



HAL
open science

Oxidation resistance of hard boron-rich chalcogenides B₆X and B₁₂X (X = S, Se)

Vladimir Solozhenko

► **To cite this version:**

Vladimir Solozhenko. Oxidation resistance of hard boron-rich chalcogenides B₆X and B₁₂X (X = S, Se). *Journal of Superhard Materials*, 2021, 43 (6), pp.455-456. 10.3103/S1063457621060101 . hal-03555990

HAL Id: hal-03555990

<https://hal.science/hal-03555990v1>

Submitted on 3 Feb 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Oxidation resistance of hard boron-rich chalcogenides B_6X and $B_{12}X$ ($X = S, Se$)

Vladimir L. Solozhenko*

LSPM–CNRS, Université Sorbonne Paris Nord, 93430 Villetaneuse, France

Oxidation resistance of new boron-rich chalcogenides, orthorhombic B_6X and rhombohedral $B_{12}X$ ($X = S, Se$), was studied by thermal analysis (TG-MS). It has been established that in air boron-rich sulfides remains stable up to $\sim 580^\circ\text{C}$, while boron-rich selenides start to oxidize already at $\sim 550^\circ\text{C}$.

Keywords: boron-rich chalcogenides, oxidation resistance, thermal analysis.


Four new boron-rich chalcogenides – orthorhombic B_6S and B_6Se [1] and rhombohedral $B_{12}S$ and $B_{12}Se$ [2] – have been recently synthesized by direct reactions of the elements at high pressures and high temperatures. As follows from experimental [3] and theoretical [1] studies, all these compounds are characterized by high Vickers hardness (31-33 GPa) and, thus, could be of applied interest. However, in this regard their thermal and chemical stability are also rather important. In the present Letter we report the oxidation resistance of boron-rich chalcogenides.

Boron-rich chalcogenides (powders of grain size ranging from 1 to 10 μm) have been synthesized by direct reactions of the elements in a toroid-type high-pressure apparatus according to the methods described elsewhere [1,2]. X-ray diffraction study (TEXT 3000 Inel, $\text{CuK}\alpha 1$ radiation) has shown that recovered samples contain well-crystallized single-phase boron-rich chalcogenides with lattice parameters close to the literature data [1,2]. Oxidation resistance in air at temperatures to 1400°C has been studied at a heating rate of 10 K/min by simultaneous thermogravimetric (TG) and mass spectroscopy (MS) analysis using Netzsch STA 409 PC/PG thermal analyzer coupled with QMS 403 Aëolos quadrupole mass spectrometer.

According to the results of thermogravimetric study, both boron-rich sulfides B_6S and $B_{12}S$ remain stable in air up to 580°C (the onset temperatures from TG curves) (Fig. 1a). At higher temperatures, oxidation starts on the sample surface resulting in formation of boron (B_2O_3) and sulfur (SO_2) oxides. Mass spectrometry analysis of the evolved gases revealed the presence of parent SO_2 ($m/z = 64$) and fragment ion SO^+ ($m/z = 48$) for both boron-rich sulfides (see Fig. 2).

Orthorhombic B_6Se remains stable in air up to 550°C (the onset temperature from TG curve) (Fig. 1b). At higher temperatures, oxidation results in formation of boron (B_2O_3) and selenium (SeO_2) oxides. The oxidation resistance of $B_{12}Se$ is remarkably higher, probably due to the lower selenium content of the phase. Mass spectrometry analysis of evolved gases in the case of boron-rich selenides was not possible due to the high sublimation temperature of SeO_2 ($> 315^\circ\text{C}$ [4]).

Thus, despite the high hardness of new boron-rich chalcogenides, their relatively low oxidation resistance may somewhat limit their applicability.

*  <https://orcid.org/0000-0002-0881-9761>; vladimir.solozhenko@univ-paris13.fr

The author thanks Dr. V.A. Mukhanov for the samples preparation, and Dr. A.N. Baranov for assistance in thermoanalytical study. This work was financially supported by the European Union's Horizon 2020 Research and Innovation Programme under the Flintstone2020 project (grant agreement No 689279).

1. Cherednichenko, K.A., Mukhanov, V.A., Wang, Z., Oganov A.R., Kalinko A., Dovgaliuk I., Solozhenko, V.L. Discovery of new boron-rich chalcogenides: orthorhombic B_6X ($X = S, Se$). *Sci. Rep.*, 2020, vol. 10, 9277.
2. Cherednichenko, K.A., Mukhanov, V.A., Kalinko A., Solozhenko, V.L. High-pressure synthesis of boron-rich chalcogenides $B_{12}S$ and $B_{12}Se$. [arXiv:2105.04450](https://arxiv.org/abs/2105.04450)
3. Solozhenko, V.L. Hardness of new boron-rich chalcogenides $B_{12}S$ and $B_{12}Se$. *ChemRxiv*. Cambridge: Cambridge Open Engage, 2021. (DOI: [10.33774/chemrxiv-2021-4pn07](https://doi.org/10.33774/chemrxiv-2021-4pn07))
4. Stull, D.R. Vapor pressure of pure substances. Organic and inorganic compounds. *Ind. Eng. Chem.*, 1947, vol. 39, No. 4, pp. 517-540.

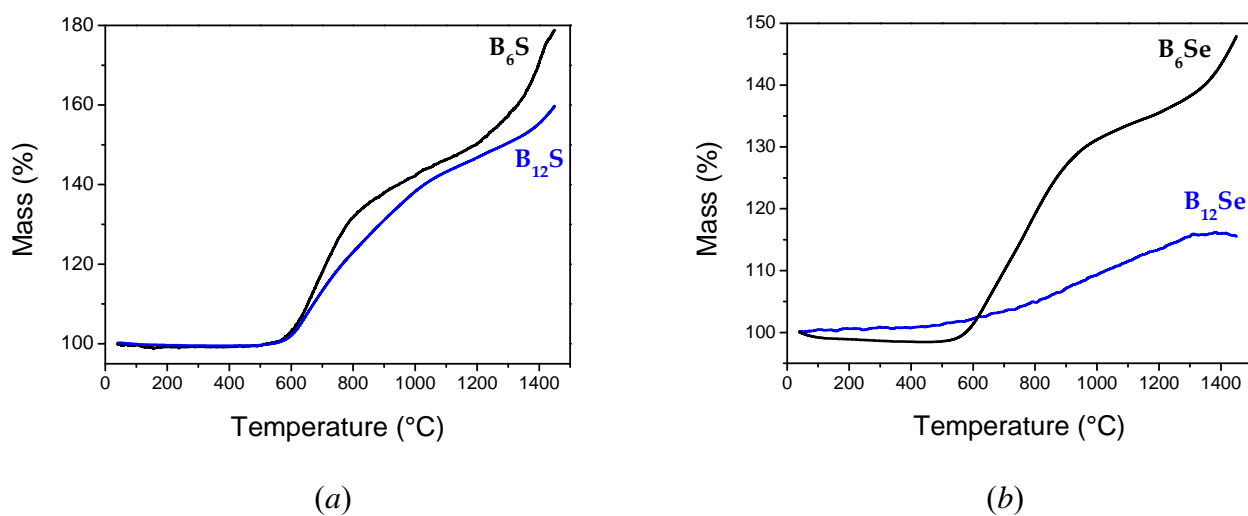


Fig. 1 Thermogravimetric data (in air) for boron-rich sulfides (a) and selenides (b).

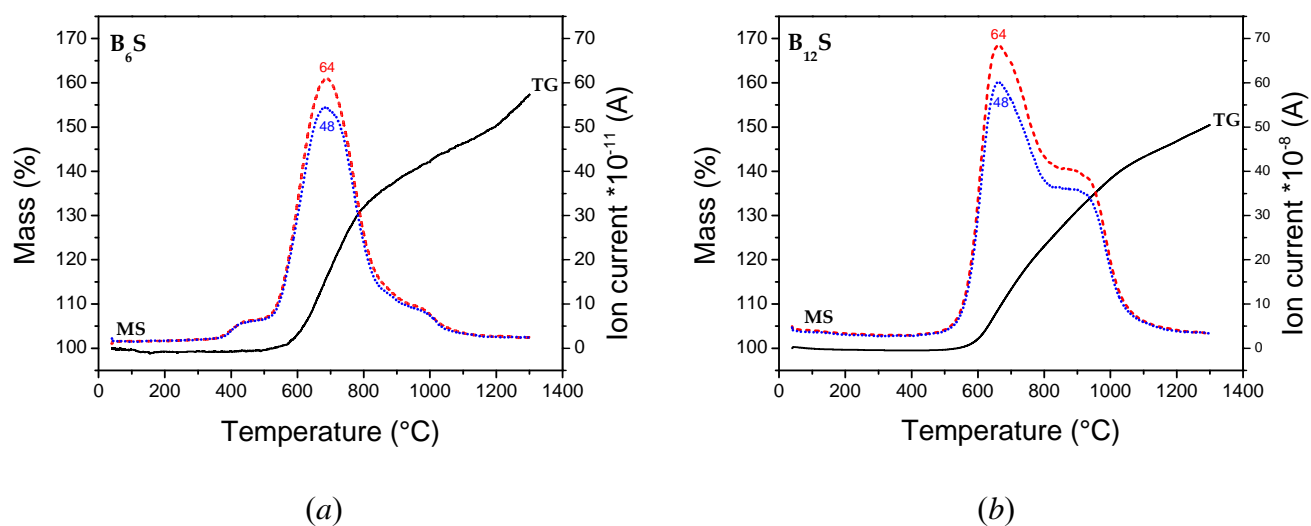


Fig. 2 Thermogravimetric (TG) and ion detection (MS) curves of boron-rich sulfides B_6S (a) and $B_{12}S$ (b). Dashed and dotted lines correspond to mass/charge ratios 64 and 48.