

Structural and electrical study of ZnCuTiO_4 , ZnCuSnO_4 and ZnCuGeO_4 synthesised using metallic copper

M P TARE, R R TRIPATHI, S SAMPATH and S M TARE

Department of Chemistry, Institute of Science, Nagpur 440 001, India

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Abstract. The structural study of ZnCuTiO_4 , ZnCuSnO_4 and ZnCuGeO_4 reveals that while the cooperative J - T effect of Sn^{4+} is responsible for the orthorhombic symmetry of ZnCuSnO_4 , the hexagonal influence of Ge^{4+} is more predominant in ZnCuGeO_4 . Ti^{4+} is uninfluential either in initiating the distortive tendency or cooperating with other ions for the same. The XRD, ρ_{RT} , ΔE and the nature of the charge carriers, all suggest that the air oxidation of metallic copper leads to the minority concentration of Cu^+ along with a majority concentration of Cu^{2+} , as demanded by the stoichiometric considerations of these compositions.

Keywords. Cooperative J - T effect; metallic copper; symmetry; cation distribution.

1. Introduction

The structural resemblance between TiO_2 and SnO_2 (rutile structure with comparable lattice parameters) and similar site preference energies of Ti^{4+} and Sn^{4+} in the spinel structure for octahedral sites (Reznitskii 1976) ($\text{Ti}^{4+} = -11$ kcal/g ion and $\text{Sn}^{4+} = -14$ kcal/g ion) has kindled our interest in ternary spinel type systems with Ti^{4+} and Sn^{4+} .

In ternary systems with tetrapositive Ti^{4+} and Sn^{4+} (preferring B sites), one of the accompanying ions should have a distinct A site preference to facilitate the crystallization in the spinel lattice. The reverse is also found true in terms of systems with Ge^{4+} , as Ge^{4+} has a distinct preference for A sites (Tellier and Lenglet 1976).

Thus Zn_2TiO_4 (Krivobok *et al* 1984), Co_2TiO_4 (Begum *et al* 1970), ZnNiTiO_4 (Mulla and Darshane 1983) and ZnCuTiO_4 (Yamaguchi 1953) are known to be spinels. Surprisingly however, while ZnCuTiO_4 is reported to be a spinel, ZnCuSnO_4 is reported to be tetragonally distorted (Deshpande *et al* 1977). Since the origin of this distortion cannot be due to Sn^{4+} , it was considered worth while to search for the analogous compound with Ge^{4+} , for the sake of comparison. GeO_2 crystallizes in two different symmetries. It shows both primitive tetragonal (Hazen and Finger 1981) and hexagonal symmetry (Swanson and Tatge 1950). Ge^{4+} prefers A sites in contrast to Ti^{4+} and Sn^{4+} . A similar phenomenon is observed in ternary compounds with Ge^{4+} , viz. crystallization in a spinel lattice is easier when one of the accompanying ions has a distinct preference for octahedral sites and as such ZnNiGeO_4 (Durif *et al* 1956) and CoNiGeO_4 (Romeijn 1953) are known to be spinels at room temperature and pressure.

Thus to evaluate the effects of Ti^{4+} and Sn^{4+} independently, in association with ($\text{Zn}^{2+} + \text{Cu}^{2+}$) and for comparing these effects with that of Ge^{4+} in presence of the same two divalent ions (in determining the symmetry), the three title compounds were synthesized by oxide method. Further, to explore the possibility of getting the more stable and the more easily formed +2 oxidation state of copper (during synthesis), cheaper metallic copper was used in place of cupric oxide.

2. Experimental

The title compounds were prepared using the standard ceramic technique (Economos 1955). The constituent oxides and finely powdered metallic copper were taken in the appropriate molar ratio and thoroughly mixed, using AR acetone as the medium. The pellets were prepared using polyvinyl acetate as a binder. Firing was then carried out in stages at 400, 800 and 1100°C for 20, 20 and 45 h respectively.

A Philips X-ray diffractometer using Ni-filtered CuK_α radiation was used for obtaining the structural details. Pellets of premeasured dimensions were coated with colloidal graphite as contact material, checked for continuity and their resistivities measured using a Markoni Bridge (for resistance $\leq 10^6$ ohms) and a BPL Megohm meter (for resistance $> 10^6$ ohms).

3. Results and discussions

The XRD patterns of the compounds were indexed using standard indexing procedures (Henry *et al* 1960). The patterns are characterized by the absence of lines due either to the constituent oxides or to the different possible phases and that of metallic copper, excepting those of SnO_2 . The SnO_2 lines, though present, are not in their proper intensity ratios as reported in the ASTM data file. This suggests that SnO_2 lines constitute a part of the single phase pattern and that perhaps SnO_2 is showing a solvent action (Walia 1971). The composition ZnCuTiO_4 , as expected, was found to crystallize in the spinel structure. However the XRD patterns of ZnCuSnO_4 and ZnCuGeO_4 could be indexed only on the orthorhombic and hexagonal symmetry respectively. The detailed XRD pattern of the compounds is given in tables 1, 2 and 3. The intensity calculations were carried out to determine the site distribution of ions in ZnCuTiO_4 . The structure factor for planes 220, 400 and 422 was calculated since these planes are very sensitive to cation distribution (Azaroff 1968). The diffraction intensity of these reflections was estimated from the peak area and compared with calculated values, using the expression

$$I_{hkl} = |F_{hkl}|^2 \cdot P \cdot L_p$$

Table 1. X-ray crystallographic data of ZnCuTiO_4 .

Symmetry: Cubic.

$a_0 = 8.452 \text{ \AA}$.

I/I_0	d (obs) (\AA)	hkl	d (cal) (\AA)
6	4.881	111	4.880
36	2.989	220	2.988
100	2.549	311	2.548
6	2.440	222	2.440
12	2.111	400	2.113
2	1.872	420	1.890
13	1.723	422	1.725
34	1.625	511	1.627
31	1.492	440	1.494

Table 2. X-ray crystallographic data of ZnCuSnO₄.

Symmetry: Orthorhombic.

 $a_0 = 10.025 \text{ \AA}$; $b_0 = 6.719 \text{ \AA}$; $c_0 = 10.437 \text{ \AA}$.

I/I_0	d (obs) (\AA)	hkl	d (cal) (\AA)
56	5.010	200	5.013
58	3.363	020	3.360
46	3.058	121	3.047
34	2.653	213	2.631
100	2.614	004	2.610
64	2.508	400	2.506
43	2.475	222	2.461
9	2.404	303	2.411
30	2.380	320	2.369
16	2.326	204	2.315
58	2.170	322	2.158
14	2.136	131	2.139
13	1.985	015	1.994
40	1.771	305	1.771
15	1.680	040	1.680
55	1.669	430, 600	1.671, 1.670
9	1.595	042	1.599
70	1.526	126	1.527
13	1.510	135	1.510
15	1.501	340	1.501
14	1.463	235	1.461
15	1.441	117	1.441
10	1.413	044	1.413
10	1.368	533	1.373
30	1.319	151	1.321
30	1.316	720	1.317
18	1.313	045	1.309
28	1.305	008	1.305
17	1.302	713	1.299
10	1.287	152	1.291

where F_{hkl} = structure factor, P = multiplicity factor, and L_p = Lorentz polarization factor.

The atomic scattering factor was taken from the literature (Klug and Alexander 1974). The intensity ratios I_{220}/I_{400} and I_{422}/I_{400} were calculated, and compared with the observed intensity ratios, for various ionic configurations, of which the configurations given in table 4 are in good agreement.

It is clear from table 4 that for the first configuration the value of I_{220}/I_{400} (cal.) is close to the observed I_{220}/I_{400} ratio and for the third configuration I_{422}/I_{400} (cal.) is close to the observed I_{422}/I_{400} ratio. Hence it is logical to arrive at the conclusion that some concentration of Cu^+ exists in the composition ZnCuTiO_4 and the most probable cation distribution is $\text{Zn}[\text{Cu}_{0.9}^{2+}\text{Cu}_{0.1}^+\text{Ti}^{4+}]_2\text{O}_4$. The observed orthorhombic symmetry of ZnCuSnO_4 synthesised here is different from its reported tetragonal symmetry. This may be due to the coexistence of a small amount of Cu^+ (about 10% as determined from the intensity calculation of ZnCuTiO_4), along with a majority of Cu^{2+} . The orthorhombic symmetry of

Table 3. X-ray crystallographic data on ZnCuGeO₄.

Symmetry: Hexagonal.

 $a_0 = 14.198 \text{ \AA}$; $c_0 = 8.558 \text{ \AA}$.

I/I_0	d (obs) (\AA)	hkl	d (cal) (\AA)
20	7.196	200	7.100
40	4.095	220	4.098
60	3.534	400	3.549
70	3.164	302	3.174
70	2.903	411	2.914
100	2.683	330	2.683
35	2.495	510	2.504
30	2.380	223	2.377
30	2.350	313	2.343
10	2.130	610	2.126
25	1.884	710	1.880
12	1.689	334	1.684
12	1.616	623	1.620
10	1.580	225	1.579
12	1.542	405	1.542
8	1.504	803	1.507
30	1.443	425	1.443
22	1.389	605	1.387
18	1.360	306	1.366
10	1.331	316	1.341
8	1.281	625	1.292
12	1.251	824	1.255
10	1.232	805	1.232
10	1.180	307	1.184

Table 4. Cation distribution in ZnCuTiO₄ from the intensity ratios.

Cation distribution	I_{220}/I_{400}		I_{422}/I_{400}	
	Obs.	Cal.	Obs.	Cal.
Zn ²⁺ [Cu ²⁺ Ti ⁴⁺]O ₄		2.899		1.097
Zn ²⁺ [Cu _{0.9} ²⁺ Cu _{0.1} ⁺ Ti ⁴⁺]O ₄	2.913	2.893	1.092	1.095
Zn ²⁺ [Cu _{0.8} ²⁺ Cu _{0.2} ⁺ Ti ⁴⁺]O ₄		2.889		1.094

ZnCuSnO₄ may also be understood here in terms of the Sn⁴⁺ ion cooperating with Cu²⁺ in enhancing the distortive capacity of Cu²⁺ (Jogalekar and Sinha 1967). This phenomenon seems to be aided by the coexistence of Cu⁺. The observed hexagonal symmetry of ZnCuGeO₄ synthesized here is different from the reported cubic one (Robbins and Baltzer 1965). This may be attributed to the different firing conditions and the use of metallic copper here. The linear dependence of logarithmic resistivity on T^{-1} as also the low ΔE values (0.2–0.8 eV) show the semiconducting nature of the title compounds in the temperature range studied. The linearity of the graphs also suggests that the stoichiometry is almost constant. It is reported (Verwey *et al*

1951; Jogalekar and Sinha 1967) that in spinels the presence of a metal ion in two different oxidation states, differing by unity, if present at the same site, leads to lowering of ρ_{RT} which in such a case is $\sim 10^2$ to 10^4 ohms cm. In the present case only ZnCuTiO_4 crystallises in the spinel lattice in which case ρ_{RT} refers to the nonlinear portion of the graph. Thus the three compounds are semiconducting in nature and further, as indicated by thermo-emf measurements, are *p*-type semiconductors.

References

- Azaroff L V 1968 *Elements of X-ray crystallography* (New York: McGraw Hill)
- Begum R J, Rao M, Murthy L and Satya N S 1970 *Proc. Nucl. Phys. Solid State Phys. Symp.* **3** 693
- Deshpande P D, Kulkarni D K and Khandekar P V 1977 *Indian J. Pure Appl. Phys.* **15** 675
- Durif V A, Bertaut E F and Pauthenet R 1956 *Ann. Chim. (Paris)* **13** 525
- Economos G 1955 *J. Am. Ceram. Soc.* **38** 241
- Hazen R M and Finger L W 1981 *J. Phys. Chem. Solids* **42** 143
- Henry N F M, Lipson H and Wooster W A 1960 *Interpretation of X-ray diffraction photography* (London and New York: Macmillan)
- Jogalekar P P and Sinha A P B 1967 *Indian J. Pure Appl. Phys.* **5** 9
- Klug H P and Alexander L E 1974 *X-ray diffraction procedures for polycrystalline and amorphous materials* (New York: John Wiley and Sons) p. 880
- Krivobok V I, Gorbitova T A and Shaginyan L R 1981 *Izv. Akad. Nauk. SSSR, Neorg. Mater.* **20** 2057
- Mulla B A and Darshane V S 1983 *Proc. Indian Acad. Sci. (Chem. Sci.)* **92** 139
- Reznitskii L A 1976 *Izv. Akad. Nauk SSSR Neorg. Mater.* **12** 1909
- Robbins M and Baltzer P K 1965 *J. Appl. Phys.* **36** 1039
- Romeijn F C 1953 *Philips Res. Rept.* **8** 304
- Swanson and Tatge 1950 J C FEL Reports
- Tellier J C and Lenglet M 1976 *C. R. Hebd. Seances Acad. Sci.* **C282** 827
- Verwey E J W, Brown P B, Gorter E W, Romeijn F C and Vansanten J H 1951 *Z. Phys. Chem.* **198** 6
- Walia D S 1971 *Compass Sigma Gamma Epsilon* **49** 27
- Yamaguchi G 1953 *Bull. Chim. Soc.* **26** 204