasses; the sodium ion is interstitially compensated by a non-bridging oxygen in which the lone pair orbital is occupied by two electrons. If the above suggestion is true, and since the magnitude of the band is independent of NiO content in the glasses, it may be concluded that the non-bridging oxygen present in $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ glasses remains almost unchanged upon addition of nickel in small quantity. This supports our IR measurements. X-ray diffraction studies of the unannealed samples indicated their amorphous nature. The annealed samples at 500°C as shown in Fig. 2 provided positive evidence of crystallization occurring in these glasses.

The results of conductivity measurements as a function of temperature in the range 300 to 700 K for different compositions are shown in Fig. 3. It is clear that the conductivity of undoped sodium tetraborate glass is higher than for those doped with NiO. Khan *et al.* [15] studied the electrical conductivity of semi-conducting vanadium germanate glasses on unannealed samples and some annealed samples, and found that at about 300°C the appearance of a crystalline phase results in an increase of conductivity.

Fig. 4 shows the temperature dependence of the d.c. conductivity of annealed samples. It is clear that heat treatment caused progressive microstructural changes which dramatically affected the electronic conductivity (σ) and the activation energy for conduction (w). Khawaja *et al.* [16] reported a decrease of conductivity of sodium digermanate glasses upon doping with iron. Mackenzie [17] observed a similar effect in $\text{SiO}_2\text{--Na}_2\text{O--MO}$ glasses where M is a metal.

In the present study the observed decrease of conductivity upon doping with NiO ions could possibly be explained as follows.

In 1957 Slater [18] pointed out that the anti-ferromagnetic superlattice would split the e_g band in nickel oxide into two equal halves, with a gap between them; one half would be occupied and the other half empty, so the insulating and transparent nature was

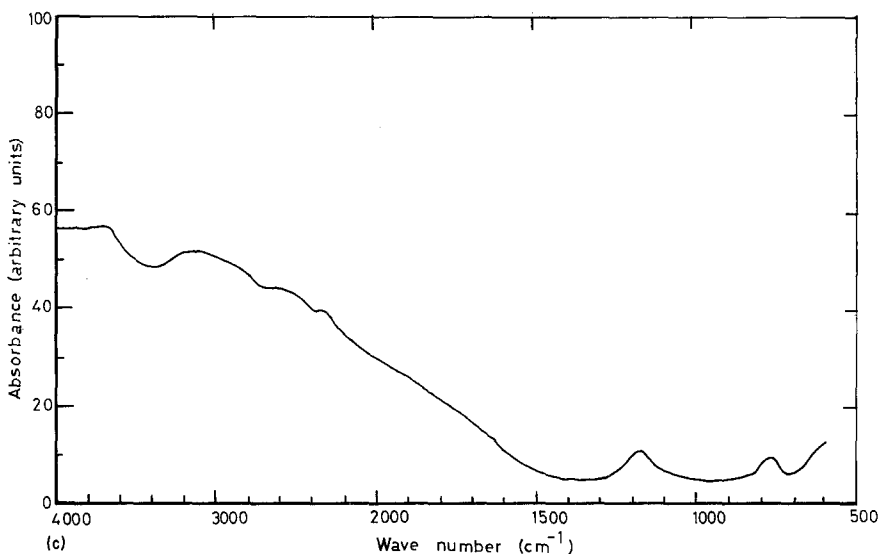
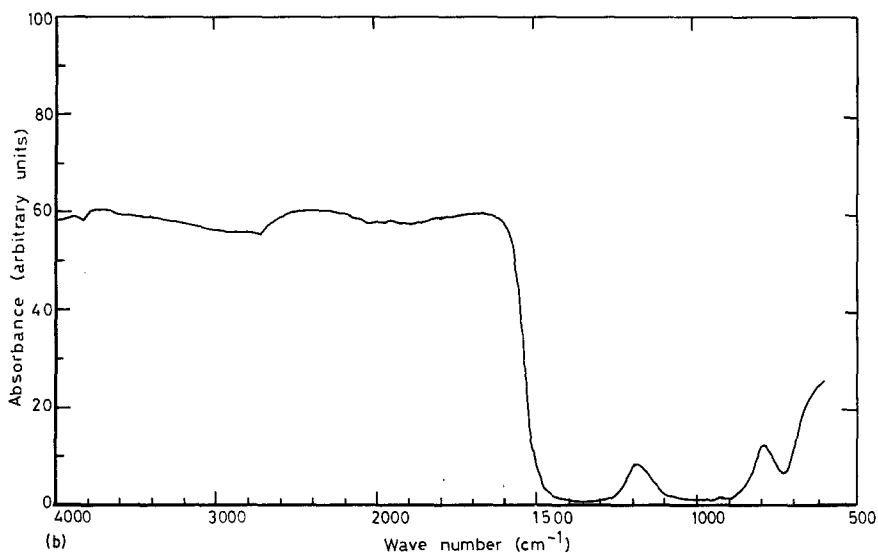
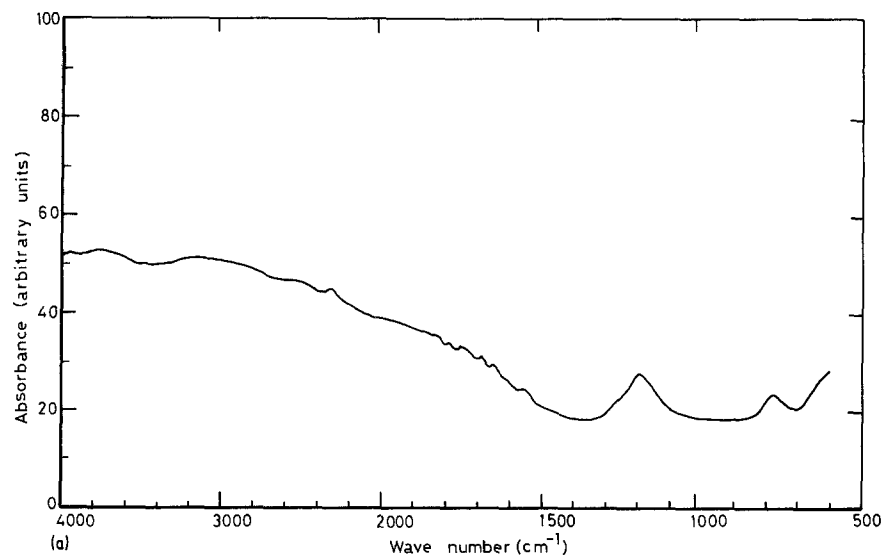


Figure 1 The infrared absorption spectra of sodium tetraborate glass (a) without nickel doping taken with KBr pellets; (b) taken with thin blown film; (c) after annealing at 500°C for 2 h; (d) containing 5 mol % of NiO taken unannealed; (e) containing 5 mol % of NiO taken after annealing at 200°C for 2 h; (f) containing 5 mol % of NiO taken after annealing at 500°C for 2 h.

explained. But this was not the complete story, because if the superlattice were indeed the origin of the insulating property, this should disappear at the Néel temperature, and above this temperature nickel oxide should be a metal. This is far from being the case. A full understanding then, of the insulating property goes some way beyond band theory and does depend on electron–electron interaction.

A better understanding really dates from Hubbard's (1964) [19] introduction of a new Hamiltonian and of

the concept of "Hubbard bands" in the early 1960s. Stripped of the mathematics, the physical concept is as follows.

In nickel oxide, a current can be carried if Ni⁺ or Ni³⁺ ions are present. These electronic configurations can move through the lattice of Ni²⁺ ions, with a definite wave number for the wave function, just as an electron, a hole or an exciton can. The motion of the Ni³⁺ configuration is described as "in the lower Hubbard band," that of the Ni⁺ as "in the upper

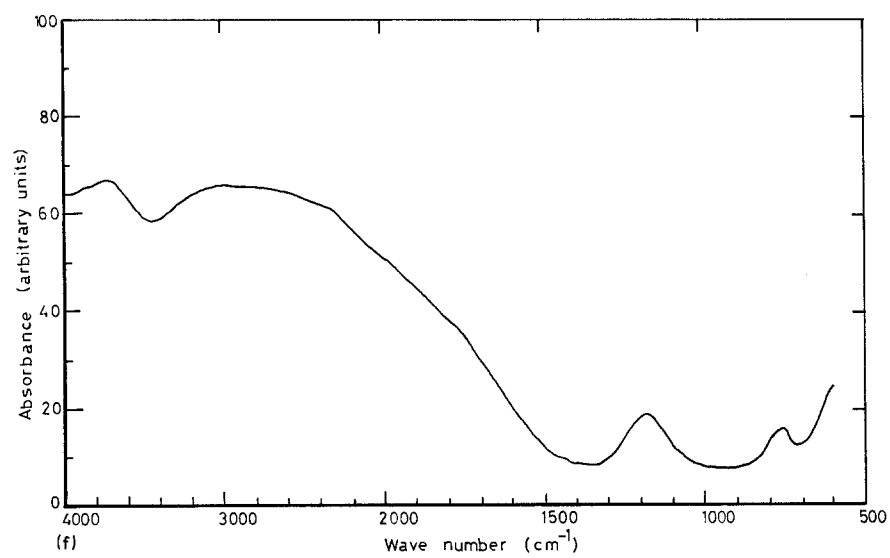
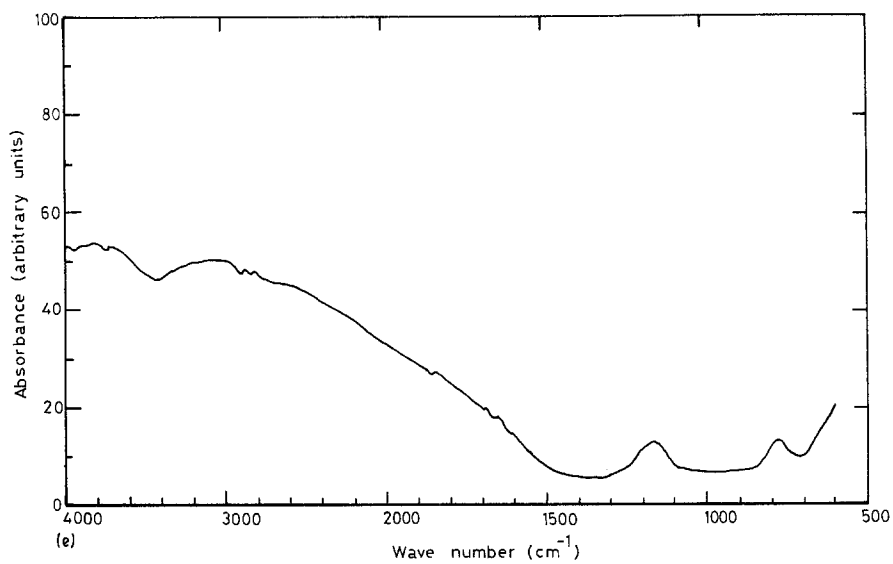
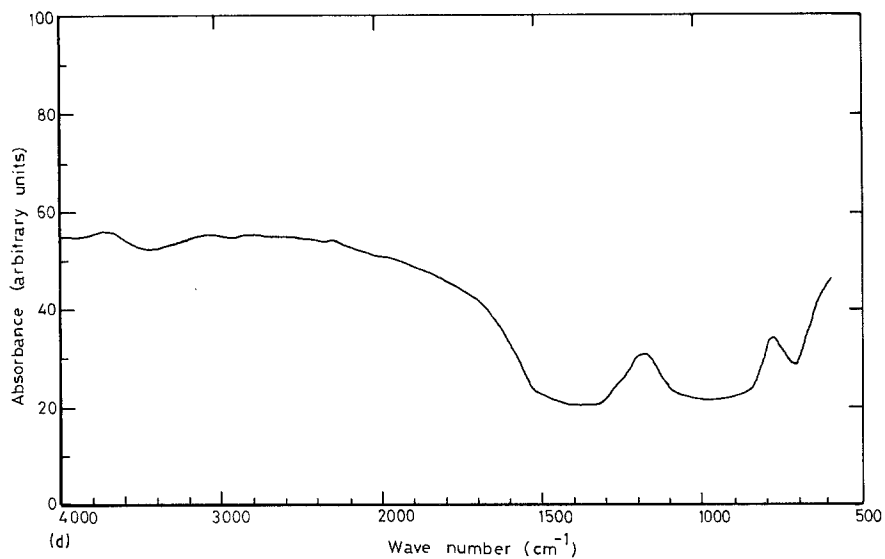
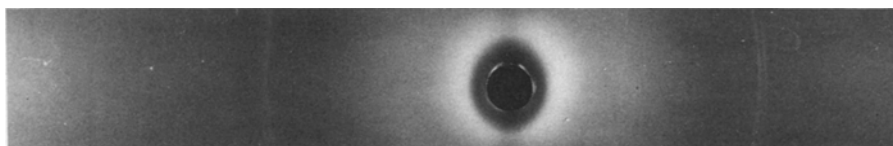


Figure 2 X-ray diffraction pattern of sodium tetraborate glass containing 3 mol% of NiO after annealing at 500°C.



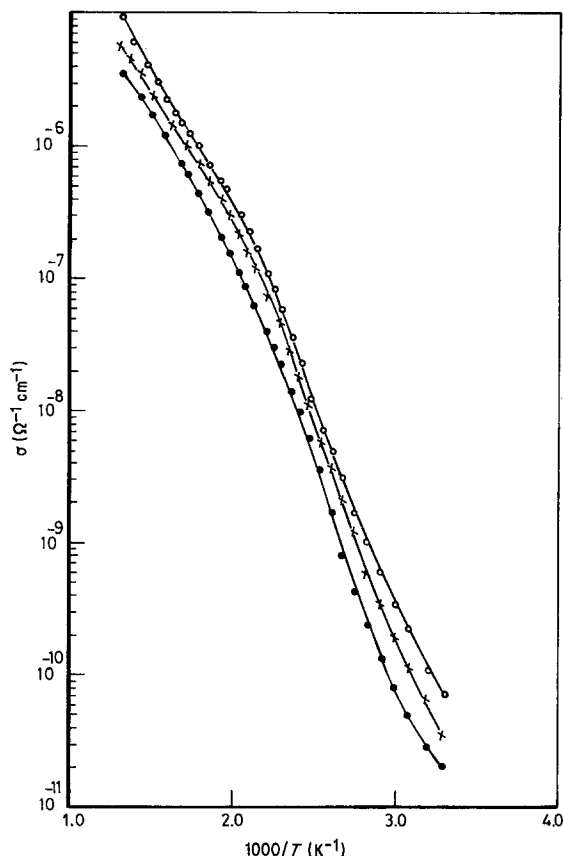


Figure 3 Electrical conductivity as a function of reciprocal temperature for a series of NiO-Na₂O-2B₂O₃ unannealed samples. NiO content (○) 1 mol %, (×) 3 mol %, (●) 5 mol %.

Hubbard band." For both of these, bandwidths B_1 and B_2 can be defined; we suppose these to be of the tight binding type, and so with a density of states symmetrical about the midpoint. The energy required to create these two configurations, if ions are a long way from each other, is called the Hubbard U and is

$$U = I - E$$

I in this case is the energy required to remove an electron from Ni²⁺ to form Ni³⁺, and E is the energy gained when a free electron at rest is added to Ni²⁺ to form Ni⁺. If, however, the ions are in the crystal, the energy required to produce the pair of carriers is

$$U - \frac{1}{2}(B_1 + B_2)$$

If this is positive, an energy gap exists and the material is an insulator; if not, it is a metallic conductor.

Figs. 3 and 4 show that the conductivity of sodium tetraborate glasses decreases with NiO content in the glasses. A somewhat simple but plausible explanation seems to be in a "blocking effect" of nickel ions on the overall mobility of sodium ions. A similar argument was considered by Mackenzie and others [17, 20] where the conductivity of SiO₂-Na₂O-MO glasses was established to decrease with increasing concentration of MO (where MO was MgO, PbO, BaO and CaO). This was attributed to the low mobility and effective blocking by the divalent ions of the sodium ion.

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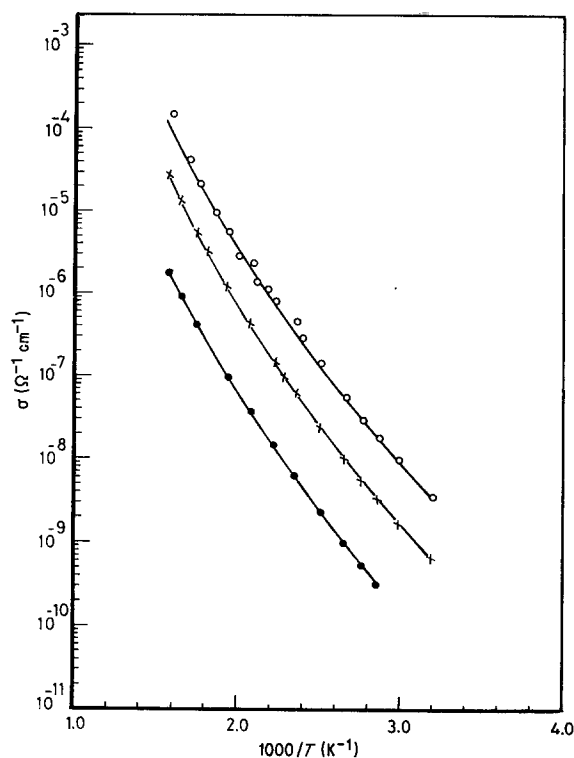


Figure 4 Electrical conductivity as a function of reciprocal temperature for a series of NiO-Na₂O-2B₂O₃ annealed samples. NiO content (○) 1 mol %, (×) 3 mol %, (●) 5 mol %.

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