

## X-ray powder diffraction study of $\text{ZnLi}_{0.5}\text{Mn}_{0.5}\text{SnO}_4$

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**Abstract.** X-ray crystallographic investigation of the title complex oxide composition reveals the presence of two phases. The first is a spinel phase which is somewhat consistent with  $\text{Zn}_2\text{SnO}_4$  with  $a_0 = 8.646 \text{ \AA}$ . The other phase has been identified as a non-spinel phase of  $\text{LiMnSnO}_4$ , the presence of which was confirmed by synthesizing it and comparing its XRD pattern with that of the title composition. The exact composition of the two phases has been determined by intensity calculations. It seems that while cooperative J–T effect is responsible for the observed symmetry of  $\text{LiMnSnO}_4$ , the distribution of phase along with separation of phases is attributed to the solubility limit of  $\text{Sn}^{4+}$  in such quaternary compositions.

**Keywords.** Spinel phase;  $\text{LiMnSnO}_4$ ; intensity calculations; cooperative J–T effect; solubility.

### 1. Introduction

Zinc orthostannate  $\text{Zn}_2\text{SnO}_4$  (Gupta and Mathur 1968; Ioffe *et al* 1975; Fujita *et al* 1988), which is a 4:2 inverse spinel with cationic distribution  $\text{Zn}_A[\text{ZnSn}]_B\text{O}_4$ , has been widely studied and reported. The ternary derivatives of  $\text{Zn}_2\text{SnO}_4$  cited in literature include  $\text{ZnCdSnO}_4$  (Panakh-Zade *et al* 1985),  $\text{ZnNiSnO}_4$  (Yamaguchi 1953),  $\text{ZnCoSnO}_4$  (De Strooper 1977),  $\text{ZnCuSnO}_4$  (Tare *et al* 1990) and  $\text{ZnMgSnO}_4$  (Chang and Kaldon 1976). In all these ternary derivatives obtained by substitution of  $\text{Zn}^{2+}$  with different divalent ions, the replacement has to occur at B-sites only as the A-sites are occupied by  $\text{Zn}^{2+}$  ions with maximum A-site preference energy (Miller 1959). On the other hand, quaternary derivatives of  $\text{Zn}_2\text{SnO}_4$ , have not been widely studied. In the present investigation, the B-site  $\text{Zn}^{2+}$  ion in  $\text{Zn}_A[\text{ZnSn}]_B\text{O}_4$  has been substituted with an equimolar mixture of monovalent and trivalent ions. The monovalent ion chosen here is  $\text{Li}^+$ , the trivalent ion being  $\text{Mn}^{3+}$ . It is expected that the structural parameters of such a planned quaternary stannate,  $\text{ZnLi}_{0.5}\text{Mn}_{0.5}\text{SnO}_4$ , could be influenced by the covalent nature of  $\text{Li}^+ - \text{Mn}^{3+}$  bond, distortive nature of  $\text{Mn}^{3+}$ , and the thermodynamic stability of  $\text{Sn}^{4+}$  in such a quaternary composition.

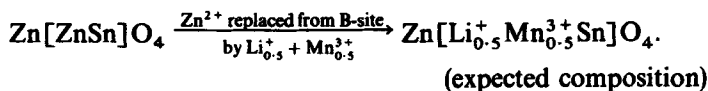
### 2. Experimental

Synthesis of the planned composition was carried out by the standard ceramic technique (Economos 1955). The AR grade oxides  $\text{ZnO}$ ,  $\text{Li}_2\text{O}$ ,  $\text{Mn}_2\text{O}_3$  and  $\text{SnO}_2$  were mixed in appropriate molar ratios and fired at 400, 600 and 800°C for 20 h each and finally at 1100°C for 45 h. Ni-filtered  $\text{CuK}_\alpha$  was used to obtain the XRD charts.

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### 3. Results and discussion

A close observation of the XRD pattern reveals the presence of a predominant spinel phase similar to that of  $Zn_2SnO_4$  in addition to a second non-spinel phase (table 1). Hence, to identify and study the nature of second phase, the ASTM data for different constituent oxides and possible oxidic phases were checked and compared with those for this phase. Interestingly, the comparison revealed that the additional lines (non-spinel phase) mostly coincided with those of  $SnO_2$ . It was logical, therefore, to imagine the possibility of a separation of  $SnO_2$ . Thus, the observed  $SnO_2$  lines were compared with the ASTM data for  $SnO_2$ . It was observed that though the maximum intensity line ( $d = 3.35 \text{ \AA}$ ) remains the same, the other lines do not obey the exact intensity ratio as referred to in the ASTM data for  $SnO_2$ . Hence to understand the mode of separation of  $SnO_2$  the following scheme was considered:



From the observation of the intensities of the lines due to  $SnO_2$  phase, it was estimated that about 20% of  $SnO_2$  type phase separates. To confirm the possibility of separation of  $SnO_2$ , intensity calculations were carried out.

The intensities for non-zero reflections were computed by using the formula

$$I_{hkl} = [F_{hkl}]^2 P \cdot \frac{1 + \cos^2 2\theta}{\cos \theta \sin^2 \theta}$$

**Table 1.** X-ray crystallographic data for  $ZnLi_{0.5}Mn_{0.5}SnO_4$  (radiation:  $CuK_\alpha$ ).

$l/l$	Observed $d$ ( $\text{\AA}$ )	$hkl$	Calculated $d$ ( $\text{\AA}$ )
13	4.963	111	4.990
17	3.353*	—	—
15.5	3.060	220	3.057
2.3	2.853*	—	—
12	2.630*	—	—
100	2.607	311	2.607
13	2.490	222	2.496
4	2.374*	—	—
17.3	2.161	400	2.161
16	1.766*	422	1.765
4.5	1.683*	—	—
26	1.664	511, 333	1.664
2	1.577*	—	—
43	1.529	440	1.528
2	1.502*	—	—
3.5	1.460*	—	—
7.5	1.318*	—	—
2.6	1.209*	—	—

Symmetry: Face centred cubic.  $a_0 = 8.646 \text{ \AA}$ .

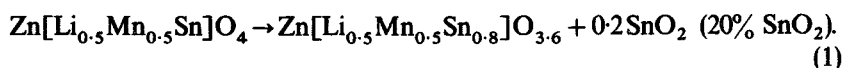
\*Second non-spinel phase.

where  $F_{hkl}$  is the structure factor for plane  $hkl$ ,  $p$  the multiplicity of reflection, and last factor  $L_p = \frac{1 + \cos^2(2\theta)}{\cos\theta \sin^2\theta}$  is the Lorentz polarization factor for the powder method.

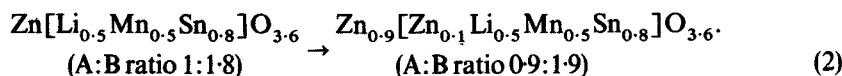
The values of atomic scattering factor  $f_r$  for the different ions, viz.  $Zn^{2+}$ ,  $Li^+$ ,  $Mn^{2+}$ ,  $Mn^{3+}$  and  $Mn^{4+}$  (Klug and Alexander 1974) and  $Sn^{4+}$  (Umanskago 1961), were used to calculate the structure factor  $F_{hkl}$ . From the knowledge of  $F_{hkl}$  values, intensities for various reflections were calculated.

As the 200, 400 and 422 planes are more sensitive (Azaroff 1968) to the change in cation distribution for spinel structure, intensity ratios  $I_{220}/I_{422}$  and  $I_{422}/I_{400}$  are compared with the observed intensity ratios for various ionic configurations, from which the site distribution is determined.

Now, for the possibility that 20% of  $SnO_2$  is separating, the following scheme is suggested:

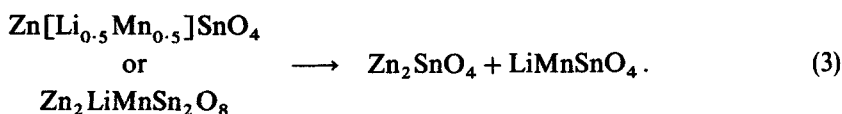


Equation (1) is nonstoichiometric and even if the quaternary composition was to crystallize in spinel lattice the intensities calculated should substantiate the existence of  $Li_{0.5}$ ,  $Mn_{0.5}$  and  $Sn_{0.8}$  in B-site of the lattice, since A-sites are preoccupied by  $Zn^{2+}$ . But the intensity calculations for the quaternary composition in (1) do not match with the observed ratios. The second scheme considered to maintain the ratio of ions in A and B sites of spinel structure was the following:

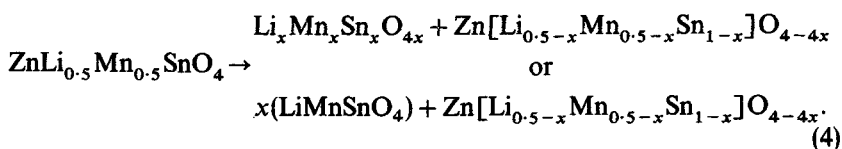


However, (2) is also ruled out on the basis of intensity calculations.

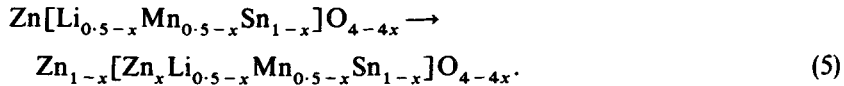
It is clear from the above that  $SnO_2$  phase is not separating alone. It was considered, therefore, that other ions, viz.  $Li^+$  and  $Mn^{3+}$ , are separating along with  $SnO_2$  in equal proportions as shown below:



This envisages the total separation of  $LiMnSnO_4$  (non-spinel phase) with the result that the spinel phase must be  $Zn_2SnO_4$  alone. To verify this possibility, intensity calculations for  $Zn_2SnO_4$  type spinel phase was carried out. It was observed that the intensities of the observed spinel phase do not match with those of  $Zn_2SnO_4$  (ASTM), ruling out the possibility of the total separation of  $Zn_2SnO_4$  and suggesting the solubility of some  $LiMnSnO_4$  in  $Zn_2SnO_4$ . In other words, the separation of  $LiMnSnO_4$  is also not total. But the extent of such a separation is controlled by the solubility of  $LiMnSnO_4$  in  $Zn_2SnO_4$ . The following scheme explains the above contention:



The ionic distribution in (4) can be expressed in terms of spinel stoichiometry by rearranging as follows:



The ionic distribution given above is comparable to that existing in  $\text{Zn}_2\text{SnO}_4$  or  $\text{Zn}[\text{ZnSn}]\text{O}_4$ . Scheme (5) suggests that the value of  $x$  should be less than 0.5 and more than 0.2 (computed from 20% separation of  $\text{SnO}_2$  type). Hence the intensity calculations were carried out for  $0.5 > x > 0.2$ .

The results are summarized in table 2. It is clear from the table that the distribution is



as there is maximum agreement for this configuration between observed and calculated intensity ratios. It is clear from intensity calculations that the second phase consists of  $\text{LiMnSnO}_4$  type composition, which is found to crystallize in tetragonal symmetry with  $a_0 = 6.748 \text{ \AA}$ ,  $c_0 = 10.758 \text{ \AA}$ .

To confirm that the second phase is  $\text{LiMnSnO}_4$ , it was independently synthesized using AR grade constituent oxides in the proper molar ratio, keeping exactly the

**Table 2.** Site distribution from intensity ratios in  $\text{Zn}_{1-x}(\text{Zn}_x\text{Li}_{0.5-x}\text{Mn}_{0.5-x}\text{Sn}_{1-x})\text{O}_{4-4x}$ .

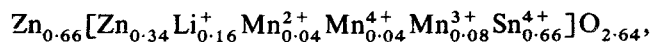
Site distribution	$I_{220}/I_{422}$		$I_{422}/I_{400}$	
	observed	calculated	observed	calculated
$\text{Zn}_{0.76}(\text{Zn}_{0.24}\text{Li}_{0.26}\text{Mn}_{0.16}^{3+}\text{Mn}_{0.02}^{2+}\text{Mn}_{0.02}^{4+}\text{Sn}_{0.76}^{4+})\text{O}_{3.04}$		2.528		0.460
$\text{Zn}_{0.70}(\text{Zn}_{0.30}\text{Li}_{0.20}\text{Mn}_{0.12}^{3+}\text{Mn}_{0.04}^{2+}\text{Mn}_{0.04}^{4+}\text{Sn}_{0.70}^{4+})\text{O}_{2.80}$	2.50	2.529	0.360	0.410
$\text{Zn}_{0.68}(\text{Zn}_{0.32}\text{Li}_{0.18}\text{Mn}_{0.10}^{3+}\text{Mn}_{0.04}^{2+}\text{Mn}_{0.04}^{4+}\text{Sn}_{0.68}^{4+})\text{O}_{2.72}$		2.529		0.401
$\text{Zn}_{0.66}(\text{Zn}_{0.34}\text{Li}_{0.16}\text{Mn}_{0.08}^{3+}\text{Mn}_{0.04}^{2+}\text{Mn}_{0.04}^{4+}\text{Sn}_{0.66}^{4+})\text{O}_{2.64}$		2.530		0.390

**Table 3.** X-ray diffraction data for  $\text{LiMnSnO}_4$  observed (as a second phase) and  $\text{LiMnSnO}_4$  synthesized.

$\text{LiMnSnO}_4$ observed				$\text{LiMnSnO}_4$ synthesized			
$d(\text{obs})$ ( $\text{\AA}$ )	$d(\text{cal})$ ( $\text{\AA}$ )	$I/I_0$	$hkl$	$d(\text{obs})$ ( $\text{\AA}$ )	$d(\text{cal})$ ( $\text{\AA}$ )	$I/I_0$	$hkl$
4.960	4.800	25	110	4.799	4.772	51	110
3.353	3.374	100	200	3.352	3.374	100	200
2.853	2.858	20	202	—	—	—	—
2.630	2.632	70	212	2.644	2.632	80	212
2.374	2.386	33	220	2.368	2.386	28	220
1.766	1.767	48	322	1.762	1.768	71	322
1.683	1.687	25	400	1.675	1.687	18	400
1.577	1.574	12	331	1.593	1.591	15	330
1.502	1.499	13	107	1.497	1.498	15	107
1.460	1.463	23	117	1.467	1.463	7	117
1.318	1.319	5	108	1.317	1.314	7	511
1.209	1.209	4	416	1.213	1.209	11	416

Symmetry, tetragonal;  $a_0$  6.748  $\text{\AA}$  and  $c_0$  10.758  $\text{\AA}$ .

same firing schedule. The XRD pattern of this composition, to our surprise, was almost identical to that of the separated non-spinel phase, confirming that it is due to  $LiMnSnO_4$ . Table 3 gives the comparison of  $LiMnSnO_4$  observed as second phase and  $LiMnSnO_4$  synthesized. Thus the quaternary composition  $Zn[Li_{0.5}Mn_{0.5}Sn]O_4$  from a detailed study of XRD intensities was found to contain the spinel phase, viz.



and a non-spinel phase of  $LiMnSnO_4$  which can be obtained by subtracting the observed spinel composition from  $Zn[Li_{0.5}Mn_{0.5}Sn]O_4$ , i.e. the planned composition, leaving  $Li_{0.34}Mn_{0.34}Sn_{0.34}O_{1.36}$  or  $LiMnSnO_4$ .

#### 4. Conclusions

- (i) The present investigation reveals that the solubility (Puri *et al* 1983) of  $Sn^{4+}$  in the quaternary spinel type stannate is around 0.66 mol per formula unit. This observation is in near-agreement with the reported solubility of  $Sn^{4+}$  in quaternary systems.
- (ii) Intensity calculations have been extremely useful to establish the stoichiometry of spinel phase as



from which the second phase was identified as  $LiMnSnO_4$ .

- (iii) A close observation of the crystallographic data for  $LiMnSnO_4$  showing the lines of  $SnO_2$  strongly indicates the solvent action of  $SnO_2$  (Tare *et al* 1990).
- (iv) The symmetry and lattice parameters of  $LiMnSnO_4$  suggest that  $Sn^{4+}$  and  $Mn^{3+}$  (J-T ion) cooperate to enhance the distortion leading to increasing  $c/a$  ratio ( $c/a$  for  $SnO_2$  is 1.46 and that for  $LiMnSnO_4$ , 1.59). This contention, that the role of  $Sn^{4+}$  to act as a J-T ion along with  $Mn^{3+}$  (in  $LiMnSnO_4$ ), receives further support from the fact that the corresponding titanate  $LiMnTiO_4$  (Blasse 1963) crystallizes in f.c.c. symmetry, where  $Ti^{4+}$  ion shows no such cooperative J-T effect.

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