Note

THE EFFECT OF MECHANICAL TREATMENT ON THE THERMAL BEHAVIOUR OF THE Cu_{2-x}Te PHASE

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Some examples of the effect of grinding on the DTA curves of inorganic materials have been reported [1-3]. These effects were caused either by kinetic influences or by the presence of impurities. During our work on the Cu-Te phase diagram we found that the DSC curves of the Cu_{2-x} Te phase were affected by grinding in a ball mill under argon atmosphere.

The samples presented in this paper were prepared from pure copper and tellurium by encapsulating them under vacuum in silica ampoules, melting in a flame and homogenizing for two months at 573 K. The instrument used was a Perkin-Elmer DSC-2. (Heating rate 10 K min⁻¹.)

The DSC curves obtained from finely ground samples of crystallites are shown in Figs. 1 and 2. The figures reveal that some transitions can be suppressed by a mechanical treatment in a ball mill under argon atmosphere.

The reason for this behaviour lies in the complicated superstructures of the simple hexagonal Cu_{2-x} Te lattice, which were reported by various



Fig. 1. DSC curves of a sample with 33.83 mole % Te. 1, Crystalline sample; 2, sample ground for 8 min in a ball mill; 3, ground sample, second run in DSC.

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Fig. 2. DSC curves of a sample with 34.5 mole % Te. 1, Crystalline sample, 2, after 8 n grinding; 3, after 40 min grinding.



Fig. 3. X-Ray pattern (Guinier-4, Cu K_{α_1}) of a sample with 34.8 mole % Te. 1, Crystalline ground sample.



Fig. 4. Thermal effects of ground $Cu_{2-x}Te$.

authors [4-8]. These superstructures are destroyed during the grinding procedure. This idea is supported by a comparison of the X-ray patterns of ground and crystalline samples (Fig. 3) which show that grinding produces a pattern with the same strong lines but without the weak lines due to the superstructures.

After thermal treatment the ground samples return to the equilibrium state. Figure 1 shows that after one run in the DSC the DSC trace pattern of the crystalline sample returns, though the transformation temperatures are still different.

The observed effects may be one of the reasons for the differences in the temperatures and enthalpies of transformation of Cu_2Te which were reported in the literature.

The very complicated phase region of Cu_{2-x} Te [8,9] with at least nine different structures is simplified by grinding as shown in Fig. 4.

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REFERENCES

- 1 A. Negishi and T. Ozawa, Thermochim. Acta, 2 (1971) 89.
- 2 M. Wada and Y. Ida, Jpn. J. Appl. Phys., 8 (1969) 1569.
- 3 R.M. Gruver, J. Am. Ceram. Soc., 31 (1948) 323.
- 4 M. Kieu Van Con and H. Rodot, C.R. Acad. Sci., 260 (1965) 1908.
- 5 F. Guastabino, H. Luquet and J. Bounot, Mater. Res. Bull., 8 (1973) 935.
- 6 A.L.N. Stevels, Philips Res. Rep. Suppl., 9 (1969) 1.
- 7 R.V. Baranova and Z.G. Pinsker, Zh. Strukt. Khim., 11 (1970) 637.
- 8 R. Blachnik, M. Lasocka and U. Walbrecht, J. Solid State Chem., in press.
- 9 S. Miyatani, S. Mori and M. Yanagihara, J. Phys. Soc. Jpn., 47 (1979) 1152.