

EPR SPECTROSCOPY APPLIED TO THE STUDY OF ANCIENT CERAMICS: PRELIMINARY RESULTS FOR BRONZE AGE POTTERY FROM ILISUA

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ABSTRACT. Ceramic pottery fragments of Ilişua archaeological site were studied by Electron Paramagnetic Resonance (EPR). The Fe³⁺ EPR spectra evidence the disposal of ferric ions in different environments depending on their thermal history. The firing temperatures of the raw clays used in manufacturing of the investigated ceramic samples were compared based on the relative intensity of the resonance lines.

Keywords: EPR; ancient ceramics.

Introduction

Since 1960's, the Electron Paramagnetic Resonance (EPR) has been successfully applied for post-accident dose reconstruction in the environment [1], investigation of human tissues [2, 3] or other various substances including geological systems [4-8]. Apart of dating of stalactites [9], or sediments [10] a number of other geological materials, e.g. cherts [11], volcanics [12, 13], clays [14-16], travertines [17] and some minerals [18, 19] were also subjected to EPR studies.

Moreover, the EPR is widely used in archaeometry, for tooth enamel and bones dating [20-24], for the study of mosaic glasses [25], organic food remnants [26] and other compounds [27]. For ceramics, the EPR application regards mainly dating as well as information on firing temperature and atmosphere [28-31]. The ceramics is suited for EPR studies because it is made of natural clays containing iron. However, whether upon firing iron occurs as "free" oxides, ferric or ferrous ions trapped inside glass or crystalline firing phases, or adsorbed on the surface of phyllosilicates remains unknown.

The aim of this paper is to present preliminary EPR results on ceramic pottery fragments of Ilişua archaeological site and to compare with the previous results obtained by optical microscopy and Electron Microprobe analyses on same shards.

Samples and method

The Ilişua archaeological site is located in the northern part of the Transylvanian Basin, in Romania, on a high terrace of the Someşu Mare River near the confluence

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with the Şieu River [32]. Beneath the remains of a Roman *castrum* [33], cremation tombs containing bronze artefacts and shards of ceramic bowls, cups, plates, small vessels were found. These were assigned to the so-called Late Bronze Age “Noua” Culture, dated between 1400-1200 B.C. [34].

Fragments of ceramic pottery, labelled B2, B4, B6, B7, B8 and B11, were provided by Bistrița-Năsăud County Museum (Romania) for mineralogical and physical studies. The ceramic samples show a brown to greyish-brown body-colour and a relatively homogeneous appearance, with visible pores and shrinkage cracks.

The EPR measurements were performed at room temperature on powdered samples of same mass, at room temperature, in X band (9.4 GHz), with 4 G modulation amplitude, on an ADANI spectrometer.

Results and discussion

The EPR spectra (Fig. 1) are dominated by a large, relatively symmetric resonance line with $g_{\text{eff}} \approx 2.1$. No narrow signal can be observed close to $g_{\text{eff}} = 2$, that usually arises in clays from paramagnetic centers due to the natural radiation which induces the formation of radicals of trapped electrons and holes [35]. Such irradiation induced defects disappear when the calcination temperature increases, i.e. they are thermally removed [36]. Their lacking in the EPR spectra suggests firing temperature above 800 °C for the ceramic sample [29, 31]. This is in good agreement with the Electron Microprobe data based on mineral chemistry, which assume a firing temperature between 850-950 °C for the Ilisua ceramic samples [32].

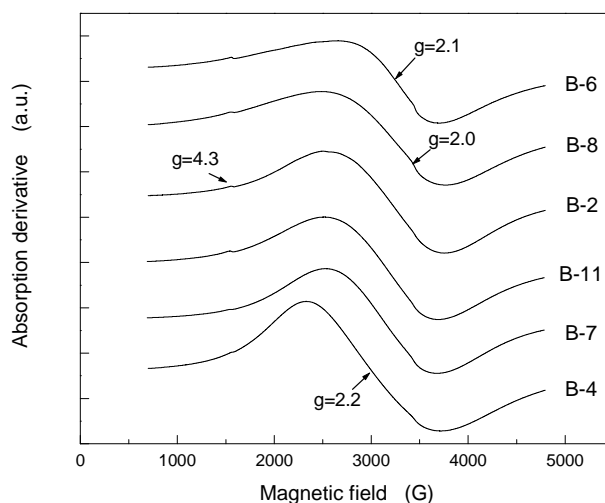


Fig. 1. The room temperature EPR spectra of ceramic samples.

A weak resonance signal occurs at $g_{\text{eff}} \approx 4.3$ and is assigned to Fe^{3+} ions in sites of tetrahedral or rhombohedral symmetry, characterized by high crystal fields. As this resonance line is typical for Fe^{3+} ions trapped in glasses [37], its intensity might be a rough measure of the quantity of the glass phase present in the ceramics and implicitly a qualitative estimation of the firing temperature. The intensity of this signal is better evidenced in Fig. 2. According to the intensity of these resonance signals, the highest firing temperature was applied to sample B6 and the lowest to samples B7 and B4.

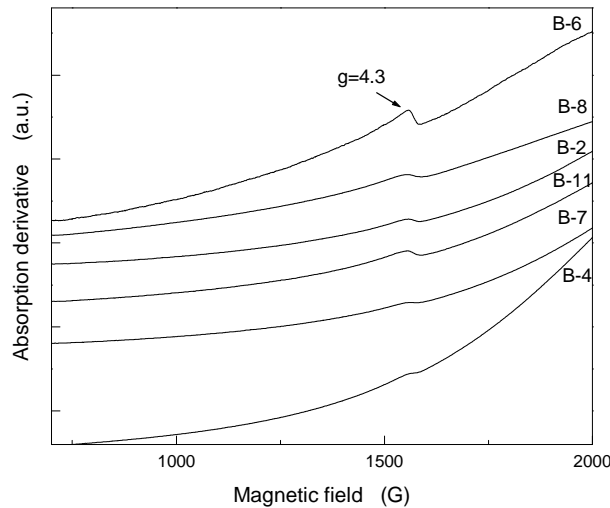


Fig. 2. Detailed EPR spectra of ceramic samples in the low magnetic field region.

The large and symmetric resonance line with $g_{\text{eff}} \approx 2.1$ is assigned to Fe^{3+} ions in sites of octahedral symmetry, with low crystal fields, and is specific to disordered oxide systems with high Fe_2O_3 content wherein most probably hematite and/or magnetite particles occur [38, 39]. In thin sections, hematite, Ti-magnetite and Fe_2O_3 -bearing ilmenite were identified [32]. The resonance line at $g_{\text{eff}} \approx 2.1$ is shifted to lower values of the magnetic field, up to $g_{\text{eff}} \approx 2.2$, in following order: B6, B8, B2, B11, B7 and B4 (Figs. 1 and 2). These results can be assigned to the development of ferromagnetic multi-domain particles in the ceramics samples. The width of $g_{\text{eff}} \approx 2.1$ line increases in the same order of samples and suggests a wide range of ferromagnetic particles size. Conversion of Fe^{3+} ions into Fe^{2+} ions could also contribute to the observed evolution of the Fe^{3+} EPR intensity. The lowest intensity of the EPR signal is recorded for the B6 sample, showing lowest Fe^{3+} content.

It has to be noticed that the EPR spectra of the samples B-6 and B-8 are quite similar and differ from the other ones. Whereas the EPR spectra for the latter are rather symmetric, those of the B6 and B8 samples are more asymmetric, indicating a shape of the magnetic domains far from ideal sphere. Even though at such Fe_3O_3 concentrations a line narrowing, due to super-exchange interactions, is expected, this narrowing is not observed. It might be presumed that any narrowing in some clusters is masked by the dipolar broadening or by the structural disorder in the iron rich phases.

Conversion of Fe^{3+} ions into Fe^{2+} ions could also contribute to the observed evolution of the Fe^{3+} EPR intensity, that can be exploited for the investigation of firing temperature. The lower intensity of the EPR signal recorded for the B-6 sample (Fig. 1) shows that the Fe^{3+} content in this ceramic is lower than in the other ones, probably due to higher firing temperature.

Conclusions

The EPR results on pottery fragments of Ilişua archaeological site show that the iron present in clays which are now thermally transformed is located in two types of sites. The resonance lines at $g_{\text{eff}} \approx 4.3$ and 2.1 might be assigned to the Fe^{3+} ions in sites of low symmetry characterized by high crystal fields, and to the Fe^{3+} ions in sites of octahedral symmetry, with low crystal fields, respectively. The relative firing temperature was comparatively estimated based on the relative intensity of the resonance absorption lines. These indicate the highest temperature for the sample labelled B-6. The lack from the RPR spectra of the radiation-induced defects suggests firing temperature above 800-850 °C for all investigated samples. This is consistent with the mineral chemistry based on electron microprobe data [32] which assumed a firing temperature between 850-950 °C for the Ilişua ceramic samples.

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