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Blue luminescence in the WO_3—P_2O_5—ZnO glass system

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ABSTRACT

Luminescence in WO_3—P_2O_5—ZnO glasses was measured and its origin was investigated. With XRD measurements, the amorphous phase of the glasses was determined to exclude a crystalline-phase region as the source of luminescence. A blue emission by 320 nm excitation was observed, similar to that in $ZnWO_4$ crystals. The decomposition of the emission spectra into three bands and the Stokes shift were close to the results for $ZnWO_4$ crystals. The laser spectroscopy revealed decay behavior similar to that for $ZnWO_4$ crystals. Raman spectroscopy on the glasses showed the presence of WO_6 groups in the glass. We conclude that the origin of the luminescence of the glasses is the same as that of $ZnWO_4$. The luminescence in the glass is an intrinsic feature of the WO_6 group. It results from the electronic excitation of O(2p) to W(5d) energy levels and the following decay in the WO_6 groups of the glass.

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1. Introduction

The search for rare-earth-metal-free luminescent glasses is still an active research field, and new rare-earth-metal-free glasses based on zinc phosphate have been found [1,2]. One of those glass systems is WO_3—P_2O_5—ZnO. The luminescence of WO_3—P_2O_5—ZnO glass was first observed by Inoue et al. [3] using a combinatorial glass-melting apparatus. They observed luminescence only in a small region of the ternary-phase diagram. However, the origin of the luminescence was never determined. In the preliminary work of this study, the same glass compositions were prepared and orange luminescence was found.

Blue luminescence has been reported in MWO_4 (M cations: Zn [4–9], Ca [9], Cd [7,8,10], Pb [11,12]) crystals. Depending on the cation, two possible complex anions, the tetrahedral $(WO_4)^{2-}$ group and the octahedral $(WO_6)^{6-}$ group, exist in MWO_4 crystals. It is known that the atoms in these complexes are tightly bound.

It is reasonable to choose $ZnWO_4$ as a basis for comparison with our data due to the materials used. Its blue luminescence is an intrinsic feature of the distorted octahedral WO_6 groups in the crystal [13]. We began our study with the assumption that the WO_6 groups are preserved in the glass. This publication shall clarify the reason for the blue luminescence observed in the ternary glass system. The clarification of the origin is important in developing new luminescent glasses free from rare-earth ions.

2. Experimental

Pure WO_3 (Rare Metallic Co.), $NH_4H_2PO_4$ (Kanto Chemical Co.) and ZnO (Kanto Chemical Co.) with purities of 99.9%, 99.0% and 99.9% were used, respectively, for the glass batches. The three compounds were mixed for several minutes, and 5-g amounts were added to alumina and silica crucibles, respectively. The mixed powders were melted under two different melting conditions. Under condition 1, the powders were melted at a temperature of 1200 °C for 30 min. Under condition 2, the powders were placed in the furnace at a temperature of 600 °C for 1 h, heated up to 1300 °C with a heating rate of 10 °C/min and kept at that temperature for 2 h. The glasses were melted using a combinatorial glass melting apparatus [3] and a furnace (Advantec KSH-2S).

For the X-ray powder diffraction (XRD) measurement, a Rigaku RINT2200V diffractometer was used in continuous mode with Cu Kα radiation (40 kV/40 mA). The samples were scanned from 10° to 70° with a scan speed of 1 deg./min. Raman spectra were measured using a Nd:YAG laser (λ = 1064 nm, power = 1000 mW) of a NIR-FT Raman spectroscope (Perkin Elmer Spectrum GX2000R). Raman shifts were measured from 200 cm^{-1} to 1200 cm^{-1} at room temperature. The resolution was set to 4 cm^{-1}. To measure the luminescence, the glasses were polished. The excitation and emission spectra were obtained with 520 nm and 320 nm light from a Hitachi F4500 spectrometer. Decay times were obtained with a Ti:sapphire laser using a wavelength of 267 nm and an output power of 800 mW.

3. Results and discussion

The ternary diagrams for melting condition 1 and condition 2 using alumina crucibles are shown in Fig. 1. The phases for the

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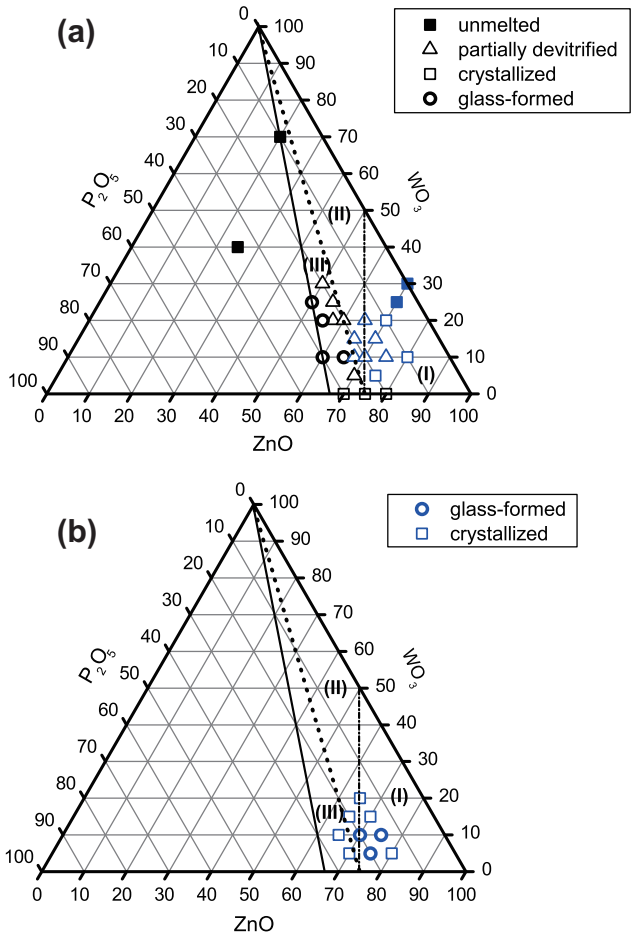

Fig. 1. Ternary diagrams for melting conditions 1 (a) and 2 (b); the lines represent binary systems: WO_3—$Zn_2P_2O_7$ (black line), WO_3—$Zn_3(PO_4)_2$ (dotted line) and $ZnWO_4$—$Zn_3(PO_4)_2$ (dash-dotted line); phases of region (I)–(III) are given in the text; blue symbols represent the samples that showed luminescence. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

crystallized WO_3—P_2O_5—ZnO system have already been investigated by Yin et al. [14]. The lines in Fig. 1 are taken from their publication and represent binary systems. The phases of each triangle are: (I) $Zn_3(PO_4)_2$, $ZnWO_4$, ZnO; (II) $Zn_3(PO_4)_2$, $ZnWO_4$, WO_3; (III) $Zn_3(PO_4)_2$, $ZnWO_4$, and $Zn_2P_2O_7$. Under melting condition 1, glasses were obtained with P_2O_5 contents of 25% or higher. Those glasses had a dark blue color and showed no luminescence. The other samples showed luminescence, but they were partially or completely crystallized. Under melting condition 2, glasses were obtained in only a small area of the ternary diagram. Further, glasses were only formed when heated in alumina crucibles. Those glasses were colorless and transparent, showed luminescence under irradiation with UV-light and were covered with a surface layer of white crystals. Small white inclusions of the glass near the surface were also visible to the naked eye.

Glass with less surface crystallization and inclusions was obtained with the batch composition of $10WO_3$—$20P_2O_5$—70ZnO (in mol%). The glass transition temperature T_g was determined to be 470 °C. This composition corresponds to a binary system consisting of $ZnWO_4$ and $Zn_3(PO_4)_2$ in the crystallized state; see the dash-dotted line in Fig. 1.

Luminescent samples (crystals and glasses) show emission in the region (I)–(III) containing crystallized $ZnWO_4$, which is known for its blue luminescence [4,5]. $Zn_3(PO_4)_2$ was also present, but is not likely to have been the origin of the blue luminescence, since zinc phosphate usually acts as a glass former. Furthermore, luminescence has only been observed in $Zn_3(PO_4)_2$ crystals containing additional ions such as Ag or Mn [1,15]. This indicates that the origin of the luminescence in the glass and in the $ZnWO_4$ crystal may have been the same.

Table 1 shows the result of chemical analysis of a crystallized and a glassy sample (ratios given in mol%) which were prepared under condition 1 and condition 2 in alumina crucibles, respectively. Besides the three expected elements, Al_2O_3 was found in large amounts. The compositions of the crystallized sample (melted under condition 1) and the glass (melted under condition 2) were almost identical. The different heat treatments seem to have been the reason for the different phases. The analyzed and expected concentrations for WO_3 and P_2O_5 differed up to 1 mol%. Measured values for ZnO were somewhat surprising; the expected ZnO contents were greater than the measured ones. This indicates that the glass melt reacted with the alumina crucibles. Al_2O_3 is known to be an intermediate oxide in glasses and may play a role in the glass formation because only samples heated in alumina crucibles became glass, as mentioned above.

The XRD measurements of the glass samples were performed after removing the crystallized surface layer by polishing. Fig. 2 shows the XRD patterns of two compositions, with Fig. 2b and c showing patterns of $10WO_3$—$20P_2O_5$—70ZnO and $5WO_3$—$20P_2O_5$—75ZnO, respectively, melted under condition 2. Pattern (a) is the $10WO_3$—$20P_2O_5$—70ZnO composition melted under condition 1. The peaks in pattern (a) were identified as $ZnWO_4$ (JSPDS No.: 88-0251) and α- and γ-$Zn_3(PO_4)_2$ crystals (JSPDS No.: 29-1390, 30-1490) and coincide with the ternary phase diagram. Patterns (b) and (c) are almost completely amorphous. In addition, the crystals themselves were not responsible for the blue emission in the glass, as clarified below.

The Raman spectra of $10WO_3$—$20P_2O_5$—70ZnO and $5WO_3$—$20P_2O_5$—75ZnO glasses are shown in Fig. 3. For the $10WO_3$—$20P_2O_5$—70ZnO glass, there are main peaks at 332 cm^{-1}, 564 cm^{-1} and 980 cm^{-1}. The band at 332 cm^{-1} has a small shoulder and can be deconvoluted into two bands of 333 cm^{-1} and 405 cm^{-1}. The band peaking at 980 cm^{-1} also has a shoulder and was decomposed into two bands at 980 cm^{-1} and 954 cm^{-1}. For the bands of $5WO_3$—$20P_2O_5$—75ZnO glass, a small shift could be observed.

According to Brow et al. [16], the following peaks can be assigned to zinc phosphate glass: 333 cm^{-1}, 564 cm^{-1} and 980 cm^{-1}. Comparing these data with the Raman spectra of $ZnWO_4$ crystals [17,18], we assigned the peaks at 405 cm^{-1} and 954 cm^{-1} to the internal modes of WO_6 groups—bending and symmetric stretch modes, respectively—although these peaks were shifted about 60 cm^{-1} to higher wavenumbers than those of the crystals. In the case of Rb_2O—MgO—WO_3—P_2O_5 glass, the Raman peak assigned to WO_6 octahedra appeared at 930 cm^{-1}, which is 20 cm^{-1} higher than in the crystals [19]. The distortion of the WO_6 octahedra is suggested to be more pronounced than that of the crystals. On the other hand, the band peak at 954 cm^{-1} is close to the observed one in WO_3—TeO_2 glasses, and has been assigned to W=O stretching vibrations [20]. In the $ZnWO_4$ crystals, the structures are supposed to be composed of ZnO_6 and WO_6 octahe-

Table 1
Measured compound concentration in the $10WO_3$—$20P_2O_5$—70ZnO ternary system for a crystallized sample (melted under condition 1) and a glass (melted under condition 2) in mol%.

Compounds	Al_2O_3	WO_3	P_2O_5	ZnO
Crystal	6.4	9.4	21.0	63.2
Glass	7.2	9.8	20.0	63.0

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