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Compositional dependence of lattice constants in solution grown single crystals of $Ni_xZn_{1-x}SO_4.7H_2O$ by X-ray diffraction method

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Abstract: $NiSO_4.7H_2O$ (morenosite) and $ZnSO_4.7H_2O$ (goslarite) are hydrogen bonded crystals having wide applications in various fields. In an attempt to understand the formation and properties of mixed crystals based on $NiSO_47H_2O$ and $ZnSO_47H_2O$, we have grown by the free evaporation method at room temperature and characterized $Ni_xZn_{1-x}SO_4.7H_2O$ single crystals (with x having the values 0.0, 0.2, 0.4, 0.5, 0.6, 0.8 and 1.0).X-ray diffraction studies have been carried out on solution grown mixed crystals of Nickel–Zinc sulphate (Ni–Zn) over the entire range of composition. Lattice parameters *a*, *b* and *c* are experimentally determined using Computer program POWD. The dependence of the lattice parameters on dopant concentration in $Ni_xZn_{1-x}SO_4.7H_2O$ solid solutions is not linear. Lattice parameter a decreases continuously upto x=0.4, then has a high spike at x=0.5, thereafter, shows slightly increase in nature. Lattice parameter b gradually decreases upto x=0.2, after that it almost saturates. Lattice parameter c almost follows a sinusoidal nature with a sharp depression at x=0.5 and 0.8. However, the value of the lattice volume v decreases monotonically with concentration x with a sharp depression at x=0.5. Hence, it can be said that the lattice parameters a,b and c follow anomalous Vegerd's law. Results are analyzed in the light of packing consideration of the individual atoms.

Keywords: Crystal growth, Mixed crystals of Nickel–ZincSulphate, X-ray techniques, Lattice parameters

I. INTRODUCTION

The study of mixed crystals of nickel-zinc sulphate $Ni_xZn_{1-x}SO_4.7H_2O$, (NS-ZS) has attracted considerable attention in recent years, as they present a new class of materials with intrinsic interest due to their potential applications in the area of research for both academic and industrial applications in various areas like medical, agricultural and chemical industry [1]. There already exist some investigations which include structural, spectroscopic, dielectric, electrical conductivity measurements [2-4]. But there have been practically no report available in respect of concentration dependence of lattice constants in this mixed system which is anomalous in nature. From this point of view, an attempt has been made to characterize the mixed crystals of nickel sulphate (NS) and zinc sulphate (ZS), the other analogue of the same family which forms a continuous series of mixed crystals NS.

II. EXPERIMENTAL

Mixed crystals of NSH-ZSHare grown at room temperature ≈ 30^0C by slow evaporation of the aqueous solution of the mixed salts with wide variation of molar concentrations x (x = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8 and 1.0). Large number of small transparent crystals crystallizes at the bottom of the crystallizing dish over the entire range of composition.

III. CHARACTERIZATION

Densities of the grown crystals were measured by the flotation method [5, 6] within an accuracy of ±0.008 g/cm3. The rarer and denser liquids that have been used in the process are Carbon tetrachloride of density 1.594 g/cm^3 and boroform of density 2.890 g/cm^3 respectively. The chemical compositions are estimated from the density data following the method adopted by Theivanayagom and Mahadevan [7]. The densities of single phased mixed crystals have been found to be very nearly additive obeying the relation,

$$d = xd_1 + (1-x)d_2 \qquad [1]$$

where d is the density of the mixed crystal and d_1 and d_2 are the densities of the end members. Atomic absorption spectroscopic (AAS) measurements were also carried out using an atomic absorption analyzer (Model AA-6300) to determine the Ni and Zn atom contents in the mixed crystals.

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X-ray diffraction (XRD) data were collected from powder samples of crystals using an automated X-ray powder diffractometer (PANalytical) with monochromatic Cu $K_\alpha$radiation (k = 1.54056 Å), scan speed 2^0/ min and scintillation counter at a temperature of 25 ± 1^0C in the 2h range 10–70^0. The reflections were indexed following the procedures of Lipson and Steeple [8]. Lattice parameters were determined from the indexed data using high angle reflections by considering a set of three reflections and forming three simultaneous equations using the relation,

$$4 \sin^2/ \lambda^2 = h^2/a^2 + k^2/b^2 + l^2/c^2 \quad [2]$$

(k is the wavelength of radiation, h, k and l are the indices of reflection and a, b and c are the lattice parameters) and solving the same for the unknown lattice parameters. In each case, several sets were considered and the averages of the, b and c values obtained are reported.

IV. RESULTS AND DISCUSSIONS

i. Density measurement and consequences with Vegard's Law

It is an empirical finding (heuristic approach) resembling the rule of mixtures. Here lattice parameter of a solid solution of two constituents is approximately a weighted mean of the two constituents' lattice parameters at the same temperature and can be defined has:

$$\alpha_{A(1-x)}B_x = (1-x)\ \alpha_A + x\ \alpha_B \quad [3]$$

Vegard's law assumes that both components A and B in their pure form (i.e. before mixing) have the same crystal structure. $a_{A(1-x)}B_x$ is the lattice parameter of the solid solution, a_A and a_B are the lattice parameters of the pure constituents, and x is the molar fraction of B in the solid solution.The densities of single phased mixed crystals have been found to be very nearly additive obeying the relation,

$$d = xd_1 + (1-x)d_2 \quad [4]$$

The above relation implies a linear compositional dependence.
The grown single crystals can be represented as:

$$ZSH \rightarrow ZnSO_4.\ 7H_2O \text{ crystal;}$$

$(NSH)_{0.2}(ZSH)_{0.8} \rightarrow Ni_{0.2}Zn_{0.8}SO_4.7H_2O$ crystal; $(NSH)_{0.4}(ZSH)_{0.6} \rightarrow Ni_{0.4}Zn_{0.6}SO_4.7H_2O$ crystal;
$(NSH)_{0.5}(ZSH)_{0.5} \rightarrow Ni_{0.5}Zn_{0.5}SO_4.7H_2O$ crystal; $(NSH)_{0.6}(ZSH)_{0.4} \rightarrow Ni0.6Zn_{0.4}SO_4.7H_2O$ crystal;
$(NSH)_{0.8}(ZSH)_{0.2} \rightarrow Ni_{0.8}Zn_{0.2}SO_4.7H_2O$ crystal; $NSH \rightarrow NiSO_4.7H_2O$ crystal.

The densities of metal atom (Ni and Zn) contents observed in the present study are provided in Table 1. The chemical compositions estimated using the measured densities and using the metal atom contents obtained through AAS measurements are also provided in Table 1. The density values obtained in the present study for the end members compare well with those reported in the literature [7, 9]. The composition (x) obtained in the present study using the density values compare nearly with that obtained using the metal atom contents determined through AAS measurements. Figure 1 and 2 show the graph of Zn content (%) and Ni content (%) as a function of chemical composition (x). Figure 3 is a plot of density versus concentration of the as-grown mixed crystals.

TABLE 1 DENSITIY OF DIFFERENT METAL ATOMS IN MIXED CRYSTALS

Crystal	Density	Ni content (%)	Zn Content (%)	chemical composition (x)	
				Density data	AAS data
NSH	1.881	100	0	1.0	1.0
$(NSH)_{0.8}(ZSH)_{0.2}$	1.898	83.2	16.2	0.793	0.832
$(NSH)_{0.6}(ZSH)_{0.4}$	1.917	67.3	32.7	0.561	0.673
$(NSH)_{0.5}(ZSH)_{0.5}$	1.925	59.6	40.4	0.463	0.596
$(NSH)_{0.4}(ZSH)_{0.6}$	1.932	50.6	49.4	0.378	0.506
$(NSH)0.2(ZSH)_{0.8}$	1.948	28.8	71.2	0.183	0.288
ZSH	1.963	0	100	0	0

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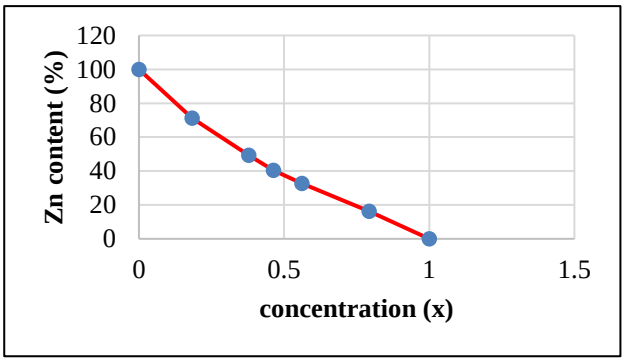


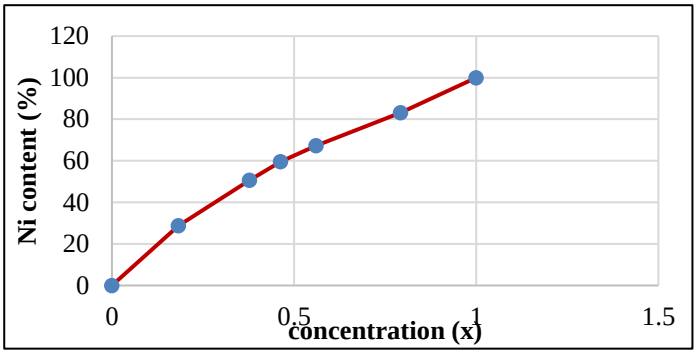


Fig. 1 Plot of Zn content (%) as a function of concentration x Fig. 2 Plot of Ni content (%) as a function of concentration x

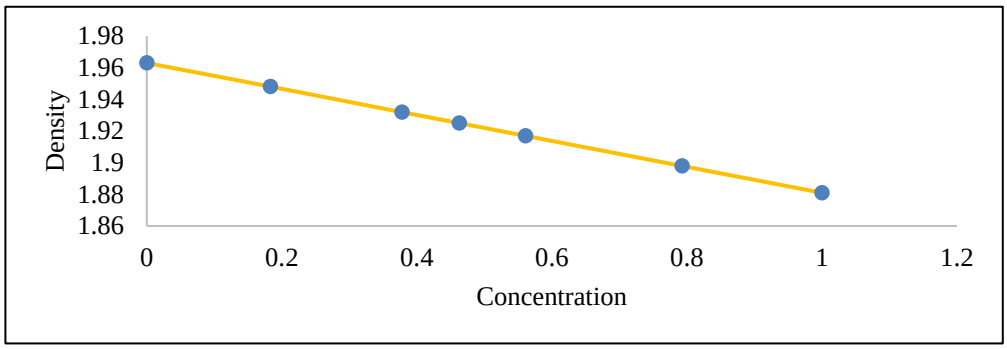


Fig. 3 Plot of Density of the mixed crystal as a function of concentration

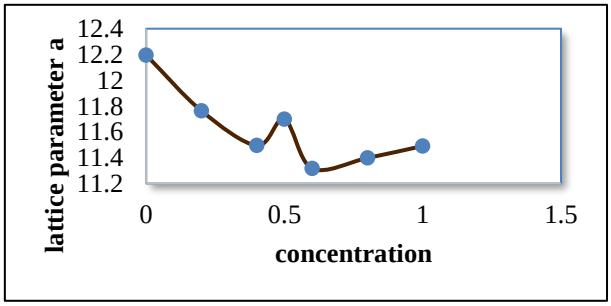
The linear dependence of density with composition shows that it obeys Vegard's law. It is also clear that there exists a good agreement in density with the composition.

ii. Measurement of lattice constants and consequences with Vegard's Law

The lattice constants of the as-grown mixed crystals are calculated using the linear relation of the form

$$a = xa_1 + (1-x)a_2,\ b = xb_1 + (1-x)b_2,\ c = xc_1 + (1-x)c_2 \quad [5]$$

And compared with the experimental values and shown in the figure 4-7.



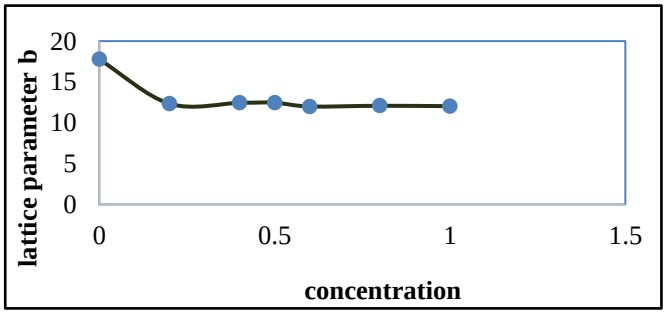


Fig. 4 Plot of lattice parameter A vs. concentration

Fig. 5 Plot of lattice parameter B vs. concentration

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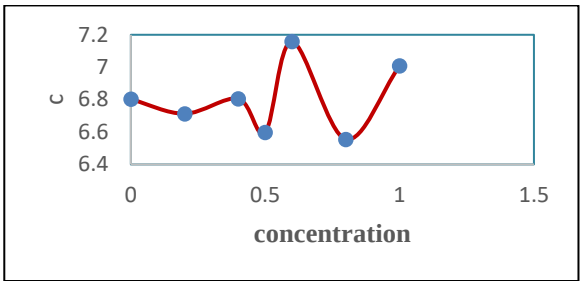

Fig. 6 Plot of lattice parameter C vs. concentration

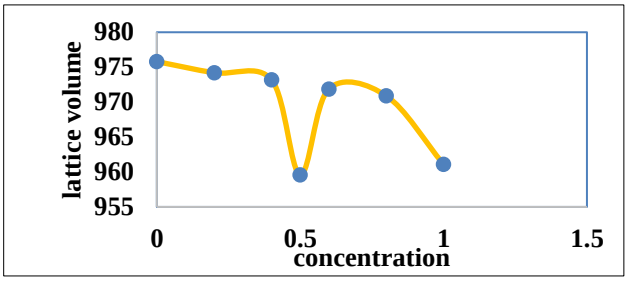

Fig. 7 Plot of cell volume A vs. concentration

Lattice parameters *a*, *b* and *c* are experimentally determined using Computer program POWD. The dependence of the lattice parameters on dopant concentration in $Ni_xZn_{1-x}SO_4.7H_2O$ solid solutions is not linear. Lattice parameter a decreases continuously upto x=0.4, then has a high spike at x=0.5, thereafter, shows slightly increase in nature. Lattice parameter b gradually decreases upto x=0.2, after that it almost saturates. Lattice parameter c almost follows a sinusoidal nature with a sharp depression at x=0.5 and 0.8. However, the value of the lattice volume v decreases monotonically with concentration x with a sharp depression at x=0.5.Dependence of lattice parameters a and b with molar concentration are almost linear, where as that of c is completely different. The linear dependence of lattice parameters with composition can also be corroborated with the presence of single phase of NSH and ZSH system. Although at some points, experimental values (using POWD program) and calculated values (using standard data) are not matching, but the overall trend is linear. Mixed crystal with equimolar composition (x = 0.5) has not been reported in the literature earlier.

V. CONCLUSION

Replacement of Ni^{2+} by Zn^{2+} is not expected to distort the crystal structure significantly. The presence of Zn^{+} in place of Ni^{+}induces strains in the structure due to different ionic radii. The radii of .69 and .60 nm resulting in stronger Ionic bonding for zinc salt. As NSH and ZSH are isomorphous, packing consideration indicate that the replacement of Ni^{2+} by Zn^{2+} would contract that lattice in all the three directions the thereby reducing the dell volume gradually.

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