# 論文 / 著書情報
# Article / Book Information

| | |
|---|---|
| 論題(和文) | |
| Title | Redox equilibrium of Rare-Earth Ions in Chlorine-and Bromine-Doped Fluoroaluminate Glasses |
| 著者(和文) | 矢野哲司, 山崎 浩二, 柴田 修一, 山根正之, 井上悟 |
| Authors | Tetsuji Yano, Kouji Yamazaki, S. Shibata, masayuki yamane, Satoru Inoue |
| 出典 / Citation | J. Ceram. Soc. Jpn, Vol. 105, No. , pp. 635 |
| Citation(English) | J. Ceram. Soc. Jpn, Vol. 105, No. , pp. 635 |
| 発行日 / Pub. date | 1997, |

Journal of the Ceramic Society of Japan 105 [8] 635-637 (1997) Paper

# Redox Equilibrium of Rare-Earth Ions in Chlorine- and Bromine-Doped Fluoroaluminate Glasses

Tetsuji YANO, Koji YAMAZAKI, Shuichi SHIBATA, Masayuki YAMANE and Satoru INOUE*

*Department of Inorganic Materials, Faculty of Engineering, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152*
**National Institute for Research in Inorganic Materials, 1-1, Namiki, Tsukuba-shi, Ibaraki 305*

# 塩化物イオン及び臭化物イオン添加フッ化アルミニウム系ガラスにおける希土類金属イオンの酸化還元平衡

矢野哲司・山崎浩二・柴田修一・山根正之・井上 悟*

東京工業大学工学部無機材料工学科，152 東京都目黒区大岡山 2-12-1
*無機材質研究所，305 茨城県つくば市並木 1-1

**The effect of chloride and/or bromide ions on the redox equilibrium of rare-earth ions, Sm and Yb, was investigated in an $AlF_3$-based YABC glass system. The large absorption bands of 4f-5d transition of $Sm^{2+}$ and $Yb^{2+}$ ions were found in the chlorine-doped samples in the visible and ultra-violet regions, respectively. Their intensities increased with the degree of incorporation. Change in the redox equilibrium of Yb ions was found to be a function of both the quantity and type of non-fluoride halide ions used as dopants. $Br^-$ was about 6 times more efficient than $Cl^-$ and co-doping resulted in a greater number of divalent $Yb^{2+}$ ions. X-ray photoelectron spectra of Y3d and the thermodynamics data of various halide compounds and molecules reveal that the direct bond formation between rare-earth ions and non-fluoride ions and the lower free energies of mixed halide molecules would play key roles in the formation of divalent rare-earth ions in the glass melts.**

[Received March 5, 1997; Accepted May 9, 1997]

***Key-words :*** *Redox equilibrium, Fluoroaluminate glasses, Rare earth, Chlorine, Bromine*

## 1. Introduction

Multicomponent fluoride glass systems have been studied extensively owing to their inherent advantage as host materials for laser-active rare-earth metal ions. When compared to oxide glass systems, multicomponent fluoride glass systems attain high efficiency with high gain in laser oscillation. Most studies, however, have focused on the 4f-4f transitions of rare-earth ions, although there are some unique characteristics which are known about laser oscillation based on 4f-5d transitions in reduced state. Characteristics of 5d orbitals sensitive to the crystal field strength lead to vibronic broadening of the laser transition. For instance, a $Ce^{3+}$-doped $LiSrAlF_6$ crystal shows laser oscillation in the ultra-violet range by pumping FHG Nd : YAG laser and high gain has been reported.[1] In fluoride glass systems, the formations of $Eu^{2+}$ ions in $ZrF_4$-$BaF_2$ based ZBLANP,[2] and $Ce^{3+}$, $Sm^{2+}$, $Eu^{2+}$ and $Yb^{2+}$ in $AlF_3$-based fluoride glass[3] by melting each type of glass in an atmosphere containing hydrogen has been reported. In the case of $AlF_3$-based fluoride glass, strong and broad luminescence has been observed in the ultra-violet region for $Ce^{3+}$ and in the blue to green region for $Yb^{2+}$ ions. In addition, high quantum efficiencies have been estimated to be near 100% compared with that of oxide glass matrices. However, the samples obtained had a somewhat black appearance probably due to a change in the matrix glass components due to the use of a strongly reducing atmosphere. This is an important issue in the preparation of laser glass materials containing rare-earth ions in a reduced valence state. Amongst various fluoride glass systems, the $AlF_3$-based YABC system is considered to be one of the most resistant glasses to a reducing atmosphere, and has potential optical properties as a laser host material with properties such as high transparency in the ultra-violet region, and a low nonlinear refractive index.

In this report, we present a procedure for the formation of reduced rare-earth ions in a $YF_3$-$AlF_3$-$BaF_2$-$CaF_2$ system without using reducing atmospheric control, but through the incorporation of the non-fluoride halide ions, $Cl^-$ and $Br^-$. In the discussion, the mechanisms determining the effects of the halide ions in this glass system are discussed.

## 2. Experimental procedures

The base composition of the glass studied was $20YF_3$-$40AlF_3$-$20BaF_2$-$20CaF_2$ (mol%). Rare-earth ions ($SmF_3$ or $YbF_3$) and non-fluorine halides ($BaCl_2$ and/or $BaBr_2$, $YBr_3$) were incorporated by replacing parts of the $BaF_2$ and $YF_3$, respectively. The amount of rare-earth fluoride dopants was fixed at 1 mol%, and the amount of non-fluoride halide compounds were varied from 0 to 7.5 mol%. All procedures from batch preparation to annealing were performed in a glove box filled with $N_2$ gas. A 20 g-batch mixture of high-purity fluoride, chloride and bromide raw materials (>99.9%, Rare Metallic Co.) was placed in a vitreous carbon crucible and heated at a rate of 10°C/min. At 1000°C, it was held constant for 2h. Inside the furnace (inner volume $\approx 2$ *l*), the atmosphere was controlled by flowing $N_2$ gas (99.9995%, $pO_2 \sim 0.01$ Pa) through at a rate of 300 ml/min. The melt was poured into a preheated carbon mold at 380-400°C and held at just above the glass transition temperature for 1h, after which it was slowly cooled at 2°C/min. The dimensions of the glass samples obtained were about 15 mm × 40 mm × 10 mm. In order to obtain standard samples in which all the rare-earth ions were in a trivalent state, the oxidation agent, $InF_3$, was added to the base glass with 1 mol% rare-earth elements, and batches were melted under a $NF_3/N_2$ atmosphere. For comparison, other samples were also prepared by melting under a $H_2$/Ar atmosphere, to ascertain the effect of an atmosphere containing hydrogen.

The sample compositions were analyzed using inductively-coupled plasma spectroscopy (SII, SPS-1500VR) for cations and ion-chromatography (Dionex, 4520i) for anions.

The samples were dissolved in 1N $HNO_3$ aqueous solution and diluted to the appropriate concentration for respective analysis.

The absorption spectra of the glass samples were recorded in the range of UV to near IR. The sample thickness was changed depending on the absorbance of the transitions of the rare-earth ions. The ratio of divalent/trivalent rare-earth ions was estimated from changes in absorption of the 4f-4f transitions of the trivalent ions, because the transition probabilities are less sensitive to the matrix changes.

## 3. Results

All the obtained glass samples melted under $N_2$ atmosphere were transparent and did not contain any blackish inclusions. The samples containing Yb ions were colorless, while those with Sm ions appeared orange due to the 4f-5d transition of $Sm^{2+}$ ions. However, the samples that had been melted under $H_2$/Ar atmosphere had a blackish or yellowish color and did not have a high degree of transparency for thicker samples. This same phenomena was reported by Verway and Blasse[3] and is probably due to the change in the matrix components induced by the reducing atmosphere.

Figures 1 and 2 show the absorption spectra of the Sm- and Yb-doped samples with various chlorine content,

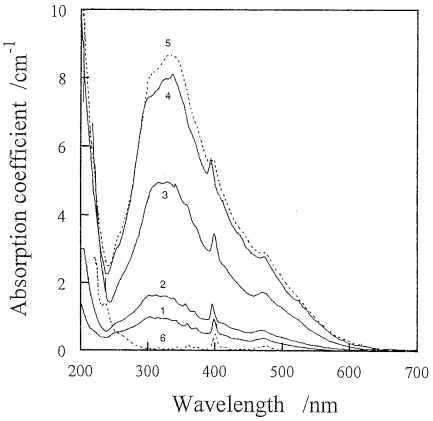


Fig. 1. Absorption spectra of Sm-doped sample glasses of various chlorine content. Solid lines 1-4: samples with 0, 1.9, 3.8, 5.8 anion% $Cl^-$ melted , respectively. Dashed line 5: sample with 5.8 anion% $Cl^-$ melted under $H_2$/Ar atmosphere. Dashed line 6: $Cl^-$-free sample melted under $NF_3/N_2$ atmosphere.

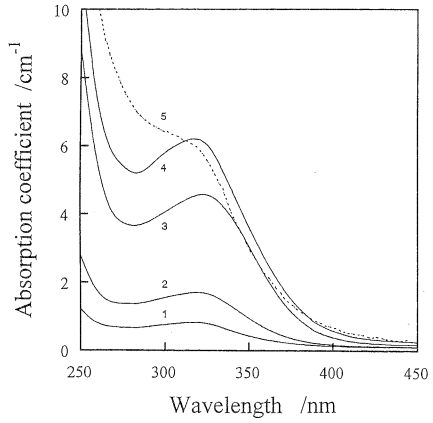


Fig. 2. Absorption spectra of Yb-doped sample glasses of various chlorine content. Solid lines 1-4: samples with 0, 1.9, 3.8, 5.8 anion% $Cl^-$. Dashed line 5: sample with 5.8 anion% $Cl^-$ melted under $H_2$/Ar atmosphere.

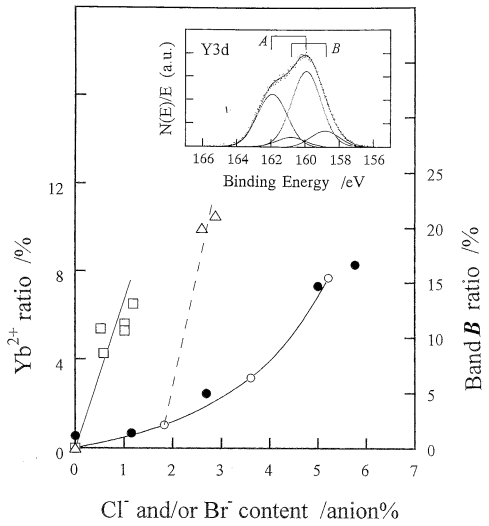


Fig. 3. Plots of $Yb^{2+}/(Yb^{2+}+Yb^{3+})$ ratio against non-fluorine concentration. Inset figure shows the Y3d XPS spectrum of the 5.8 anion% $Cl^-$-doped YABC glass sample taken from Ref. 7). The closed circles show the band ratio of the band *B* in XPS spectra.

respectively. For reference, the figures include the spectra of samples melted under oxidation and reduction conditions using $NF_3$ and $H_2$ gas, respectively. Chlorine incorporation clearly produced a large absorption band which had a peak at 400 nm in the Sm-doped samples and at 310 nm in the Yb-doped samples, respectively. These peaks can be assigned to the 4f-5d transition of rare-earth ions in a divalent state. The band intensity increased with chlorine concentration, and that of the sample with 5.8 anion% chlorine was comparable with that of the sample melted under a reducing atmosphere. In the case of Yb-doped systems, the spectra of all the samples containing chloride ions had a well-resolved 4f-5d transition peak at 310 nm, while that of the glass melted under a $H_2$-gas atmosphere showed a broad shoulder at the same wavelength. In order to evaluate the effect of the chlorine in producing divalent rare-earth ions, the ratio in the amount of divalent rare-earth ions was estimated from changes in the peak intensity of the $^2F_{7/2}$-$^2F_{5/2}$ transition of $Yb^{3+}$ in the near IR range. Figure 3 shows the ratio of $Yb^{2+}/(Yb^{2+}+Yb^{3+})$ to $Cl^-$ and/or $Br^-$ ions dopants. As the quantity of $Cl^-$ ions increased, the $Yb^{2+}$ ratio increased in a quadratic manner with about 8% of the ytterbium ions having been converted from a trivalent to a divalent state at 5.8 anion% $Cl^-$ doping. In case of $Br^-$ ions, their incorporation showed a higher efficiency in the reduction of $Yb^{3+}$ ions, with about 6 times the amount of $Yb^{2+}$ ions being produced with the same amount of incorporation. The open-triangle plots in Fig. 3 represent the results for the $Cl^-$ and $Br^-$ co-doped samples, where the contents of ($Cl^-$, $Br^-$) were (1.88, 0.72) and (1.78, 1.10) in anion%, and the $Yb^{2+}$ ratios were 10.0 and 10.5%, respectively. These values were about 20% greater than the sum of the values collected for single-doped cases. This suggests the existence of some multiple effects between $Cl^-$ and $Br^-$.

## 4. Discussion

Redox equilibria of metal ions in glass have been extensively studied in the oxide system and the effect of the glass composition has been interpreted by considering the formation of oxyanions in melts, where the redox equilibrium is represented as follows;

$$[M^mO_x]^{(2x-m)-} + (n/2)O^{2-} = [M^{m-n}O_x]^{(2x-m+n)-} + (n/4)O_2$$

The melting atmosphere influences this reaction through the partial pressure of $O_2$ gas and the glass composition has an effect through oxide-ion activity $[O^{2-}]$. The latter is usually scaled arbitrary in terms of the basicity of glass. For halide systems, Angell and Bennett[4] measured the optical basicities of some chloride melts and Bruce and Duffy[5] measured those of fluoride melts. Their results suggest that the optical basicity concept would be applicable in each system. However, it has not been clearly ascertained whether the basicity concept is applicable to fluoride and mixed-halide glass systems such as the glasses investigated in this study. Nakamura et al.[6] investigated the optical basicity of fluoride and chloride compounds using data for $Pb^{2+}$ s-p transition spectra in $CaF_2$ and $CaCl_2$ and obtained $\Lambda$ values of 0.67, 0.72, 0.78 and 0.84 for $CaF_2$, $CaCl_2$, $BaF_2$ and $BaCl_2$, respectively. Since the quantities of non-fluoride dopants are small, changes in the glass basicity are also considered to be small. Consequently, it is probably reasonable to assume that the effect on rare-earth ions through the addition of non-fluoride halide ions into this glass system is not on the average of anion activity of the glass melt, but by some selective interaction. The authors[7] have previously reported evidence of the formation of direct bonds between yttrium and chlorine ions by Y3d X-ray photoelectron spectroscopy for $Cl^-$-doped YABC glasses as shown in an inset in Fig. 3. This yttrium ratio was estimated from the intensity of the band $B$ at lower binding energies. The data are also plotted along with the chlorine concentration in Fig. 3 (closed circles). It is increasing manner with $Cl^-$ content correlates quite well with that of the $Yb^{2+}$ ratio. Since the roles of $Y^{3+}$ and $Yb^{3+}$ ions in glass formation are identical,[8] non-fluorine ions are also incorporated into the polyhedra of rare-earth ions and the changes in the redox equilibrium should be induced by direct interaction between rare-earth ions and non-fluorine ions.

The differences in the efficiency of the redox changes found in $F^-$, $Cl^-$ and $Br^-$ can be ascertained by using thermochemical data.[9] As a simple example, the energy diagrams of calcium halide melts and various other halide molecules at 1300 K are shown in Fig. 4. Generally, fluoride compounds have a larger $-\Delta G_f$ value than those of chlorides and bromides, while mixed-halide systems have an even larger $-\Delta G_f$ value due to entropy. But since the glass melts investigated in this study contain such small quantities of non-fluoride ions, the respective melts can be said to have approximately the same $-\Delta G_f$ value. However, the different mixed-halide molecules each have quite unique $-\Delta G_f$ values. In the case of FCl and FBr molecules, their $-\Delta G_f$ values are 58.5 and 80.0 kJ/mol at 1300 K, while ClBr is 8.3 kJ/mol. This means that the free energy of a redox equilibrium depends mainly on the type of the gas molecule involved in the reaction. For the glass containing $Cl^-$ and/or $Br^-$ ions, the formation of FCl and/or FBr gas molecules are more probable energetically than that of $F_2$ gas. Similarly, the larger $-\Delta G_f$ value of FBr over that of FCl can account for the difference in the reducing efficiency between $Cl^-$ and $Br^-$ doping. Finally, the redox equilibrium of rare-earth ions in the fluoride glass melts investigated here might be expressed thus;

$$Re^{3+}(\text{in melt}) + 1/2F^-(\text{in melt}) + 1/2X^-(\text{in melt}) \leftrightarrow Re^{2+}(\text{in melt}) + 1/2FX(g)$$

where X=F, Cl or Br, and again, the equilibrium constant changes depending on the type of FX molecules at constant temperature and atmosphere.

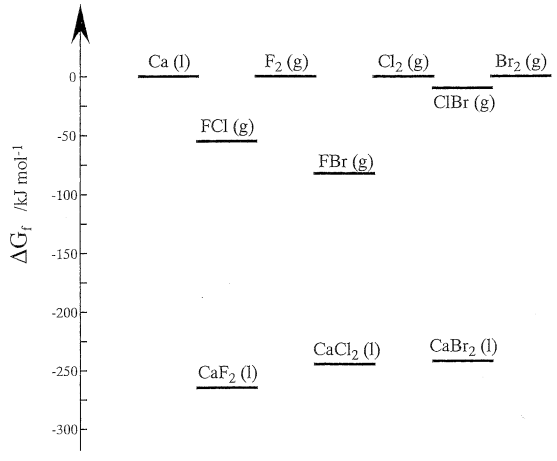


Fig. 4. Schematic energy diagram of various halide compounds and molecules at 1300°C. The energy values taken from the Ref. 9).

## 5. Conclusion

The formation of divalent rare-earth ions of $Sm^{2+}$, $Yb^{2+}$, in chlorine- and/or bromine-doped $AlF_3$-based fluoride glasses has been detected. The amount of reduced rare-earth ions increased with the dopant content. In case of 5.8 anion% chloride glass, the reducing effect was comparable with that of using a reducing atmosphere containing $H_2$ gas. The matrix of the glass did not lose optical quality. Bromine ions have a higher reducing efficiency than chlorine ions but co-doping with both chlorine and bromine was even more efficient. XPS and thermodynamic data suggested that non-fluoride ions interact directly with rare-earth ions and it is proposed that the formation of mixed halide molecules plays a key role in the redox equilibrium in melts.

## References

1) M. A. Dubinski, V. V. Semashko, A. K. Naumov, R. Yu. Abdulsabirov and S. L. Korableva, *J. Modern Opt.*, 40, 1–5 (1993).
2) P. W. France, M. G. Drexhage, J. M. Parker, M. W. Moore and J. V. Write, "Fluoride Glass Optical Fibres," Blackie, London (1990).
3) J. W. M. Verway and G. Blasse, *J. Phys. Chem. Solids*, 53, 1157–62 (1992).
4) C. A. Angell and P. D. Bennett, *J. Am. Chem. Soc.*, 104, 6304–09 (1982).
5) A. J. Bruce and J. A. Duffy, *J. Chem. Soc. Faraday Trans.*, 78, 907–14 (1982).
6) T. Nakamura, Y. Ueda and J. M. Toguri, *J. Jpn. Inst. Metals*, 50, 456–61 (1986).
7) T. Yano, J. Mizuno, S. Shibata, M. Yamane, S. Inoue and Y. Onoda, *J. Non-Cryst. Solids*, in press.
8) F. Lin, H. Zhang, H. Hu and F. Gan, *Mater. Sci. Forum*, 32–33, 595–600 (1988).
9) JANAF Thermochemical Tables, Third ed., in the series of J. Phys. Chem. Ref. Data, Vol. 14, Ed. by M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald and A. N. Syverud (1985).