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ELECTRICAL CONDUCTIVITY AND SUPERIONIC TRANSITIONS IN PURE SILVER AND LITHIUM SULPHATES

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Abstract

Pure samples of polycrystalline Silver and Lithium sulphates (Ag_2SO_4 and $Li_2SO_4.H_2O$) were heated to a temperature of about 600°C from 27 °C .The transition temperatures for Superionic conduction was determined together with the activation energies for the conduction as 290°C, 0.35eV and 260°C and 0.57eV respectively, for lithium and silver ions. Similarly, the character of the changes in resistance has been described. The silver and lithium sulphates samples were subjected to several heating runs and the same parameters were determined. Superionic transition was observed in the silver sulphate sample but not in the lithium sulphate. It was observed that thermal cycles reduced the sample resistance.

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

Introduction

Current trends in research have been geared towards the search for compact energy sources in the solid state, i.e. Solid state electrolytes or superionic conductors (Yamazoe and Miura, 1995). Solid state energy sources have many advantages over liquid electrolytes in terms of compactness, versatility and mobility. They are used for rechargeable batteries and also as electrolytes in fuel cells (Cuenca, 2002;Onuma and Kaimai et al, 1998). These rechargeable batteries are found in microbatteries, sensors and smart windows (Balkanski, 1990;Miura and Ono et al, 1998; Narita and Can et al, 1995; Worrel, 1998) and in mobile phones, laptop computers, among others. Lithium compounds are commonly used in lithium ion batteries. Their conductive properties are principally derived from ions rather than electrons and this is normally achieved at high temperatures during which superionic transition is said to set in.

The current lithium-based compounds have a lot of problems (Weller, 2000), current research is therefore geared towards developing materials that are cheaper, stable, environmentally friendly, have high charge capacity/density and in particular, high conductivity at room or ambient temperatures (Hull and Keen, 2003), temperature at which most appliances operate. The most widely used materials are $LiCoO_2$ and $LiMnO_2$. The former has been associated with one or more of the above desirable parameters. There is the need to improve the electrical properties of these compounds, such as their electrical conductivity and mobility. Hence the research in silver and lithium sulphates are important because of the good electrical conductivity and polarisability of silver on the one hand, and the small size of lithium ion and its light weight, which make it easily diffuse and contribute to electrical conductivity.

The lattice structure of silver sulphate is orthorhombic whereas lithium sulphate is monoclinic. Silver sulphate is a better conductor than lithium, however, its cost puts it at disadvantage. Several research have been carried out on these compounds (Teterycyz and Kózlowski, 1998;Teterycyz and Nitsch, 2000), for example, using thick-film technology in gas sensors for environmental pollution detection.

In the present study, report is presented on samples of silver and lithium sulphates, in Pelletized powder forms. The objective is to determine the superionic transition temperatures, the activation energies and electrical conductance of

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...compounds and compare them, including the effect of repeated heating ...ons on these parameters. This is believed will facilitate further study of these compounds to enhance their conductivity by forming solid solutions of the compounds.

The Arrhenius plot (lnGT vs. I/T) was used to analyze the results. The conductivity is related to temperature by: $\sigma = \sigma_o /T\exp(-E_a/T)$, where σ_o is the pre-exponential factor, E_a is the activation energy for conduction and T is the absolute temperature. However, the conductance has been used instead of the ...ivity, σ.

... silver and ... alytical

(APLAB,India, 1200°C maximum); digital Multimeter (Gold Model, WG022) and Copper/Constantan thermocouple were used for the measurements. Acetone and deionised water were the cleaning agents. Current and voltages were measured three times, from which the resistance (and average resistance) was calculated, from room temperature to about 600°C, for each temperature. The conductance (G) was calculated from the computed values of the average resistance. A plot of lnGT Vs I/T (Arrhenius plot) was obtained from which the activation energy, E_a was deduced from the slope of the graph.

Results and Discussions

The materials investigated revealed high ionic conductivity at elevated temperatures, in particular, silver sulphate. It has been generally difficult to obtain stable lithium sulphate at high temperatures (>320°C) due to cracking or ... of the samples at these ... Fig.1 shows a low ... conductivity of a ... that cracked ...

e observed owing to sample
lity beyond 290◦C.
However, the Arrhenius plot of
sulphate, room temperature to
, showed superionic transition with
ation energy at transition temperature
.32eV comparable to that reported
rycyz and Nitsch, 2000), while being
vation energies) 0.83eV and 0.57eV at
r temperature respectively, for the
rted (Teterycyz and Nitsch, 2000) and
work. Correspondingly, room
perature resistance fell from 1.71KΩ to
4Ω at maximum temperature.

Superionic transition was observed
occur at 260 ◦C compared to 420 ◦C
eterycyz and Nitsch, 2000). Fig. 2 shows
plot from which it can be inferred that
transition temperature is not well
fined as factors such as preparative,
ermal history; composition and
ystallinity may affect the transition
mperature (Sunandana and Kumar,
004). Thus the low activation energy may

The second thermal
580◦C) has average resista
temperature of 33KΩ.
activation energies were
in these regions an
temperature was 350◦C
cycle (C3)(27-490◦C
resistances as 122Ω
corresponding act
0.07eV and 1.32
temperature of
suggest a system
the sample was
particular the
lower temper
beyond the
character
pointing t
the heati
Also it
temper
to the
and
heat
tra

ıble up to 640°C. This may
irregular features, attributed
ıly high resistance of lithium
ıith corresponding high
ıemperature, and to the
nature of the sample,
ı homogeneity and polarization.
wever, the second sample could
ed to another heating cycle (C1)

0°C , where resistance reduced to
, from 11.00MΩ at room
ıture. The activation energy
ıng 0.59eV throughout the regions
o sharp transitions observed, fig.4. A
ır thermal cycle (C2) reduced the

and to 705.00Ω ... temperature of 600°C . The form of the graph is essentially the same as C1 with activation energy almost uniform at 0.69eV. It must be remarked that most researchers have not focused on the systematic study of thermal cycles of superionic conductors, this is emphasized here, fig.5. Up to 500°C was reached for the third cycle (C3) of silver sulphate in which the resistance was 1.4Ω at room temperature, the activation energies were 0.021eV and 1.2eV at the lower and high temperature regions respectively, fig.6.

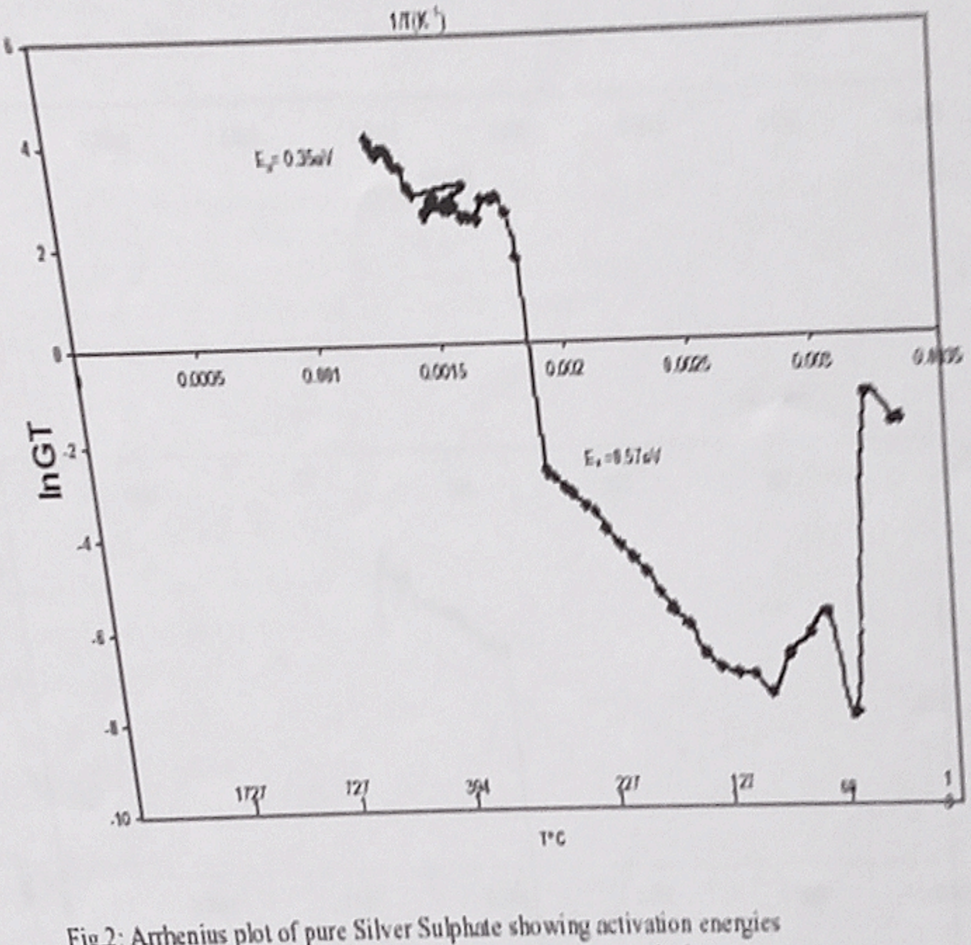
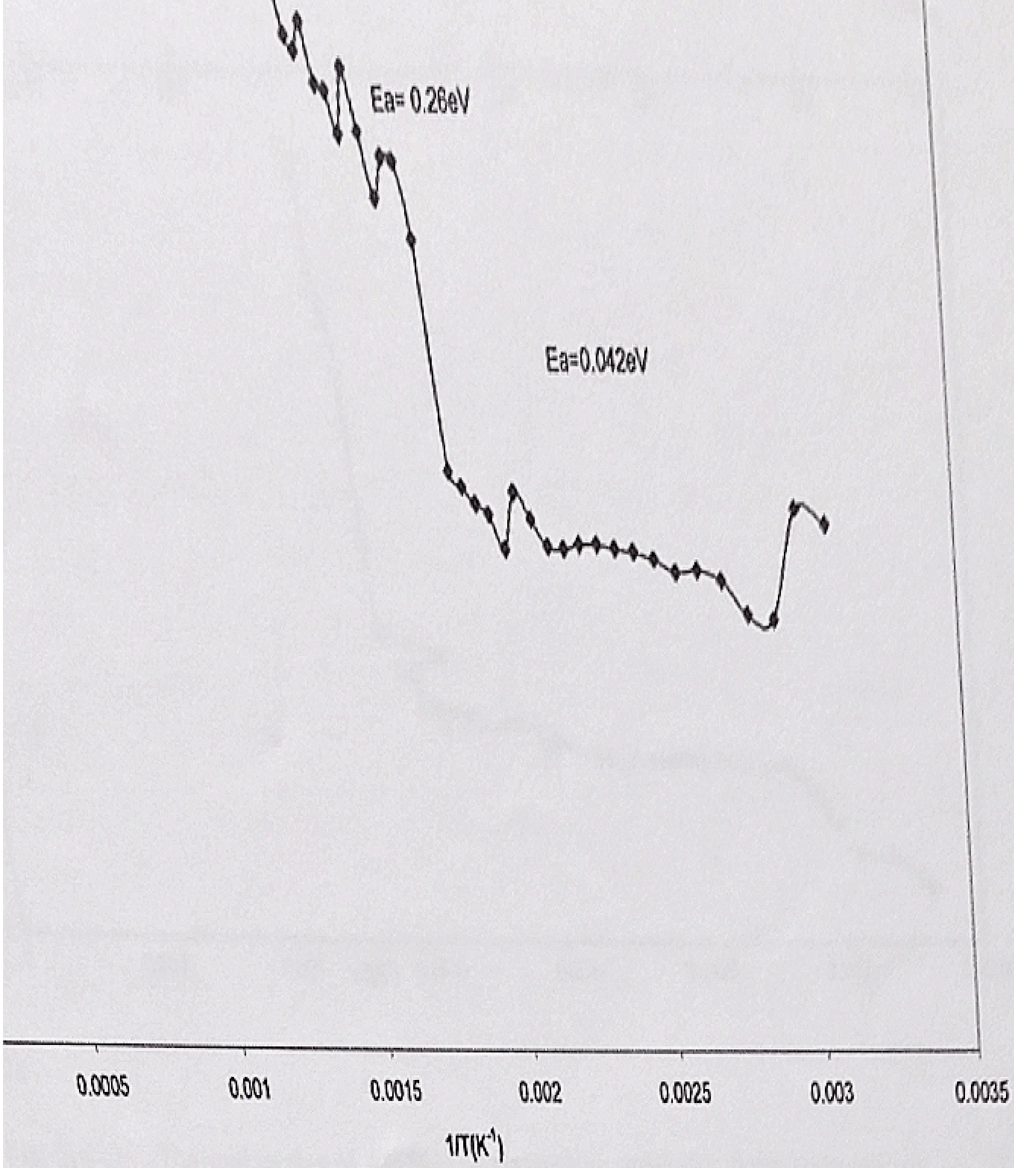
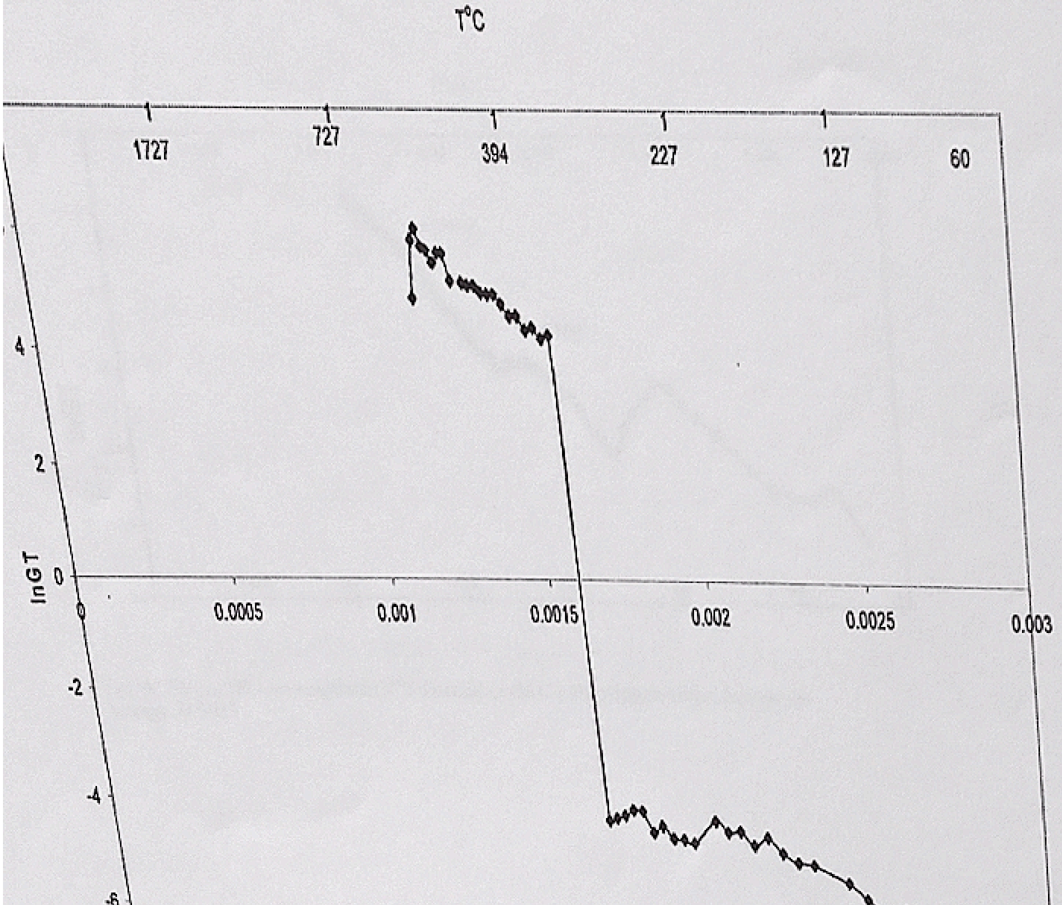
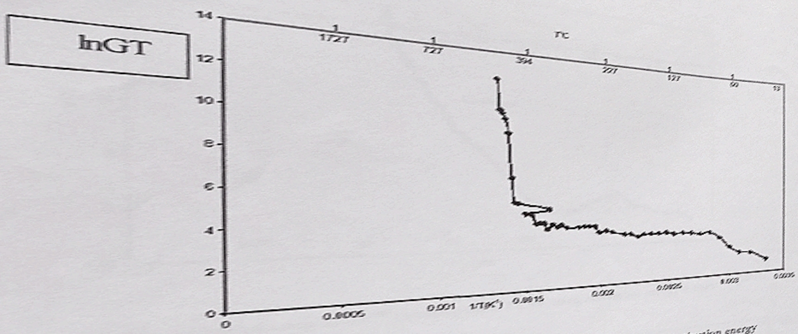


Fig.2: Arrhenius plot of pure Silver Sulphate showing activation energies 0.57eV and 0.35eV at lower and higher temperature respectively. The transaction temperature is 260°C.


Ea= 0.26eV
Ea=0.042eV
0.0005
0.001
0.0015
0.002
0.0025
0.003
0.0035
1/T(K-1)


T°C
1727
727
394
227
127
60
lnGT
4
2
0
-2
-4
-6
0
0.0005
0.001
0.0015
0.002
0.0025
0.003



(c)

Fig. 3(a-c): Thermal cycles of Ag_2SO_4, in successive order (a): Activation energy E_a = 0.042eV at lower temperature. The transition temperature is 250°C; (b): E_a = 0.21eV at lower temperature and 0.38eV at temperatures; transition is 350°C and (c): 0.07eV at lower temperatures; transition temperature is 350°C.

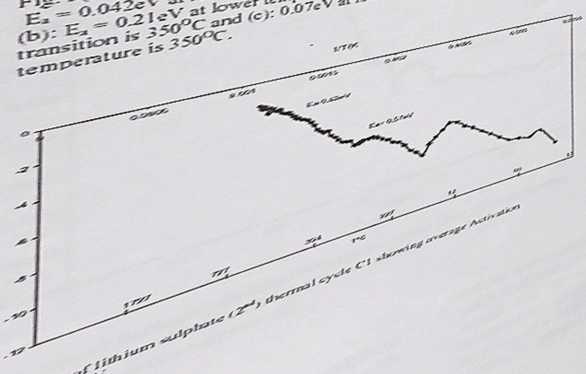
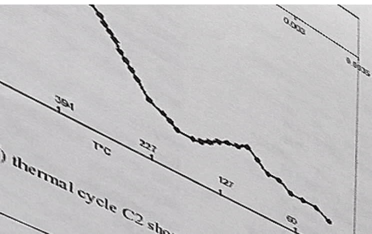


Fig. 4: Plot of lithium sulphate (2nd) thermal cycle C1 showing average Activation ...rgy, 0.59eV.



...5: Plot of lithium sulphate (2nd) thermal cycle C2 showing activation energy 0.69eV

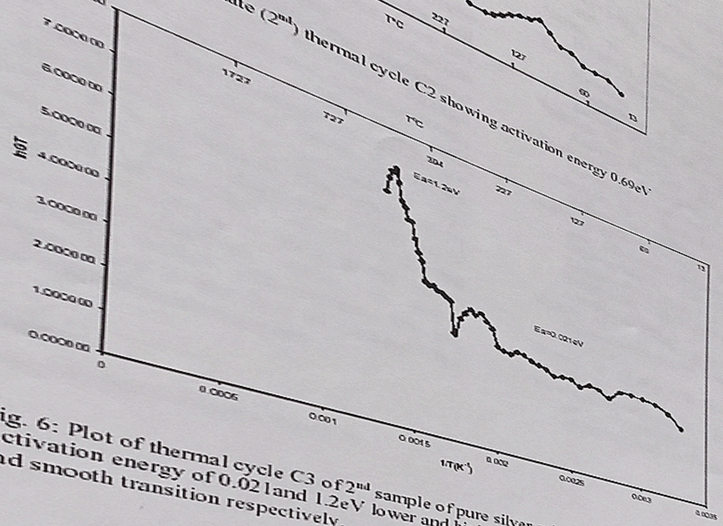


Fig. 6: Plot of thermal cycle C3 of 2nd sample of pure silver sulphate showing Activation energy of 0.021and 1.2eV lower and high temperature and smooth transition respectively.

Conclusion

All the samples of lithium sulphate exhibited increase conduction with temperature, and reduced activation energies in the lower temperature regions in the thermal cycles. Though some samples were highly unstable and cracked, others were stable, yet behaved irregularly, such that transition to the superionic state could not be observed, given the high temperature required. Polarization and the hygroscopic nature of the sample was a problem, particularly, in humid weather

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a.c. conductivity measurements could reduce this problem.

Samples of pure sulphate however, were generally more stable and had better cohesion. Thus it was relatively possible to reach higher temperatures. The pure and some of the thermally cycled samples have Arrhenius character, though some of the samples showed poor stability too. Transition temperature for one of the pure samples was 260°C, whereas the thermally cycled ones were 250, 350 and 400°C, for the three cycles obtained for the first sample.

The research established that silver sulphate is good superionic conductor and that repeated heating of samples does not necessarily reduce the transition temperature, even though the resistance reduced. Also, lithium sulphate, though highly resistive at ambient temperatures, reduced in resistance with increasing thermal cycles. The thermal cycles do not show a marked transition, rather, generally a gradual build up in conduction was observed. It is proposed that since silver sulphate is better conductor, when solid solutions of the two are formed, by doping one with the other, it may bring about enhanced conduction, even at room temperatures, which still remains the big challenge. This is the line of research the authors intend to investigate.

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