

MAJOR FACTORS AFFECTING THE EMISSION OF DILITHIUM-FLUORIDE CLUSTER ION IN THERMAL IONIZATION MASS SPECTROMETRY

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The process of generating dilithium fluoride ion from the samples of LiF, LiF/C₆₀, LiF/LiI, and LiF/LiI/C₆₀ using a double and a triple filament thermal ionization source for a mass spectrometer was studied. This cluster belong to the “superalkali” class that can form the building block for new nanoscale cluster assembled materials. The results show that in the case of the double filament thermal source when the solution of LiF/C₆₀ was used the Li₂F⁺ ion was detected in the longest temperature range of the evaporation filament. On the other hand, the best abundances of Li₂F⁺ ion was obtained when the solution of LiF/C₆₀ were loaded on the evaporation filaments of the triple filament thermal ionization source. It has also been found that several different processes are involved in the generation of Li₂F⁺ by the triple filament thermal source: (1) Li₂F₂ → Li₂F⁺ + F; (2) Li⁺+LiF → Li₂F⁺; and (3) Li⁺(from LiI)+LiF → Li₂F⁺. Reaction (1) is dominant at the low temperatures of evaporation filament (Te), reaction (2) it appears at Te > 1000 °K, for all four above mentioned samples. Reaction (3) appears when the samples were the solution of LiF/LiI and LiF/LiI/C₆₀ at the high temperature of the evaporation filament.

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1. Introduction

Studies of heterogeneous non-stoichiometric alkali halides clusters by mass spectrometry are generally considered a bridge between gas-phase chemistry and new cluster assembled materials.^[1-4] For illustration of the similar role of mass spectrometry in a significant new field of condensed-phase chemistry is the discovery of fullerenes.^[5]

Fundamentally, non-stoichiometric clusters such as M_nX and M_nX_{n-1} are particular importance because violate stoichiometry based on the octet rule; it is reason they named hypervalent species. The bonding in hypervalent clusters of the type M_nX can be described in terms of a negatively charged electronegative atom embedded in a positively charged lithium “network”. The “extra” electrons are accommodated in molecular orbital consisting of atomic orbital of all the metal atoms forming metal “network”.^[6-9] The non-stoichiometric clusters with one excess metal atom such as M_nX_{n-1} have electronic structure segregated into an ionic part and metallic atom. These clusters are of considerable interest in research as a prototype for understanding the interaction of the between the part with metallic bonding and part polar bonding on structural characteristics of these species.^[10, 11]

It is important to note that the clusters of the type M_nX⁺ have the ionization energies lower than that of alkali metal atoms, while clusters of the type MX_n⁻ have electron affinities higher than that of halides element, it is reason these clusters named “superalkali” and “superhalogen”, respectively.^[12-17] Additionally, it has been theoretically demonstrated that by combining “supralakali” with “superhalogen”, it is possible to form small superatom clusters. The studies

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indicate that “supralakali” may serve as potential building blocks for the new cluster assembled materials with unique structural, electronic, optical, magnetic, and thermodynamic properties.^[18-20] Also, Li et al. are predicted a series of “superalkalies” - “superhalogen” compounds which exhibit special bonding nature and extraordinarily large nonlinear optical (NLO) response.^[21] Generally, the non-stoichiometric clusters are intrinsically challenging to characterize experimentally because they may lie at the core of current search for novel materials with tailored properties.^[1]

On the other hand, a thermal ionization or surface ionization mass spectrometry (TIMS or SIMS) is a method for generating ions at a hot metal surface (filaments).^[22] Earlier, the thermal ionization has used extensively in mass spectrometry for determination of isotope abundances with solid sample. Alkaline and alkaline-earth metal have many stable isotopes, including odd-number isotopes, and these elements are good subject for the study by thermal ionization mass spectrometry. Thermal ionization ion sources with double or triple filament are appropriate for such analysis.^[23-25] Also, the thermal or surface method has been used for study the ionization of lithium, lithium halides, lithium nitrate, and lithium sulphate on rhenium surface.^[26-28] For example, in a previous paper Fujii et al. have studied experimentally the thermal ionization of lithium halides in the temperature region 1000-1500 °K. They have discussed the correlation between the ionization efficiencies and thermodynamic properties of lithium halide for this reason the ionic current of ${}^7\text{Li}^+$ has been monitored in the cases of LiF, LiCl, LiBr, and LiI.^[29] Kawano et al. have investigated the threshold temperature range causing sharp change in the ionization efficiency of alkali halide molecules. Also, same authors have studies temperature dependence of the effective work function for thermal positive ion production from lithium atoms incident upon a rhenium surface.^[30]

An important feature of the thermal ionization mass spectrometry is the possibility of measuring ionization energies and it has been applied successfully for atomic and inorganic species. To date it has been found that the ionization is proportional to the evaporation pressure, and therefore the absolute vales of ion currents depend on the volatility of the chemical forms of the samples.^[22, 31]

In more recently it has been found that the thermal ionization method offers the possibility of formation M_nX and M_nX_{n-1} (M-alkali metal, X-halide element, $n>2$) clusters and the measurement of their ionization energies.^[32-38] However, both the effects of the chemical composition of sample and the arrangement of the filament set in the thermal ionization mass spectrometer on the produced positive ion of these clusters have not been fully elucidated.

In a class of the metal-rich clusters the one extensively studied experimentally, is dilithium fluoride (Li_2F).^[39-48] It is reason, in this work we have studied the possibility of obtaining the dilithium fluoride ion using the double and triple filaments thermal ionization source for a magnetic sector mass spectrometry. Also, it has been investigated the temperature dependence of positive ion Li_2F^+ clusters production from different the samples such as lithium fluoride salt, a mixture lithium fluoride/fullerene (C_{60}), a mixture lithium fluoride/lithium iodide salt and a mixture lithium fluoride/lithium iodide/ fullerene (C_{60}). The goal of this study is elucidate the condition to obtaining of the best abundances of dilithium fluoride ion.

2. Experimental

In this work the double and the triple filaments thermal ionization source for a magnetic sector mass spectrometry were used for obtaining Li_2F^+ ion. The arrangement of the double filaments set is shown in Fig. 1.

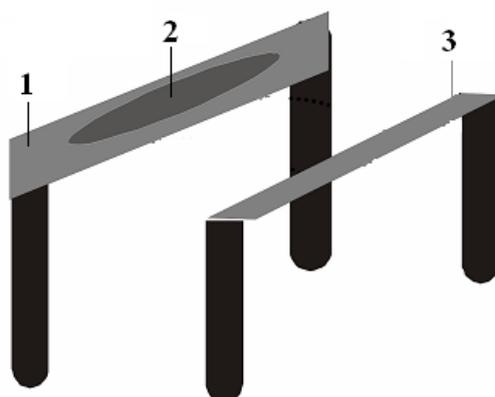


Fig. 1. The double filaments set of the TIMS: 1-the evaporation filaments (Re); 2-sample salts LiF or the mixture LiF/LiI dissolved in C_2H_5OH . 3- the ionization filament (Re).

The triple filaments thermal ionization source for a mass spectrometer with a two evaporation filaments (EF) and ionization filament (IF) has been given elsewhere.^[33, 34, 38] In thermal ionization mass spectrometry a rhenium filament is used for the ionization because of its chemical stability, high melting point, and high work function of 5.1eV. Rhenium (Re) ribbon (height 8mm, width 1mm, and thickness 0.05mm) was used for both the ionization filament and evaporation filament. The samples were LiF salt or mixture LiF/LiI dissolved in C_2H_5OH . These samples were loaded on the evaporation filament and heated to dryness in air in each experiment. In the case when the samples were LiF/ C_{60} or LiF/LiI/ C_{60} , the evaporation filament was first coated with the solution of C_{60} /toluene; the slurry was allowed to go nearly to dryness before sample solutions of LiF or LiF/LiI were added.

The filaments were heated using an electric current and the temperature was determined with an optical pyrometer. The advantage of double or triple filament technique of thermal ionization is possibility of heating evaporation filaments and ionization filament separately.

In order to identify and measure the ions produced by thermal or surface ionization a magnetic sector mass spectrometer was used. The pressure in the analyser region was maintained below 10^{-8} Torr, while the operating pressure in the source region was below 5×10^{-7} Torr.

3. Results and discussion

In the present study, it has been measured only the ion intensity of dilithium-fluoride cluster using both the double and the triple filament thermal ionization source for a magnetic sector mass spectrometry. In earlier paper we have investigated the optimal conditions for measuring the ionization energies of Li_nX (X-halogen element) clusters by the TIMS. The Li_nX^+ ($n = 2$ and 3) ions were detected by the solution of LiX/LiI. The evaporation filament was heated to the appropriate temperature for the sample evaporation, and then the temperature of this filament kept constant. It has been found that the highest intensity of Li_2F^+ ion appearance at temperature of the ionization filament of 1694 °K.^[33, 34] For this reason, in order to obtain the maximum abundance of Li_2F^+ ion the temperature of the ionization filament was kept constant at 1694 °K, while the temperature of the evaporation filament was gradually heated. The solution of LiF, LiF/ C_{60} , LiF/LiI, and LiF/LiI/ C_{60} were loaded on the evaporation filament for both the double and the triple filament set of the TIMS.

As a first step, the ion intensities of dilithium-fluoride cluster as a function of the temperature evaporation filament of the double filament thermal ionization source were measured. The temperature dependence of the intensities of Li_2F^+ ion are represented in Figure 2 as $\ln(I(Li_2F^+))$ versus T_e .

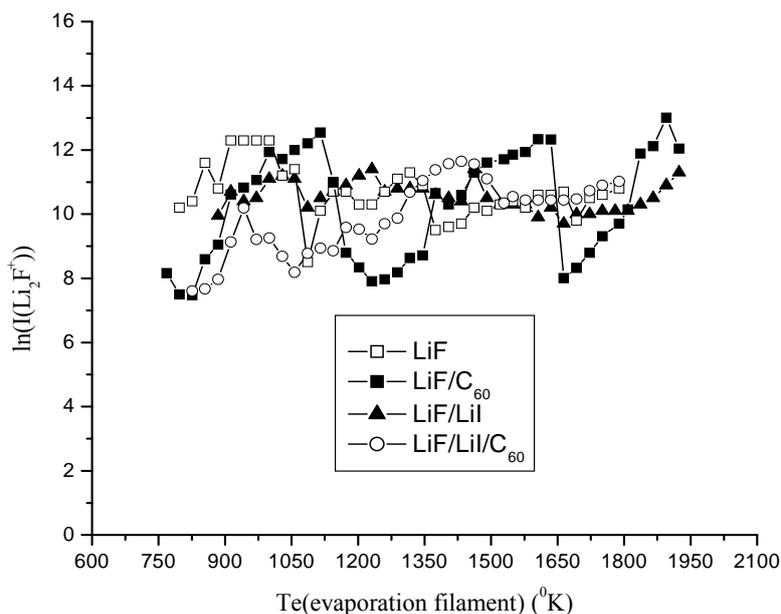


Fig. 2. Evolution of the logarithm of the ion intensity for Li_2F^+ vs. the temperature of evaporation filament of double filament set of the TIMS: open square – sample was the solution of LiF salt; solid square- sample was the solution LiF/ C_{60} ; solid up triangle- sample was the solution of a mixture LiF/LiI; open circle- sample was the solution of mixture LiF/LiI/ C_{60} .

Secondly, the ion intensities of dilithium-fluoride cluster as a function of the temperature evaporation filaments of the triple filament set of the TIMS were measured, too. These results are presented in Figure 3.

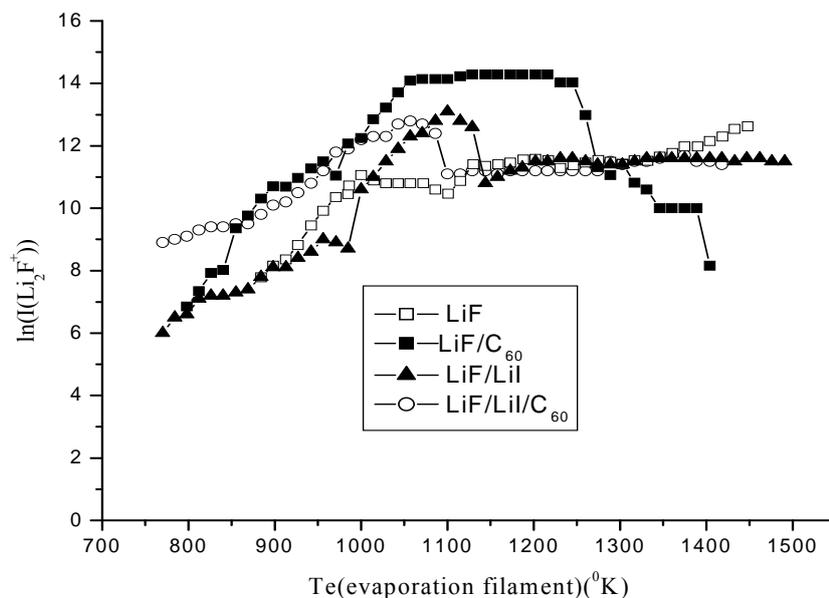


Fig. 3. Evolution of the logarithm of the ion intensity for Li_2F^+ vs. the temperature of evaporation filament of triple filament set of the TIMS: open square – sample was the solution of LiF salt; solid square- sample was the solution LiF/ C_{60} ; solid up triangle- sample was the solution of a mixture LiF/LiI; open circle- sample was the solution of mixture LiF/LiI/ C_{60} .

The experimental conditions employed for curves in Figures 2 and 3 are summarized in Table 1.

Table 1. The temperature range of evaporation filament for the double and triple filament set in the TIMS. The samples were LiF, LiF/C₆₀, LiF/LiI and LiF/LiI/C₆₀.

Sample	Temperature range of the evaporation filament of the TIMS	
	double filament (°K)	triple filament (°K)
LiF	792 – 1786 (ΔT 994)	882 – 1449 (ΔT 567)
LiF/C ₆₀	761 – 1924 (ΔT 1163)	797 – 1405 (ΔT 720)
LiF/LiI	890 – 1924 (ΔT 1034)	771 – 1491 (ΔT 608)
LiF/LiI/C ₆₀	830 – 1783 (ΔT 950)	771 – 1419 (ΔT 648)

When the solutions of LiF, LiF/C₆₀, LiF/LiI, and LiF/LiI/C₆₀ were used to produce the Li₂F⁺ ion the temperature range of the evaporation filament were 792-1786 °K, 761-1924 °K, 890-1924 °K, and 830-1783 °K, respectively. It has been observed that the temperature ranges of the evaporation filament in the case of the triple filament set are slightly shorter than those of the double filament set, for detection the above mentioned ion. The data those obtained show that in the case of the double filament set, when the solution of LiF/C₆₀ was used, the Li₂F⁺ ion was detected in the longest temperature range of the evaporation filament.

A comparison of the data plotted in Figure 2 for double filament and Figure 3 for triple filament shows that the two sets of data are different. In the case the double filament set, all the intensities of dilithium-fluoride ion with increase temperature have no clearly trend. In contrast, for the triple filament set, all the shapes curves of the ln(I(Li₂F⁺)) vs. Te have three-stage. It can be seen from Figure 3 that, in a first stage, the intensities of Li₂F⁺ ion increase with increasing temperature of the evaporation filaments. In second stage, the ln(I(Li₂F⁺)) increase to a maximum and then ln(I(Li₂F⁺)) decrease. In third stage, the temperature of evaporation filaments increasing while the intensities of Li₂F⁺ ion was almost same in each case.

As can be also seen in Figure 3, the shape and the intensities of the I_{max}(Li₂F⁺) are dependent on the composition of sample. The curves of the ln(I(Li₂F⁺)) vs. Te has two slightly marked I_{max}(Li₂F⁺) around 1000 °K and 1100 °K for the solution of LiF salt, while I_{max}(Li₂F⁺) is in the temperature range 1055-1236 °K for the solution of LiF/C₆₀. The maximum intensity of Li₂F⁺ ion occurs around 1098 °K and 1052 °K for a mixture LiF/LiI and LiF/LiI/C₆₀, respectively.

Earlier it has been established that the lithium fluoride vaporizes in the form of the monomer (LiF) and dimer (Li₂F₂). The dimer-to-monomer flux ratios were found to increase with increasing temperature in the temperature range 970-1070 °K.^[47] Also it was known previously that, during thermal ionization on rhenium filament lithium ion were formed from LiF and LiI in the temperature range 1140-1620 °K and 950-1250 °K, respectively.^[29]

For this reason, for all four samples, it has been considered that the process dissociative ionization of Li₂F₂ is dominant to the generating Li₂F⁺ (Li₂F₂ → Li₂F + F then the neutral cluster are ionizes to form Li₂F⁺) at low temperature (Figure 3, the first stage). At temperature above 1100 °K the forming of Li₂F⁺ involves three distinct processes: LiF decomposes (LiF → Li + F), then ionizes Li to form Li⁺ (Li → Li⁺), and the ion-molecules reactions where Li⁺ combines with non-decomposed LiF to form Li₂F⁺ (Li⁺+LiF → Li₂F⁺). These facts suggest that in the case of lithium fluoride, the dissociative ionization of Li₂F₂ leading to the maximum intensity of Li₂F⁺ around 1000 °K, while the beginning of ion-molecules reactions may be responsible for the I_{max}(Li₂F⁺) around 1100 °K. It has been observed that the emission of Li₂F⁺ ion is enhanced using a mixture

LiF/C₆₀. This is probably associated with the existence of the graphite monolayer on the evaporation filament, which leads to the decreases of thermal dissociation of this cluster. Namely, previously it was established that adsorbed C₆₀ molecules retain the fullerene structure on the surfaces of rhenium heated up to 800 °K. In the temperature range 1000-1600 °K the adsorbed fullerene molecules decompose and forms a graphite monolayer on the rhenium surface. [49-52]

Further, for the solution of LiF/LiI the ion-molecules reaction $\text{Li}^+(\text{from LiI}) + \text{LiF} \rightarrow \text{Li}_2\text{F}^+$ was also possible above 950 °K. The lithium iodide was used as the source of Li^+ ions, which may be the main reason why the intensity of $I_{\text{max}}(\text{Li}_2\text{F}^+)$ for the solution of a mixture LiF/LiI is higher than the $I_{\text{max}}(\text{Li}_2\text{F}^+)$ for the solution of LiF (Figure 3). This means that three processes simultaneously may contributing to obtaining Li_2F^+ ion from the solution of LiF/LiI: the dissociative ionization of Li_2F_2 , the ion-molecules reactions $\text{Li}^+ + \text{LiF} \rightarrow \text{Li}_2\text{F}^+$ and $\text{Li}^+(\text{from LiI}) + \text{LiF} \rightarrow \text{Li}_2\text{F}^+$, around 1098 °K. It has also been observed that the intensity of Li_2F^+ ion is enhanced in the case of LiF/LiI/C₆₀, probably because graphite monolayer on the evaporation filament. These results indicated that the best abundances of dilithium fluoride ion was obtained when the solution of LiF/C₆₀ were loaded on the evaporation filaments of the triple filament thermal ionization source for a mass spectrometer.

4. Conclusion

The process of generating dilithium fluoride ion from the samples of LiF, LiF/C₆₀, LiF/LiI, and LiF/LiI/C₆₀ using the double and the triple filament thermal ionization source for a mass spectrometer was studied. It was found that the intensity of Li_2F^+ ion depends on both the temperature of the evaporation filament and the chemical composition of sample.

The above results and considerations lead to the following conclusions. All the intensity of dilithium-fluoride ion with increase temperature have not clearer definite trend for the double filament thermal source. By contrast, it has been shown that for the triple filament thermal source all the shapes curves of the ion intensities of dilithium-fluoride cluster vs. the temperature evaporation filament have three-stage. Also several different processes are involved in the generation of Li_2F^+ by the triple filament thermal source: (1) $\text{Li}_2\text{F}_2 \rightarrow \text{Li}_2\text{F}^+ + \text{F}$; (2) $\text{Li}^+ + \text{LiF} \rightarrow \text{Li}_2\text{F}^+$; and (3) $\text{Li}^+(\text{from LiI}) + \text{LiF} \rightarrow \text{Li}_2\text{F}^+$. Reaction (1) is dominant at the low temperatures of evaporation filament, reaction (2) is appears at $T_e > 1000$ °K, for all four above mentioned sample. Reaction (3) appears when the samples were the solution of LiF/LiI and LiF/LiI/C₆₀ at the high temperature of the evaporation filament. In this case the shape and the intensities of the $I_{\text{max}}(\text{Li}_2\text{F}^+)$ are dependent on the composition of sample. The best abundances of dilithium fluoride ion was obtained when the solution of LiF/C₆₀ were loaded on the evaporation filaments of the triple filament thermal ionization source for a mass spectrometer. However, in the case of the double filament thermal source, when the solution of LiF/C₆₀ was used, the Li_2F^+ ion was detected in the longest temperature range of the evaporation filament.

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