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Local structure of lanthanum in fluoride or oxyfluoride at high temperature

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Introduction

Some of the light rare earth fluorides and oxyfluorides have the feature of superionic conductance at high temperature. To design the functional ceramics with fluorine conductance, the in-situ evaluation of local structure would be important. To obtain supercooling phase at ambient temperature effectively, the composition of the compounds and its ratio with inert matrix material are key parameters. In this report, the local structure of lanthanum in LaF_3, LaOF, LiF-LaF_3, and LiF-LaOF with boron nitride at various temperatures have been evaluated .

Experimental

EXAFS spectra of La L_{III}-edge (5.489 keV) were collected with a fixed time scan method by using Si (111) double crystal monochromator in transmission mode. Mixtures of LiF-LaF_3 (x_{LaF3} = 0.5) and LiF-LaOF (x_{LaOF} = 0.5) were melted once in a glassy carbon crucible at 1173 K in a glove box filled with an argon atmosphere in high purity. Then, they were mixed with boron nitride powder, and pressed into pellets. The mixing ratio is fixed to be 1 to 2.5 weight times of BN. To prevent from the chemical reaction during heating process in EXAFS measurements, these pellets were installed in a cell made with pyrolytic boron nitride and the electric furnace was filled with He gas under 30 kPa. EXAFS data were analysed by using the WinXAS ver.3.1.

Results and discussion

Figure 1 shows the Fourier transformed structure functions of each samples at various temperatures. In the case of (a) LaF_3, the 1st coordination distance which is corresponding to La^{3+} - F^- starts expanding over 700 °C, and does not go back to the value of initial one (2.049 – 2.199 – 2.099 Å). LaF_3 at higher temperature shows superionic conductance, thus this expanding feature of La^{3+} and F^- would be highly reflected by superconductivity. Due to high thermal conductivity of boron nitride matrix, the feature of superionic conductance would be partly kept after the sample cooled down. In the case of (b) LaOF, the nearest inter-ionic distance (La^{3+} - F^- or O^{2-}) once reduces at 500 °C and expands upto 900 °C. In this case also the distance does not go back to initial value but the descrepancy is less than that of previous case (2.049 – 2.274 – 2.074 Å). This specific feature depending on temperature was expected by the relocation of F^- and O^{2-} anions, but this ratio with matrix would not well match to this compound. The most striking feature shows in the case of (c) LiF-LaF_3, 1 to 1 mixture. The 1st coordination distance starts expanding again at 700 °C, but rapidly than in the case of (a). After the sample cooled down, the 1st coordination distance keeps still larger value (1.949 – 2.324 – 2.074 Å). This sample was expected to be molten at higher temperature, thus this feature would enhance keeping supercooled phase until ambient temperature. In the case of (d) LiF-LaOF, 1 to 1 mixture, the variation of spectra depending on temperature is similar to case (b) (2.049 – 2.224 – 2.099 Å), thus the sample would not be homogeniously molten. In the next step, the similar experiments with varied size and amount of boron nitride would be expected for optimization of the material design.

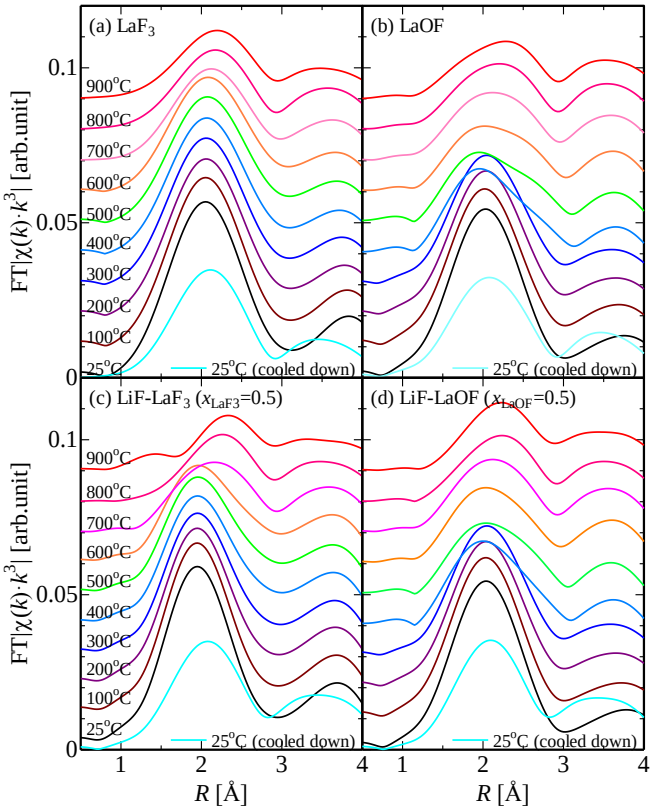

Fig. 1 EXAFS structure functions of (a) LaF_3, (b)LaOF, (c) LiF-LaF_3 (x_{LaF3} = 0.5), and (d) LiF-LaOF (x_{LaOF} = 0.5) at various temperatures upto 900 °C.

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