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Abstract: We have investigated the generation of THz radiation in lithium ternary compounds LiInSe₂, LiGaSe₂, LiInS₂, LiGaS₂ and characterized these materials by THz time-domain spectroscopy. Using 800 nm femtosecond excitation pulse, all crystals produce THz radiation due to an optical rectification corresponding to the nonlinear optical coefficient d_{33} . We have measured refractive indices along the x-axis and the z-axis for all crystals in the range 150-700 μm and fitted them by using Sellmeier equation. With respect to the obtained results, velocity-matching between the incident laser pulse and the generated THz wave cannot be achieved at 800 nm, but for shorter wavelengths. Hence, an enhanced THz generation in Lithium ternary compounds may be observed by using a laser emitting below 800 nm.