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Thermal and Spectroscopic Studies on $AgTlSO_4$

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Abstract

AgTlSO4, synthesized by mixing Ag_2SO_4 and Tl_2SO_4(1:1 ratio) is characterized by XRD to possesses a orthorhombic structure submitted monovalent double sulphate.Thermal characteristicsby DSC of $AgTlSO_4$ shows peaks at 459.7^0C, 505.4^0C, 503.4^0C and 520^0C that could be attributed to several phase transition from ordered to disordered structure.Raman spectra of $AgTlSO_4$ exhibit small triplets (ν_3) at about 1085 and 1080 cm^{-1}respectively, intense singlets (ν_1) at 953 cm^{-1} for Tl derivatives and 968 cm^{-1} for Ag derivative very small triplets (ν_4) at about 605 and 615 cm^{-1} and medium doublets near 450 cm^{-1} which indicates a multiplicity of Z=2, the new spectroscopic unit-cell consisting of two SO_4 ions. ESR gain is due to CO_3^- radicals and the corresponding g value is 2.365. The g- anisotropy of the CO_3^- is quite sensitive to the surroundings in which it is stabilized.

Introduction

A number of solids undergo solid-solid phase Transitions accompanied by a sharp jump in ionic Conductivity in the high temperature phase [1-13]. The conductivity log(σT) versus T^{-1} plot for these solids, e.g. alkali sulphates, Ag_2SO_4, Agl, Li_2MCl_4spinels, resembles the site percolation probability function, i.e. P(p) plot [14-21], suggesting the percolation model forion transport in these compounds. The discontinuity in ionic conductivity profile accompanying the solid-solid phase change provides another avenue to probe the mechanism of ion transport. Also the conductivity profile can provide an insight into the mechanism of the structural change occurring during the phase transition.The mixed sulphates - AgLiSO4, NaLiSO4, RbAgSO4, KLiSO4 and $AgTlSO_4$ with two monovalent cations are known

to be good solid electrolytes. Some of these compounds exhibit ferroelectric and ferroelastic properties [19]. Dueto large polarisability of Tl+, Ag+, and Rb+ cations, Raman scatteringcan provide information about the local structure and the static or dynamic disorder prevailing in both host frame work and conducting ions sublattice [20].Fast –ion conduction in solids has been considered a paradigm for a structure-property relation. The sharp jump in ionic conductivity, up to a factor of 10^4, accompanying the structural change at the phase transition is consistent with this relation. The structure factor can involve coordination geometry number, face-sharing sites and lattice disorder. On the other hand non-structural factors can also contribute significantly such as activated ion concentration, ion-ion interaction or bonding characteristics, vibration amplitudes of neighbouring ions, lattice pressibility or resiliency, ion size, polarisability of the oppositely charged ion and rotational motion ofsulphateions. An assessment of the relative contributions by these factors will provide a better understanding of the transport mechanism [21].$AgTlSO_4$ and RbAgSO4 compounds undergo phase transitions at about 440 C (713 K) and 190 C (463 K) respectively to high conducting state [18].Tl^+ ions are known to react very fast with hydrated electron producing Tl^0. The Tl^0 species is in equilibrium with Tl_2^+ and subsequently forms thallium clusters (Tl_n) on further irradiation.Radiolytic reduction of Ag+ ions in the aqueous medium is one of the most extensively studied systemsamong the different metal ions. Various transient intermediates such as ag^0, Ag^{2+}, Ag_3^{2+} Ag_4^{2+}etc, have been characterized by the technic of pulse radiolysis, and finally results in larger silver clusters with development of plasmon absorption band at ~380- 400 nm [22].In this work the thermal and spectroscopic properties of $AgTlSO_4$ synthesized by a novel mechnochemical method developed earlier by Bharati Mohan and Sunandana [23].

Experimental

Synthesis

The material used in this experiment was Ag_2SO_4 (AR 99% pure) and Tl_2SO_4ALDRICH(99.9%)have been mixed in 1:1 ratio and grinded for one hour in a agate mortor and then transferred to heater. The powder is heated at 200^0C for 10 hours, and subsequently cooled to room temperature. $AgTlSO_4$ was again thoroughly grinded and used for further characterization.

Instrumentation

The crystal structure of $AgTlSO_4$ samples is characterized by X-ray powder diffractometer using Co Kα radiation (λ = 1.7889 A). To analyse the morphologies and chemical composition of these samples were obtained by Field emission scanning microscopy (FESEM) and for chemical composition using energy dispersive X- ray scattering (EDS) analysis (a model no ULTRA- 55, ZEISS, Japan).Raman spectra recorded at 300k in a backscattering geometry with Horiba Jobin Yvon, LabRAM-HR800 micro-Raman system using 514.5 nm excitation from Ar+ gas laser. The differential scanning calorimetry (DSC) was done using DuPont 9900 model DSC instrument. Finally, the electron spin resonance spectra recorded on a JEOL(FE-3X)

x-Band spectrometer under optimized conditioned of modulation amplitude, receiver gain, time constant and scan time.

Results and Discussion

Structure and morphology

The XRD pattern of $AgTlSO_4$is shown in Fig 1A, The experimental and theoretically obtained XRD of AgTlSO4 have more or less similar signature. Orthorhombic phase with a space group of Pnam (structure of TlLiSO4) has taken as input structure for AgTlSO4. After optimization, the structure has been modified and resulting to same as TlLiSO4. The obtained 2θ values of XRD pattern matches well with the standard data (JCPDS card no.50-0611). The lattice parameters are within orthorhombic symmetry, and the atomic positions are distorted due to the replacement of Li atoms with Ag atoms. This is may be due the mismatch of atomic sizes of Li/Ag atoms. The crystal structure and density of states of AgTlSO4 as shown in Fig 2. AgTlSO4 has a band gap of 2.85 eV indicating it is an insulator. This gap is less compared to other sulphates.The optimised lattice parameters and the atomic coordinates obtained from GGA values of AgTlSO4 along with LiTlSO4 are shown in table 1and 2.The nano regime of $AgTlSO_4$ were observed in FESEM to investigate the morphology and surface characteristics. This sample shows nano particle with average size of the particle is ~80 nm as shown in Fig.1B. The elemental analysis of $AgTlSO_4$ sample was determined by using EDS technique. The EDS clearly shows the formation of Tl, Ag, O and S elements, formation of$AgTlSO_4$ and the EDS analysis confirms that the chemical composition of $AgTlSO_4$ is almost in stoichiometric ratios.

Table.1: The optimised lattice parameters obtained from GGA values of AgTlSO4 along with LiTlSO4

Parameters	AgTlSO4	LiTlSO4
a (Å)	9.301409	8.893
b (Å)	9.628723	9.348
c (Å)	5.902327	5.387
V(Å3)	528.616464	447.9

Table.2: The atomic coordinates obtained from GGA calculations of AgTlSO4 and

	Atoms		AgTlSO4		LiTlSO4	
	x/a	y/b	z/c	x/a	y/b	z/c
Ag/Tl	0.318878	0.427416	0.230289	0.495208	0.218639	0.745971
Li/Tl	0.501460	0.227482	0.722854	0.322172	0.412074	0.245216
S	0.220113	0.078072	0.251392	0.207435	0.079567	0.245553
O (1)	0.068945	0.114173	0.314122	0.041108	0.093221	0.250113
O (2)	0.284913	0.188921	0.107915	0.275100	0.214654	0.149477
O (3)	0.306477	0.061271	0.466860	0.264212	0.050570	0.502670
O (4)	0.223651	-0.058058	0.125368	0.252223	-0.042030	0.079800

Raman Spectroscopy and phase transition

The obtained Raman spectroscopy has shown in Fig.3A. Raman spectra confirms the existance of either a stable or metastable sequence for thallium derivatives. $AgTlSO_4$ samples exhibit spectra with small triplets (ν_3) at about 1085 and 1080 cm^{-1}respectively, intense singlets (ν_1) at 953 cm^{-1} for Tl derivatives and 968 cm^{-1} for Ag derivative very small triplets (ν_4) at about 605 and 615 cm^{-1} and medium doublets near 450 cm^{-1} which indicates a multiplicity of Z=2, the new spectroscopic unit-cell consisting of two SO_4 ions[7].We observed 91cm^{-1} as ν_{ext}. The intense peak at 956 cm^{-1} is denoted as ν_1, whereas 435$cm^{-1}$is under the ν_2 band. The peak 1164 cm^{-1}as ν_3 band.

Electron spin resonance

Electron spin resonance is a specific microscopic probe with which to examine molecular environments in crystalline and disordered systems. Under favourable circumstances, it is possible to create and stabilize paramagnetic radicles which may reflect certain aspects of dynamics- which may be characteristic of the system itself. Presently we describe our efforts to stabilize and identify molecular paramagnetic radicles in AgTlSO4.ESR spectra of $AgTlSO_4$ consists of an anisotropic resonance (see Fig.3B). This resonance is gain due to CO_3^- radicals and the corresponding g value is 2.365. The g- anisotropy of the CO_3^- is quite sensitive to the surroundings in which it is stabilized. This is a strong indirect microscopic evidence in support of the stabilization of the dynamical disorder of SO_4^{2-}.

Differential Scanning calorimetry

Fig.3C shows the DSC scan of the material $AgTlSO_4$ in the temperature range 50 to 550 ^{0}C.The DSC curve of $AgTlSO_4$ shows small water peak at 184.6^{0}C. An endothermic peaks at 459.7^{0}C, 505.4^{0}C, 503.4^{0}C and 520^{0}C respectivily. The endothermic peaks could be due to the phase transition from ordered to disordered low temperature structure. The first endothermic is less intense compared to other endothermic peaks at 503.4^{0}C and 520^{0}C. But there is astrong endothermic peak at 505.4^{0}C. As is common with hydrated systems, these peaks represent dehydration of $AgTlSO_4$.

Fourier Transform Infrared Spectroscopy

In order to get some structural information of $AgTlSO_4$ solid solution, IR absorption spectra of a mechanically mixed powder of $AgTlSO_4$ sample are shown in Fig.3D. The free sulphate SO_4^{2-} ion belongs to the high symmetry point group. For the four fundamental internal vibration modes, the symmetric stretching mode ν_1 and the doubly degenerate symmetric bending mode ν_2 are IR inactive; the asymmetric stretching mode ν_3 and ν_4 are both triply degenerate and IR active. In crystalline solids, the sulphate group is influenced by its structural environment. As the symmetry lowers, the degeneracy in ν_2, ν_3, and ν_4 may be expected to be wholly or partially removed and ν_1 and ν_2 may become i.r. active. The new phase shows an increase of i.r. transmission, inactive absorption ν_1 around 597.26 cm^{-1} and ν_2 around 1052.05 cm^{-1}. More over the broadening of the i.r. active absorption ν3 around

1112.33 cm^{-1} and ν_4 around 624.66 cm^{-1} indicates the decrease in symmetry of the SO_4^{2-} ions due to the incorporation of Li+ ions in to the interstitial positions and/or Ag+ lattice sites, resulting in the change of structural environment. That is, IR spectra indirectly demonstrate the formation of $AgTlSO_4$ phase.

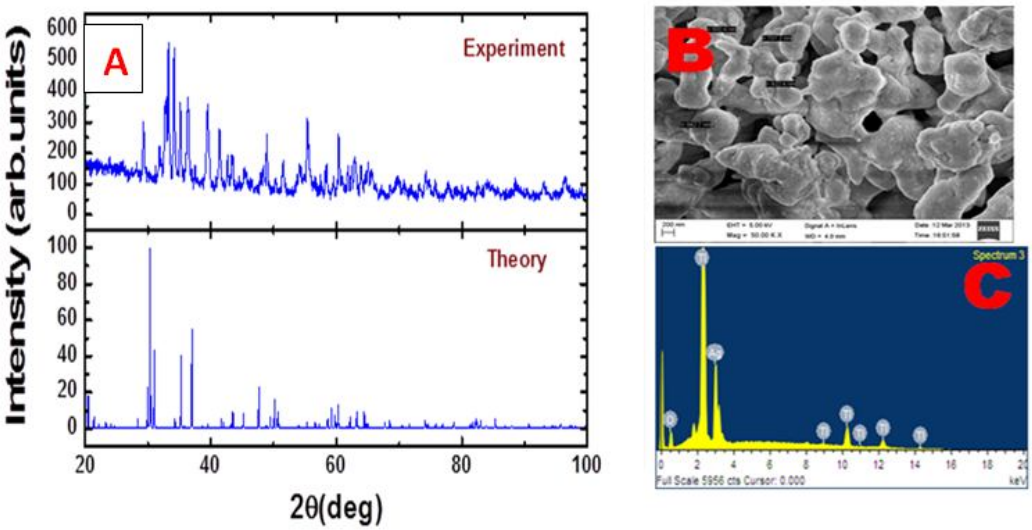

Fig.1. The(A) X-ray diffraction, (B) FESEM and (C) EDS of $AgTlSO_4$.

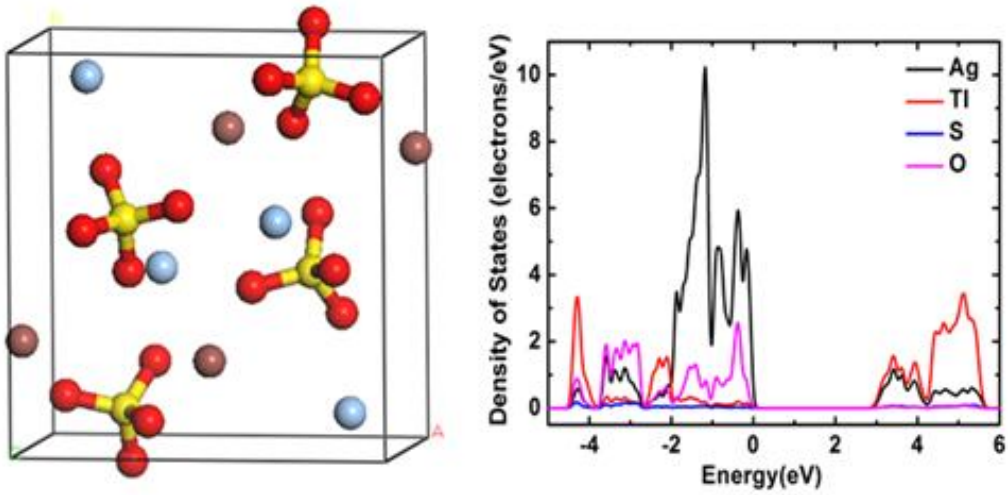

Fig.2. The (A) Crystal structure (B) Density of states of AgTlSO4

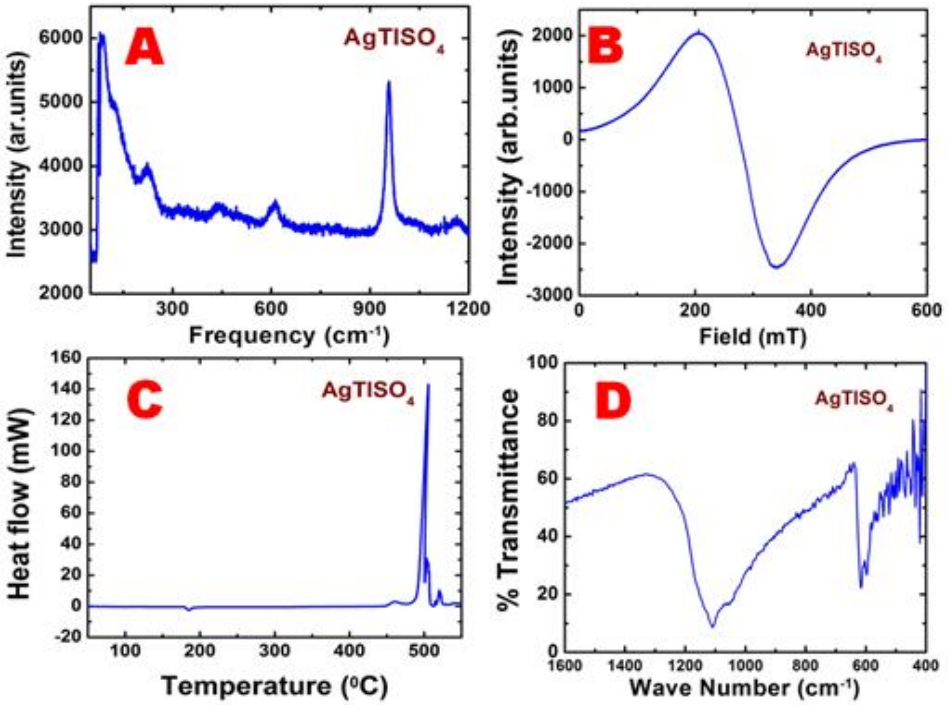

Fig.3. (A) Raman spectroscopy, (B)ESR, (C) DSC and (D) FTIR of $AgTlSO_4$

Conclusions

AgTlSO4, is prepared by mixing Ag_2SO_4 (AR 99% pure) and Tl_2SO_4ALDRICH (99.9%) with 1:1 ratio and grinded for one hour. The obtained XRD pattern is in well agreement with the previous studies.Raman spectra of $AgTlSO_4$ exhibit small triplets (ν_3) at about 1085 and 1080 cm^{-1}respectively, intense singlets (ν_1) at 953 cm^{-1} for Tl derivatives and 968 cm^{-1} for Ag derivative very small triplets (ν_4) at about 605 and 615 cm^{-1} and medium doublets near 450 cm^{-1} which indicates a multiplicity of Z=2, the new spectroscopic unit-cell consisting of two SO_4 ions. ESR gain is due to CO_3^- radicals and the corresponding g value is 2.365. The g- anisotropy of the CO_3^- is quite sensitive to the surroundings in which it is stabilized. The DSC curve of $AgTlSO_4$ shows small water peak at 184.6^0C. An endothermic peaks at 459.7^0C, 505.4^0C, 503.4^0C and 520^0C respectivily. The endothermic peaks could be due to the phase transition from ordered to disordered low temperature structure.

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