Theoretical and applied implications of structural order of vermiculite irradiated.

C. Marcos

Dpto. Geología & Inst. de Química Organometálica "Enrique Moles", Univ. Oviedo, Jesús Arias de Velasco s/n, 33005, Oviedo, Asturias, Spain.

Phone: 34 985 10 31 00, Fax: 34 985 10 31 03

E-mail: cmarcos@uniovi.es

Abstract

Vermiculite is a layered silicate with a crystalline complex structure, even in the case of the most pure vermiculite (e.g. Santa Olalla, Huelva (Spain)), characterized by the existence of a large density of defects. As a result of their lamellar structure, vermiculite presents a broad diversity of behaviour and it is an interesting mineral from both the applied and basic point of view. Vermiculite is used to examine interesting physical properties such as mixed-cation effects and two-dimensional magnetism. The existence of frustration and disorder is a key feature for understanding the mechanisms of spin-glass (SG), for example. The dimensionality of magnetic interactions, which plays a central role in controlling the critical dynamics of SG systems, is still not resolved. Probably, magnetic studies on ordered structurally vermiculites will allow elucidate the true nature of the spin-glass-like phases. One way to provide structurally ordered vermiculites might be by irradiation with ultraviolet or gamma rays. These types of radiation induce structural order in vermiculites leading to materials with the enhanced opto-electrical properties and improving its utility as an electronic insulator and a thermoluminescence dosimeter for innovative dosimetry applications in radiation rich environment (Kaur et al., 2014). Other layered minerals irradiated with gamma rays can enhance their radiation shielding capacity and electronic insulating property.

Key words: Vermiculite, radiation, structural order, magnetism, opto-electrical properties.

Body text

Kaur et al. (2014) investigated, for the first time, the opto-structural, dielectric, chemical and thermoluminescence properties of gamma-irradiated vermiculite and concluded that irradiation induced structural changes that led to the creation of a material with enhanced opto-electrical properties. They observed a notable increase in the dielectric constant of the vermiculite with a gamma dose of 1000 kGy which improved its utility as an electronic insulator. They also concluded that vermiculite is a good material for thermoluminescence dosimeter for innovative dosimetry applications in radiation rich environment.

Vermiculite is a layered silicate whose basic building block is composed of two sheets of SiO_4^- tetrahedra coupled symmetrically to another sheet of MgO_6^{4-} octahedra in a tetrahedral-octahedral-tetrahedral layer lattice. As a result of their lamellar structure, vermiculite presents a broad diversity of layer charge associated with numerous isomorphic substitutions, disorder effects, ability for dehydration-rehydration and swelling process. Consequently, vermiculite is an interesting mineral not only from the applied point of view (Strand & Stewart, 1983; Hindman, 1992; Suzuki et al. 1989, 2001; Bergaya et al. 2006; Klein and Dutrow, 2007; Abollino et al. 2008; Zhang et al. 2009; Marcos et al., 2012; Marcos et al., 214), being an attractive material due to its high thermal and insulation applications and sensitivity to ionizing radiation as gamma rays, but it is also remarkably important as a model system in physics, chemistry and the biological sciences (Satapathy et al., 2011; Wu et al., 2011; Eom et al., 2011).

The complex crystalline structure of the Santa Olalla vermiculite (Huelva, Spain), one of the most studied vermiculites due to is purity, is characterized by the existence of a large density of defects as demonstrated by Marcos et al. (2004). It has been successfully refined from X-ray powder diffraction data by a method based on a recursive description of faulted structures by using the DIFFaX+ software (Argüelles et al. 2009 and 2010). This disordered structure has also been confirmed for the iron- and nickel-intercalated vermiculite prepared from the Mg-vermiculite by means of an ion exchange (Argüelles et al. 2011). Therefore, the structural disorder appears to be the most common configuration of vermiculite.

Because of the large *c*-axis repeat distance, vermiculite is used to examine interesting physical properties such as mixed-cation effects and two-dimensional magnetism (Zhou et al., 1993; Suzuki et al., 2001). In particular, it is well known that the existence of frustration (i.e. competing interactions of spins) and disorder are key features for understanding the mechanisms of spin-glass (SG), crystallographic disorder or a geometrically frustrated lattice being the principal reasons usually preventing the magnetic moments of a magnetic system from being long-range ordered. The subject of SG has been challenging both experimentalists and theoreticians for more than forty years (Dekker et al., 1989). The dimensionality of magnetic interactions plays a central role in controlling the critical dynamics of spin-glass (SG) systems: the lowest critical dimensionality of short-range Ising SG is between two and three. In the case of dimensionality three, equilibrium of ordered phase is reached at a finite temperature, whereas for two-dimensional systems, this situation is only achieved at 0 K in which competing ferromagnetic and anti-ferromagnetic interplanar exchange interactions are responsible for the complex magnetic behaviour found. Additional experiments will be needed in order to elucidate the true nature of the spin-glass-like phases.

Marcos et al. (personal communication) also have observed structural order in different commercial vermiculites irradiated with ultraviolet radiation. The structural

ordering of the irradiated vermiculite with gamma or ultraviolet radiation could be attributed to the improvement in the crystallinity due to an increase of crystallite size, reduction of defects and a decrease in structural disorder and microstrain.

Magnetic studies on ordered structurally vermiculites will allow researchers to better elucidate the true nature of the spin-glass-like phases. One way to provide structurally ordered vermiculites might be by irradiation with ultraviolet or gamma rays. Additionally, other layered minerals irradiated with gamma rays can enhance their radiation shielding capacity and electronic insulating property.

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