Thermally stimulated processes in Li and Cu doped alkali fluorides irradiated with electron beams of ultra-high dose

Zh K Mamytbekov[1], A N Tcherepanov[1], A I Slesarev[1], M M Kidibaev[2], Q Shi[1,3], K V Ivanovskikh[1], V Yu Ivanov[1], A A Egamberdieva[2] and B V Shulgin[1]

[1]Ural Federal University, 620002, Ekaterinburg, Russia
[2]National Academy of Sciences KR, 720071, Bishkek, Kyrgyz Republic
[3]Taiyuan University of Technology, 030024, Taiyuan, China

E-mail: zzhayloo@gmail.com

Abstract. The thermally stimulated luminescence (TSL) and exoemission (TSE) in Li and Cu doped NaF and LiF single crystals irradiated with electron high energy electron beams of (10 MeV, doses 0.75 and 2 MGy) have been investigated. The results obtained reveal important properties that suggest that the crystals have a sufficient radiation stability and sensitivity for high energy electron beams and are promising for application as high-dose detectors of electron radiation.

1. Introduction

Considerable progress has been made over the last decades in the development and characterization of many kinds of thermoluminescence (TL) phosphors among which alkali fluorides have always been of notable importance [1-4]. Lithium and sodium fluorides are characterized by low effective atomic number (Z_{eff}) that makes them useful for the development of tissue-like thermoluminescence dosimeters (TLDs). The remaining potassium, rubidium, and cesium fluorides are highly hygroscopic and do not attract significant attention.

A drawback of undoped LiF consisted in a complicated TL response that was dependent on its radiation and thermal history. In attempting to solve the problem, a quite significant attention was drawn to the development and study of LiF doped with B, Si, Mg, Cu, Ti and other dopants including lanthanides (see [4-12] and reference therein). Nowadays, commercial TLDs based on LiF:Mg,Ti (TLD-100/600/700) and LiF:Mg,Cu,P (TLD-100H/600H/700H) and their modifications are well accepted in the industry. The second practically important representative of the alkali fluorides family is NaF which thermally stimulated properties have also been extensively studied over the last decades. The development of NaF based TLDs is challenging due to a complex manner of its TL properties influenced by factors like type and energy of ionizing radiation, thermal and radiation dosage history, etc. [1-3, 13-17]. Both LiF and NaF like many others have drawback consisted in a low sensitivity to low doses and an early saturation at higher doses.

Nowadays, we observe rising demand for high-level TL dosimetry materials due to the development of new radiation technologies applicable in materials testing, sterilization and processing, nuclear medicine, etc. Some of them are based on using electron and ion beam facilities as irradiation sources. It was recently shown that LiF based TLD may be prospective for application in extremely wide dose range of up to twelve orders of magnitude (see [18] and references therein). This inspired us to test thermally stimulated processes of NaF and LiF doped with Li and Cu irradiated with ultra-high dose of electron beam. To this end we performed an experimental study of TL and thermally stimulated exoemission (TSEE) glow curves of LiF and NaF doped with Li and Cu irradiated with ultra-high doses of 10 MeV electron beams. The results obtained suggest that the crystals have a sufficient radiation stability and sensitivity for high energy electron beams and can be promising for application as ultra-high-dose detectors of electron radiation.

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2. Experimental

Single crystals of NaF:1mol%Li (NaF:Li), NaF:1mol%Li, 0.1mol%Cu (NaF:Li,Cu), NaF:0.1mol%Cu (NaF:Cu), and LiF:0.3mol%Cu (LiF:Cu) were grown in platinum crucibles by the Kiropoulos method [19] at the Institute of Physics of Kyrgyz National Academy of Sciences. The crystals were 5 mm in diameter and about 3 cm long. To perform the measurements the crystals were cut into 1 mm thick slices using a diamond saw and polished. The samples were then examined for their basic luminescence properties in order to confirm the entry of impurity ions into the lattice.

The samples were irradiated with 10 MeV electron beam from a MT-20 microtron (Russia) at Ural Federal University. The samples were mounted on a massive cupper sample holder in order to minimize possible heating. Typically, dose acquired by a sample in one minute was 15-16 kGy that was monitored with SO PD(F)R-5/50 standard fenazin dosimeters (Russia) with uncertainty of up to 10%. The samples were exposed to electron beams for 50 and 133 minutes in order to acquire dose of 0.75 and 2 MGy, respectively.

TL and TSEE glow curves were recorded with an automated exoemission spectrometer [20] equipped with a VEU-6 electron multiplier (Russia) to detect electron emission and a FEU-142 solar-blind photomultiplier (Russia) sensitive in the spectral range of 112–365 nm to detect the luminescence. The setup allows linear heating of samples in 300–800 K range with 0.1–1.0 K/s rate. The measurements were performed in vacuum of ~10^{-5} Torr.

3. Results and discussion

Figure 1 shows TSEE glow curves recorded for NaF:Li and NaF:Li,Cu crystals irradiated by electron beams with 750 kGy and 2 MGy dose. Obviously, the glow curves have a complex structure resulted from superposition of multiple TSEE peaks. The curves were fitted assuming the first order kinetics of thermal processes [21]. The TSEE (and TL) activation energies were calculated using halfwidth of the elementary emission bands obtained from deconvolution of the initial glow curves [22]. The quality of fittings done in the frame of this research was to be satisfactory done if figure-of-merit (FOM) was less than 1%. Kinetics parameters obtained for TSEE glow curves of NaF:Li and NaF:Li,Cu crystals that include peak maxima (T_m), activation energies (E_a), and frequency factor (S) are gathered in table 1 along with the data obtained for LiF:Cu and NaF:Cu considered below.

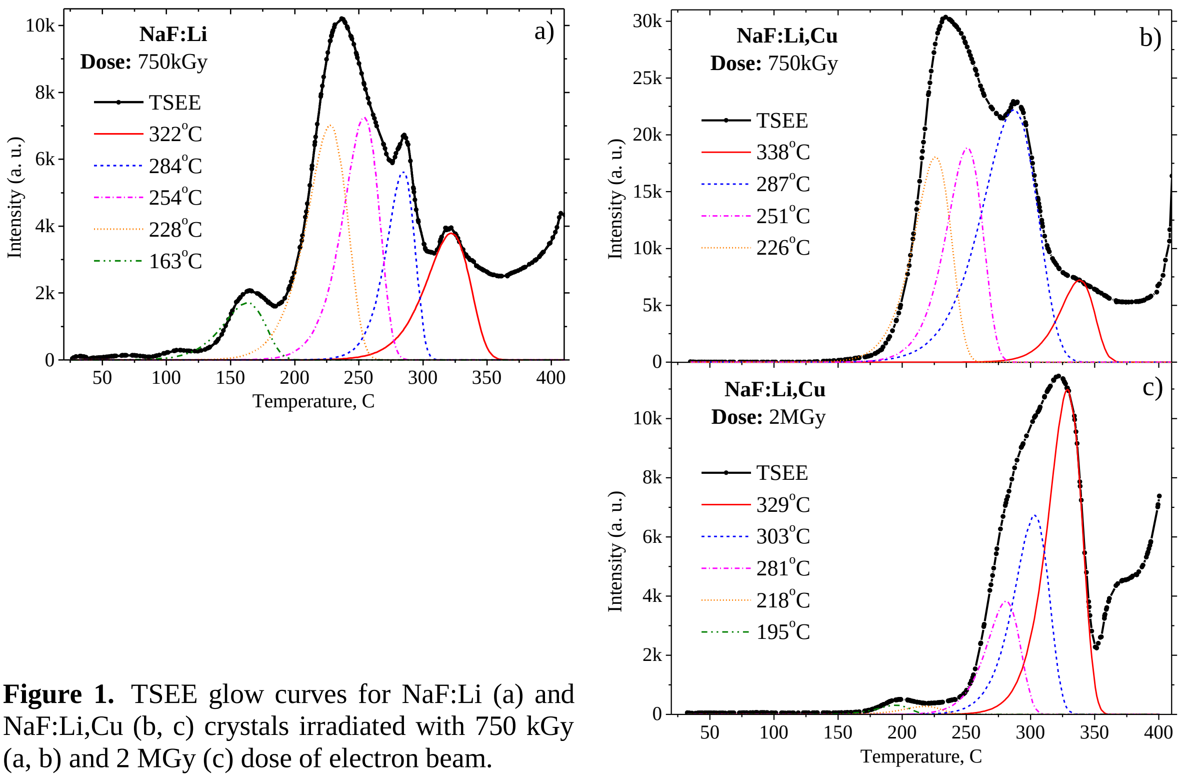

Figure 1. TSEE glow curves for NaF:Li (a) and NaF:Li,Cu (b, c) crystals irradiated with 750 kGy (a, b) and 2 MGy (c) dose of electron beam.

The shape of the glow curves obtained for the crystals exposed to 750 kGy of electron beams is dominated by a peak centered near 237 °C that is composed of two elementary peaks with maxima near 226–228 °C and 251–254 °C. The peak is accompanied by a high-temperature peak at 284–287 °C that becomes more intense in Cu-co-doped crystal. It is worth noting that co-doping with Cu leads to noticeable rise of the TSEE yield. Increasing the dose of irradiation up to 2 MGy leads to dramatic modification of the glow curve that reveals redistribution of populated traps towards deeper ones. Shallow traps responsible for TSEE features detected below 250 ^{o}C are not effectively populated at such a high irradiation dose, making less than 1% of the total observed TSEE yield.

Figure 2 shows TL and TSEE glow curves recorded for LiF:Cu and NaF:Cu crystals exposed to 2 MGy dose of electron beams. Both crystals demonstrate well pronounced anticorrelation of the corresponding TL and TSEE glow curves up to about 320 ^{o}C. Thermally stimulated processes switch from the domination of electron exoemission to luminescence near 180 ^{o}C and 210 ^{o}C for LiF:Cu and NaF:Cu crystals, respectively. The TSEE glow curve of LiF:Cu crystal is dominated by the peak at 174 ^{o}C. The features located at lower temperatures (peaks at 258, 212, and 160 ^{o}C) make less than 15% of the total exoemission yield. NaF:Cu crystal demonstrates a well pronounced TSEE peak at 198 ^{o}C. Contribution of a broad TSEE feature centered near 293 ^{o}C does not exceed 1%. The TL glow curves of LiF:Cu and NaF:Cu crystals reveal broad non-elementary features spread from about 180 to 300 ^{o}C and from 190 to 320 ^{o}C, respectively. Both crystals demonstrate rise of TL and TSEE intensity above about 330 ^{o}C. We note that the appearance of high-temperature TL features is typical of alkali fluorides irradiated with high and ultra-high dose of ionizing radiation (see [18] and references therein). Kinetics parameters obtained for TSEE and TL glow curves of NaF:Li and NaF:Li,Cu crystals can be found in table 1.

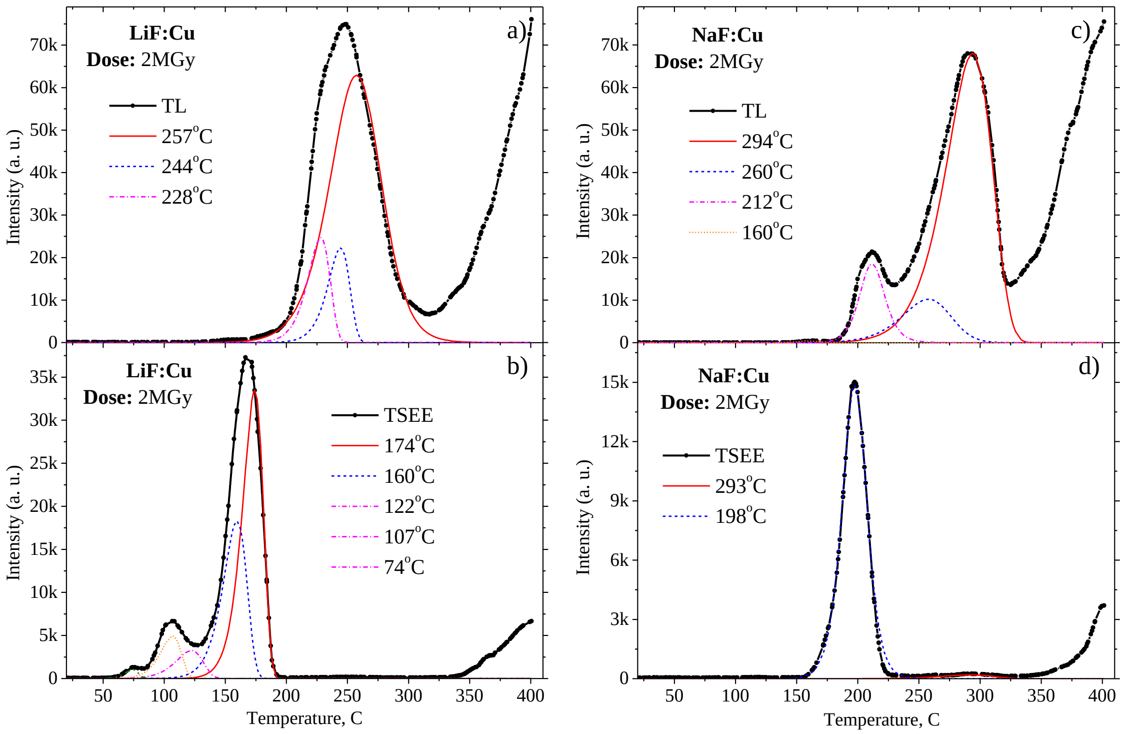

Figure 2. TL (a, c) and TSEE (b, c) glow curves for LiF:Cu (a, b) and NaF:Cu (c, d) crystals irradiated with 2 MGy dose of electron beam.

The above described experimental results can be explained in terms of the model of electronic and ionic excitations in the crystals [23]. The model assumes the presence of a highly mobile electron-hole, ion-ion, and ion-vacancy pairs which are responsible for accumulating of energy released by primary electronic excitation and subsequent transfer of the stored energy to the surface. The latter is known to be enhanced upon high energy electron bombardment [24]. The results documented by some of us earlier in [15-17, 19, 23, 25] along with the results presented in [26, 27] suggest that the energy range of active exoemission in the crystals studied here correlates well with the energy range related to the thermal destruction of F-centers along with aggregated F_2, F_2+ and F_2– centers. We note, that destruction of F-centers may also be connected with their recombination with the hole (H-) centers, which have an increased thermal stability in doped crystals [3, 16, 24]. The TL features related to this kind of thermal processes are likely to contribute to the TL peaks observed around 320–350^{o}C. Obviously, the thermal processes staying behind the TL and TSEE features observed in this work are quite complicated. From the same point of you, we can assume that both the fitting and interpretation of the TL and TSEE glow curves can be ambiguous. One of the reasons for that comes from the fact that the commonly applied fitting method, when a glow curve is considered to be a superposition of several single glow peaks each related to a first-order process, does not account such processes as cascade detrapping or retrapping of carriers and saturation of traps [21, 22]. This peculiarity may results in getting somewhat physically irrelevant kinetics parameters and particularly to extremely high values of the frequency factor [28], that is partly the case in our fitting results. Applying the second-order kinetics or more advanced models is a challenging task that requires additional a priori data on energy structure and concentration of defects. Although defects in alkali halides have been extensively studied so far, understanding of defects due to high and ultra-high dose electron beams is lacking today.

From the practical point of view, it is worth noting that dopants play an important role in formation of trapping and recombination centers responsible for both the TL and TSEE phenomena. Extension of this experimental work would benefit from comprehensive study of TL and TSEE response of the crystals depending on dopant concentration, dose and energy of electron beams.

Table 1. Kinetics parameters for TL and TSEE processes in NaF and LiF doped with Li and Cu irradiated with ultra-high dose electron beams

Sample	Dose[a]	Process	Kinetic parameter[b]	Peaks 1	2	3	4	5
NaF:Li	750	TSEE	T_m	322	284	254	228	163
			E	1.76	2.46	1.71	1.36	0.97
			S	1.4E+13	5.0E+20	4.6E+14	9.0E+11	2.9E+09
NaF:Li,Cu	750	TSEE	T_m	338	287	251	226	
			E	2.39	1.23	1.64	1.46	
			S	1.1E+18	1.7E+09	1.3E+14	1.1E+13	
	2000	TSEE	T_m	329	303	281	218	195
			E	2.39	2.11	2.03	1.37	1.48
			S	2.1E+18	5.6E+16	5.9E+16	2.3E+12	1.8E+14
LiF:Cu	2000	TSEE	T_m	174	160	122	107	74
			E	2.06	1.67	1.22	1.48	1.92
			S	5.1E+21	8.6E+17	8.7E+13	1.3E+18	4.0E+26
		TL	T_m	257	244	228		
			E	1.40	2.61	2.39		
			S	3.0e+11	7.8e+23	3.7e+22		
NaF:Cu	2000	TSEE	T_m	293	198			
			E	1.27	2.56			
			S	2.7e+9	1.1e+26			
		TL	T_m	294	258	212	160	
			E	1.43	1.34	2.87	2.37	
			S	7.3e+10	7.6e+10	2.5e+28	1.8e+26	

[a] Dose is measured in kGy.
[b] Units for T_m, E, and S parameters are ^oC, eV, and s^{-1}, respectively.

4. Conclusion

Single crystals of NaF:Li, NaF:Li,Cu, NaF:Cu, and LiF:Cu were synthesized using the Kiropoulos method and irradiated with ultra-high dose electron beams of 10 MeV. All the samples revealed good radiation resistance and sensitivity to the irradiation doses applied. The results of TSEE and TL measurements suggest complicated structure of defects in the crystals that can hardly be modelled with the commonly applied model of first-order process. In connection with the observed TL and TSEE glow curves, it is possible to tentatively propose application of the crystals for application in ultra-high dose TL and TSEE dosimetry. This proposition, however, should be further supported by in-depth investigation of TL and TSEE response of the crystals depending on dopant concentration, dose and energy of electron beams.

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