Spectral Diagnostics of Vapor Composition over Molten Na$_2$WO$_4$ and Na$_2$O–BaO–B$_2$O$_3$ System

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Abstract—The high-temperature Raman spectra recording technique was found applicable also to study luminescence of atoms and individual molecular groups in vapors over some overheated molten compounds. Sodium atomic luminescence excited with a yellow (578.2 nm) copper vapor laser line was detected in vapors over overheated molten Na$_2$WO$_4$ and Na$_2$O–BaO–B$_2$O$_3$ system. The possibility of recording the sodium doublet spectrum by excitation with the 578.2 nm copper vapor laser line in vapors of any melts containing sodium was shown. Overheated melts in the Na$_2$O–BaO–B$_2$O$_3$ system disproportionate and lose boron oxide as evidenced by the recording of luminescent spectra of BO$_3$ molecular radicals in vapors over relevant melts.

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INTRODUCTION

Most laser materials are synthesized from melts at temperatures over 1000 K. For technological reasons, before starting the synthesis, melts are overheated for the purpose of homogenization. Such procedures can cause undesirable changes in their composition, which in turn complicates the synthesis of single crystals.

Among nonlinear optical crystals, borate compounds are distinguished by formation of structural types having significant optical nonlinearity [1]. One of the most universal nonlinear crystals is β-BaB$_2$O$_4$. Synthesis of the low-temperature β phase of barium borate uses the multicomponent molten Na$_2$O–BaO–B$_2$O$_3$ system containing 22 to 30 mol% Na$_2$O within the temperature range of 1175 to 1204 K. The melt is preliminarily homogenized for a long time (up to 36 h) at a temperature exceeding the melting point by 50 K [1].

The goal of this work is to study the structure of molecular fragments in vapors over melts of the Na$_2$O–BaO–B$_2$O$_3$ system and the effect of the overheating degree of the melts on their disproportionation processes in air by means of Raman spectroscopy and luminescent spectroscopy.

EXPERIMENTAL

Our studies were carried out with an original experimental setup designed earlier for Raman spectroscopy of melts at high temperatures [2]. The excitation source was a copper vapor laser operated in periodic pulse mode with the pulse frequency of 15 kHz and duration of 10 ns. The average radiation power was about 3 W.

Two laser lines were used: $\lambda_1 = 510.5$ nm and $\lambda_2 = 578.2$ nm. To avoid the thermal background effect of the specimen, we used the recording technique in the mode of gated photon count [2]. By means of an optical system, the scattered radiation by the specimen was directed to the entrance slit of a SPEX-Ramalog 1403 double monochromator and recorded with an FEU-136 photodiode-electric multiplier. Control was provided with a SCAMP processor.

The test specimens in platinum crucibles were placed into a vertical resistance tube furnace of Pt–6% Rh wire. The temperature was measured with a Pt–10% Rh/Pt–30% Rh thermocouple with an accuracy of 5 K. Such an arrangement of specimens enables one to provide a 180° observation geometry and to apply excitation through the top boundary of the studied molten compounds at any overheating degree. The optical system enables one to regulate the focal depth and to record spectra of vapors rather than only melts below. To record luminescence, a platinum screen was placed over the melt surface to prevent the laser beam from hitting the melt surface and to discriminate the Raman signal.

We studied the following compositions of the Na$_2$O–BaO–B$_2$O$_3$ system in the form of polycrystals: sodium and barium metaborates NaBO$_2$ and BaB$_2$O$_4$, eutectic composition BaB$_2$O$_4$ + 30% Na$_2$O, working composition for synthesis of β-BaB$_2$O$_4$ (BaB$_2$O$_4$ + 20% Na$_2$O), and boron oxide B$_2$O$_3$. Moreover, a specimen of sodium orthotungstate Na$_2$WO$_4$ was used to study the luminescence of sodium atomic vapors in other melts.

All the studies were carried out in air corresponding to the real synthesis conditions of BaB$_2$O$_4$ single crystals.
As was detected in [3, 4] by means of mass spectrometry, vapors over alkaline metaborates consist of monomeric metaborate molecules $\text{MBO}_2$ and an insignificant number of dimers ($\text{MBO}_2)_2$. A higher temperature (melt overheating degree) results in metal atoms M and $\text{B}_2\text{O}_3$ molecules appearing in vapors [4]. With respect to oxygen concentration, other molecules and molecular radicals (BO, $\text{B}_2\text{O}_2$, and BO$_2$) can be formed in vapors over molten borates.

We should note that mass spectrometric experiments do not enable one to study the vaporization nature and composition of vapors over melts in air, which is important for simulating the borate single crystal growing conditions. In this connection, it is pressing to develop simple spectrometric methods for this purpose.

The possibility of such studies was found in the course of experiments to study the structure of boron–oxygen groups in various molten borates by means of high-temperature Raman spectroscopy [6–9]. We recorded new phenomena for strongly overheated molten borates. Thus, upon excitation with a yellow copper vapor laser line of 578.2 nm, a study of sodium-containing borates revealed, in addition to Raman spectra of boron–oxygen groups ($R_1$, $R_2$, and $R_3$), a doublet of lines: $L_1 = 16978 \text{ cm}^{-1}$ and $L_2 = 16961 \text{ cm}^{-1}$. Figure 1 shows this phenomenon for molten sodium metaborate at various overheating degrees. This doublet was recorded only upon excitation with a yellow copper vapor laser line ($\lambda_2 = 578.2 \text{ nm}$) rather than upon excitation with a green line ($\lambda_1 = 510.5 \text{ nm}$). In the latter case, we recorded only the Raman spectrum of boron–oxygen groups in the melt. The positions of peaks $L_1$ and $L_2$ correspond to the known yellow doublet of atomic sodium (see, for example, [10]).

The possibility of atomic sodium excitation with radiation of wavelength 578.2 nm was noted in [11]. As we see in the energy diagram of atomic sodium (Fig. 2), the quantum energy of $\lambda_2 = 578.2 \text{ nm}$ is equal within the accuracy of 0.01 nm to half the energy gap between the ground ($3^2S_{1/2}$) and excited ($4^2F_{5/2,7/2}$) states of sodium atoms. In the given case, we observe double-photon excitation of sodium atoms to level $4^2F_{5/2,7/2}^{0 \lambda_2}$, followed by a cascade transition through level $3^2D_{3/2,5/2}$ to levels $3^2P_{1/2}^{0 \lambda_2}$ and $3^2P_{3/2}^{0 \lambda_2}$, corresponding to the known doublet of sodium.

Detection of atomic sodium luminescence in vapors of overheated molten sodium metaborate upon excitation with the yellow copper vapor laser line enabled us ...