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XAFS analyses of molten metal fluorides

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ABSTRACT

X-ray absorption fine structure studies of molten metal fluorides containing the materials related to nuclear engineering are intensively summarized. By using XAFS spectra data of divalent and trivalent cation metal fluorides in molten state which have been collected by authors' group for a few years, local structure have been extracted and discussed systematically in conjunction with other spectroscopic studies and numerical calculations. In molten divalent fluorides, tetrahedral coordination of fluorides around a cation is predominant. In the case of pure molten trivalent fluorides, structure with more than 6-coordination has been suggested in some cases, but octahedral coordination structure is much stabilized at heavier rare earth metal fluorides. By mixing with alkali metal fluorides, it is a general trend that inter-ionic distances keep constant, but coordination number of fluorides decreases. In experimental chapter, all the details of sample preparation, furnace installation, X-ray optics setups and data analyses procedures are explained. Finally, future expectations of XAFS technique are also suggested.

1. Introduction

1.1. Molten metal fluoride in nuclear engineering: its brief history

Molten metal fluorides have often been utilized as media in pyro-metallurgic processes. One of the successful industrial processes is aluminium metallurgy. Also in nuclear technology, molten fluorides have attracted many interests. One of which is to apply for liquid fuel reactor system, e.g., molten salt reactor. This concept was proposed by Oak ridge national laboratory, and in practice, molten salt reactor experiment was performed successfully in 1960s. Unfortunately, this project was abandoned soon, but in the beginning of 2000s, molten salt reactor was selected to be developed as one of promising fission reactor candidates in Generation IV programme [1]. Compared to fission reactors using solid fuel, fuel recycle process would be rather simpler. However, a liquid fuel cleaning by metallic extraction of multi-processes is required to remove accumulated fission products and/or corrosion materials. Electrochemical methods depending on elements would be considered to be introduced.

Another possibility in the application of molten fluorides is pyrochemical reprocessing of nuclear fuels from fission reactors. Pyrochemical process has an advantage of compactness, and it leads to reduce secondary wastes evolved from treatment. At the moment, there is no concept using only molten fluorides from the beginning to the end of nuclear treatment processes, but its specific feature of completely different ordering of redox potential referring to that of molten chloride would evolve innovative concept. The processes by adding certain amounts of fluorides into molten chlorides have been examined to be applying to electrochemical treatment of spent nuclear fuels [2].

On the contrary to the wide application to fission reactor systems, there are quite a few examples applied to molten salt technology in the nuclear engineering field, one of which is molten fluoride system used as a blanket candidate in fusion reactors. Molten salt is utilized as a coolant as well as a tritium breeder medium. Historically, Flibe has mainly been considered to be used [3], but $LiF–PbF_2$ is also an alternative candidate in fusion reactor [4].

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Another application of molten salt is used as incineration media of radioactive materials at an accelerator driven system [5]. In this concept, the advantageous characteristics of large solubility of incinerated elements and good chemical resistance from irradiation can be utilized.

1.2. Several tasks for materialization of chemical processes using molten fluorides

The main problem of molten fluorides is strong corrosive nature, thus oxides should be avoided to be used as any material directly contacted. Because of this reason, the materialization using molten fluorides for industrial processes has been regarded to be difficult, but according to accumulation of several experiences in using fluorides, Ni-based alloys, refractory metals, glassy carbon, boron nitride and oxide-free ceramics, e.g., SiC and AlN are considered to have enough stabilities to the reaction with molten fluorides. However, to apply to nuclear technology process, these materials are kept under irradiated condition, thus in several cases, the development of multi-composite material would be required.

Molten salt is a typical model of liquids where coulombic interaction is predominant, thus compared with water and organic solutions, the numerical examination study would be much easier performed. Once the global model is constructed, it is easy to simulate the chemical behavior of species in experimentally difficult systems, since local structures and dynamic properties related to directly chemical engineering parameters in the processes should be highly correlated. However, compared with molten chlorides, structural information of molten fluorides has still been relatively limited. According to recent innovation of the investigation tools as well as accumulated experiences of handling materials, several publications appear in this decade.

1.3. Spectroscopic studies

Classical infrared and ultraviolet–visible spectroscopic techniques have been well utilized at evaluation of chemical species in liquids. In the case of molten fluorides, as mentioned above, these techniques are extremely difficult, since oxide glasses as optical windows are impossible to be used. Probably these techniques are applicable if either the samples in multi-component fluorides at reduced temperature or the samples containing less concentration of fluoride can be prepared.

Raman spectroscopy is frontier technique in the investigation of molten fluorides. Classically Oak ridge national laboratory performed it to obtain the spectra [6]. Since Belgian group designed carbon windowless cell, a lot of publications have appeared until now [7]. Greek group has published a lot of systematic investigations [8]. Raman spectroscopy is an excellent tool to investigate strong covalent interacted liquids, such as network-like structure, but when more than two contributions of species are overlapped in the spectra, it is very difficult to identify each contribution. If we would expect to obtain the spectra in high resolution, the concentration focused should be enough to be observed, ca. more than 5 mol% of composition of the molten mixture systems. Referring to crystal structure of known solid phase, several species can be conjectured to exist in molten state, however, the information obtained is global, and main discussion can be done by how is the difference from symmetrical structure.

Nuclear magnetic resonance (NMR) spectroscopy is also an excellent tool of the investigation on molten fluoride, since the chemical shifts of ^{19}F and ^{139}La nuclei are very sensitive to the variation of local environment. French group has special probes only adapted to high temperature samples [9]. In this measurement, the samples confined in boron nitride crucible are heated by CO_2 laser heating system. An advantage of this technique is to look at local environment around focused atom in variety of compositions and compounds at various temperatures. But the structural information can be discussed by referring to the chemical shift values of crystal structures already known, and some nuclei which do not depend on the variation of local environment, e.g., ^{7}Li have been empirically recognized and some rare earth nuclei are difficult to be observed by NMR because of their paramagnetic characteristics.

X-ray absorption fine structure (XAFS) can be applied to various compounds and conditions to elucidate the local structure around a given atom. Its great advantage from other techniques is to be possible to derive concrete values of structural parameters, such as inter-ionic distances, coordination numbers and temperature factors, etc. [10]. French and Japanese group independently have developed how to materialize measurements on molten fluorides using synchrotron radiation X-rays. The advantage of XAFS is its flexibility on sample environment, but of course, there are limitations. This technique is mainly applied to the elements heavier than Sc, because of the energy range of X-ray. Historically, the analytical procedure tends to contain human's artifacts and model dependence.

In this review, we focus on XAFS studies on molten fluoride. First, we show some results of molten divalent and trivalent cation metal fluorides and their mixtures with alkali metal fluorides, and compare with the structural parameters obtained each other, referring to the information derived by the other spectroscopic investigations. Second, we explain experimental configuration and data treatment in details to show how we try to avoid human's artifact from analytical procedure. Lastly, the perspective of this research and the way to combine with other techniques are described.

2. Divalent cation metal fluorides and their mixtures

2.1. PbF_2 and LiF–PbF_2 mixture

Molten LiF–PbF_2 has been proposed for application to an alternative candidate as the liquid blanket material for fusion reactor systems [4]. Also, the specific characteristics that pure PbF_2 undergo phase transition from orthorhombic (α) to cubic (β) at 589 K and cubic (β) to superionic phase at 711 K below its melting point (1128 K) [11], would attract much interests from engineers to develop ionic sensor materials. Thus, XAFS spectra of both pure PbF_2 and LiF–PbF_2 at various temperatures have been collected to investigate local structural variation [12] and concentration dependence of LiF–PbF_2 mixtures [13] have also been examined.

The most difficulty of this system was how to treat multiple excitation effect associated with 2p4f at ca. 180 eV above the absorption edge [14]. Also, α phase of PbF_2 has already known to be an asymmetric crystal structure from the viewpoint of Pb atom, thus only structural parameters regarded as averaging 1st coordination shell can be derived by XAFS spectra.

Although these restrictions of XAFS analyses on this system exist, superionic phase transition was clearly observed by indication of drastic phase shifts in XAFS spectra, which is corresponding to rapid increase on dynamics of fluorides [12]. By means of molecular dynamics simulations of PbF_2 at various temperatures using polarizable ionic model [15], the above features at solid phases including superionic phase are well reproduced surprisingly [13]. However, both EXAFS signals and structural parameters of molten PbF_2 are not successfully reproduced by the MD simulation, thus still both efforts on careful re-evaluation of experimental data and potential optimization is required for this system.

In the LiF–PbF_2 mixtures, the structural parameters show 4 fluorides coordinated tetrahedral geometry is predominant except