Research paper

Vermiculites irradiated with ultraviolet radiation

C. Marcos *, I. Rodriguez

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

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A B S T R A C T

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.

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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; Viewiöra 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

* Corresponding author. Tel.: +34 985 10 31 00; fax: 34 985 10 31 03.
E-mail address: cmarcos@uniovi.es (C. Marcos).

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0169-1317/© 2015 Elsevier B.V. All rights reserved.
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 hand-picking. Chemical analyses of the untreated sample of Libby was performed by means of energy dispersive spectroscopic analysis using a CAMEBAX-MBX50 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 Star 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 cm² 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 after 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; λ = 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-Kα radiation; λ = 1.5418 Å), 2θ range of 3–10,

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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 (%).

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Santa Olalla</th>
<th>China G</th>
<th>Libby</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>35.167</td>
<td>35.647</td>
<td>38.665</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.317</td>
<td>1.161</td>
<td>1.174</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>15.097</td>
<td>10.996</td>
<td>13.022</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.062</td>
<td>0.389</td>
<td>0.999</td>
</tr>
<tr>
<td>FeO</td>
<td>3.225</td>
<td>4.626</td>
<td>8.598</td>
</tr>
<tr>
<td>MnO</td>
<td>0.103</td>
<td>0.037</td>
<td>0.048</td>
</tr>
<tr>
<td>MgO</td>
<td>22.016</td>
<td>21.813</td>
<td>20.580</td>
</tr>
<tr>
<td>CaO</td>
<td>0.279</td>
<td>0.916</td>
<td>0.028</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.073</td>
<td>3.545</td>
<td>0.248</td>
</tr>
<tr>
<td>NiO</td>
<td>0.060</td>
<td>0.056</td>
<td>0.028</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.048</td>
<td>5.614</td>
<td>9.682</td>
</tr>
<tr>
<td>Water content (%)</td>
<td>25.6</td>
<td>12.3</td>
<td>10.3</td>
</tr>
</tbody>
</table>

---

**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).
The starting sample of Santa Olalla in powder form and in thin sheet consisted basically of 2-WLHS phase with two hydrates related to the phase with d highlighted and underlined, the other phases were barely noticeable.

In the China sample in powder form coexisted different phases: 2-WLHS hydrates (at 15.010 Å and 13.076 Å, respectively); 2-1 WLHS (at 12.571 Å and 12.272 Å, probably a random interstratification of 2- and 1-WLHS), reflections at 10.301–10.245 Å (interstratified 1-0 WLHS), and probably two superstructures at 28.829 Å and 27.010 Å, as a result of layer alternance with basal spacings of 15.010 Å and 13.076 Å in the first and of 15.010 Å and 12.272 Å in the second. All the phases were very noticeable. In thin sheet the 2-WLHS, 2-1 WLHS and interstratified 1-0 WLHS phases coexisted with other phases, probably superstructures with interplanar distances inferior to the ones of the sample in powder.

In the Libby sample in powder form coexisted hydrates 1-0 WLHS (at 10.148 Å), very noticeable and as expected in many K-vermiculites (MacEwan and Wilson, 1980), with 2-1 WLHS (at 12.571–12.284 Å) and 1 WLHS (at 11.276 Å) and two almost imperceptible superstructures (at 28.766 Å and 27.064 Å). The thin sheet sample appeared to retain the basal spacing of the 1-0 WLHS (at 10.180 Å) as the sample in powder form.

In the XRD of the irradiated vermiculites at ambient conditions (Figs. 2–4; in which 1, 24 and 168 denote the irradiation hours) the intensity and position of the reflections varied compared to those of the non-irradiated samples.

In the samples of Santa Olalla in powder form and in thin sheet irradiated with short- and long-UV radiation in ex situ the position of their most characteristic reflection (002) shifted slightly toward higher values of 2θ in relation to the non-irradiated UV sample, except in the powdered sample irradiated with short-UV for 24 h (Fig. 2a–e and Tables 3–4). The intensity order of the reflection (002) with irradiation time was for:

- powdered samples:
  a) short-UV: non-irradiated > 1 > 24 > 168,
  b) long-UV: non-irradiated > 24 > 168 > 1;

<table>
<thead>
<tr>
<th>Phases</th>
<th>Santa Olalla</th>
<th>China</th>
<th>Libby</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>d (Å)</td>
<td>15.810</td>
<td>15.010</td>
<td>Powder</td>
<td></td>
</tr>
<tr>
<td></td>
<td>14.286</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>13.132</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>15.844</td>
<td>14.656</td>
<td>14.532</td>
<td>Thin sheet</td>
</tr>
<tr>
<td></td>
<td>14.314</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>13.303</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-WLHS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-1 WLHS</td>
<td>12.623</td>
<td>13.076</td>
<td>28.066</td>
<td>Powder</td>
</tr>
<tr>
<td></td>
<td>12.632</td>
<td>24.766</td>
<td>27.010</td>
<td>Thin sheet</td>
</tr>
<tr>
<td>1-WLHS</td>
<td>11.494</td>
<td>11.220</td>
<td>11.276</td>
<td>Powder</td>
</tr>
<tr>
<td>0-WLHS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interstratified 1-0 WLHS</td>
<td>10.301–10.245</td>
<td>10.148</td>
<td>Powder</td>
<td></td>
</tr>
<tr>
<td>Superstructures</td>
<td>27.999</td>
<td>10.052</td>
<td>10.180</td>
<td>Thin sheet</td>
</tr>
<tr>
<td></td>
<td>26.834</td>
<td>27.010</td>
<td></td>
<td>Powder</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27.064</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>28.066</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>28.602</td>
<td>27.731–27.211</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>27.109</td>
<td>24.766</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20.760</td>
<td>23.354</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20.070</td>
<td>22.614–22.257</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>17.207</td>
<td>21.647</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>16.230</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
thin samples:

- short-UV: 168 > 24 > 1 > non-irradiated, and in situ = 24 > 1 > non-irradiated.
- long-UV: 24 > 168 > 1 > non-irradiated.

The reflections of the China vermiculite in powder form and in thin sheet irradiated ex situ with short- and long-UV (Fig. 3a–d) correspond to different phases coexisting (hydration states, interstratified phases and superstructures) (see Table 4). The position of these reflections shifted toward higher 2θ values, except for the powdered samples irradiated for 24 h with short-UV and 1 h with long-UV. The intensity order of the reflections with irradiation time was for:

- powdered samples:
  - short-UV: non-irradiated > 1 > 24 > 168,
  - long-UV: non-irradiated > 1 > 168 > 24;

- thin samples:
  - short-UV: vermiculite phase – 24 > non-irradiated > 1 > 168–, interstratified phase – non-irradiated > 1 > 24 > 168;

The reflections of the Libby vermiculite in powder form irradiated with short- and long-UV ex situ (Fig. 4a–d) correspond to different phases coexisting (hydration states, interstratified phases and superstructures) (see Table 5) with very low intensity in general, except that corresponding to the interstratified 1-0 WLHS which is the most important reflection of this sample. The intensity order of the reflections with irradiation time was for:

- powdered samples:
  - short-UV: interstratified 1-0 WLHS–non-irradiated = 24 > 1 > 168–, interstratified 2-1 WLHS – 24 > 1 > non-irradiated > 168– (see in the inset of Fig. 4a);
  - long-UV: interstratified 1-0 WLHS–non-irradiated > 168 > 24 > 1–, interstratified 2-1 WLHS–non-irradiated > 24 > 168 > 1– (see in the inset of Fig. 4b);

- thin samples:
  - short-UV: interstratified 1-0 WLHS – 1 > 168 > 24 > non-irradiated, interstratified 2-WLHS – 24 > 1 > non-irradiated, and
the reflection intensity of this phase was negligible compared to the interstratified 1-0 WLHS and disappeared with 168 h of irradiation (see in the inset of Fig. 4c);

b) long-UV: interstratified 1-0 WLHS − 24 > 1 > 168 > non-irradiated, interstratified 2-WLHS − 168 > non-irradiated, but the reflection intensity disappeared for 1 and 24 h of irradiation (see in the inset of Fig. 4d).

A remarkable difference was found in the process induced by UV irradiation on thin sheet samples and powder form. The changes were more pronounced in the China and Libby vermiculites than in the purest of Santa Olalla, and most pronounced in powder form. In thin sheet, Santa Olalla and Libby vermiculites reacted to UV radiation in a similar manner, the position of the principal reflection shifted toward higher \(2\theta\) values and the intensity increased. China vermiculite behaved in a slightly different way since the intensity of the most important reflections decreased with short-UV and increased with long-UV. Thus, the intensity and position of the most characteristic reflections in the irradiated UV vermiculites depending on the vermiculite type, irradiation time and sample size and preparation (powder or thin sheets).

All of recognized phases in the investigated vermiculites both non-irradiated and irradiated were previously reported (Collins et al., 1992; Reichenbach and Beyer, 1994; Ruiz-Conde et al., 1996; Marcos et al., 2003).

4. Discussion

The fact that the XRD intensity of the non-irradiated vermiculites was higher in thin sheet than in powder and the hydration state was reversed, is due to the difficulty shown by the thin sheet samples in avoiding the removal of water molecules according to Marcos et al. (2003).

The slight shift of the most characteristic reflections recorded by XRD toward higher values of \(2\theta\) observed in the irradiated UV samples for 1, 24 and 168 h can be associated to the slight dehydration suffered with the irradiation, as corroborated by thermogravimetry.

As with other treatments such as heating at elevated temperature or vacuum (Reichenbach and Beyer, 1994; Ruiz-Conde et al., 1996; Marcos et al., 2003; Marcos et al., 2009), the changes caused by UV radiation can be related to interlayer-cations (\(\text{Mg}^{2+}\) and \(\text{K}^+\)) and iron and water contents. \(\text{Mg}^{2+}\) cation has a high affinity to water molecules while \(\text{K}^+\) ion has a relatively low hydration energy, and \(\text{Fe}^{2+}\) ion would facilitate the fixation of the \(\text{K}^+\). In the powder samples of the three vermiculites irradiated with short- and long-UV, the broadening of the most characteristic reflections with irradiation time, the decreasing intensity and the slight increase of the \(2\theta\) values indicated a more disordered structure. In contrast, the structure of the samples in thin sheets would be more ordered. The difference in the structural order in powdered and thin sheets samples could be explained according to Marcos et al. (2003) as the difficulty showed by the first in avoiding the removal of water molecules, as consequence the surface to volume ratio is less in thin sheet than in powder samples and the enclosed volume that could not dehydrate was greater. This suggested that the external layers of the samples became a barrier between the outer atmosphere and the internal layers, avoiding dehydration.

The greater transformation to UV radiation experienced by China vermiculite in powder form could be explained by the coexistence of different hydration states, interstratifications and superstructures in the starting vermiculite and higher \(\text{Mg}^{2+}\) and \(\text{K}^+\) interlayer contents than in the other studied vermiculites.

Increasing the intensity of the reflections with irradiation time might be related to the increase in structural order caused probably by the slight water adsorption (Marcos et al., 2009). At the same time, the structural order could be attributed to the improvement in the crystallinity due to the increase of crystalite size, reduction of the defects and the decrease in structural disorder and lattice strain. On the other hand, the subsequent decrease in intensity could denote some
destruction of the structural order of the original crystal and loss of crystallinity. X-ray diffraction reflections broaden when the crystal lattice becomes imperfect (Klug and Alexander, 1974; Warren, 1990; Snyder and Hala, 1999; Mittemeijer and Scardi, 2004; Ungár, 2004), and therefore the reflection broadening carries direct information about the lattice imperfections. In general, these lattice imperfections are classified into two types: nanometer-sized crystals and lattice defects (Klug and Alexander, 1974; Warren, 1990; Snyder and Hala, 1999; Mittemeijer and Scardi, 2004; Ungár, 2004). Thus, the crystal sizes and lattice microstrains of materials are evaluated using the line-broadening theory of X-ray powder diffractometry. Authors like Pérez-Maqueda et al. (2001) or Pérez-Rodríguez et al. (2002) used these parameters in delamination experiments of vermiculite, and Kaur et al. (2014) used them with gamma-irradiated vermiculite. The crystallite size was calculated from the full width half maximum (FWHM) measurements using Debye Scherrer formula (Scherrer, 1918; Patterson, 1939):

$$\text{crystallite size} = \frac{\lambda K}{\text{FWHM} \cos \theta}$$

where, $K$ is the shape factor which is usually close to the default value 0.9, $\lambda$ (1.541 Å) is the wavelength of X-ray , $\theta$ is the diffraction angle or Bragg’s angle. The values of FWHM and $\theta$ were obtained from the diffraction patterns (Figs. 1–4). The lattice strain arising from crystal imperfection and distortion was calculated using formula (Stokes and Wilson, 1944):

$$\text{lattice strain} = \frac{\text{FWHM}}{4 \tan \theta}$$

As expected, larger the crystallite size the fewer lattice strain and defects (Table 6). The crystallite size was greater in thin sheet samples than in powder form, except for China which was reversed probably due to its more complex structure. In general, larger the crystallite size in the powder samples irradiated with short- and long-UV was provided by China vermiculite and in thin sheet samples by Santa Olalla. The larger the crystallite size in the thin sheet samples corroborated the intensity increase of the most important reflections of the vermiculites studied in thin sheet. The larger the crystallite size in the thin samples implied

![Fig. 4. X-ray diffraction pattern for non-irradiated and irradiated ex situ vermiculites from Libby. With short ultraviolet radiation in powder form (a) and in thin sheet (b), with long ultraviolet radiation in powder form (c) and in thin sheet (d).](image-url)
reduction of the defects, improvement in the crystallinity and therefore greater structural order.

The fact that UV-radiation can provoke structural order in vermiculites might be very important to elucidate the true nature of the spin-glass-like phases from magnetic studies. The dimensionality of magnetic interactions, which plays a central role in controlling the critical dynamics of spin-glass systems, subject that has been challenging both experimentalists and theoreticians for more than forty years (Dekker et al., 1989), is still not resolved in vermiculite due probably to its disordered structure. Also, this will probably allow enhance their physical properties as optoelectronic properties in a similar way to with gamma rays (Kaur et al., 2014) and which would make it suitable for optoelectronic devices, although more investigation is needed.

5. Conclusions

It was the first time that structural changes, as structural order–disorder and dehydration–rehydration, induced by short- and long-
ultraviolet (UV) radiation in commercial vermiculites were analyzed by X-ray powder diffraction. The results of XRD analysis indicated that these changes occurred in a similar way to as temperature and vacuum do. The changes were more significant for vermiculites in powder form due to the difficulty showed by the first in avoiding the removal of water molecules. Also, these results were more significant for the China vermiculite in powder form than for the Santa Olalla and Libby 7 vermiculites probably by the coexistence of different hydration states, interstratifications and superstructures in the starting China vermiculite and higher Mg$^{2+}$ and K$^+$ interlayer contents than in the other vermiculites. The structure of the samples in thin sheets was more ordered than in powder form as consequence of the larger of the crystallite size. Further, ultraviolet radiation, being less penetrating and easier and cheaper to obtain than gamma radiation, could be used as an alternative to induce structural order in vermiculites in thin sheet, very important to elucidate the true nature of the spin-glass-like phases from magnetic studies and probably also to enhance their physical properties as optoelectronic properties, although more investigation is needed.

Acknowledgments

The authors wish to acknowledge the scientific–technical services of the University of Oviedo (Spain) for the X-ray diffractometry.

Table 5

| Phases coexisting in the Libby vermiculite in powder form and thin sheet irradiated with short- and long-ultraviolet radiation for 1, 24 and 168 h (WLHS: Water Layer Hydration States – 0, 1, 2-). Note: d highlighted and underlined correspond to the most intense and characteristic reflections). |
|---|---|---|---|---|---|---|---|---|
| Irradiation time (hours) | 1 | 24 | 168 |
| 1-0 WLHS | 27.5480 | 27.834 | 27.5480 |
| 1-WLHS | 27.5670 | 27.5670 | 27.5670 |
| 2-1 WLHS | 28.3644 | 28.3644 | 28.3644 |
| Superstructures | 28.450 | 28.450 | 28.450 |
| Samples | Powder | Thin sheet |

References


Table 6

| Values of crystallite size (Å) and lattice strain (%) obtained for vermiculites from Santa Olalla, China and Libby. |
|---|---|---|---|---|---|---|
| Sample type | UV-radiation | Time (hours) | Peak (°) | FWHM (°) | Crystallite size (Å) | Lattice strain (%) |
| Powder | Non-irradiated | Short | 5.585 | 5.883 | 8.706 | 0.052 | Santa Olalla | 1530 | 1530 | 821 | 0.465 | 0.422 | 0.536 |
| | | 1 | 6.227 | 5.841 | 8.805 | 0.058 | 0.052 | 0.084 | 1372 | 2486 | 949 | 0.465 | 0.274 | 0.476 |
| | | 24 | 6.156 | 6.177 | 8.757 | 0.090 | 0.065 | 0.065 | 884 | 1224 | 1226 | 0.730 | 0.526 | 0.370 |
| | | 168 | 6.228 | 6.177 | 8.806 | 0.058 | 0.052 | 0.058 | 1372 | 1530 | 1374 | 0.465 | 0.421 | 0.329 |
| Thin sheets | Non-irradiated | Short | 6.170 | 6.026 | 8.679 | 0.045 | 0.052 | 0.065 | 1768 | 1530 | 1226 | 0.364 | 0.431 | 0.374 |
| | | 1 | 6.196 | 6.018 | 8.823 | 0.039 | 0.058 | 0.045 | 2040 | 1372 | 1771 | 0.314 | 0.481 | 0.254 |
| | | 24 | 6.174 | 6.025 | 8.792 | 0.032 | 0.071 | 0.052 | 2486 | 1120 | 1532 | 0.259 | 0.589 | 0.295 |
| | | 168 | 6.246 | 6.061 | 8.800 | 0.058 | 0.103 | 0.058 | 1372 | 772 | 1374 | 0.464 | 0.849 | 0.329 |
| | Long | 1 | 6.308 | 6.138 | 8.802 | 0.045 | 0.078 | 0.045 | 1768 | 1020 | 1771 | 0.356 | 0.635 | 0.255 |
| | | 24 | 6.229 | 6.095 | 8.798 | 0.052 | 0.058 | 0.045 | 1530 | 1372 | 1771 | 0.417 | 0.478 | 0.255 |
| | | 168 | 6.228 | 6.070 | 8.799 | 0.045 | 0.058 | 0.045 | 1768 | 1372 | 1771 | 0.361 | 0.477 | 0.255 |


