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Special effects of YbF_3 on the structural changes for fluorophosphate glass

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Abstract

From Raman and IR spectra, obvious differences of the glass structure were observed in non-Yb^{3+}-doped and Yb^{3+}-doped fluorophosphate glasses. Results showed that Yb^{3+} ions can induce, in a better glass, polymerization and network uniformity. Compared with the monophosphate-mastered Yb^{3+}-free glass, Yb^{3+}-doped glass has a pyrophosphate environment. The main building blocks in Yb^{3+}-doped samples are metaphosphate groups, pyrophosphate groups ($P_2(O,F)_7$,PO_3F), $Al[F_6]+Al[O,F]_6$ and $F_3Al–O–AlF_3$ while those of the Yb^{3+}-free glasses are monophosphate groups $P(O,F)_4$, little pyrophosphate groups, $Al[F_4]+Al[F_6]+Al[O,F]_4+Al[O,F]_6$ and $F_3Al–O–AlF_3$. The DSC analysis also showed a slight increase in crystallization stability.

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1. Introduction

In recent years, Yb^{3+}-doped fluorophosphate (FP) glass has been recognized as one of the laser materials fit for high-power ultra-short-pulse amplifications and tunable laser sources [1,2]. A great variety of rare-earth (RE)- doped FP glasses were developed and most of the researches focused on the studies for the spectroscopic and lasing properties of the glasses [3–5]. But little work is done on the structure of these RE-doped glasses, especially for the structural and glass-forming ability changes caused by RE fluorides. It is known that glass properties are governed by its structure, which in turn depends on its chemical composition. Zhang and Poulain [6] figured out that RE fluorides are dopants as well as glass-forming components, but did not give out

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experimental demonstration. Also, the structure of FP glass is very complicated, because with different P/F ratios, glass structure changes greatly. But many characteristic vibration bands relating to some phosphate groups and fluorides can still be distinguished. Then, with the combination of IR and Raman spectra, the possible structure of the glass can be roughly determined. The aim of this work is to investigate the structural change of a FP glass caused by the introduction of Yb^{3+} ions and the effect of Yb^{3+} ions on the glass-forming abilities.

2. Experiments

Four original glasses were prepared according to the glass compositions listed in Table 1. Then another four glasses of the same compositions but with extra 1 mol% YbF_3 were made, and continuing experiment was done to determine the glass-forming range of this system with the method of RF_2 substituting BaF_2. 4 N purity of YbF_3 is used in the experiment. All other raw materials are reagent grade. Each batch was melted at 1000 °C in a covered platinum crucible with a nitrogen downpipe for stirring. After refining, melts were cast into a steel mould and properly annealed to room temperature.

Raman spectra were recorded by the LabRam-IB Micro-Raman Spectrometer, a 6 mW He–Ne laser was used as the excitation source. The IR absorption spectra of powder samples in the range 500–1500 cm^{-1} were taken using KBr by the Thermo Nicolet NEXU FT–IR Spectrophotometer. T_g and T_x values are recorded by DSC method.

Table 1
Glass composition

Glass no.	Composition
1	$20Al(PO_3)_3 \cdot 72BaF_2 \cdot 8MgF_2$
2	$20Al(PO_3)_3 \cdot 57BaF_2 \cdot 23MgF_2$
3	$20Al(PO_3)_3 \cdot 57BaF_2 \cdot 23CaF_2$
4	$20Al(PO_3)_3 \cdot 57BaF_2 \cdot 23SrF_2$
5	$20Al(PO_3)_3 \cdot 72BaF_2 \cdot 8MgF_2 \cdot 1YbF_3$
6	$20Al(PO_3)_3 \cdot 57BaF_2 \cdot 23MgF_2 \cdot 1YbF_3$
7	$20Al(PO_3)_3 \cdot 57BaF_2 \cdot 23CaF_2 \cdot 1YbF_3$
8	$20Al(PO_3)_3 \cdot 57BaF_2 \cdot 23SrF_2 \cdot 1YbF_3$

3. Results and discussion

Fig. 1 is the Raman spectra of samples 1–4 which are YbF_3 free.

$Al(PO_3)_3$ has three main vibration bands: metaphosphate groups at 1220 cm^{-1}(O–P–O) and 715 cm^{-1}(P–O–P) , and Al–O bond at 310 cm^{-1}. With the addition of F^-, 1220 cm^{-1} band will split into a pyrophosphate vibration at 1030–1070 cm^{-1} and a metaphosphate vibration at 1100–1140 cm^{-1} [7]. In studied glasses, no metaphosphate band is observed in 1100–1140 cm^{-1} in samples 1–4, this showed the heavy depolymerization of the metaphosphate chains in Yb^{3+}-free glasses. According to the literature [8,9], the bands around 995 cm^{-1} can be associated with monophosphate groups $P(O,F)_4$, and the bands at 750 and 1050 cm^{-1} with diphosphate groups, while at the same time, Videau et al. [10] and Zhmyreva et al. [11] assigned the 750 cm^{-1} band to the vibrations of P–F of fluoride chain formation. Compared with the 715 cm^{-1} band in $Al(PO_3)_3$, the 750 cm^{-1} band in this FP system has a ~35 cm^{-1} shift to large wave number, indicating that the vibration groups change from metaphosphate (POP) to

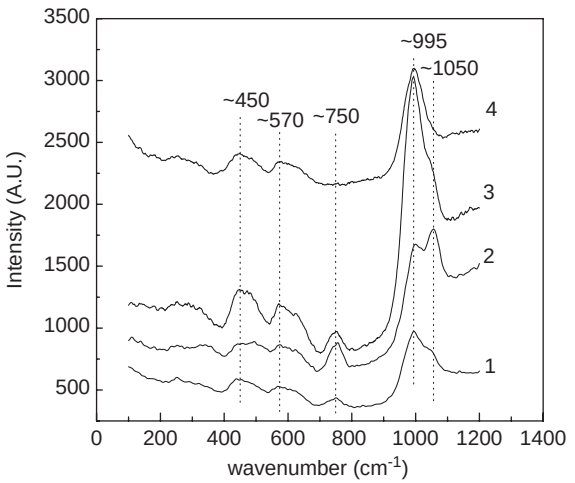

Fig. 1. Raman spectra of non-Yb^{3+}-doped FP glasses with different alkali-earth fluorides.