X-Ray and Thermal Studies on $\text{Zn}_x\text{Mg}_{1-x}\text{SO}_4\cdot 7\text{H}_2\text{O}$ Crystals

P. SUMITHRAJ PREMKUMAR and X. SAHAYA SHAJAN

Centre for Scientific and Applied Research, School of Basic Engineering and Sciences
PSN College of Engineering and Technology, Melathediyoore, Tirunelveli - 627152, India

shajan89@gmail.com

Received 19 February 2010; Accepted 1 May 2010

Abstract: Single crystals of pure and mixed $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$ and $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ crystals were grown by slow evaporation method. The grown crystals were characterized by x-ray diffraction, atomic absorption spectral analysis and thermal analysis. The lattice parameters were calculated by from the XRD data. Atomic absorption spectral analysis showed that the Mg and Zn atoms were present in the mixed crystals. The thermal analysis by TGA and DTA showed that the mixed crystals have higher thermal stability than the pure crystals.

Keywords: Zinc sulphate heptahydrate, Magnesium sulphate heptahydrate, Mixed crystals, Crystal growth, Thermal analysis.

Introduction

Magnesium sulphate heptahydrate (MSHH), nickel sulphate heptahydrate (NSHH) and zinc sulphate heptahydrate (ZSHH) crystals can be considered as metal sulphate ($\text{MSO}_4\cdot 7\text{H}_2\text{O}$) single crystals. These crystals are isomorphous to each other and they all belong to the orthorhombic system with space group $P2_1P2_1P2_1$. They have tetramolecular unit cell and are important due to the availability of several hydrogen bonds.

Microelectronics industry needs replacement of dielectric materials in multilevel interconnect structures with new low dielectric constant materials. Impurity addition and mixing lead to change in the electrical properties of dielectric material crystals. In this aspect, ZSHH and MSHH play a key role as best dielectric materials. Growth of MSHH, ZSHH and NSHH crystals were reported in the literature¹⁻³. However literature apparently shows that there is no systematic study have reported on the growth of mixed crystals of ZSHH and MSHH so far. In the present study, we have attempted to grow pure and mixed MSHH and ZSHH crystals by slow evaporation method. The growth conditions were optimized and crystals of dimensions $50 \times 15 \times 10 \text{ mm}^3$ were obtained in the present study. The grown crystals were characterized by AAS, x-ray and thermal analysis. The details are reported herein.

Experimental

Recrystallized samples of analytical reagent grade $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and doubly distilled water were used in the present work for the growth of single crystals from aqueous solution by slow evaporation method. The saturated concentration of the ZSHH and MSHH growth solution at room temperature was found to be 3.5 M and 3.2 M respectively. Mixed crystals were grown by mixing appropriate ratios of MSHH and ZSHH. The growth solution was kept in a constant temperature bath (acc. ± 0.01 °C, Sub-Zero make) in the predetermined temperature. Crystals of maximum size were obtained in about 5-7 days. The maximum size of the grown crystals was $50 \times 15 \times 10 \text{ mm}^3$.

The mixed crystals were characterized by AAS analysis (VARIAN Model SPECTRAA 220) in order to confirm the entry of Mg and Zn atoms into the crystal lattice. The material of the grown crystals was confirmed by x-ray diffraction analysis (PANalytical make, Model X'per PRO). The thermal stability of the grown crystals was studied using TGA and DSC (Perkin-Elmer thermogravimetric analyser) analysis. The heating rate was 10 °C/min in nitrogen environment.

Results and Discussion

AAS analysis

The grown crystals were characterized by AAS analysis. The molar concentration of Zn and Mg present in the growth solution and that incorporated into the crystal were presented in Table 1.

Table 1. Molar concentration of zinc and magnesium in the growth solution and the grown crystals

Molar concentration taken for growth experiment		Molar concentration present in the crystal	
Zinc	Magnesium	Zinc	Magnesium
0.8	0.2	0.92	0.08
0.6	0.4	0.76	0.24
0.4	0.6	0.57	0.43
0.2	0.8	0.41	0.59

Table 1 show that the incorporation of Zn^{2+} ions into the (Zn-Mg) SHH mixed crystal lattice is more favoured than Mg^{2+} ions. This might be due to the fact that Zn^{2+} can easily replace Mg^{2+} ions since because they are isomorphous in nature. Similar observations are reported in the literature for calcium and strontium tartrate tetrahydrate single crystals^{4,5}.

X-Ray diffraction analysis

The x-ray diffraction data were indexed and the lattice parameters were determined. The indexed data of ZSHH and MSHH was compared with JCPDS data [File No. 09 0395] and [File No. 36 0419] respectively and are presented in Table 2. The material of the grown pure crystals (end members) is thus confirmed to be ZSHH and 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 observed in the present study indicates that the grown crystals are mixed ones.

Table 2. Indexed x-ray diffraction data for pure ZSHH and MSHH crystal grown in the present study

S No	ZSHH				MSHH			
	Present study		JCPDS Data		Present study		JCPDS Data	
	2 θ	Intensity %	2 θ	Intensity %	2 θ	Intensity %	2 θ	Intensity %
1	14.856	35.4	14.703	10	15.057	35.4	14.914	16
2	15.44	40.4	14.978	8	16.799	23.9	16.695	20
3	16.665	96.3	16.525	80	20.046	9.1	19.83	12
4	18.116	32.9	19.624	8	21.322	100	21.071	100
5	20.372	100	21.085	100	23.765	19	23.522	12
6	21.279	53.2	21.238	50	26.069	9.3	26.015	10
7	22.268	69.9	23.39	12	28.294	4.3	28.14	4
8	23.615	20	23.771	20	30.149	5.6	30.119	3
9	24.966	9.7	25.749	25	31.287	13.9	31.051	20
10	26.225	6.3	26.102	10	32.626	1.3	32.632	18
11	28.286	13.5	28.199	6	33.828	9.8	33.719	25
12	29.594	2	29.909	16	36.174	0.6	36.04	2
13	30.975	29.7	30.241	10	41.072	6.7	40.946	10
14	32.697	42	32.484	20	45.203	1.9	45.176	3
15	33.994	29.5	33.381	18	46.627	3.4	46.538	2
16	36.112	10.2	36.357	8				
17	37.844	5.7	37.538	4				
18	39.717	24.1	39.892	4				
19	41.39	19	41.088	18				
20	42.558	49	42.464	8				
21	44.023	4.9	44.028	8				
22	45.503	9.2	45.812	10				
23	47.878	10.8	47.78	10				
24	48.996	19.8	48.157	12				
25	53.601	10.6	53.682	10				

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

Crystal	Lattice parameter ($\text{\AA}$)			Lattice volume ($\text{\AA}^3$)
	a	b	c	
Zn $\text{SO}_4 \cdot 7\text{H}_2\text{O}$	11.822	11.977	6.834	967.64
$\text{Zn}_{0.8}\text{Mg}_{0.2}\text{SO}_4 \cdot 7\text{H}_2\text{O}$	11.792	11.995	6.843	967.91
$\text{Zn}_{0.6}\text{Mg}_{0.4}\text{SO}_4 \cdot 7\text{H}_2\text{O}$	11.802	11.996	6.845	969.09
$\text{Zn}_{0.4}\text{Mg}_{0.6}\text{SO}_4 \cdot 7\text{H}_2\text{O}$	11.801	11.989	6.852	969.44
$\text{Zn}_{0.2}\text{Mg}_{0.8}\text{SO}_4 \cdot 7\text{H}_2\text{O}$	11.881	11.911	6.861	970.93
Mg $\text{SO}_4 \cdot 7\text{H}_2\text{O}$	11.852	11.973	6.851	972.18

Thermal analysis

The thermograms recorded for all the grown crystals and are presented in Figures 1 to 6. The thermograms show that these crystals decompose on heating. An increase in the thermal stability was observed for the mixed crystals. The decomposition temperature for ZSHH and MSHH were found to be 109.10 $^{\circ}\text{C}$ and 117.23 $^{\circ}\text{C}$ respectively. However for $\text{Zn}_{0.8}\text{Mg}_{0.2}\text{SO}_4 \cdot 7\text{H}_2\text{O}$ crystal the decomposition temperature was found to be 135 $^{\circ}\text{C}$.

Figure 1. Thermogram of pure ZSHH

Figure 2. Thermogram of $\text{Zn}_{0.8}\text{Mg}_{0.2}\text{SO}_4 \cdot 7\text{H}_2\text{O}$

Figure 3. Thermogram of $\text{Zn}_{0.6}\text{Mg}_{0.4}\text{SO}_4 \cdot 7\text{H}_2\text{O}$

Figure 4. Thermogram of $\text{Zn}_{0.4}\text{Mg}_{0.6}\text{SO}_4 \cdot 7\text{H}_2\text{O}$

Figure 5. Thermogram of $\text{Zn}_{0.2}\text{Mg}_{0.8}\text{SO}_4 \cdot 7\text{H}_2\text{O}$

Figure 6. Thermogram of pure MSHH

Two stages of decomposition are found while heating the crystals from ambient to 900 °C. In the both the stages of decomposition, water molecules are liberated. ZSHH becomes anhydrous at 109 °C whereas all other crystals become anhydrous around 300 °C. $\text{Zn}_{0.2}\text{Mg}_{0.8}\text{SO}_4 \cdot 7\text{H}_2\text{O}$ crystals become anhydrous at 442.06 °C all the stages of decomposition are supported by the corresponding exothermic and endothermic dips observed in the thermograms. The expected loss of molecules in each stage of decomposition and corresponding percentage weight loss are tabulated in Table 4.

Table 4. Percentage of weight loss in the different stages of decomposition of (Zn-Mg)SHH mixed crystals

Grown Crystals	Decomposition temperature, °C	percentage of weight loss		Expected loss of molecules
		observed	calculated	
ZSHH	109.1	58.4	56.16	7H ₂ O
	433.23	63.42	60.36	2O ₂
$\text{Zn}_{0.8}\text{Mg}_{0.2}\text{SO}_4 \cdot 7\text{H}_2\text{O}$	122.93	26.71	26.57	4H ₂ O
	300.17	8.9	8.69	H ₂ O
$\text{Zn}_{0.6}\text{Mg}_{0.4}\text{SO}_4 \cdot 7\text{H}_2\text{O}$	129.01	36.78	36.21	5H ₂ O
	334.09	14	14.72	2H ₂ O
$\text{Zn}_{0.4}\text{Mg}_{0.6}\text{SO}_4 \cdot 7\text{H}_2\text{O}$	129.52	24.48	23.97	4H ₂ O
	334.09	19.13	18.02	2H ₂ O
$\text{Zn}_{0.2}\text{Mg}_{0.8}\text{SO}_4 \cdot 7\text{H}_2\text{O}$	135.1	30.26	28.28	4H ₂ O
	442.06	27.22	29.58	3H ₂ O
MSHH	117.23	23.12	21.92	3H ₂ O
	289.87	32.74	32.75	4H ₂ O

Conclusion

Mixed crystals of ZSHH and MSHH were grown by slow evaporation method. Crystals of dimensions 50 x 15 x 10mm³ were obtained in the present study. The grown crystals were subjected to AAS, XRD and TGA/DSC analysis. The material of the grown crystals was confirmed by XRD analysis. AAS confirmed the presence of Mg and Zn atoms in the mixed crystals. Enhancement of thermal stability was observed for mixed crystals. The crystals were found to decompose through two stages of decomposition.

References

1. Kasatkin I A, *Cryst Res Technol.*, 2002, **37**(2-3),193.
2. Xinxin Zhuang, Genbo Su, Guofu Wang, Guohui Li and Zixiang Huang, *Cryst Res Technol.*, 2004, **39**, 754
3. Kanagadurai R, Durairajan R, Sankar R, Sivanesan G, Elangovan S P and Jayavel R, *E- J Chem.*, 2009, **6**(3), 871-879.
4. Sahaya Shajan X and Mahadevan C, *Cryst Res Technol.*, 2005, **40**, 598-602.
5. Gowri B and Sahaya Shajan X, *Mater Lett.*, 2006, **60**(11), 1338-1340.