



Mechanochemical synthesis of binary phosphorus telluride: Short range structure and thermal properties



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ABSTRACT

A binary phosphorus telluride sample (20 at% Te) was synthesized by mechanochemical solid state reaction from elemental powders. The X-ray diffraction pattern and neutron total structure factor show no detectable Bragg peaks, indicating that the sample is amorphous with respect to X-ray and neutron diffraction. The neutron and X-ray total pair distribution functions show correlation peak arising from P–Te heteropolar bonds in addition to those arising from P–P and Te–Te bonds. The Te–Te bond length is slightly shorter than that in the crystal structure of trigonal tellurium, suggesting a different environment from a polymeric chain structure. The thermal analysis results show that the binary phosphorus telluride is thermally unstable, that is, it decomposes above 200 °C into trigonal tellurium crystals and gaseous phosphorus, where phosphorus begins to gasify at a lower temperature than the sublimation temperature of red phosphorus.

1. Introduction

Phosphorus reacts readily with sulfur and selenium, yielding a large number of binary compounds, but is difficult to react with tellurium due to the instability of P–Te bonds [1]. Many attempts have been made to synthesize binary phosphorus tellurides by several researchers [1,2]. Montignie reported a method to synthesize P₂Te₃ by heating white phosphorus and tellurium powder at 320 °C during 1 h in a sealed tube [2]. However, Monteil and Vincent tried unsuccessfully to follow the same procedure, resulting in a mixture of red phosphorus and tellurium [1]. They examined several mixtures of red phosphorus and tellurium at various ratios through differential thermal analysis (DTA) measurements but the DTA curve on heating showed only two endothermic peaks due to the melting of the elements. Jörgens et al. reported that binary P–Te species are present in the form of [P₄Te₂]²⁻ ions in a BaP₄Te₂ ternary crystal compound and there are two P–Te covalent bonds, i.e. $r_{\text{P-Te}} = 2.469(6)$ Å and $r_{\text{P-Te}} = 2.537(5)$ Å [3]. Later Chung et al. reported the synthesis an alkali tellurophosphate compound K₄P₈Te₄ [4]. They showed that the compound features infinite chains of [P₈Te₄]⁴⁻ with P–Te covalent bonds and exhibits reversible crystal–glass phase–change behaviour. To our knowledge, however, binary phosphorus tellurides have not been reported up to the present date.

Mechanochemical synthesis is a technique that employs solid state reactions at a room temperature and it is useful to synthesize

compounds that are hardly synthesized by a conventional method. In this article, we report the mechanochemical synthesis of binary phosphorus telluride (20 at% Te), and its structural and thermal properties. The pair distribution functions obtained from neutron and X-ray diffraction measurements are used to investigate the short range structure and a direct evidence for the existence of P–Te bonds will be presented. Furthermore, thermal decomposition characteristics will be discussed on the basis of thermogravimetric (TG) and DTA results.

2. Theory of neutron and X-ray diffraction

The neutron and X-ray total structure factors, $S^{\text{N,X}}(Q)$, where Q is the momentum transfer, are obtained from scattering intensities, $I^{\text{N,X}}(Q)$, based on the Faber-Ziman definition [5]. The total pair distribution function and the total structure factor are related as follows:

$$g^{\text{N,X}}(r) = 1 + \frac{1}{2\pi^2 r \rho_0} \int_0^\infty Q(S^{\text{N,X}}(Q) - 1) \sin Qr dQ, \quad (1)$$

where ρ_0 is the average number density.

The neutron and X-ray total pair distribution function of a P–Te binary mixture can be described as a weighted sum of three partial pair distribution functions, $g_{i-j}(r)$:

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$$g^N(r) = \frac{c_P^2 b_P^2}{\langle b \rangle^2} g_{P-P}(r) + \frac{2c_P c_{Te} b_P b_{Te}}{\langle b \rangle^2} g_{P-Te}(r) + \frac{c_{Te}^2 b_{Te}^2}{\langle b \rangle^2} g_{Te-Te}(r). \quad (2)$$

$$g^X(r) = \frac{c_P^2 f_P(Q)^2}{\langle f(Q) \rangle^2} g_{P-P}(r) + \frac{2c_P c_{Te} f_P(Q) f_{Te}(Q)}{\langle f(Q) \rangle^2} g_{P-Te}(r) + \frac{c_{Te}^2 f_{Te}(Q)^2}{\langle f(Q) \rangle^2} g_{Te-Te}(r). \quad (3)$$

where

$$\langle b \rangle = \sum_i c_i b_i, \quad (4)$$

$$\langle f(Q) \rangle = \sum_i c_i f_i(Q), \quad (5)$$

where c_i , b_i and $f_i(Q)$ are respectively the concentration, the neutron coherent scattering length and the X-ray atomic form factor of the component atom i .

3. Experimental procedure

3.1. Sample preparation

Red phosphorus (Furuuchi Chemical, 99.9999% purity) and trigonal tellurium (Kojundo chemical laboratory, 99.9999% purity) were used as a starting material. Each element sample was crushed and ground into a fine powder by using an agate mortar. These powders were mixed in the appropriate ratio and the mixture (approximately 2 g) was put into a sealable zirconia vial (80 cm³ volume) with 20 zirconia balls (10 mm diameter). All handlings of chemicals and seals of vials were undertaken in highly pure argon atmosphere glovebox (1 ppm or less of oxygen, -70 °C or less of dew point). A planetary ball mill (Fritsch P-6) was used for milling at a rotating speed of 180 rpm. The ball milled samples have a hygroscopic nature and hence all measurements described below were performed in highly pure argon (or helium) atmosphere.

3.2. Density measurement

The densities were measured at room temperature using a gas pycnometer (Quantachrome, Micro-Ultrapyce 1200e) with helium (99.9999% purity) as the displacing fluid. Each sample was placed into a 4.25 cm³ container. Before the measurements, the sample chamber was evacuated for 60 s by using a rotary pump. A plurality of measurements was performed on each sample and their average value and standard deviation were calculated.

3.3. X-ray and neutron diffraction

The X-ray diffraction measurements were carried out at room temperature by using a θ - 2θ diffractometer (Rigaku MiniFlex 600) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 15 mA. Each sample was placed in the enclosed sample holder with kapton window.

The neutron diffraction measurement was carried out in BL21 (NOVA) spectrometer at the MLF pulsed neutron source of J-PARC facility. The sample was placed into a vanadium can with an inner diameter of 6 mm and a 0.1 mm thickness. The neutron total structure factor, $S^N(Q)$, was obtained from the scattering intensity after correction for the background, absorption [6], and multiple scattering [7] and normalization with a vanadium rod. The neutron scattering lengths and cross sections were taken from Ref. [8].

The X-ray diffraction measurement for pair distribution function analysis was carried out using a θ - 2θ diffractometer (Rigaku RINT Ultima) with Mo K α radiation ($\lambda = 0.7093 \text{ \AA}$) at 40 kV and 30 mA. After corrections for the background, absorption [9] and Compton scattering [10], the scattering intensity was converted to the X-ray total structure factor, $S^X(Q)$ [11]. The X-ray atomic form factors were taken from Ref. [12].

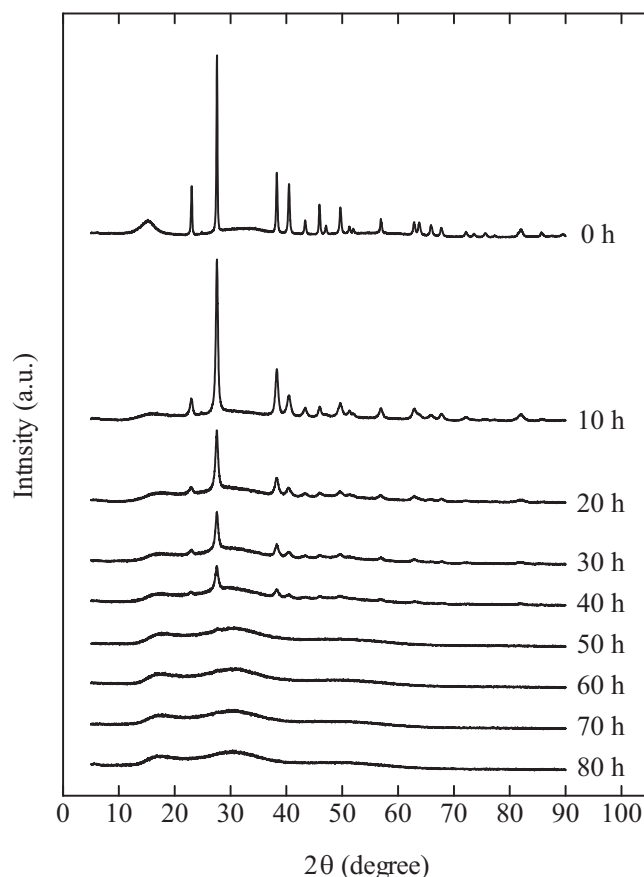


Fig. 1. The X-ray diffraction patterns of $P_{0.8}Te_{0.2}$ mixture sample in the course of milling.

3.4. Thermal analysis

The TG/DTA measurement was performed by using Rigaku TG8120 at a heating rate of 10 °C/min in highly pure argon flow (50 ml/min), from room temperature to 550 °C. Approximately 10 mg of sample was placed into an open alumina pan. An alumina powder was used for reference. A blank measurement was also performed in the same condition and the TG/DTA curve was obtained by correction using the blank measurement data.

4. Results and discussion

4.1. Mechanochemical reaction of P-Te mixture

Fig. 1 shows the X-ray diffraction patterns of $P_{0.8}Te_{0.2}$ mixture sample in the course of milling. The diffraction pattern of the mixture sample before milling (0 h of milling) shows structural characteristics of both red phosphorus and trigonal tellurium crystal. The broad peak observed at approximately $2\theta \sim 15^\circ$ is attributed to the amorphous structure of red phosphorus and it is referred to as the first sharp diffraction peak (FSDP) [13]. The FSDP decreases in intensity and its position shifts to higher angle with increasing milling time. On the other hand, all Bragg peaks observed in the X-ray diffraction patterns are attributed to the crystal structure of trigonal tellurium [14]. They decrease in intensity with increasing milling time and disappear at 50 h of milling. There is no significant change in the diffraction patterns after 60 h of milling. The milled sample was a fine powder and its colour was black.

The mixture sample with different tellurium content (10 and 30 at% Te) were also examined to form a binary compound in the same manner. The X-ray diffraction patterns of $P_{0.9}Te_{0.1}$ sample after 60 h of

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