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Mechanochemical syntheses of bismuth selenides

E. Klose, R. Blachnik*

Institut für Chemie, Universität Osnabwück, Barbarastraße 7, D-49069 Osnabrück, Germany

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Abstract

Bi + Se mixtures in the molar ratios of 2:3, 1:1, and 2:1, as well as a Bi + Sb + Se mixture in the molar ratio of 1:1:3 were treated in a planetary ball mill. The compounds Bi_2Se_3, BiSe, and $BiSbSe_3$ were formed after short milling periods.

The Bi + Se mixture in the molar ratio of 2:1 was less reactive, after 60 min besides the X-ray reflections of Bi, only few weak lines of an unidentified product were observed.

Keywords: Bismuth selenides; Mechanochemistry

1. Introduction

The phase diagram Bi–Se is dominated by the congruently melting compound Bi_2Se_3. Variations of its tetradymite structure increase the number of compounds in this system to 16 [1]. All are usually synthesized by reaction of the constituent elements or of educt compounds at higher temperatures. Tschakarov et al. have investigated the syntheses of various binary chalcogenides [2]. They reported that the chalcogenides of Zn, Cd, In, Sn, and Pb were formed in an explosive reaction after milling times in the range 12–365 min. We tried the mechanochemical method in the synthesis of some bismuth selenides.

2. Experimental

The thermal analyses were performed with a DTA device, developed by Gather [3]. The system was calibrated with the melting points of gallium, indium, lead, antimony, and silver. The samples were sealed in evacuated silica ampoules (length: 55 mm; diameter: 4.0 mm; wall thickness: 0.5 mm). The DTA experiments were done in the range 25–600°C with a heating rate of 10 K/min, a sample mass of 0.12–0.18 g, silicon as reference, and Ni/NiCr thermocouples.

X-ray measurements were carried out with the aid of a transmission powder diffractometer STADI P (Stoe), using Cu Kα1 radiation (154.051 pm), germanium single crystal monochromator, and linear position sensitive detector. Temperature dependent X-ray measurements were performed with a high temperature attachment.

Mechanical alloying was performed with a planetary ball mill (Pulverisette 7, Fritsch) with tungsten carbide bowls ($V = 12$ ml) and milling balls (∅ 12 cm) under argon. The rotational speed was 400 rpm and the mass of samples approximately 4 g. The mill was stopped in intervals and small parts of the powder mixture were taken for analysis to control the progress of the reaction. Bi, Sb (99.999%, Preussag) and Se (99.9%, ABCR) were used.

* Corresponding author. Fax: +49-541-969-3323.
E-mail address: bl@chnik.de (R. Blachnik).

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3. Results

Educt mixtures were prepared in the molar ratios of Bi:Se of 2:3, 1:1, and 2:1. These mixtures were treated in the planetary mill with total milling times between 1 and 60 min. Samples were investigated by difference thermal analyses and X-ray powder methods.

Mixtures corresponding to the composition Bi_2Se_3 and BiSe behave similarly. The diffractograms reveal that the educts react within 5 min to the compounds.

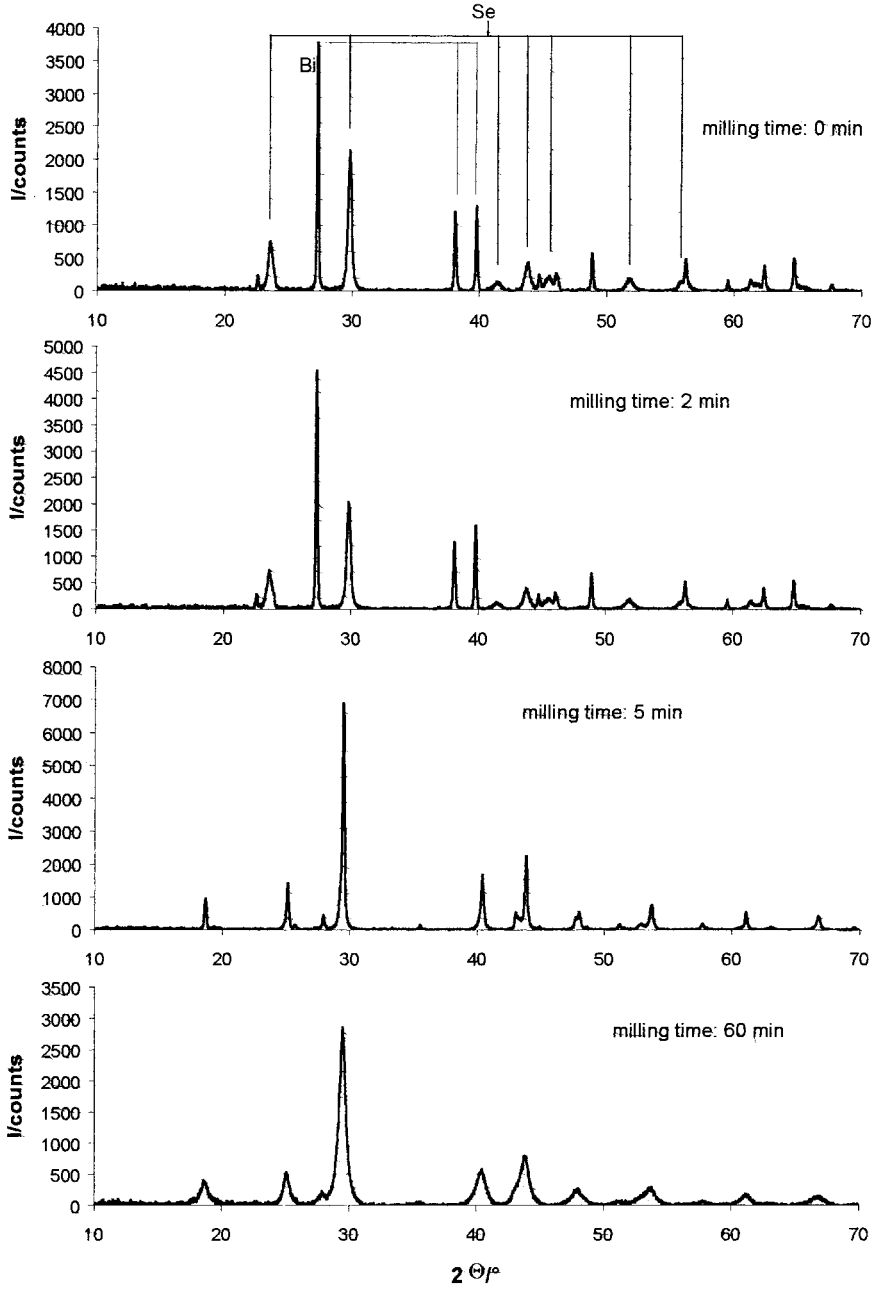

Fig. 1. Diffractograms of a 2Bi + 3Se reaction mixture after 0, 2, 5, and 60 min milling time.

With longer milling times broadening and decaying intensities of the reflection peaks indicate a decrease of particle size and start of amorphisation (Fig. 1). DTA traces of mixtures of untreated samples in the molar ratio 2:3 and of those milled for 2 min show the endothermic melting effect of selenium at 223°C immediately followed by the exothermic formation of Bi_2Se_3. The small endothermic effect at 620.0°C

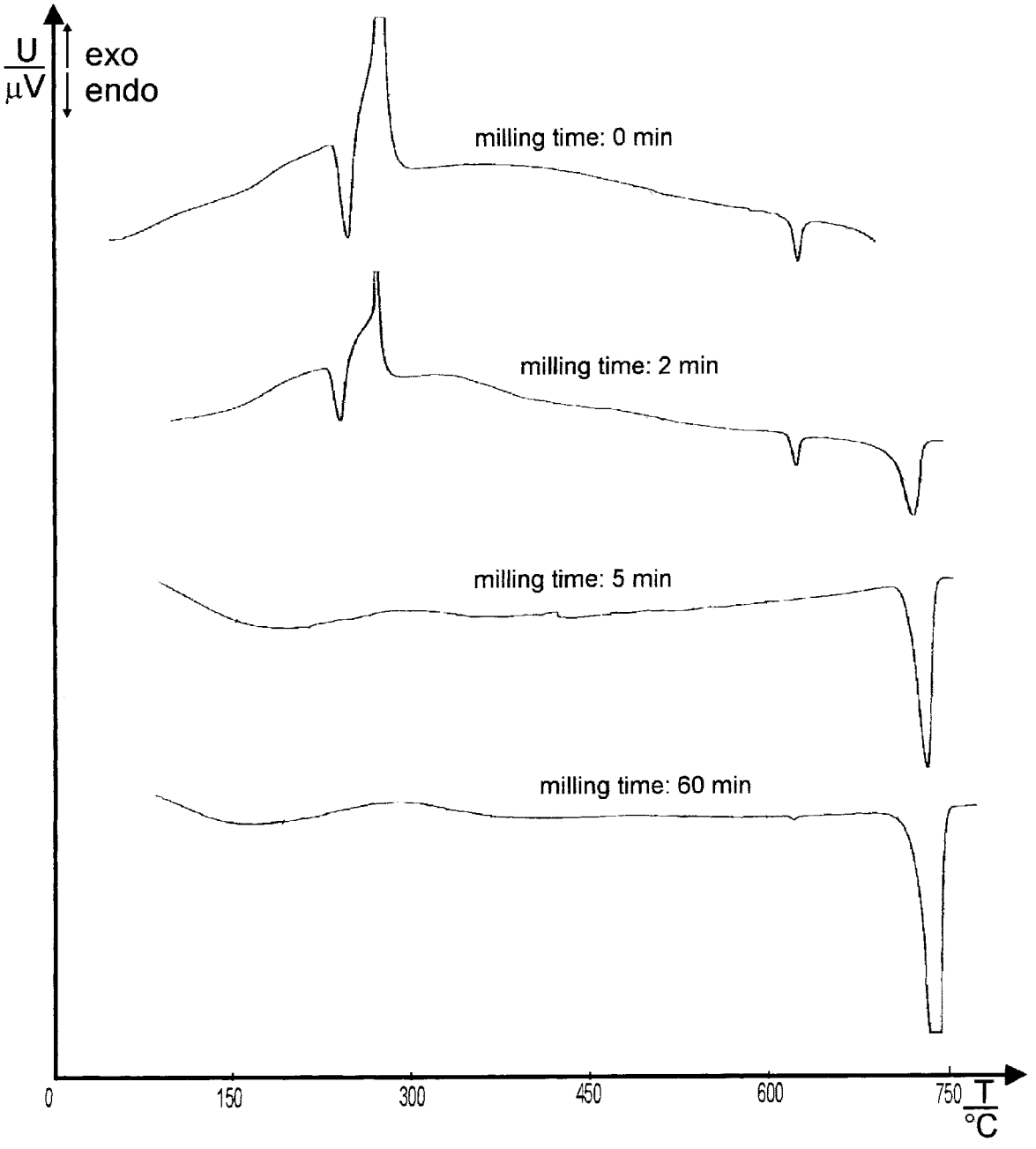

Fig. 2. DTA traces of a 2Bi + 3Se reaction mixture after 0, 2, 5, and 60 min milling time.

corresponds to the temperature of the monotectic in the system Bi–Se and that at 696.6°C to melting of Bi_2Se_3. After a milling time of 5 min, only the latter is found (Fig. 2).

Educt mixtures corresponding to BiSe have after 2 min at lower temperatures the same thermal effects in the DTA (Fig. 3) as those for Bi_2Se_3. After milling times of 5 min, a broad endothermic doublet on the

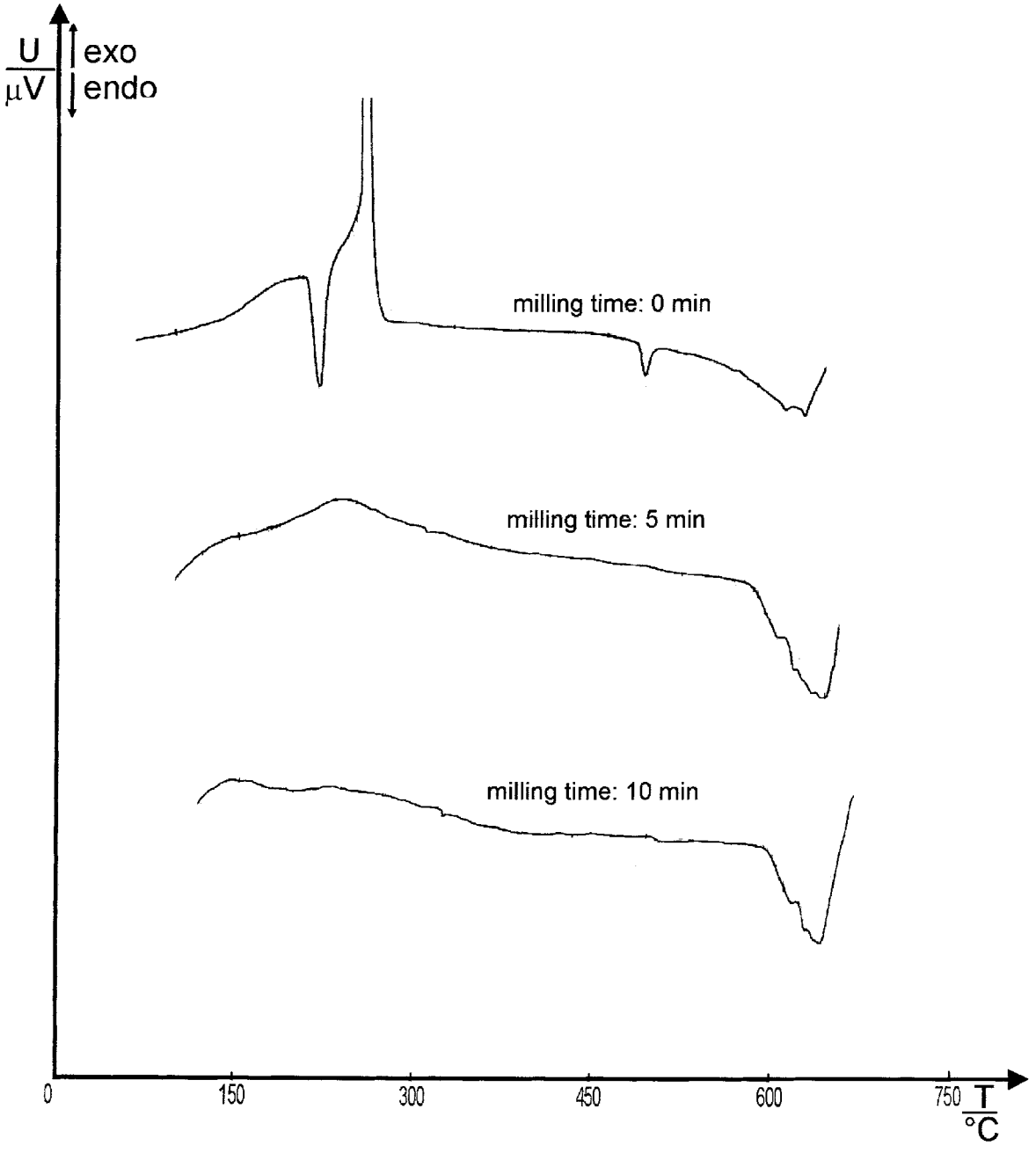

Fig. 3. DTA traces of a Bi + Se reaction mixture after 0, 5, and 10 min milling time.

DTA traces indicates the peritectic temperature of BiSe and the Bi–Se liquidus curve. Longer milling periods lead to amorphisation.

The educt mixtures in the ratio 2:1 are less reactive. The DTA trace of the Bi_2Se educt mixture which had been milled for 60 min shows a small exothermic effect at 193.9°C, melting of bismuth at 268.8°C and a broad liquidus effect at 600°C. The diffractogram contains reflections of bismuth and some weak lines of a product which could not be identified.

Encouraged by these results, we have tried to synthezise a ternary phase, $BiSbSe_3$. This composition

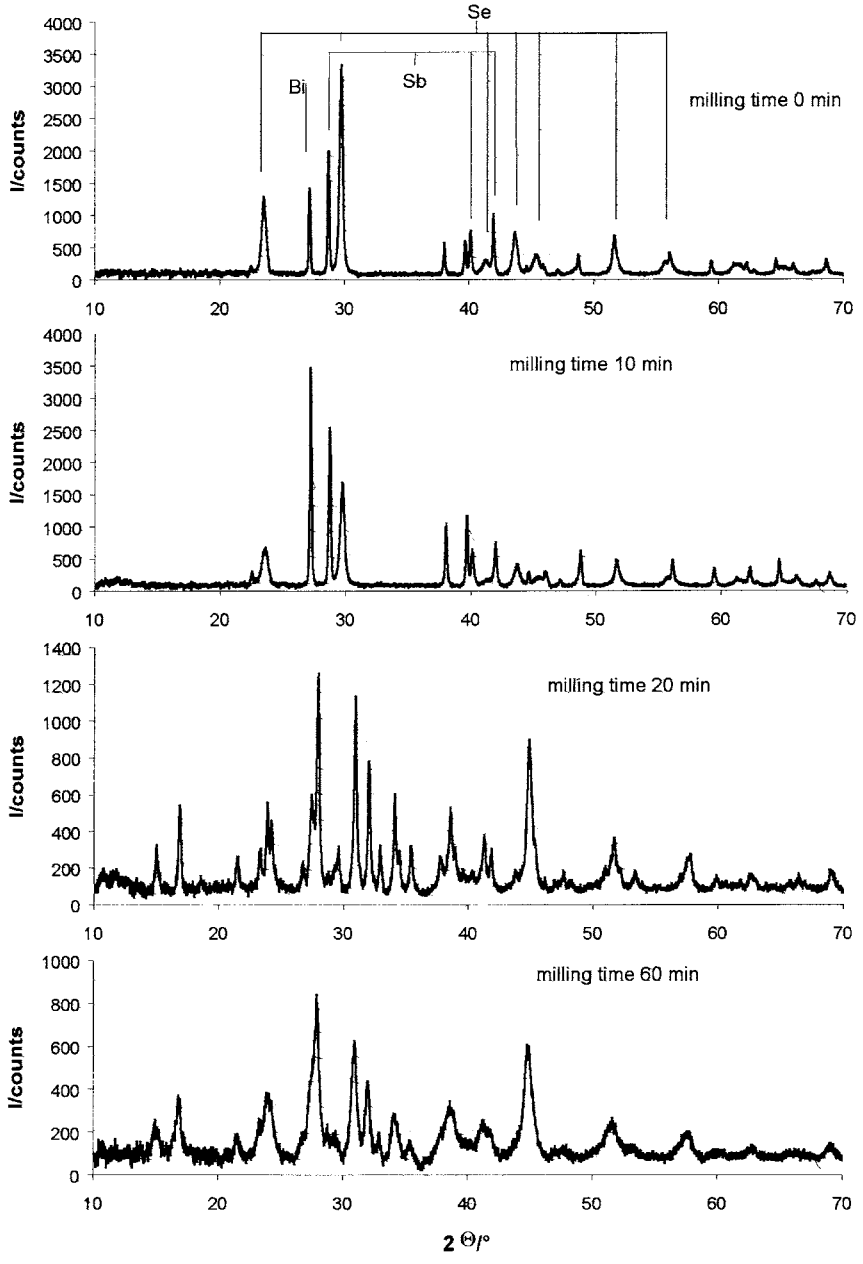

Fig. 4. Diffractograms of a Bi + Sb + 3Se after 0, 10, 20, and 60 min milling time.

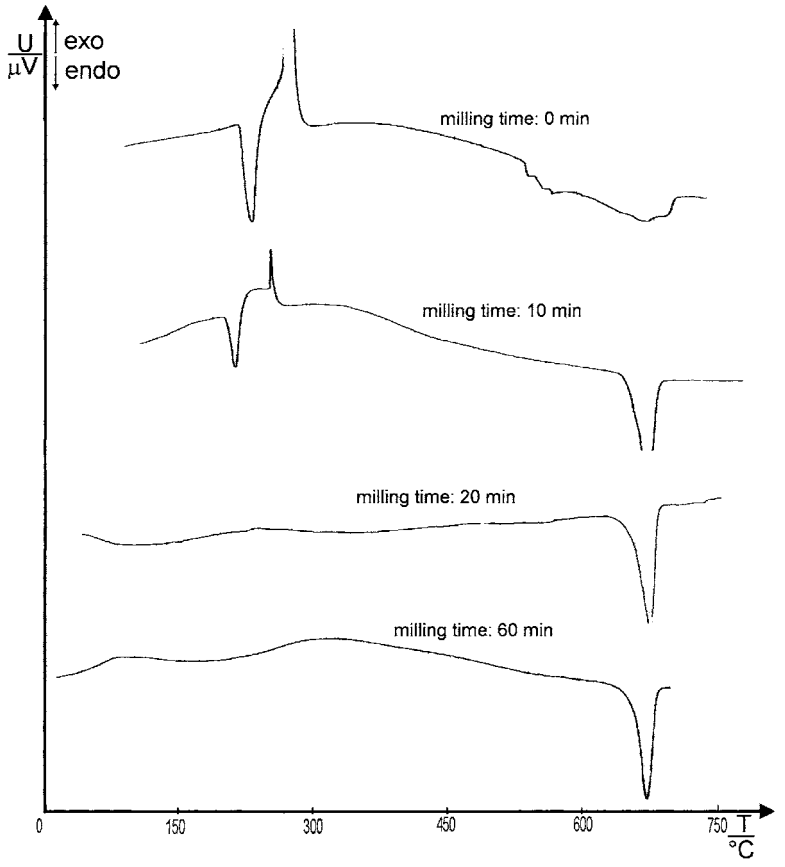

Fig. 5. DTA traces of a Bi + Sb + 3Se reaction mixture after 0, 10, 20, and 60 min milling time.

is part of the Bi_2Se_3–Sb_2Se_3 phase diagram which is characterized by complete solubility in both solid and liquid state [4]. The reaction to the solid solution was completed after 20 min (Fig. 5). The phase obtained melts at 640°C and has lattice parameters of $a = 1159.1$ pm, $b = 1179.4$ pm, and $c = 404.2$ pm (Fig. 4). These values are in very good agreement with the data given by Kuznetzov et al. [4] ($T_m = 640$°C, $a = 1161.0$ pm, $b = 1173.5$ pm, $c = 401.2$ pm).

The investigation has shown that powders of the compounds in the binary Bi–Se system and the ternary Bi–Sb–Se system can be obtained in short times by treating the educt mixtures in a planetary mill.

Acknowledgements

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