



Lanthanide mechanoluminescence

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ABSTRACT

Mechanoluminescence (ML) is the emission of light consecutive to a mechanical force or stress imposed to a crystalline material. Many inorganic and organic compounds present this phenomenon that is known for over 400 years. Lanthanide and uranyl salts were among the first substances investigated for this property. Mechanoluminescence, also referred to as triboluminescence, is often considered as being a badly understood phenomenon. In fact it is because of two main reasons. Firstly, a variety of different mechanical stresses, from simple rubbing, to applied pressure, crushing, impact of a weight, ultrasound, laser-generated shock wave, crystallization, dissolution of crystals, or even wind can trigger it. Secondly, ML is very sensitive to the purity and morphology of the sample: in inorganic compounds, generation of traps by doping “impurities” (e.g. lanthanide ions) is responsible for light emission so that the exact composition of the sample has to be known to a very detailed level; for chelates, the crystallization conditions are crucial since they often generate extended networks of weak interactions that are instrumental in triggering ML when they are broken. In fact mechanisms of ML are relatively well known and theories and models often reproduce very well the experiments. Additionally, practical applications are at hand, for example stress, crack, and impact sensors based on $\text{SrAl}_2\text{O}_4:\text{Eu}^{\text{II}}$ or $\text{Et}_3\text{NH}[\text{Eu}(\text{dbm})_4]$ are used to test structures and materials as diverse as road bridges, reinforced concrete elements, pressurized containers or airplane wings and to image the propagation of cracks or stress distribution. Military and security applications involve detecting the passage of vehicle or soldiers and producing counterfeiting inks while more joyful applications are luminous balls, wrapping papers and adhesive tapes. Not only bulk materials, but micro- and nanoparticles feature mechanoluminescent properties and single particle manipulation under an AFM allows one to produce light sources that could be useful to several photonic applications, including bio-applications.

The review starts with a short historical background of ML, discussing definitions, and providing some theoretical bases. It then presents instrumental setups before covering all aspects of lanthanide mechanoluminescence, starting with simple salts, then doped inorganic compounds (irradiated and non-irradiated) and finally chelates. Mechanoluminescent sensors are described with various actual and potential applications. Literature is covered until April 2017. The wealth of information gathered during the past 20 years in the field and the broad understanding of the phenomenon attained show that the field is presently ready for a quantitative leap forward. Many subjects are waiting to be developed, including NIR mechanoluminescence or bio-applications based on single mechanoluminescent particle light sources; in addition, designing new types of mechanoluminescent materials with techniques paralleling the developments in other aspects of lanthanide photonics could prove extremely rewarding.

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1. Introduction

Many crystalline inorganic and organic compounds emit sparks of light under crushing or mechanical stress; estimates for their proportion range from 24% (1883 compounds tested)¹ to 50%.² Mechanoluminescence (ML) has been observed for conductors,

semiconductors, and insulators and has been known or studied for over 400 years. During this span of time, scientists progressively realized that this type of light emission is rather subtle, arising from several excitation mechanisms and being frequently accompanied by other forms of luminescence.³ Mechanical excitation can be widely diverse, resulting from strain induced by rubbing, pressure,

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