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

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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 ~580°C, while boron-rich selenides start to oxidize already at ~550°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  $\mu$ m) 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, 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<sub>6</sub>S and B<sub>12</sub>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<sub>2</sub>O<sub>3</sub>) and sulfur (SO<sub>2</sub>) oxides. Mass spectrometry analysis of the evolved gases revealed the presence of parent SO<sub>2</sub> (m/z = 64) and fragment ion SO<sup>+</sup> (m/z = 48) for both boron-rich sulfides (see Fig. 2).

Orthorhombic B<sub>6</sub>Se 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<sub>2</sub>O<sub>3</sub>) and selenium (SeO<sub>2</sub>) oxides. The oxidation resistance of B<sub>12</sub>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<sub>2</sub> (> 315°C [4]).

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

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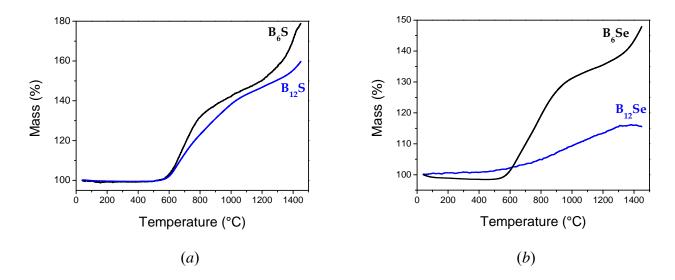


Fig. 1 Thermogravimetric data (in air) for boron-rich sulfides (a) and selenides (b).

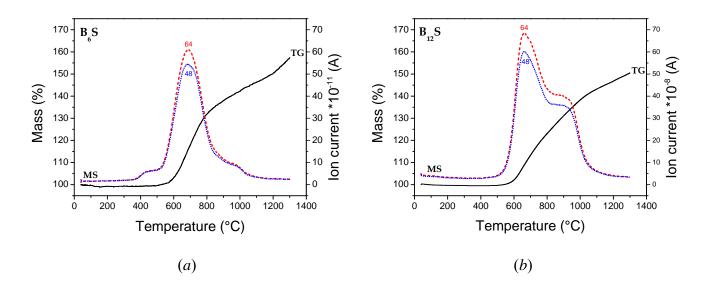


Fig. 2 Thermogravimetric (TG) and ion detection (MS) curves of boron-rich sulfides  $B_6S$  (*a*) and  $B_{12}S$  (*b*). Dashed and dotted lines correspond to mass/charge ratios 64 and 48.