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 ~580ºC, while boron-rich selenides start to oxidize already at ~550ºC.

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, CuKα1 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 1400ºC 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 580ºC (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 550ºC (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 (> 315ºC [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

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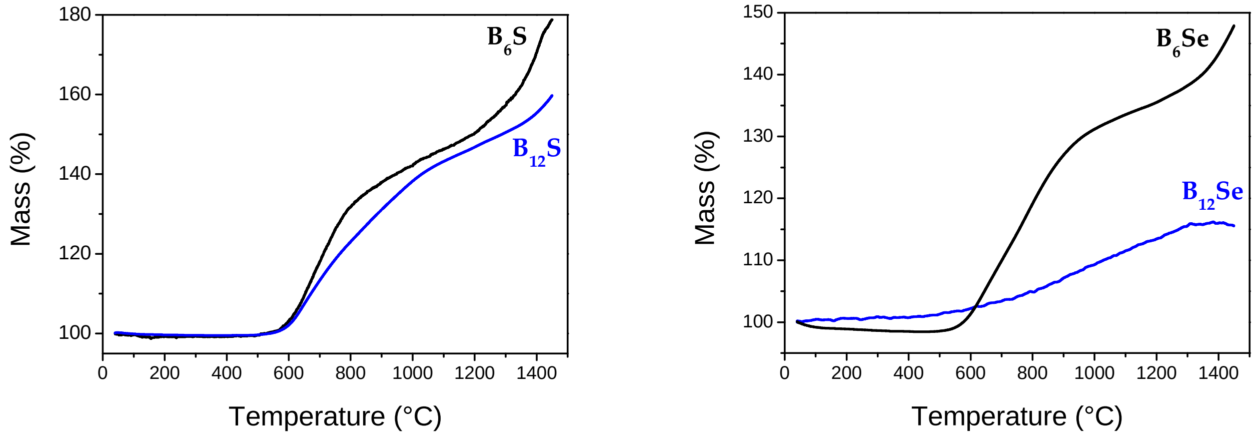
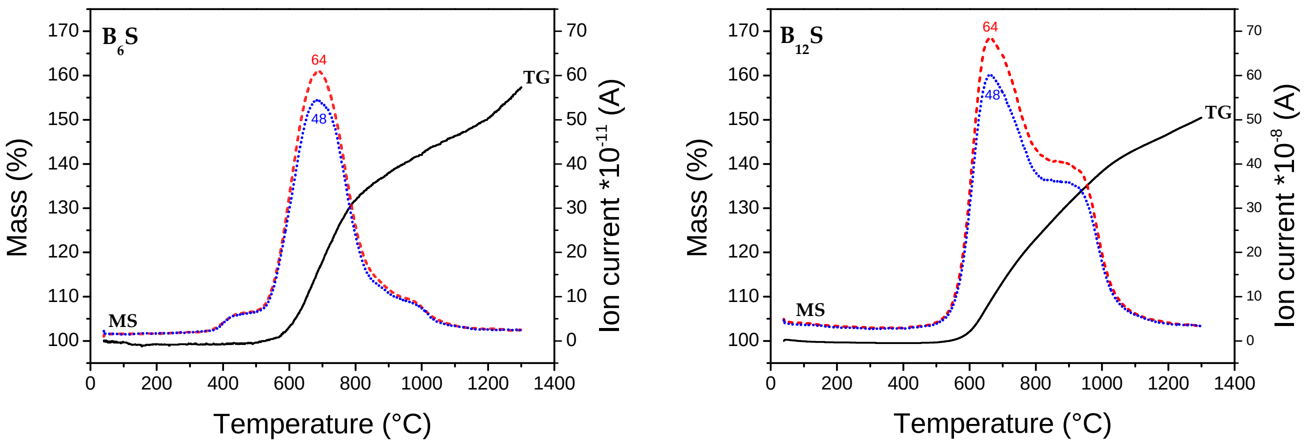


(*a*) (*b*)

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



(*a*) (*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.