CHEMISTRY LETTERS, pp. 1329-1330, 1982.

A NEW TERNARY PHASE $Zn_2Ti_{18}S_{32}$

Masanobu SAEKI* and Mitsuko ONODA
National Institute for Research in Inorganic Materials,
1-1, Namiki, Sakura-mura, Niihari-gun, Ibaraki 305

New phase was found in composition of $Zn_2Ti_{18}S_{32}$. It was prepared from Ti metal, zinc sulfide and titanium sulfide at 1200°C. The structure was of cubic cell with lattice constant of a = 9.843 Å.

Many conpounds have so far been reported in the M-Ti-S (M = metal) system, especially for M = alkali metal[1)] and the first-row transition elements[2)]. In these compounds except for the case of M = Cu[3)], the symmetry of the sulfur coordination about each metal atom is either octahedral or trigonal prismatic. On the other hand, no information is given in the literature on the system of M = Zn which prefer tetrahedral coordination. We tried to prepare the compound of the Zn-Ti-S system with expecting a new phase. It resulted in the formation of $Zn_2Ti_{18}S_{32}$. The present report aims at describing the existence and synthesis of the $Zn_2Ti_{18}S_{32}$.

Synthesis was carried out by the reaction of Ti metal, titanium sulfide (4H type) and zinc sulfide. Titanium sulfide (4H type) was prepared at first. Ti metal (purity 99.0%) and sulfur (purity 99.9999%) were mixed together in a calculated ratio (S/Ti = 1.70) and sealed in an evacuated silica tube. The mixture was then allowed to react for 3 days at 350°C, after which temperature was raised to 900°C and hold for 3 days. The mixture of titanium sulfide (4H type) obtained thus, zinc sulfide (purity 99.9%) and Ti metal, whose ratio was $Zn_2Ti_{18}S_{32}$, was put into a silica tube and sealed under vacuum, and heated at 1200°C for 5h. Upon the completion of the reaction, the specimen was quenched in water.

The quenched specimen was examined by a powder X-ray diffractometer with CuKα radiation. Table 1 shows observed d-spacings and peak intensities. There was no evidence of either zinc sulfide or titanium sulfide detectable in the X-ray pattern. The observed peaks were indexed on the basis of a cubic cell with lattice constant of a = 9.843 Å. Calculated d-values and indices were listed together in

Table 1. Presence of only peaks with $h+k=2n$, $k+\ell=2n$ and $\ell+h=2n$ indicates that unit cell is face centered.

In electron diffraction pattern (Fig. 1) taken for the specimen, spots were observed at the position of four fold symmetry. It supports the assumption of cubic cell and indexing.

Density was measured by means of weighing buoyancy in carbon tetrachloride. It gave a value of 3.51 ± 0.02 as compared to the value of 3.49 which was calculated for a formula in the unit cell.

From the results described above and site preference of Ti and Zn atoms, it is suggested that the structure is composed of cubic close packing of sulfur, in which octahedral sites are occupied by Ti atoms and tetrahedral sites by Zn atoms.

Lattice constant varied with variation in composition. This means the existence of homogeneity range in the compound. Detailed study of the phase diagram is now in progress.

Table 1. Observed and calculated d-spacings, indices, and observed peak intensities.

d_{obs}	d_{calc}	$hk\ell$	$(I/I_0)_{obs}$
5.690	5.683	111	34
3.480	3.480	220	4
2.9683	2.9678	311	36
2.8420	2.8414	222	3
2.4609	2.4608	400	100
2.2575	2.2582	331	4
1.8945	1.8943	333,511	14
1.7400	1.7400	440	72
1.6639	1.6638	531	4
1.5010	1.5010	533	4
1.4837	1.4839	622	2
1.4209	1.4207	444	17
1.3783	1.3783	551,711	2
1.2815	1.2815	731	5
1.2303	1.2304	800	10
1.1367	1.1366	751,555	3
1.1005	1.1005	840	23

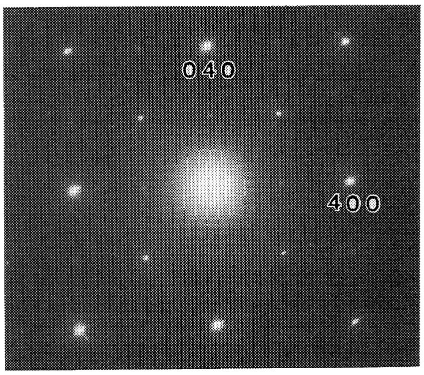

Fig.1. Electron diffraction pattern of the $Zn_2Ti_{18}S_{32}$. Incident beam is parallel to the [001] direction.

References

1) For example; J. Rouxel, J. Solid State Chemistry, 17, 223 (1976).
2) For example; M. Danot, J. Rouxel and O. Gorochov, Mat. Res. Bull., 9, 1383 (1974).
3) N. Le Nagard, O. Gorochov and G. Collin, Mat. Res. Bull., 10, 1287 (1975).

(Received June 9, 1982)