SYNTHESIS OF AMORPHOUS AND CRYSTALLINE LaBWO₆ USING MECHANOCHEMICAL ACTIVATION

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ABSTRACT

This article presents data referring to the mechanochemical activated synthesis of amorphous and crystalline LaBWO₆. A stoichiometric mixture of La₂O₃, B₂O₃ and WO₃ of a 1:1:2 molar ratio was subjected to intense mechanical treatment in air using a planetary ball mill (Fritsch - Premium line - Pulversette No. 7). The obtained samples were analyzed by XRD, DTA, IR and UV-Vis spectroscopy. The process of mechanochemical amorphization was accomplished within 20 h at a milling speed of 500 rpm at room temperature. An additional heat-treatment of the mechanochemically obtained amorphous phase was carried out in order to obtain single crystal LaBWO₆ phase. The short range order of the amorphous network was defined by BO₃, BO₄ and WO₄ structural units. Glassy LaBWO₆ was obtained by us with the application of the melt quenching method prior to these experiments. The infrared and optical spectra showed that WO₄ units were more distorted in the structure of the glassy LaBWO₆ when compared to those of both amorphous phases. The crystallization of LaBWO₆ was achieved after thermal treatment at 690°C of the mechanochemically obtained amorphous and glass composition.

Keywords: melt quenching, mechanical activation, amorphous phase and LaBWO₆.

INTRODUCTION

Amorphous materials are a subject of research interests from fundamental and industrial point of views. They are used as a component in various devices in the field of optics, electronics and opto-electronics, reflector windows and sensors due to their properties [1 - 8]. The amorphous phase is thermodynamically unstable compared to the corresponding equilibrium crystalline phase. The transformation from an amorphous to a crystalline phase depends [9] on the diffusion properties of the amorphous material and on the kinetics of crystallites nucleation and growth. Different techniques like melt quenching [10, 11], melt spinning [12], thermal evaporation [13], chemical vapor deposition [14], sol-gel [15], pressure-induced amorphization [16] and mechanically activation [17] are used to prepare bulk-, sheet-, powder-, thin film type of amorphous materials. The melt quenching technique [10, 11] is one of the most popular methods for the amorphous phase preparation. It usually requires high cooling rates (10² to 10¹⁰ K s⁻¹). Mechanical activation is also used to obtain amorphous materials. It is applied to prepare metallic amorphous alloys using ball milling [17 - 20]. Its advantage refers to the fact that the process is carried out at room temperature. Formation of amorphous or crystalline materials depends on different milling parameters as speed, time, ball to powder ratio and milling atmospheres (dry or wet) [17].

Our research team has experience in the preparation of amorphous and polycrystalline materials using melt quenching technique and mechanically activation in systems containing MoO₃, V₂O₅ and WO₃ [10, 11, 21 - 26].
Pure LaBWO₆ crystal phase and Eu³⁺ doped glass of same composition was obtained by us using the conventional melt quenching method [24 - 26]. There are data in the literature that this compound can be synthesized by the Pechini method through a solid state reaction [27 - 29]. That is why we chose to subject a mixture of nominal composition corresponding to LaBWO₆ to mechanically activation. The aim of present work is to investigate the process of amorphization and crystallization of LaBWO₆ with the application of mechanical activation. A comparative analysis of the short range order of amorphous LaBWO₆ phases obtained by melt quenching and mechanically activation is provided as well.

**EXPERIMENTAL**

Commercial powders of reagent grade La₂O₃ (Merck, p.a.), WO₃ (Merck, p.a.) and H₃BO₃ (Reachim, chem. pure) were used as starting materials. Synthesis of the glassy LaBWO₆ by melt quenching technique was previously described [24 - 26]. A stoichiometric mixture of La₂O₃:WO₃:B₂O₃ (1:1:2) was activated in a planetary ball mill (Fritsch-Premium line-Pulversette No 7) using hardened steel balls and a vial, while the ball-to-powder mass ratio was of 10:1. The milling time was fixed up to 20 h at milling speed of 500 rpm. A procedure of 15 min ball milling duration followed by a pause of 5 min was applied to avoid excessive temperature rise within the grinding chamber. The phase formation was monitored by XRD on a Bruker D8 Advance diffractometer using Cu-Kα radiation. The differential thermal analysis was performed in air by SETARAM Labsys Evo apparatus at a heating rate of 10°C min⁻¹ in an open corundum crucible. The infrared spectra were registered in the range of 1200 cm⁻¹ - 400 cm⁻¹ on a Nicolet-320 FTIR spectrometer using the KBr pellet technique. The optical properties were measured at room temperature using Evolution 300 UV-Vis spectrophotometer at wavelengths within the range of 200 nm -1000 nm.

**RESULTS AND DISCUSSION**

The phase transformation during the mechanical treatment is monitored by X-ray diffraction analysis (Fig. 1). The strong lines of the WO₃ (JCPDS-83-0951), La₂O₃ (JCPDS-22-0369), La(OH)₃ (JCPDS-36-1481) and H₃BO₃ (JCPDS-73-2158) are observed in the initial mixture (Fig. 1a). The mechanical activation induces distortion of initial crystalline structures illustrated by decrease of the diffraction lines intensity and the appearance of amorphous hallo (Fig. 1b, c and d). The diffraction lines of WO₃ are observed even after 15 h milling time indicating that WO₃ is a more stable oxide. The increase of the milling time up to 20 h leads to full amorphization of the sample (Fig. 1e). This result is in a good agreement with our previous investigations showing that milling speed of 500 rpm is high enough to obtain amorphous Bi₂WO₆ and ZnCO₃ [23, 30]. Fig. 2 gives the X-ray profiles of the amorphous samples obtained by both methods: melt quenching [26] and mechanical activation. The observed broad hallo is typical for an amorphous nature and indicates the absence of crystals in both samples.

Useful information on the structural units of the amorphous networks is obtained by IR and UV-Vis spectroscopies. The assignment of the absorption bands is made on the ground of the structural data for
LaBWO₆ [28] and our previous spectral studies [24 - 26]. According to K. Palkina et al. [28] the structure of this compound contains large ten-vertex polyhedra in the form of LaO₁₀ spenocoranas, infinite chains of BO₃ triangles and isolated WO₄ tetrahedra that are bonded to BO₃ though lanthanum. It is worth noting that there are no W-O-B bonds in the structure. The IR spectra of both amorphous phases exhibit band positions at the same locations (Fig. 3). The bands at 830 cm⁻¹ and 710 cm⁻¹ in the spectrum of the glass sample are ascribed to asymmetric stretching vibrations of WO₄ tetrahedra [24 - 26, 31]. A band at 830 cm⁻¹ is mainly observed in the spectrum of mechanochemically obtained amorphous sample. This result indicates that the WO₄ units there are of higher local symmetry compared to that of the WO₄ units present in the glass sample. The bands in the absorption region of 1400 cm⁻¹ - 1000 cm⁻¹ are due to the vibrations of BO₃ groups while the band at 1060 cm⁻¹ is due to the vibration of BO₃ groups [24 - 26, 32]. The weak band at 1060 cm⁻¹ in the glass spectrum is transformed into a shoulder in the spectrum of the mechanochemically obtained amorphous sample. Hence, it can be assumed that the BO₃ units’ number in the glass structure is slightly higher that that obtained by mechanochemically activation.

The UV-Vis spectroscopy is mainly used as a supporting structural method in order to prove the type of the structural units and their deformation. It is well known that the transitional metal oxides with d⁰ electron configuration give absorption bands in the UV-Vis region due to oxygen–metal charge transfers in various oxitungstate compounds [34 - 36]. The position of this electron transfer depends on the ligand field symmetry of the W site. As seen in Fig.4 the UV-Vis absorption spectra show a characteristic band at 240 nm and 270 nm for mechanochemically obtained amorphous sample and glass sample [26], respectively. These absorption bands are due to the O=W charge transfer in the WO₄ tetrahedra [34 - 36]. More symmetrical WO₄ units show a band at lower wavelength (240 nm), while more distorted ones exhibit a band at higher wavelength (270 nm) [35, 36]. The broad absorption band centered at higher wavelength (270 nm) is an indication for the formation in the glass network of WO₄ of different symmetry. We
used the Tauc’s method to estimate the optical band gap of the amorphous samples. As shown in the inset of Fig. 4, the optical band gaps of the mechanically obtained amorphous sample and the glassy sample are of 3.22 eV and 3.41 eV [26], correspondingly.

The thermal parameters of both amorphous samples are investigated by DTA analysis (Fig. 5). The DTA curve of the sample prepared by the melt quenching method exhibits an exothermic peak at 676°C. It is attributed to the crystallization temperature [26]. The mechanically activated sample shows an exothermic peak at 663°C associated with the amorphous-crystalline phase transformation. The DTA data obtained indicate further thermal treatment of the amorphous samples.

Fig. 6 shows the X-ray patterns of the mechnochemically obtained amorphous sample heated for 3 h at 660 and 690°C. The formation of LaBWO₆ (JCPDS-57-1076) starts at 660°C but the main diffraction peak of H₃BO₃ is also detected (Fig. 6a). That is why a thermal treatment at higher temperature (690°C) is performed. This results in crystalline LaBWO₆ formation (Fig. 6b). The temperature value pointed above is 150°C lower when compared to that required for a solid state reaction. Moreover, the synthesis duration is also decreased to 3 h [28]. Crystalline LaBWO₆ is obtained under the thermal conditions of glass composition formation [26]. Fig. 7 presents the X-ray diffraction patterns of crystalline LaBWO₆ after heating the mechnochemically synthesized amorphous sample and the glass one [26] at 690°C. It is seen that the peaks intensity and orientation of the crystalline LaBWO₆ phase obtained by mechnochemically supported solid state reaction are in a good agreement with the JCPDS standard (Fig. 7a). Preferred orientations in 002, 001 and 212 planes by variation of these peaks...
intensity is observed for the crystalline LaBWO$_6$ phase obtained upon heating of the corresponding glass composition (Fig. 7b). It can be concluded that the mechanically activation and the subsequent thermal treatment decreases the tendency toward preferential orientation. Hence, the texture evolution in our case depends on the applied method of preparation.

The IR spectra confirm the formation of crystalline LaBWO$_6$ in both samples upon heat treatment (Figs. 8a and b). The bands in the range from 1470 cm$^{-1}$ to 1170 cm$^{-1}$ correspond to the vibrations of associated BO$_3$ units building this crystalline phase [24 - 26, 32]. The bands observed at 670 cm$^{-1}$ and 620 cm$^{-1}$ correspond to typical stretching vibrations of B-O-B bonds in the BO$_3$ units borate chains. The vibrations of isolated WO$_4$ units are observed at 970 cm$^{-1}$ ($\nu_1$), between 880 cm$^{-1}$ and 720 cm$^{-1}$ ($\nu_3$) and at 480 cm$^{-1}$ ($\nu_4$) [24 - 26, 31]. It is found that they predominate in the IR spectra (fig. 8a, b). Thus, it can be concluded that they are more distorted in the crystalline phase when compared to those in the amorphous one.

The UV-Vis absorption spectra of the crystalline LaBWO$_6$ obtained by heat treatment of mechanochemically synthesized amorphous sample and a glassy one...
show a single peak at 240 nm (Fig. 9). The value of optical band gap of the crystalline LaBWO$_6$ obtained increases to 3.26 eV and 3.61 eV, respectively. This result can be attributed to the reduction of different defects during the amorphpous-crystalline phase transformation.

**CONCLUSIONS**

Amorphous and polycrystalline LaBWO$_6$ phases are synthesized by mechanically activation. Amorphization is achieved after 20 h of milling at room temperature. The structure of amorphous LaBWO$_6$ phases prepared is compared to that of glassy LaBWO$_6$ obtained by melt quenching technique. IR and UV-Vis spectroscopies show that the short range order of both amorphous samples is identical. It is determined by WO$_4$, BO$_4$ and BO$_3$ units. The WO$_4$ groups in mechanochemically obtained amorphous phase have higher symmetry as compared to the WO$_4$ building the glass sample. Less number of BO$_4$ units participates in the structure of the mechanochemically obtained amorphous phase. Crystallization of LaBWO$_6$ is accomplished at identical thermal conditions (690°C for 3 h) for both amorphous samples.

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