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ChemTech

International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN : 0974-4290
Vol.6, No.13, pp 5298-5303, November 2014

MESCon 2014 [4th -5th September 2014]
National Conference on Material for Energy Storage and Conversion- 2014

Electrical conductivity studies on pure and doped magnesium sulphate heptahydrate single crystals

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Abstract: Pure and doped (Cd^{2+} and Hg^{2+}) magnesium sulphate heptahydrate ($MgSO_4.7H_2O$) crystals were grown by slow evaporation method. The entry of the dopants into the crystal lattice was confirmed by energy dispersive x-ray (EDX) analysis. The powder x-ray data was indexed and the lattice parameters were calculated. The a.c. conductivity measurements were carried out on the grown crystals. The Arrhenius plots of these crystals show two types of conduction in these crystals — one at low temperature and the other at high temperature in the form of extrinsic and intrinsic conduction, respectively.

Keywords: Crystal growth, magnesium sulphate heptahydrate, XRD, a.c conductivity; electrical properties.

Introduction

Metal sulphate heptahydrate single crystals such as magnesium sulphate heptahydrate (MSHH), nickel sulphate heptahydrate (NSHH) and zinc sulphate heptahydrate (ZSHH) play a key role as best dielectric materials. Growth of MSHH, ZSHH and NSHH crystals were reported in the literature[1,3]. These crystals have become an important field of research for academic interest and industrial applications in various areas like medical, agriculture and chemical industry[4,5].

Electrical conductivity is an elegant experimental tool to probe the structural defects and internal purity of crystalline solids. The electrical conductivity for ionic materials is found to be very low which may be due to the trapping of some carriers at defect sites. At any particular temperature, however, Gibb's free energy of a crystal is minimum when a certain fraction of ions leave the normal lattice. As the temperature increases, more and more defects are produced which, in turn, increase the conductivity. In the high temperature (intrinsic) region, the effect of impurity on electrical conduction will not change appreciably whereas in the low temperature (extrinsic) region, the presence of impurity in the crystal increases its conductivity. The electrical conduction in dielectrics is mainly a defect controlled process in the low temperature region. The presence of impurities and vacancies mainly determines this region. The energy needed to form the defect is much larger than the energy needed for its drift. The conductivity of the crystalline material in the higher temperature region is determined by the intrinsic defects caused by the thermal fluctuations in the crystal.

It was reported that the growth of magnesium sulphate heptahydrate (MSHH) crystals from aqueous solution at low temperature[6,9] and these are found to be orthorhombic with space group $P2_1P2_1P2_1$. Literature apparently shows that very little work has been carried out on MSHH crystals. With the aim of understanding the conduction mechanism in pure and impurity added MSHH crystals we have carried out the present study. The details are presented.

Experimental

Analytical reagent grade magnesium sulphate heptahydrate ($MgSO_4.7H_2O$) and deionized water were used in the present work. To a saturated solution of $MgSO_4.7H_2O$, desired quantity of dopants (Cd^{2+} and Hg^{2+}) were added. The dopant concentration was 0.005M. The solution is filtered and kept in a constant temperature bath (Sub-Zero make (acc. = ±0.01°C)) at a predetermined temperature. Small crystals appeared in the beginning due to slow evaporation and grew into good quality larger crystals in about 2-3 weeks time. The grown crystals were harvested and used for characterization studies.

The entry of dopants into the crystal lattice was confirmed by energy dispersive X-ray (JEOL Model JED – 2300) analysis. X-ray diffraction data were collected from powder samples of crystals using PANalytical make, ModelX'per PRO. The reflections were indexed following the powder X software. Lattice parameters were determined from the indexed data using high angle reflections.

The grown crystals were powdered and made into pellets (polycrystalline) of diameter 10 mm and thickness 2 mm. The surfaces of the pellet in contact with the electrodes were coated with good quality graphite paste. The pellet was placed between the electrodes of the experimental cell. The experimental cell consists of two electrodes made up of stainless steel coated with silver and having a diameter the same as the pellet and kept parallel to each other similar to a parallel plate capacitor. This experimental cell was electrically shielded and was placed in an electric oven for temperature variation. The electrodes of the experimental cell were connected to an impedance analyzer (IM 6 ZAHNER, Germany) for measuring the bulk resistance of the sample. The sample was kept at each temperature for about 20 min before the measurements were carried out to ensure proper sample thermal equilibrium. The measurements were carried out in the temperature range 30 to 100 °C.

Result and discussion

Energy dispersive spectral analysis

The entry of the dopants (Cd^{2+}, Hg^{2+}) in to crystal lattice of the pure magnesium sulphate heptahydrate is confirmed by the energy dispersive spectra which are presented in figures 1 and 2.

The ionic radius of Mg^{2+} (0.72Å) is smaller than the ionic radius of both the dopants considered in the present study (0.97Å for Cd^{2+} and 1.02Å for Hg^{2+}). Therefore it is expected the dopants may have entered into the crystal lattice as interstitials without affecting the overall charge neutrality of the crystal.

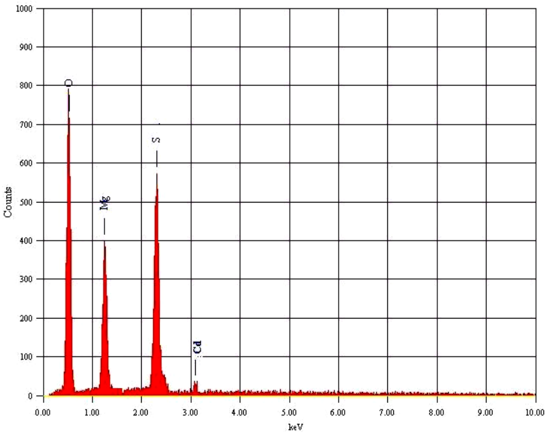

Fig 1: EDX spectrum of Cd doped MSHH

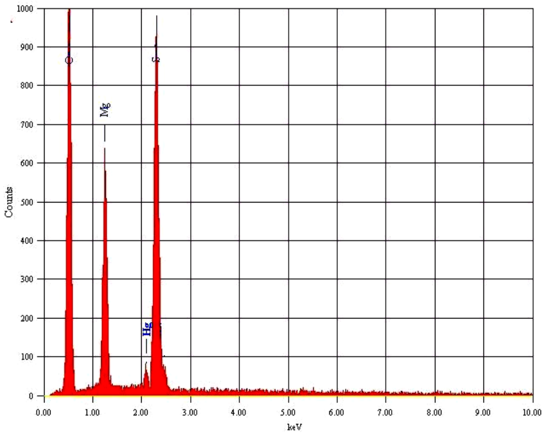

Fig 2: EDX spectrum of Hg doped MSHH

The concentration of the element is calculated by using the ratio of the intensity (number of X-ray counts) in the filtered peak for an element of interest in the sample to the intensity in the filtered peak for the standard assigned to that element. The concentration of dopants in the grown crystal was calculated and presented in table 1.

Table 1: Molar concentration of Cd^{2+} and Hg^{2+} in the magnesium sulphate heptahydrate growth solution and the grown crystals

Sample	**Element**	**Energy (keV)**	**Dopant concentration actually taken (in mole)**	**Dopant concentration in the grown crystal (in mole)**
Cd-doped MSHH	Cd	3.133	0.005	0.004782
Hg-doped MSHH	Hg	2.195	0.005	0.004514

Powder x-ray diffraction analysis

The powder x-ray diffraction for pure and doped magnesium sulphate heptahydrate single crystals were recorded and indexed using powder x software[10] and presented in the figure 3.

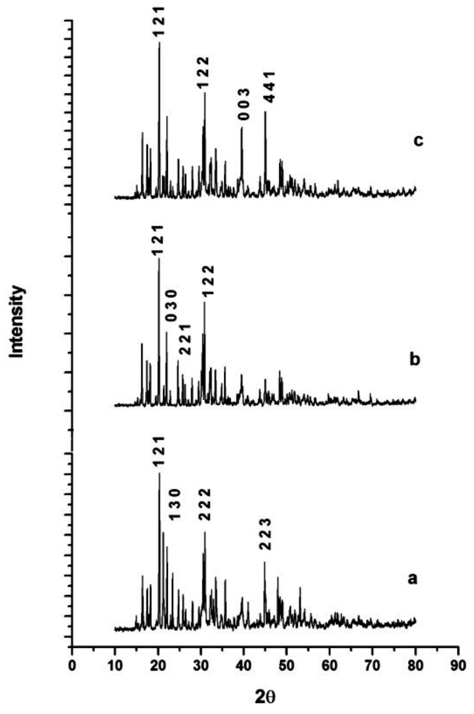

Fig 3: X-ray diffraction patterns (a) pure (b) Cd^{2+} doped, (c) Hg^{2+} doped, MSHH

The x-ray diffraction pattern of the pure and doped MSHH single crystals differed in their relative intensities and the lattice spacing of the crystals. The indexed data of pure and doped MSHH was compared with JCPDS data [File No. 36 0419] and are presented in table 2. The material of the grown pure crystals was confirmed to be MSHH.

The lattice parameters of all the grown crystals were calculated from the x-ray diffraction data. The lattice parameters obtained for the crystals grown in the present study are presented in table 3.

The variation of lattice volume of doped MSHH crystals indicates that the entry of dopant materials in to crystal lattice of pure MSHH.

Impedance analysis

A study of the electrical properties provides information about dielectric properties of the solid materials. In the present study, the grown crystals were powered and made into pellets of 2mm thickness and 10mm diameter. The pellets are placed in a two probe arrangement. Graphite is coated on both surfaces of the samples to make contact between the electrodes. The impedance were measured in the frequency range 1 Hz to 100 KHz with the applied voltage of 1.25 V. The bulk resistance (R_b) of all the samples were found out from impedance plot. The electrical conductivity of pure and doped MSHH were calculated by using the formula, $\sigma = t/R_bA$, where t is thickness of the sample, R_b is bulk resistance and A is the area of the sample.

Table 2: Indexed XRD data for pure magnesium sulphate heptahydrate crystals

hkl	From present work		From JCPDS data	
	2θ (°)	I/I_o	2θ (°)	I/I_o
0 1 1	14.8895	4.38	14.914	16
2 1 0	16.6204	10.14	16.695	20
2 0 1	19.5835	5.81	19.830	12
1 2 1	20.3688	100.00	21.071	100
1 3 0	23.4076	41.84	23.522	12
0 0 2	26.4461	14.00	26.015	10
1 1 2	28.0309	20.81	28.140	4
2 0 2	30.1297	13.07	30.119	3
2 1 2	30.9397	71.78	31.051	20
0 4 1	32.8905	22.30	32.632	18
2 2 2	33.4461	38.79	33.719	25
2 4 1	36.4433	6.87	36.040	2
5 2 0	41.0174	19.91	40.946	10
2 2 3	45.5562	11.74	45.176	3
3 1 3	47.1386	8.91	46.538	2

Table 3: Variation of lattice parameter and lattice volume of the grown crystals

Crystals	Lattice Parameters (Å)			Volume (Å^3)
	a	b	c	
Pure MSHH	11.852	11.973	6.851	972.18
Cd doped	11.758	12.109	6.910	983.83
Hg doped	11.523	12.056	6.839	950.08

A.C. Conductivity

A variation on a.c conductivity with temperature is illustrated in figure 4. It is found that the conductivity increases with increase in temperature. The electrical conductivity of the pure and doped magnesium sulphate heptahydrate was found in the order of 10^{-7} - 10^{-8} mho/m at room temperature.

In order to understand the conduction mechanism in these crystals the electrical conductivity was plotted against 1000/T shown in figure 5. All the crystals grown in the present study show Arrhenius type behaviour described by:

$$\sigma = \sigma_0 \exp\left(-E_A/k_BT\right)$$

where σ_0 is the pre-exponential factor and k_B is the Boltzmann's constant. From these plots we observe that there are two activation energies in the temperature range considered.

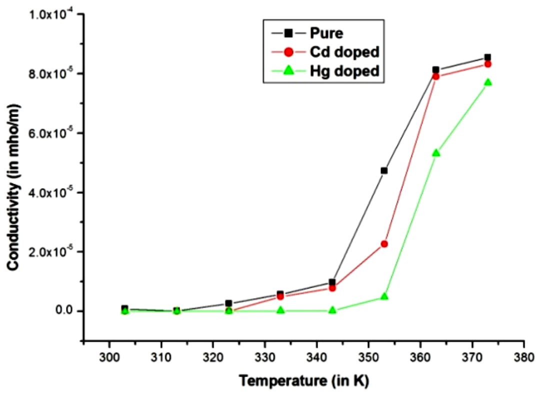

Fig 4: Variation of a.c conductivity with temperature

These plots have a nature similar to intrinsic-to-extrinsic transition found in electronic semiconductor. The presence of protons able to be exchanged between and hence able to diffuse through interspaces makes these materials protonic conductors[11,12]. The variation in electrical conductivity yields two straight lines of different slopes showing that there exist two types of conduction in these crystals. The one at low temperature is extrinsic and the other at high temperature is intrinsic. The activation energies in the extrinsic and intrinsic ranges were calculated for all the grown crystals and are presented in table 4. The low activation energies in the extrinsic region show that the conductivity is predominantly due to the movement of defects produced by thermal activation.

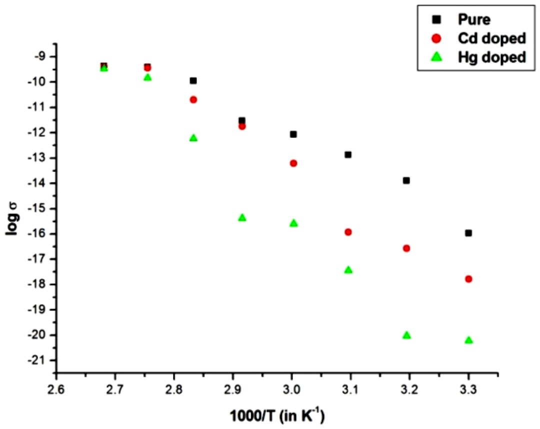

Fig 5: Arrhenius plot of pure and doped MSHH crystals

Table 4 : Activation energies E_A (in eV) calculated from Fig.5

Sample	**Activation energy E_A (in eV)**	
	Extrinsic region	**Intrinsic region**
Pure MSHH	0.9030	0.3750
Cd doped MSHH	1.3731	0.2546
Hg doped MSHH	0.5778	0.5972

Conclusion

Single crystals of pure and doped (Cd^{2+}, Hg^{2+}) magnesium sulphate heptahydrate were grown by slow evaporation method. The harvested grown crystals were subjected to EDX, XRD analysis and conductivity measurements. The energy dispersive X-ray spectrum confirmed the entry of dopants into the crystal lattices. The materials of the grown crystals were confirmed by the powder x-ray diffraction analysis. The a.c conductivity were measured at temperatures ranging from room temperature to 100°C. The present study indicates that the conductivity increases with the increase in temperature and varies with the impurity addition. These crystals exhibit two types of conduction by the way of intrinsic and extrinsic conduction.

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