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Review

Preparation and properties of rare-earth containing oxide fluoride glasses

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Abstract

The preparation of the rare earth containing oxide fluoride glasses LnF_3 (Ln; Y through Lu)–BaF_2–AlF_3–GeO_2 in which the nominal content of LnF_3 reached 60 mol% in maximum and their basic properties such as density, refractive index and glass transition temperature were investigated and summarized in detail. Especially, in order to discuss the local structure around the rare earth ion in the glass, the Judd–Ofelt analysis (discussion with Ω parameters) of the HoF_3–BaF_2–AlF_3–GeO_2 glasses was carried out. The unique fluorescent behavior and the magnetic properties of LnF_3–BaF_2–AlF_3–GeO_2 glasses (Ln = Tb and/or Sm) were also studied.

Keywords: Oxide fluoride glass; Preparation; Rare earth; Optical property; Magnetic property

Contents

1. Introduction

Our previous works have revealed that the solid electrolyte written by $Ln_2Ln'_2O_3F_6$ where Ln and Ln′ are different rare earths showed higher conductivity than that of YSZ; it has usefully stable for an oxide ion-conducting solid electrode under 700 °C [1]. Their conductivity performance depends on the combination of rare earth elements. The Nd–Sm system and Nd–Eu system showed the highest conductivity among all combinations. During the preparation process of the material of the solid electrolyte, a glass was obtained by chance. From quantitative analysis using EPMA, this glass evidently contained all starting elements (O, F and two species of rare earth elements). In addition, Si and Al, which were not contained in starting materials, were detected in the glass. The binary rare earth oxide fluoride solid electrode was prepared using a solid state reaction between a rare earth oxide (Ln_2O_3) and a rare earth fluoride ($Ln'F_3$) at a temperature higher than 1000 °C. During the mixing process, an agate ball mill was used to mix the starting materials. During calcination, the mixture was heated to over 1000 °C after it was packed into an alumina tube. The Si and Al in the glass had to be supplied from these

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materials as glass network formers. This glass was shown to contain more than 70 wt% of rare earth elements from results of the analysis using EPMA (FP method). The obtained glass was a new oxide fluoride glass containing a large amount of rare earth element. Several reports have described preparation of glasses containing rare earth elements for use as optical or magneto-optical materials [2–6]. Every rare earth element has unique optical properties because of its arrangement of electrons in the 4f orbital. It is important to find matrices in which these rare earth elements can be doped and can exhibit their performance to develop new optical and magnetic materials. Oxide fluoride glasses contain two different anions that have different valence electrons and different degrees of polarization. It is interesting to compare properties of the oxide fluoride glass with those of the oxide or fluoride glass. No reports have addressed a glass that can contain rare earth fluoride with such a high content. The properties of oxide fluoride glasses have not been summarized systematically yet, as they have been for oxide glasses or fluoride glasses. It is very interesting to study the preparation processes and characteristics of these glasses to develop new functional materials. In this paper, several recent results about rare-earth containing oxide fluoride glasses are reported.

2. Results and discussion

2.1. Preparation and basic characteristics of oxide fluoride glasses containing LnF_3

This section describes the preparation process and basic characterization of oxide fluoride glasses containing NdF_3 (light rare earth), TbF_3 (middle rare earth), and HoF_3 (heavy rare earth). Based on those results, preparation methods could be extended to other rare earth elements in the lanthanide series. Properties of those glasses were compared and summarized.

2.1.1. Preparation of oxide fluoride glasses containing LnF_3

The glass in the NdF_3–SiO_2–Al_2O_3 system has been obtained once. However, the reproducibility was not confirmed. After analyzing the glass in detail, it seemed that AlF_3 could be contained in the product in NdF_3–SiO_2–Al_2O_3 system. It means that some part of NdF_3 has been hydrolyzed to form HF and this HF has reacted with Al_2O_3 to form AlF_3. Controlling the content of AlF_3 seems to be important factor to prepare the oxide fluoride glass reproducibly. But the higher temperature for melting the sample causes large variation of the AlF_3 content in the product because AlF_3 sublimes at a temperature higher than 1000 °C remarkably. In addition, rare earth trifluorides easily undergoes pyro-hydrolysis to form their oxides over 1000 °C [7]. As the network forming oxide GeO_2 was chosen because of the lowest melting point among SiO_2 (1730 °C), Al_2O_3 (2045 °C) and GeO_2 (116 °C) in this study. In addition, various fluorides were tested as glass network modifiers and additives to lower the melting point. Consequently, the oxide fluoride glasses containing light rare earth (NdF_3) became to be obtainable in the system of NdF_3–AlF_3–GeO_2 reproducibly. Fig. 1 shows a phase diagram of the

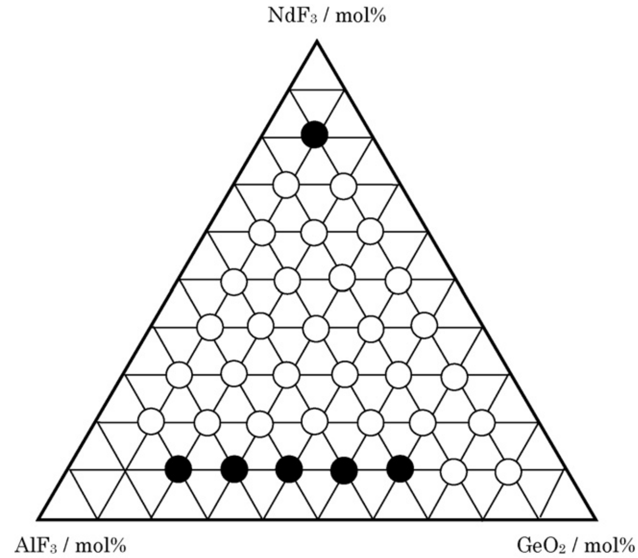

Fig. 1. Phase diagram of NdF_3–AlF_3–GeO_2 system shown by nominal composition. Closed and open circles, respectively, indicate crystal and glass phases.

NdF_3–AlF_3–GeO_2 system. It had a wide glass formation composition area. The glass was capable of containing 70 mol% NdF_3 as a nominal composition. These glasses containing NdF_3 showed the alexandrite effect. That is, the color of obtained glass showed red-violet under continuous light like sunlight and blue-violet under discontinuous light like fluorescent light. Quantitative analyses by ZAF method using EPMA showed clearly that the obtained glass was incapable of maintaining its nominal composition. Fig. 2 shows the cationic composition in the products of NdF_3–AlF_3–GeO_2 system measured by using EPMA. Contents of Al especially tended to decrease from the starting ratio. The Al contents in the glass never became greater than 34 mol%, even if the starting material contained more than 34 mol% Al. The Nd content reached 63 mol% as the maximum value. Glasses with the rare earth content more than 30 mol% have not been reported yet. These oxide fluoride glasses with a high content of rare earths are anticipated as new functional materials.

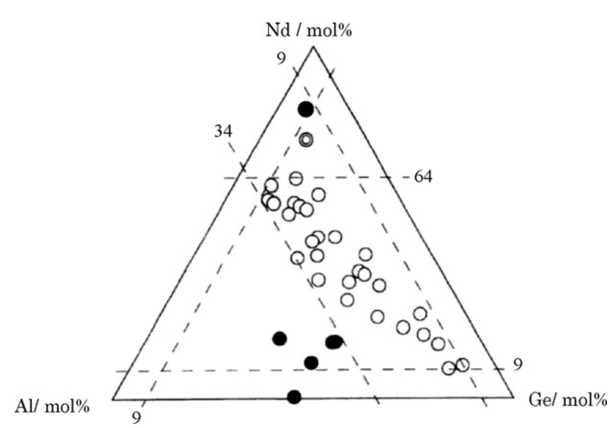

Fig. 2. Cationic composition in the glass of NdF_3–AlF_3–GeO_2 system measured by EPMA. Closed and open circles, respectively, indicate crystal and glass phases.