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Research paper

Vermiculites irradiated with ultraviolet radiation

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ABSTRACT

The present work reports the effects of ultraviolet radiation on commercial vermiculites for the first time. The changes induced by UV-radiation, dehydration–hydration and structural order–disorder, were studied by using X-ray diffraction (XRD). The results of XRD analysis indicated that these changes occurred in a similar way as temperature and vacuum do and they were more significant for vermiculites in powder form than in thin sheet. The larger crystallite size in the thin samples implied the presence of lower amounts of defects, improvement in the crystallinity and therefore increasing the structural order. Furthermore, ultraviolet radiation, being less penetrating and easier and cheaper to obtain than the gamma radiation, could be used as an alternative to induce structural order in thin sheet vermiculites. This success could be very important to solve some aspects related with the dimensionality of magnetic interactions, which plays a central role in controlling the critical dynamics of spin-glass systems (disordered magnet, where the magnetic spins of the component atoms — the orientation of the north and south magnetic poles in three-dimensional space — are not aligned in a regular pattern), and it is still not resolved in vermiculite due probably to its disordered structure. Also, the ultraviolet radiation as with gamma radiation probably might allow to enhance the physical properties of vermiculite as optoelectronic properties which would make it suitable for optoelectronic devices, although more investigation is needed.

1. Introduction

Vermiculite is the mineralogical name generally applied to a layered silicate mineral whose basic building block is composed of two silica tetrahedral sheets coupled symmetrically to another magnesium octahedral sheet in a tetrahedral–octahedral–tetrahedral layer lattice. Vermiculite has water layers between the silicate layers and, consequently, it can suffer processes of dehydration–hydration which depend on temperature, pressure, chemical composition, size and relative humidity (Mathieson and Walker, 1954; Walker, 1956; Collins et al., 1992; Vali and Hesse, 1992; Reichenbach and Beyer, 1994, 1995, 1997; Ruiz-Conde et al., 1996; Marcos et al., 2003, 2009; Marcos and Rodríguez, 2010). The hydration state of vermiculite is defined by the number of water layers in the interlayer space, with a development corresponding to different phases, such as zero-, one- and two-water layer hydration states (0-, 1- and 2-WLHS, respectively) (Suzuki et al., 1987). As an example, for Mg-vermiculites the basal spacings are 9.02 Å for 0-WLHS, 11.50 Å for 1-WLHS and 14.40 Å for 2-WLHS (e.g. Suzuki et al., 1987; Ruiz-Conde et al., 1996; Marcos et al., 2003, 2009). This layered silicate with layered structure present disorder effects, even one of the purest and studied vermiculites as Santa Olalla (Huelva, Spain) (González García and García Ramos, 1960; Velasco et al., 1981; Justo, 1984; Luque et al., 1985; Justo et al., 1989; Ruiz-Conde et al., 1996; Wiewióra et al., 2003; Marcos et al., 2004, 2009, 2012; Ramírez-Valle et al., 2006; Argüelles et al., 2009, 2010, 2011; Marcos and Rodríguez, 2010, 2014). The structural disorder appears to be the most common configuration of vermiculite. The structure has been successfully refined from X-ray diffraction (XRD) data (de la Calle et al., 1988) and X-ray powder diffraction by a method based on a recursive description of faulted structures by using the DIFFaX+ software (Argüelles et al., 2009, 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).

As a result of their layered 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 and Stewart, 1983; Suzuki et al., 1989, 2001; Hindman, 1992; Bergaya et al., 2006; Klein and Dutrow, 2007; Abollino et al., 2008; Zhang et al., 2009; Marcos et al., 2012; Marcos et al., 2014), being an attractive material due to its numerous thermal and insulation applications, but it is also remarkably important as a model system in physics, chemistry and the biological sciences (Eom et al., 2011; Satapathy et al., 2011; Wu et al., 2011). 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). 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

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Table. 1
Result of the chemical analyses for the studied samples in terms of mass content (weight %) of the oxides of the elements and the water content (%).

Oxides	Santa Olalla	China G	Libby
SiO_2	35.167	35.647	38.665
TiO_2	0.317	1.161	1.174
Al_2O_3	15.097	10.996	13.022
Cr_2O_3	0.062	0.389	0.999
FeO	3.225	4.626	8.598
MnO	0.103	0.037	0.048
MgO	22.016	21.813	20.580
CaO	0.279	0.916	0.028
Na_2O	0.073	3.545	0.248
NiO	0.060	0.056	0.028
K_2O	0.048	5.614	9.682
Water content (%)	25.6	12.3	10.3

magnetic system from being long-range ordered. Probably, magnetic studies on structurally ordered vermiculites will allow elucidate the true nature of the spin-glass-like phases which are in controversy (Suzuki et al., 2001; Marcos et al., 2012). One way to provide structurally ordered vermiculites might be by irradiation with gamma rays. Gamma radiation induces structural order in vermiculites leading to materials with enhanced physical properties (Kaur et al., 2014). Ultraviolet radiation, being less penetrating and easier to obtain than the gamma radiation, could be an alternative to induce structural order in vermiculite and probably also to enhance their physical properties.

Ultraviolet radiation (UV) with wavelengths ranging from approximately 10 to 400 nm shows the following types as being most important: long-wave UV-A (400–320 nm), mean wave UV-B (320–280 nm), and short-wave UV-C (280–100 nm) (Coblentz, 1932; Setlow, 1974; Baadsgaard, 1991; Young et al., 1998; Allen, 2001; Lim et al., 2005). UV radiation carries a lot of energy: A 300 nm photon carries roughly an energy of 400 kJ/mol, 200 nm approximately 600 kJ/mol. UV-A is thought to cause skin aging and erythema or sunburn (Bissett et al., 1989; Diffey, 2002), whereas UV-B may cause DNA damage and skin cancer (Setlow, 1974; Young et al., 1998). UV-C is the highest-energy and most dangerous type of UV radiation, but it is generally absorbed by the ozone layer in the atmosphere (WHO, 2002).

The results obtained from the research on commercial vermiculites irradiated with short and long ultraviolet radiation are presented for the first time in this work and demonstrate the structural order induced in thin sheet samples opposite to disorder and loss of crystallinity provoked in powder samples.

2. Experimental

Vermiculites from Santa Olalla (Huelva, Spain), Libby (sample provided by Montana Bureau of Mines and Geology, a department of Montana Tech of The University of Montana, U.S.) and China (sample provided by Vermiculita y Derivados S.A. company of Gijón, Spain), were used as the starting material for this study, as received after elimination of other minerals (such as quartz, iron oxides, etc.) by handpicking. Chemical analyses of the untreated sample of Libby was performed by means of energy dispersive spectroscopic analysis using a CAMEBAX-MBXSX-50 electron microprobe with an acceleration voltage of 15 kV and a beam current of 15 mA. The thermogravimetric analyses were performed between 25 °C and 1100 °C using a Mettler Toledo Stare System thermobalance and porcelain crucible with a heating rate of 10 °C/min. The total mass loss was determined gravimetrically by heating the samples in air at 1000 °C in a muffle furnace and assumed due entirely as water. The initial sample mass ranged from 18 to 29 mg.

Thin sheet samples of 1.4×1.4 cm^2 were obtained from the starting vermiculites by using adhesive tape. The powder samples were obtained by crushing with an agate mortar the samples with particle size lower than 3 mm.

Thin sheets of Santa Olalla vermiculite were irradiated *in situ* with short UV (254 nm) for 1 h and 24 h, at room conditions and 50% relative humidity and at a distance of approximately 10 cm. Immediately thereafter each irradiation with UV the sample was irradiated by X-rays. The UV lamp was located in front of the sample to be irradiated by the UV and X-rays into a Bruker D8 Discover diffractometer. The machine settings were 40 mA and 45 kV (Cu-Kα radiation; $\lambda = 1.5418$ Å), 2θ range of 5–10, 2θ step scans of 0.005°. Thin sheet and powder samples from Santa Olalla, Libby and China were irradiated *ex situ* with short- (254 nm) and long-UV (356 nm) for 1, 24 and 168 h, at room conditions and 50% relative humidity and the distance between UV-lamp and sample was approximately of 10 cm. After, the samples were exposed to X radiation using a PANalytical X'Pert Pro. The machine settings were 40 mA and 45 kV (Cu-K_α radiation; $\lambda = 1.5418$ Å), 2θ range of 3–10,

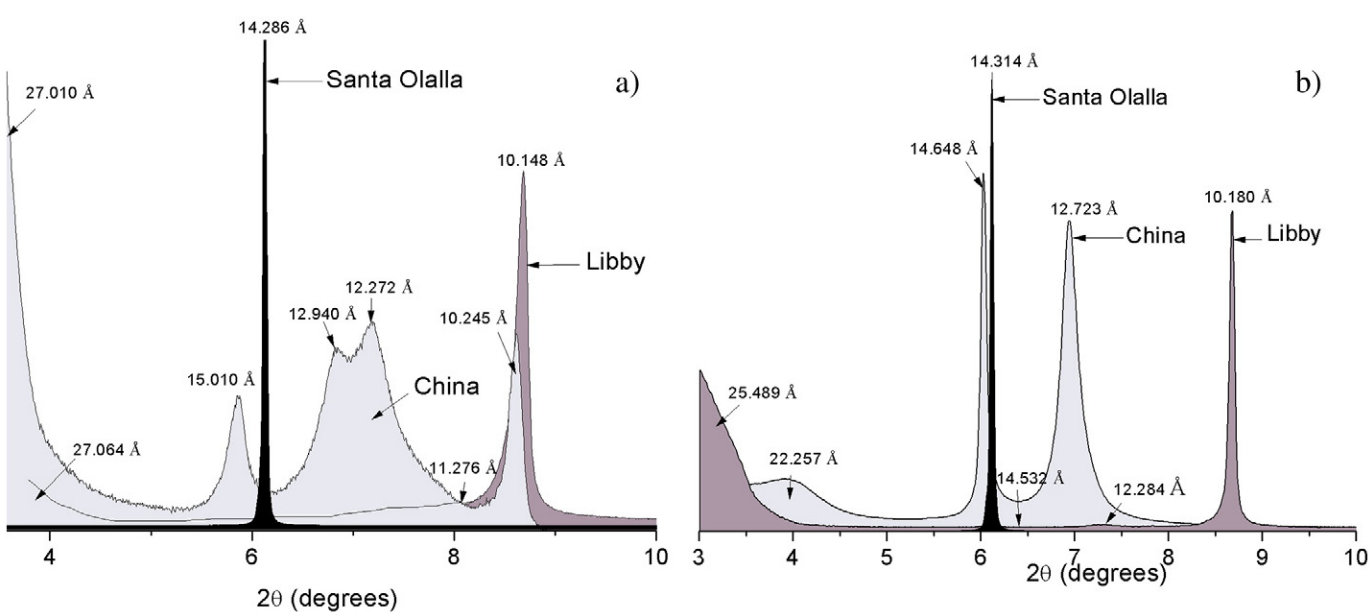

Fig. 1. X-ray diffraction patterns at room temperature of non-irradiated vermiculites from Santa Olalla, China and Libby in powder form (a) and in thin sheet samples (b).