O 1s X-ray absorption spectra of Sr$_2$RuO$_4$ and SrRuO$_3$

Juliana Manica, Miguel Abbate

Departamento de Física, Universidade Federal do Paraná, Brazil. E-mail: jm00@fisica.ufpr.br

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We studied the electronic structure of the Sr$_2$RuO$_4$ and SrRuO$_3$ using O *1s* X-ray absorption spectroscopy (XAS). The experimental spectra were interpreted in terms of the electronic states calculated using the LMTO method. For the SrRuO$_3$ is presented a magnetic solution, however, for Sr$_2$RuO$_4$ a magnetic solution is not stable. In both compounds, the Ru 4d and O 2p states are heavily mixed, especially in the valence band region, while Sr 4d band are concentrated mostly in the conduction band. This indicates that the Sr presents a more ionic character within the structure, while the Ru and O present a more covalent character within the structure. The density of states showed that the bandwidth of the Ru 4d in the SrRuO$_3$ is larger than in the Sr$_2$RuO$_4$ due to the major dispersion perpendicular to the planes. In the XAS spectra, the absorption intensity shows a good indication of covalence effects. The major differences between the Sr$_2$RuO$_4$ and SrRuO$_3$ concern in the e_g band, where, the e_g band is shifted for minor energies in the Sr$_2$RuO$_4$ in relation to the SrRuO$_3$. Also, the Sr 4d appears for smaller energy in the Sr$_2$RuO$_4$.

Layer charge of smectites: linking crystal structure with physical properties

George E. Christidis

Department of Mineral Resources Engineering, Technical University of Crete, 73100 Chania, Greece. E-mail: christid@mred.tuc.gr

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Layer charge is a fundamental property of smectites, which controls cation exchange capacity, ion exchange selectivity and swelling. Within this context, determination of layer charge and charge distribution within a bentonite deposit is of particular importance because a) it can shed light on the formation mechanism of the bentonite and any possible subsequent modifications and b) it controls the variability of bentonites in various industrial applications. This is turn can assist in an understanding of why production of Na-activated smectites from Ca-Mg smectites usually yields unpredictable results [1]. Layer charge can be determined either from the structural formula or from saturation with alkylammonium cations [2]. Recently Christidis & Eberl (2003) [3] proposed a new method which calculates the layer charge and charge distribution of smectites with X-ray diffraction (XRD). The method is based on the saturation of the $< 2\,\mu$m fraction with a cation of low hydration energy, mainly K, ethylene glycol solvation, subsequent X-ray diffraction and then determination of the layer charge and charge distribution of smectites by means of the LayerCharge program [3]. The method has been refined further to calculate the influence of tetrahedral charge on determination of layer charge. Compared to the pre-existing methods the new technique is faster and it is not affected by the presence of impurities. It has found applications in clay mineralogy, clay geology and in the understanding of physical properties of the smectites. Hence it has been used successfully to evaluate the tendency of the smectite layers to convert to illite when subjected to successive wetting and drying (WD) cycles. Also it has assisted to differentiate between high charge smectite and vermiculite and to classify the smectites according to their layer charge. This is of particular importance because so far there is no classification scheme of smectites according to the layer charge and any characterization is arbitrary. The new method also has shown the influence of layer charge on the colloidal properties of smectites which are valued by the industry. In general, increase of layer charge affects adversely most colloidal properties and high charge smectites have inferior swelling and rheological properties. Moreover in general colloidal properties seem to be affected systematically by layer charge in the range 0.425 to 0.47 per half formula unit (phfu). This range corresponds to smectites with intermediate layer charge according to [4]. Currently we use this technique to examine the distribution of layer charge of smectites in bentonite deposits. It is expected that layer charge systematics within bentonite deposits may lead to an understanding of the genesis of the deposits and the variations in the colloidal properties of the bentonites.

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