

Structural study of SeCl₄ and TeCl₄ liquids under high pressure

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The P,T- phase diagrams of TeCl₄ and SeCl₄ have been investigated. The melting curves of both substances have been determined up to 9 GPa. The moderate modification of the intermediate range order structure under high pressure has been found for SeCl₄ melt. TeCl₄ melt undergoes strong modification of intermediate range order structure at moderate pressures 1- 2 GPa and gradual change of short range order structure at higher pressures. Preliminary analysis indicates on the ionic-like structure of TeCl₄ melt at highest pressures. Both melts are quite non-viscous under high pressures and do not form glasses during melt rapid cooling.

key words: high pressures, melt, phase transitions, short range order structure

1. Objectives

The objective of the study was to investigate the structure of TeCl₄ and SeCl₄ liquids under high pressure. Chalcogen tetrahalide compounds display very interesting structural properties. It is well known that chalcogens generally have covalent bonds while halides have ionic bonds. Crystalline TeCl₄ and SeCl₄ represent molecular phases consisting of tetramers Te(Se)₄Cl₁₆. Gas phase of this compounds represents Te(Se)Cl₄ molecules. Very recently [1] there was investigation the structure of TeCl₄ liquid at normal pressure. It was found that the liquid has molecular structure consisting of dimers Te₂Cl₈. Chalcogen tetrahalide compounds have not been studied under pressure up to date both in solid and liquid phase. One can suppose that under high pressure the structure of the liquids should transform from molecular melt to covalent-network liquid. Previously we observed such structural transformation in AsS melt and possibly in P₄Se₃, P₄S₃ melts. On the other hand it is possible that liquid chalcogen tetrachlorides will transform to ionic melts similar like we observed in the case of ZnCl₂, AlCl₃. Thus the aim of present project was to make in situ x-ray diffraction study of phase diagrams of TeCl₄, SeCl₄ compounds and structural study of TeCl₄, SeCl₄ liquids in 1-10 GPa high pressure region .

2. Methods

We obtained structural data using energy dispersive x-ray diffraction method (10keV-170keV range) for the sample in a cubic-type multi-anvil press at several P,T-points in the 1-10 GPa region both at the compression and decompression cycles. We have prepared the cylinders of TeCl₄, SeCl₄ powder in Ar box. The tablets of Te(Se)Cl₄ were 1.5 mm dia and 1 mm height. Special shields and cups made of low-thermal conductivity materials were used to get highest temperatures (around 1300K). Diffraction data were taken at different two theta angles from 3 to 18 degrees.

3. Results

We have obtained more than 200 x-ray diffraction spectra of the crystalline and liquid states of both substances. In TeCl₄ the phase transition in solid state was found around 4 - 5 GPa. The preliminary analysis shows that there is the slight distortion of the molecular structure. The melting temperature of TeCl₄ at 8.8 GPa is about 900 C. The melting temperature of SeCl₄ at 8 GPa is about 880 C. The P,T- phase diagrams of TeCl₄ and SeCl₄ have been investigated. The moderate modification of the intermediate range order structure under high pressure has been found for SeCl₄ melt with significant decrease of the first sharp pre-peak. TeCl₄ melt undergoes strong modification of intermediate range order structure at moderate pressures 1- 2 GPa with huge and abrupt decrease of

the first sharp pre-peak. At higher pressures there is gradual change of short range order structure of TeCl₄ melt. Preliminary analysis indicates the ionic-like structure of TeCl₄ melt at highest pressures. Both melts are quite non-viscous under high pressures and do not form glasses during melt rapid cooling. It is interesting that TeCl₄ melt has a small undercooling mobility (100- 150 C) at all pressures whereas SeCl₄ melt has a large undercooling at 8GPa (around 400C) that means the increase of the melt viscosity in 4- 8 GPa pressure region. The detailed structural analysis of both melts is in progress.

4. Discussion and Conclusion

From the obtained data one can conclude that quasi molecular structure of both substances - TeCl₄ and SeCl₄ is quite stable under pressure in crystalline state. As for the liquid state there is no indication of molecular polymerization under pressure in both melts and one can propose that molecular- to ionic transitions occur at compression similar to ZnCl₂, AlCl₃ melts

5. References

[1] E. Bychkov et al J.Non-Cryst. Solids 354 (2008) 259