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Electrical Conductivity Measurements of Mixed Compounds of Silver and Lithium Sulphates

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Abstract: Increasing energy demands, including the search for alternative energy sources which are renewable have lead to various researchers into compact energy sources such as fuel cells and solid electrolytes or superionic conductors. We have studied mixed compositions of Lithium and Silver sulphates in order to determine the temperature range of superionic conductivity at different mole concentrations of the constituents, from room temperature to transition temperature. The electrical conductivity and the corresponding activation energies have been computed. Four different compositions have been studied. The mixed compositions reveal critical concentrations of silver sulphate that enhances electrical conductance. It also showed that doped lithium sulphate is a better conductor than the pure samples. The thermal cycles on some of the mixed compositions revealed increase conductivity.

Keywords: Doping, Lithium Sulphate, Silver Sulphate, Superionic conductor.

Introduction

The present energy crises facing Nigeria justifies the need to develop an electronic institution in the field of the solid state Physics to facilitate the development of compact energy sources to service the energy requirements of the transport sector, communications, medicine and the mobile phone market among others. These could all be achieved by investing in research on Solid state energy sources, i.e. Superionic conductors. Superionic conductivity is the phenomenon in which solids that are insulators at room temperatures suddenly become conducting by several orders of magnitude. Their conductivity becomes comparable to that in the molten state. Superionic conductors have high ionic conductivities at high temperatures compared to that in the melt at room temperatures. Typical electrical conductivities may reach 10^{-2} to $1 (\Omega\text{cm})^{-1}$ and are a consequence of extreme dynamic disorder of one or more of the constituent ionic species [1]. The temperature at which it occurs differs from material to material and within the same class of materials, depending on how it has been prepared, among others [2].

Different mechanisms for the sudden increase of conductivity of these compounds have been proposed [3,4,5]. Various factors have also been found to affect the conduction mechanism, such as structural, ion size, polarisability and the quantity of charge possessed by the ion [2].

A distinguishing character of the materials is that their conduction is due mainly to ions, rather than electrons. This is attributed to the thermal agitation of the ions, enabling a collapse of the sublattice that constitutes the mobile species [6]. Superionic conductors or solid electrolytes have extensive applications as rechargeable batteries due to their long cycling life, high charge density and capacity, among others. LiCoO_2 has been used for these purposes but has environmental problems, cost and operating temperature against it. LiMnO_2 is more suitable. The objectives of this research and indeed current ones is therefore to find better materials whose conductivity at ambient and room temperature can be improved, and that is cheap. One method is to used mixed compositions, by doping, for example lithium sulphate, a poor conductor with silver sulphate, a higher conductor but expensive, with different concentrations. In

the present work, four different mole concentrations have been studied and reported.

Experimental

The samples were all prepared at the Centre for Energy research and Training (CERT) Zaria, Nigeria. A pressure of -4.0×10^7 N/m² applied during pelletization. The samples were thoroughly mixed and ground to fine powder with binder of appropriate quantity added to enhance cohesion. Both samples were analytical reagents. A sensitive balance was used to measure their masses. Total mass of samples varied between 1.648g and their thicknesses were ~3mm and diameters ~2.5cm.

Aquadaq paint (Achenon) diluted with deionized water was painted on both sides of the sides samples. Aluminum sample holders were used, also painted with aquadaq. Prepared samples were placed in between two halves of aluminum which served as sample holders. Temperature controller by APLAB India was used with maximum temperature of 1200°C together with Copper/Constantan thermocouple as the sensor. A specially designed ceramic cylinder served as the oven with Nichrome tape wound round it. This was constructed at the Industrial Development Centre IDC, Zaria, Nigeria. Asbestos rope provided the thermal shield. D.C. electrical conductivity measurements were then carried out from room temperature to ~600°C. The compositions studied were as follow:

Samples	Mole concentrations
1. A20	- 20% Ag ₂ SO ₄ + 80%Li ₂ SO ₄
2. A30	- 30% Ag ₂ SO ₄ + 70%Li ₂ SO ₄
3. A50	- 50% Ag ₂ SO ₄ + 50%Li ₂ SO ₄
4. A75	- 75%Ag ₂ SO ₄ + 25%Li ₂ SO ₄

Results and Discussion

The sample A20 had temperature range 30-150°C with average resistance of 30MΩ at room temperature and 1.65Ω at the

maximum temperature. Electrical conductivity has increased by several orders of magnitude over the temperature range considered. The Arrhenius plot, lnGT vs. 1/T was used, where G is the conductance, in place of the conductivity (σ) and T is the absolute temperature. This is shown in Fig.1. It has two sharp transitions at 100°C and 410°C at the lower temperature region and at the transition (superionic) region respectively. The average activation energy for the two regions was constant at 0.81eV. Theory has shown that silver ions are the mobile species. The uniform activation energy may be attributed to the highly polarisable nature of silver ions which enables higher mobility and thus conduction [7].

On reheating this sample to about 300°C, the average activation energy reduced to 0.27eV. The two regions merged and became uniform. Average resistance at room temperature also reduced to 394Ω and to ~5.00Ω at the maximum temperature. It is thus concluded that reheating of samples (thermal cycling) reduces activation energy needed for conduction and thus increasing the electrical conductance. Delocalization of the silver ions reduces the potential barrier needed for the conduction as shown in . Fig. 2 .

Sample A30 had much lower average resistance at room temperature of 5.0kΩ and 2.0Ω at 550°C. It shows that increased silver concentration results in increased conductivity of sample. There is a short transition to superionic state at 470°C and average activation energy of 1.73eV for the two regions, which implies that there is not much melting o the sublattice of the conducting species and thus the presence of reasonable potential barrier due to the repulsive field of the surrounding ions Fig. 3.

The result for the reheated sample, A30-C1 shows a similar decrease in resistance to

resulting in the increase of electrical conductivity of samples compared with pure ones. This does not, however, mean that the transition temperatures reduced accordingly, as it depends on other factors, which may be structural or dynamic .

Repeated heating of samples leads to increased electrical conductivity at all temperatures. Also, increased concentration does not necessarily lead to improvement in conductance in a linear manner. Some concentrations seem to be favoured over others. The study also shows that superionic transitions may not be sudden, but may be due to gradual build up of disorder in the system. Doped lithium sulphate is a better conductor than the pure sample and increasing concentration of silver may lead to a rise in the activation energy, leading to a fall in the conduction. The research shows that doped lithium sulphate has enhanced conducting properties and could serve in such applications as portable energy sources in the area of transport, communications (mobile phone batteries), micro batteries, etc.

Fig. 1: Arrhenius Plot for Sample A20 showing the two transitions at 100 and 410°C and the activation energies.

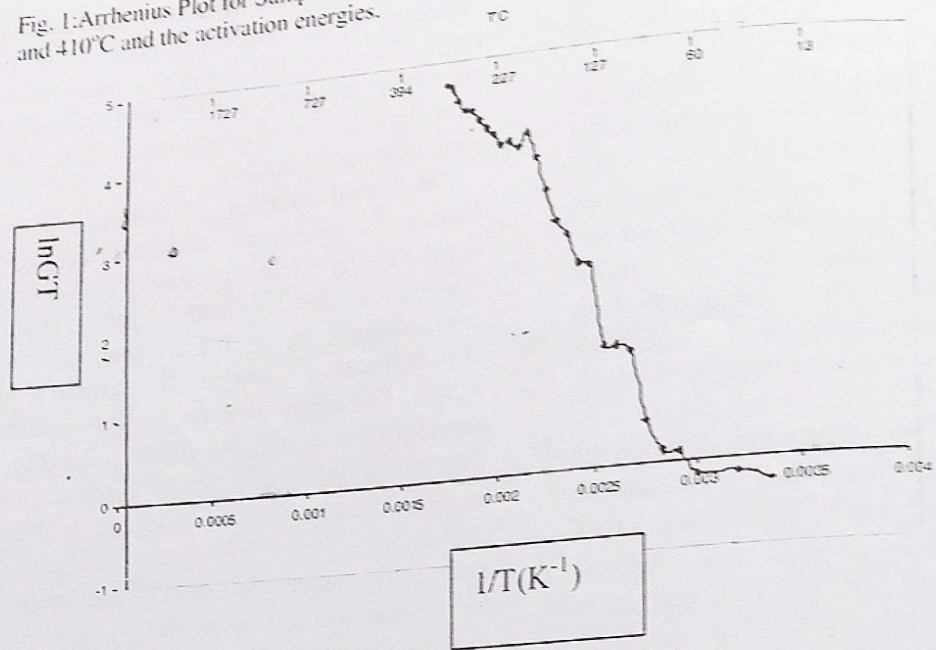


Fig. 2: Arrhenius Plot for A20-C1. Showing average energy 0.27eV.

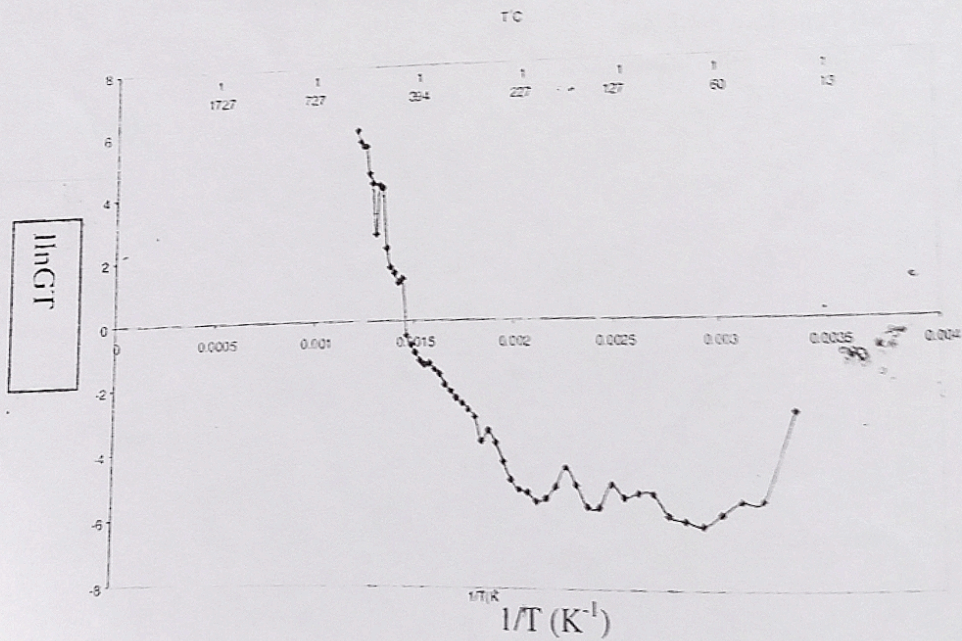


Fig. 3: Arrhenius Plot for A30 showing short transition at 470°C and average activation energy of 1.73eV.

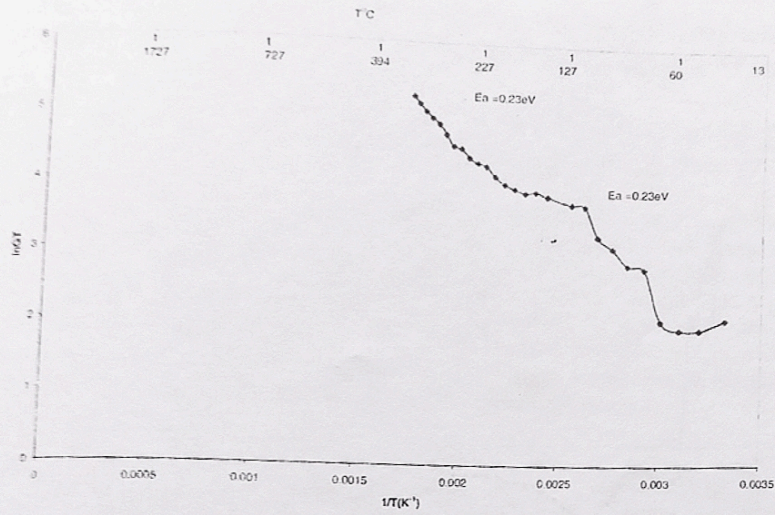


Fig. 4: Arrhenius Plot for A30-C1 showing average activation energy of 0.23eV.

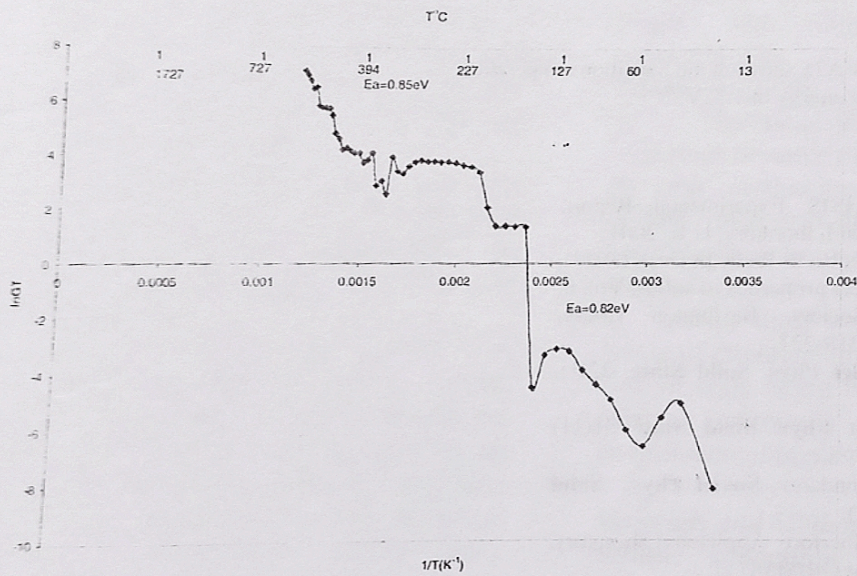


Fig. 5: Arrhenius Plot for A50 showing the various activation energies (average 0.84eV) and lower transition temperature of 150°C otherwise it is gradual buildup of disorder.

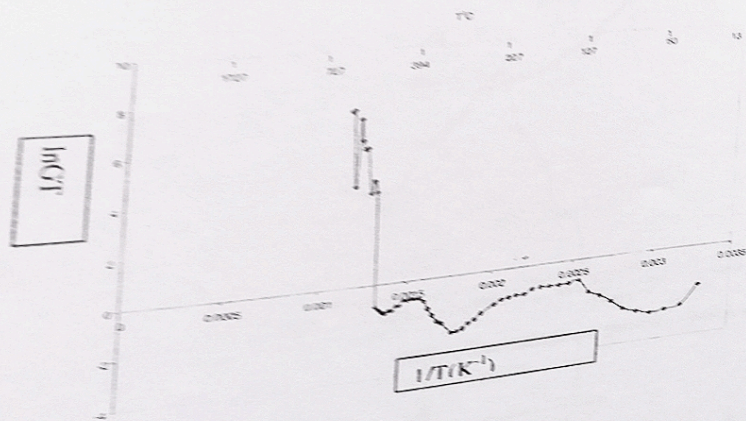


Fig. 6: Arrhenius Plot for A75 showing the transition temperature 490°C and the activation energy of 1.7eV.

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