Summary and Conclusions

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The work carried out in this thesis is presented in five main chapters.

The first chapter , is the introduction which contains the literature review and the aim of the work.

The second chapter includes highlights on the theories and the calculation methods used in this work.

The third chapter shows the preparation for each of the pure metal oxalates of [Ag(I), Cd(II), Zn(II), Cu(II), Fe(II), Co(II), Ni(II) and Mn(II)] and oxalate mixtures from silver oxalate with each one of metal oxalates investigated. This chapter includes also the techniques used in the investigation of the samples (DTA-TG, FT-IR and XRD) and in measuring the electrical and magnetic properties. The preparations of all samples before and after dissociation are also presented in details.

The fourth chapter deals with the thermal analysis (DTA-TG) results and the characterization of the products obtained from the decomposition of the samples, using FT-IR and XRD techniques.

The fifth chapter divided into three parts. The first part deals with the study of the thermal decomposition kinetics in air for some decomposition steps, which are not sharp under the experimental conditions used. The kinetic parameters results are discussed in view of various solid-state reaction models. The effect of the chemical composition on the kinetic parameters and the mechanism of decomposition have been discussed.

The second part in the fifth chapter includes the temperature dependence of electrical conductivity (σ_{DC} and σ_{AC}) for all samples investigated. The effect of presence of mixed valency and measuring frequency on the conductivity has been also investigated and discussed. The results were discussed and correlated with compositions of the samples, especially the effect of valency states on the conduction mechanism.

The third part in the fifth chapter deals with the results of the magnetic properties of the samples under investigation. The temperature dependence of the molar magnetic susceptibility; X_M has been investigated over a temperature range of 78-400°K. The magnetic results have been discussed in view of chemical composition and phases formed in the compounds investigated. The results were correlated with those obtained from electrical conductivity measurements.

The main conclusions in this work are the following:

(1) By heating silver oxalate decomposed directly into silver metal while other oxalates decomposed into metal oxides.

(2) The thermal decomposition of silver oxalate-metal oxalate mixtures ($Ag_2C_2O_4$-$CdC_2O_4.3H_2O$, $Ag_2C_2O_4$-$ZnC_2O_4.2H_2O$, $Ag_2C_2O_4$-$CoC_2O_4.2H_2O$ and $Ag_2C_2O_4$-$MnC_2O_4.2H_2O$) are occurring through three well defined steps: (i) Dehydration to silver oxalate - anhydrous metal oxalate mixtures. (ii) Decomposition of silver oxalate to silver metal to form silver-anhydrous metal oxalate

mixtures. (iii) Decomposition of the anhydrous metal oxalate to metal oxide to form silver-metal oxide mixtures.

(3) The thermal decomposition steps appearing for silver oxalate-metal oxalate mixtures of ($Ag_2C_2O_4$-$CuC_2O_4.0.5H_2O$, $Ag_2C_2O_4$-$FeC_2O_4.2H_2O$ and $Ag_2C_2O_4$-$NiC_2O_4.2H_2O$) are interfered and therefore can't be exactly defined.

(4) The thermal stability of the pure hydrated oxalates increase in the order: ZnOX > CdOX > NiOX > CuOX > MnOX > CoOX > FeOX > AgOX. Moreover it was found that the presence of silver metal in the mixture of the oxalates doesn't affect the order or the temperature at which the oxalates decomposed. This refers to the absence of silver metal in the lattice of hydrated metal oxalates

(5) The FT-IR results showed that the oxalates ions of all investigated sample are bridging together to form polymeric chains.

(6) XRD showed different crystalline structures depending on the sample composition except the anhydrous manganese oxalate or silver metal-anhydrous manganese oxalate mixture, which showed an amorphous structure.

(7) There is no only one kinetic model which can be used to interpret the thermal dehydration or decomposition of the oxalates investigated, but many kinetic models w ere used to explain the results obtained.

(8) The composite kinetic methods would allow a better choice of the reaction model since it treats all experimental data obtained at

different fraction reacted and heating rates at one time and gave results with less standard deviation.

(9) The kinetic parameters calculated for the decomposition of silver oxalate-hydrated zinc oxalate mixture showed that the silver metal catalyze the decomposition of zinc oxalate.

(10) The presence of silver metal in the mixtures didn't change the activation energies of the decomposition steps investigated.

(11) It wasn't found any correlation between ionic radius of cations and the kinetic parameters calculated for the decompositions.

(12) All the anhydrous metal oxalates are insulators ($\sigma_{DC} < 10^{-12}$ $ohm^{-1}.cm^{-1}$).

(13) At $200 < T < 400°K$, the DC conductivity values of metal oxides (except for CdO) lay in the semiconductor range, and the mobility of charge carriers are very less than 1 $cm^2.V^{-1}.s^{-1}$ indicating that the hopping mechanism predominates in the samples investigated at this temperature range..

(14) The DC conductivity obtained at 300°K for the metal oxides decreases in the order: $\sigma_{NiO} > \sigma_{Mn2O3} > \sigma_{Co3O4} > \sigma_{CuO} > \sigma_{Fe2O3} > \sigma_{ZnO}$.

(15) The DC conductivity of silver-anhydrous metal oxalate mixtures showed metallic behaviour, except for silver-anhydrous cupper oxalate. Moreover, the introducing of silver metal into oxalate samples causes increasing in σ_{DC} of these samples, indicating that the charge transfer due to electron transfer between silver atom is higher than any other charge transfer present in the metal oxalate lattice.

The conductivity of these mixtures at 300°K was found to decrease in the order: $\sigma_{Ag\text{-}CdOX} > \sigma_{Ag\text{-}ZnOX} > \sigma_{Ag\text{-}MnOX} > \sigma_{Ag\text{-}CuOX} > \sigma_{Ag\text{-}CuOX}$.

(16) The conductivity of silver-metal oxide mixtures except (Ag-Co_3O_4 and Ag-Mn_2O_3), showed metallic behaviour. It refers to that the rate of charge transfer of electrons between the different valancy states of cobalt or manganese ions (hopping mechanism) is higher than that of the electron transfer between silver atoms.

(17) The temperature dependence of the σ_{AC} for all samples except Ag-CoOX, showed similar behaviour to that found for σ_{DC}.

(18) For all samples the conductivity was found to increase with increasing the measuring frequency (due to barrier effect, which decreases with increasing frequency) except for metallic samples.

(19) The magnetic properties of compounds investigated showed the following behaviour:

(i) CoOX, MnOX, NiO and Mn_2O_3 are all antiferromagnetic.

(ii) At lower temperature range, CuO, Co_3O_4, Ag-CoOX, Ag-MnOX, Ag-NiO and Ag-Mn_2O_3 are all paramagnetic, whereas Ag-Co_3O_4 is antiferromagnetic.

(iii) At higher temperature range Co_3O_4, Ag-CuOX and Ag-CoOX are all paramagnetic, whereas Ag-MnOX is antiferromagnetic. But both Ag-Co_3O_4 and Ag-NiO are ferromagnetic.

(20) The presence of Ag metal with CuO changes the paramagnetic properties of CuO to diamagnetic one.

(21) X_M(Ag-NiO) < X_M(NiO) and (Ag-Mn_2O_3) < (Mn_2O_3), whereas X_M(Ag-Co_3O_4) > X_M(Co_3O_4). It means that the introducing of silver metal to metal oxalates and oxides causes a change in magnetic susceptibility values. This refers to introducing the silver atoms (at least partially) in the lattice structure of metal oxalates or oxides.

(22) All results showed that, the presence of more than one valancy state in the lattice of oxalates or oxides is the main factor in changing each of electrical and magnetic properties of the compounds investigated.