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Temperature-induced phase transformation in $(As_{1-x}Bi_x)_2S_3$ glasses

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INTRODUCTION

Introduction of metal dopants in the structure of chalcogenide glasses as well as a choice of the preparation technology essentially affect their physical properties, in particular, the value and type of electrical conductivity, optical and thermoelectric characteristics, photosensitivity, etc. Bithmut is a good suitable tailoring agent to tune the physical properties of chalcogenide materials for a particular technological application. Knowledge of thermal stability and glass-forming ability, as well as of mechanical behaviour is necessary to define effective working limits and overall suitability. Moreover, analysis of the glass transition kinetics can be of great importance in finding appropriate glass formulations for use in optical storage media. Stability of their operating characteristics depends on their capability of structural relaxation, including crystallisation, with increasing temperature. Significant kinetic parameters such as activation energy and reaction model can be determined using the kinetic analysis of the crystallisation phenomena.

EXPERIMENTAL

$(As_{1-x}Bi_x)_2S_3$ glasses with x= 0.08 ÷ 0.20 were prepared from pre-synthesised As_2S_3 glass and needle-shaped Bi_2S_3 crystals loaded in desired amounts into evacuated quartz ampoules heated to 1023 K at a rate of 50 K/h with subsequent aging for 3 h and cooling at 30 K/h down to 873 K followed by air quenching. These glasses were shown to possess clearly amorphous structure in the whole compositional range [1]. This was essentially different from an earlier study [2], where introduction of more than 6 at. % Bi into As_2S_3 glass resulted in noticeable phase separation in the amorphous medium by formation of elemental bismuth and crystalline Bi_2S_3 inclusions. We focus on the kinetic analysis of non-isothermal crystallisation processes in $(As_{1-x}Bi_x)_2S_3$ glasses, using the possibilities of differential thermal analysis technique. The glass heating rate was varied from 2 to 12 K/min.

RESULTS AND DISCUSSION

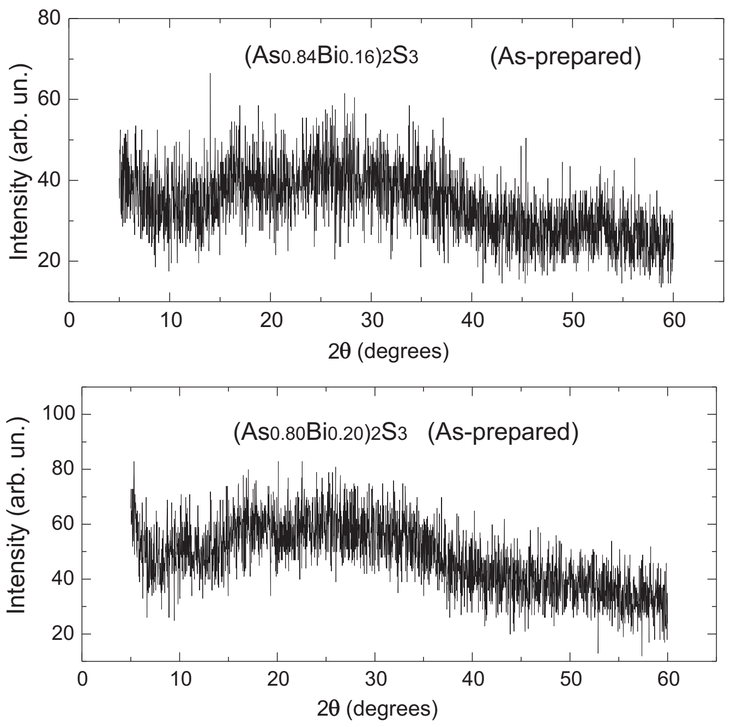

Fig. 1. Powder XRD patterns of as-prepared $(As_{1-x}Bi_x)_2S_3$ glasses

Previously [2] amorphous $(As_{1-x}Bi_x)_2S_3$ materials were fabricated with bismuth content not higher than 4÷6 at. % whereas higher Bi concentrations in the mixture resulted in the appearance of crystalline inclusions. Our method of preparation of $(As_{1-x}Bi_x)_2S_3$ glasses made it possible to create bulk samples without any noticeable crystal features. This is also confirmed by Raman spectra of the $(As_{1-x}Bi_x)_2S_3$ glasses with $0.08 \le x \le 0.20$ measured at low excitation power density [2]. They exhibit a typically amorphous behavior without any evidence for the presence of Bi_2S_3 crystallites, which could have been expected for samples with x = 0.08.

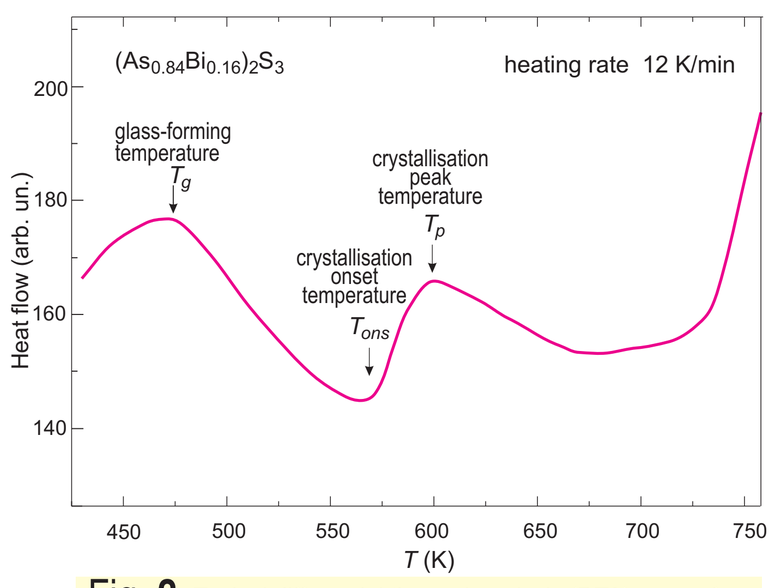

Fig. 2. Typical differential thermal analysis (DTA) trace of $(As_{1-x}Bi_x)_2S_3$ glass.

T_g and T_{ons} for all samples shift toward higher temperatures with increasing heating rate. This is attributed to the relaxation dynamics during the structural transition. For each sample DTA thermographs show a single crystallisation peak. Increasing Bi content leads to a decrease of the glass its thermal stability (characterised by Hrubý parameter).

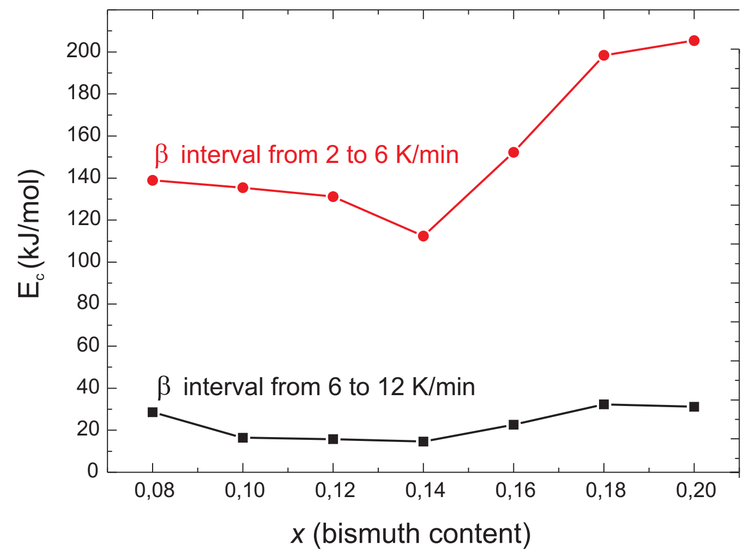

Fig. 3. Effective activation energy E_c calculations by Kissinger method for $(As_{1-x}Bi_x)_2S_3$ glasses.

The activation energy of crystallisation E_c is proportional to the slope of dependence of the crystallisation peak temperature T_p on the applied heating rate β.
The Kissinger method yields a single activation energy E_c that is consistent with the assumption of single-step kinetics. It usually gives information only about the dominant (sharpest) crystallisation peak [5, 6]. Here we found that E_c for the crystallisation process is different for two intervals of β variation. This indicates the existence of more than one energy barrier that control the crystallisation process.

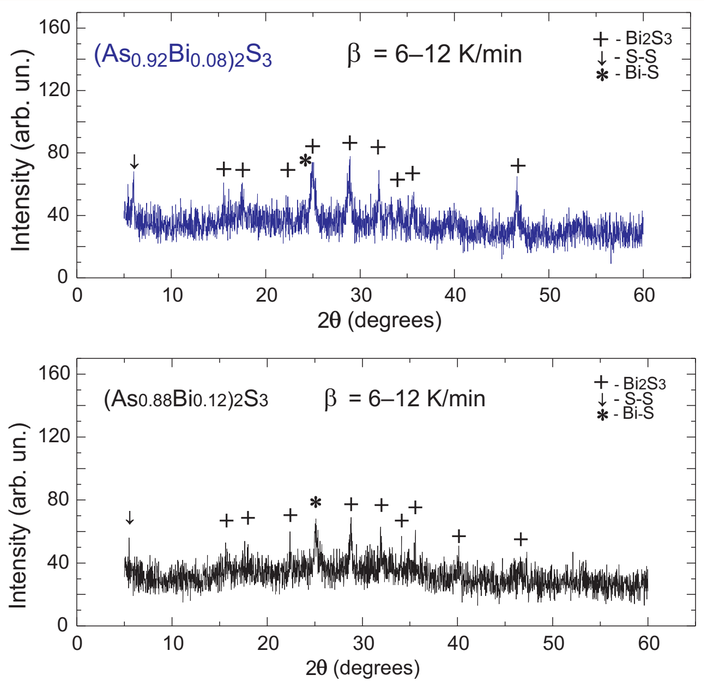

Fig. 4. XRD patterns of $(As_{1-x}Bi_x)_2S_3$ glassy samples with x = 0.08 and 0.12 after heat treatment with high heating rate

Thermal heating with a relatively larger rate leads to the formation of mainly Bi_2S_3 crystallites in the glass.

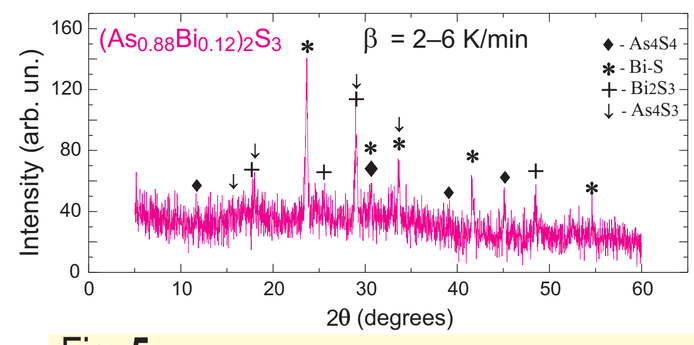

Fig. 5. XRD patterns of $(As_{1-x}Bi_x)_2S_3$ glassy samples with x = 0.12 after heat treatment with low heating rate

The transformation from the amorphous to crystalline structure involves different mechanisms of nucleation, diffusion, and growth. The evaluation by Kissinger method does not reflect the first crystallisation process (formation of Bi_2S_3 crystallites) because the second process is dominant. The two processes coexist, providing a high activation energy value at a larger β. At lower heating rates, in addition to the contribution of Bi–S bonds, As_4S_4 (As_4S_3) units with homopolar As–As bonds appear.

CONCLUSIONS

❶ X-ray diffraction (XRD) measurements for as-prepared $(As_{1-x}Bi_x)_2S_3$ glasses samples (x = 0.08÷0.20) clearly demonstrate absence of reflexes that could provide evidence for the existence of any crystallites in the samples. The XRD patterns show that all the samples with Bi concentration up to 20 mol. % are amorphous.

❷ The nonisothermal crystallisation experiments were performed using DTA technique by using the Kissinger method [3]. Kinetic analysis of the crystallisation processes in $(As_{1-x}Bi_x)_2S_3$ glasses showed the presence of two overlapping crystallisation peaks for all the glasses under investigation, when processes are controlled by more than one energy barrier. The effective activation energy E_c for different components of these processes were significantly lower at higher heating rates than for the slow heating of the samples.

❸ XRD measurements showed that at high heating rates (6–12 K/min) heating results in the dominant formation of Bi_2S_3 crystallites in the glass, whereas at lower heating rates in addition to the contribution of Bi–S bonds the number of As_4S_4 (As_4S_3) units with homopolar As–As bonds are increased.

❹ The experimentally determined crystallisation parameters E_c and T_p as well as the glass transition temperature T_g and the melting temperature T_m enabled us to analyse how the increasing Bi content in the As_2S_3-based glass affects its thermal stability. The glass thermal stability, characterised by the Hrubý parameter, decreases with the bismuth content.

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