Li/Zn ratio effect on manganese spectral properties in germanate glass-ceramics

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Introduction

Mn^{4+} ions are actively used to create phosphors in the red region of the spectrum. The most promising in terms of stabilization of the tetravalent state of manganese is the germanate matrix, since the ionic radii of Ge^{4+} and Mn^{4+} are quite close, and germanium ions are often located in the center of a structure of the GeO_6 type. When adding zinc to the composition of glass-ceramic germanate materials, it is also possible to obtain an intense green phosphorescence of Mn^{2+} ions, which replace zinc ions in the crystal structure.

Synthesis

A series of lithium-zinc-germanate glasses of the composition (30-x) Li_2O – x ZnO – 70 GeO_2, doped with 0.1 mol.% MnO_2, was synthesized; x = 5(**5Li-1ZnG**), 7.5(**3Li-1ZnG**), 10(**2Li-1ZnG**), 15(**1Li-1ZnG**), 20(**1Li-2ZnG**), 22.5(**1Li-3ZnG**) mol. %.

Due to the diversity of luminescent properties found during the polythermal heat treatment of glass samples, to obtain glass-ceramics, each glass composition was heat treated at two different temperatures (530-550°C and 640°C), which made it possible to obtain red and green luminescence.

Red emission of glass-ceramics

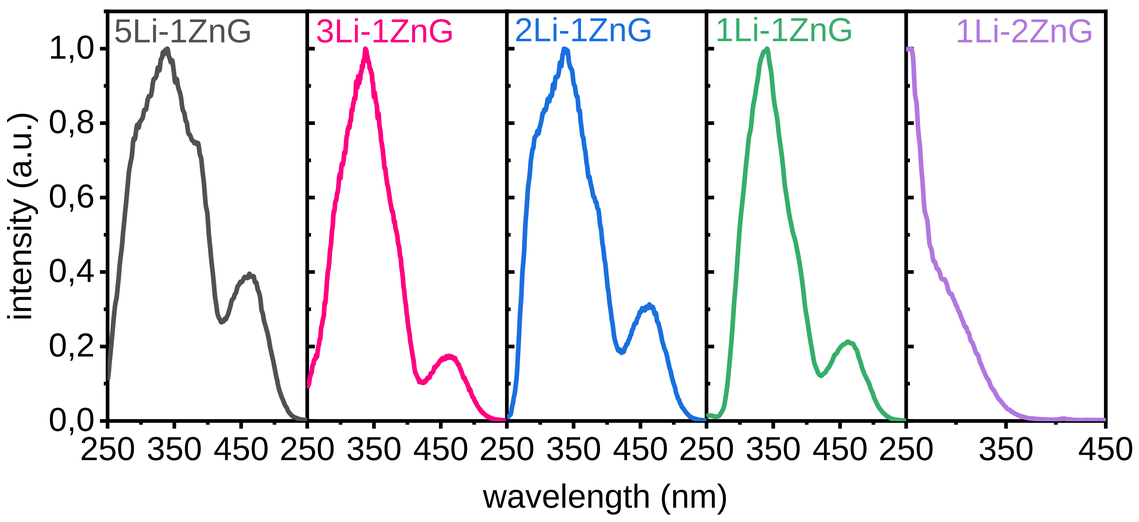

Fig. 1. PLE spectra of Mn ions in lithium-zinc-germanate glass-ceramics synthesized in the temperature range 530-550°C.

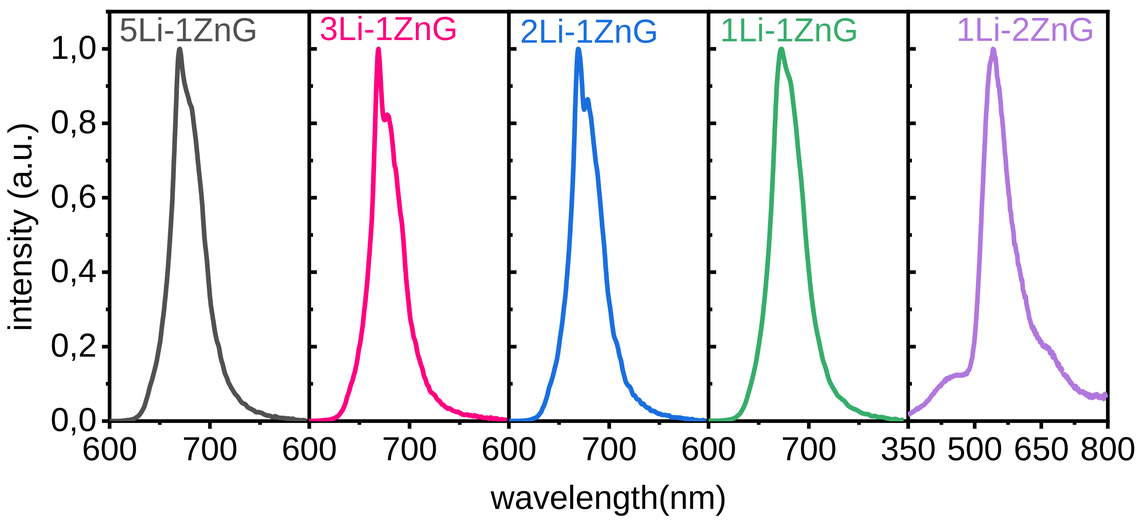

Fig. 2. PL spectra of Mn ions in lithium-zinc-germanate glass-ceramics synthesized in the temperature range 530-550°C.

Green emission of glass-ceramics

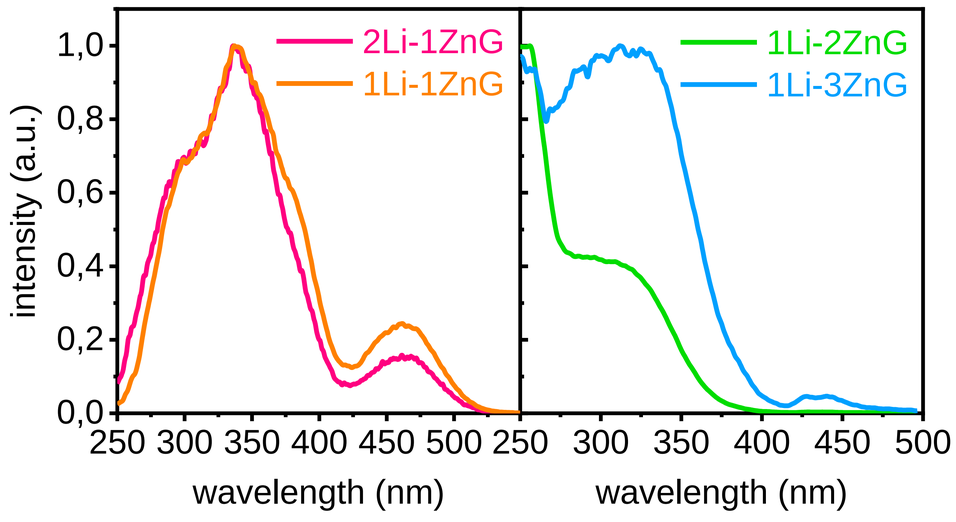

Fig. 3. PLE spectra of Mn ions in lithium-zinc-germanate glass-ceramics synthesized at 640°C.

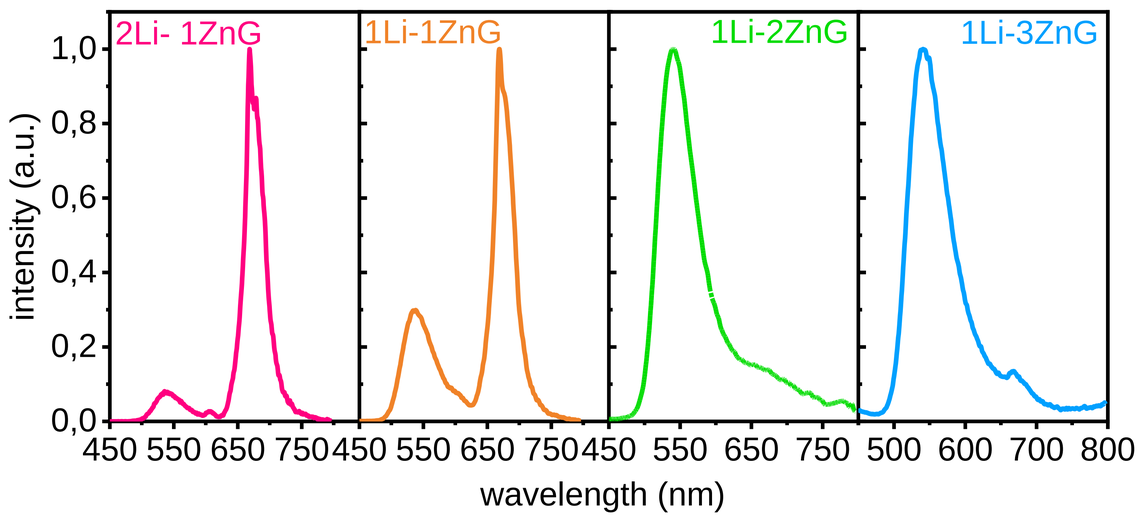

Fig. 4. PL spectra of Mn ions in lithium-zinc-germanate glass-ceramics synthesized at 640°C.

Luminescent properties

	λ_{em} = 667 nm		λ_{em} = 540 nm	
	Luminescence lifetime, ms	Quantum yield, %	Luminescence lifetime, ms	Quantum yield, %
5Li-1ZnG	1.31	52	-	-
3Li-1ZnG	1.15	42	-	-
2Li-1ZnG	1.36	61	9.41	11
1Li-1ZnG	1.34	48	8.36	21
1Li-2ZnG	-	2.5	9.69	12
1Li-3ZnG	-	-	9.79	20

Conclusion

- ✓ Lithium-zinc-germanate glass-ceramics doped with manganese can exhibit luminescence in the red and green regions of the spectrum, depending on the synthesis conditions and the Li/Zn ratio in the glass composition.
- ✓ When zinc oxide concentration is low, the luminescence spectrum is dominated by a band at 670 nm, which corresponds to Mn^{4+} ions.
- ✓ The equimolar substitution of lithium with zinc leads to the appearance of a broad band in the region of 540 nm, corresponding to Mn^{2+} ions, the contribution of which to the luminescence spectrum increases with an increase in the zinc oxide content in the glass composition.