

Preparation and Spectroscopic Characterization of Iron Doped Mullite

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Abstract. A novel method for preparation of Fe²⁺/Fe³⁺ substituted mullite is described. Aluminosilicate gels are applied as precursors instead of crystalline aluminosilicates as used in other common syntheses. The process is composed of three stages. First, iron is introduced into a homogeneous aluminosilicate gel by ion exchange. The gel is converted to a mixture of mullite and amorphous silica in a 1263 K 3 h isothermal calcination in the second stage. Finally, in order to obtain the nano-scale pure mullite phase the formed amorphous silica is removed by a dissolution in alkaline media. The components formed in various stages of the process are characterized by ⁵⁷Fe Mössbauer and Fourier transform infra red spectroscopies, X-ray diffraction method and scanning electron microscopy. Spectroscopic and diffraction methods helped the identification of the mullite phase. Mössbauer measurements revealed the presence of both Fe²⁺ and Fe³⁺ states providing a chance for perspective catalytic application of the obtained Fe-mullite.

Keywords: iron doped mullite, SEM, ⁵⁷Fe Mössbauer spectroscopy, FT-IR, XRD

1. INTRODUCTION

Mullite is a well known ceramic material. Its synthesis, properties, advantageous features and applications are described in detail *e.g.* in Ref. 1. One of the advantageous properties is its small heat expansion coefficient, thus the substance can be used as a refractory material, or *e.g.* as a support for catalysts in car engines which are being exposed to cyclic heat shocks.² Mullite can usually be formed by heating mixtures of silica- and alumina-containing appropriate precursors (minerals, oxihydroxides, *etc.*).³

Properties of mullite can be modified by insertion of a transition metal ion, such as iron, into the structure. Iron may occupy both octahedral and tetrahedral sites in the lattice.¹ Addition of iron may promote formation of mullite phase in high temperature phase transformations.⁴ Insertion of iron broadens the possibilities of perspective applications. For instance, mullite particles can be reinforced with carbon nanotubes in a composite.⁵ Presence of iron is essential for the synthesis, it catalyses the formation of carbon nanotubes.⁶ In another variation the electrical resistivity of mullite, originally an insulator, can be tuned by adding iron, thus providing a mean to prepare novel substrate materials for electronic devices.⁷ Further on, biocompatibility of iron-

containing mullite can also be utilised in various applications, namely as osteoconductive substance, or as ferrimagnetic glass ceramics for hysteresis heating of surrounding tissues.⁸

Sol-gel processes can conveniently be used for synthesis of precursors of iron-containing mullite substances. Solution of silicic acid can be mixed with appropriate solutions of Al(NO₃)₃·9H₂O and Fe(NO₃)₃·9H₂O,⁸ or further components (aluminium isopropoxide, tetraethyl orthosilicate) can also be added to the previous constituents.⁷ In the subsequent stages of preparation the gels are dried and are exposed to appropriate high temperature thermal treatments to form the mullite structure.

Sol-gel processes are also used for synthesis of precursors of various zeolites. Several zeolites have compositions close to aluminosilicate based ceramics and their thermal treatment results in the formation of various ceramic materials.^{9,10} In particular, ammonium forms of zeolite A and X are transformed to a mixture of mullite and amorphous SiO₂ in a thermal treatment at an appropriate temperature (≈ 1273 K) as demonstrated in our previous studies.^{11,12} The first step of the thermal transformation of the ammonium form of zeolite A and X is the thermally induced breaking of Si–O–Si and Si–O–Al bonds of zeolite framework resulting in the

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formation of an amorphous aluminosilicate phase. Thus, transformation of zeolite into ceramics does not proceed directly, *i.e.* by „reorganisation” (rotation, translation) of specific subunits (primary and secondary building units) of zeolite framework. Instead, nucleation and crystal growth of the secondary phase (ceramic) takes place in the matrix of the amorphous aluminosilicate.¹⁰

Basically, the process of conversion of the starting gel to zeolites and later to ceramics is completed in a two-stage thermal treatment. Zeolite structure is stabilized at a medium temperature (≈ 773 K) first, then ceramic is formed at ca. 1273 K. Composition of aluminosilicate zeolites can be modified, by varying the charge compensating cations. Among other ions, iron can also be introduced to the structure in conventional processes from aqueous solutions¹³ or by solid state ion exchange as well.¹⁴ Ion exchange can also be performed with dried aluminosilicate gels, even prior to the first thermal treatment, *i.e.* prior to the formation of crystalline zeolites. Further on, iron can also be exchanged in dried aluminosilicate gels, as has been proved with zeolite A precursors.¹⁵ It is known that mullite may crystallize at temperatures below 1273 K by annealing amorphous precursors having high chemical homogeneity (Si-Al mixing) that can be synthesized by sol-gel or spray pyrolysis procedures.⁴ The homogeneity of gels and the relatively low temperature that is required for the mullite preparation is the reason why such amorphous aluminosilicate gels were chosen to be used as precursors to prepare Fe-doped gels and in sequence synthesizing by thermal treatment Fe doped mullite. The ion exchange was performed with Fe^{2+} and Fe^{3+} ions in order to study the possibility of producing Fe^{2+} or /and Fe^{3+} mullite with respect to future perspective applications.

2. MATERIALS AND METHODS

2.1. Synthesis of iron mullite and amorphous SiO_2

The aluminosilicate hydrogel having the molar oxide composition $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.6\text{SiO}_2 \cdot 2.3\text{H}_2\text{O}$ was prepared by addition of 250 ml of sodium silicate solution (having the appropriate concentrations of Na_2O and SiO_2) into a plastic beaker contained 250 ml of stirred sodium aluminate solution (having the appropriate concentrations of Na_2O and Al_2O_3), at ambient temperature. Sodium silicate solution ($[\text{Na}_2\text{O}] = 1.668 \text{ mol dm}^{-3}$, $[\text{SiO}_2] = 1.639 \text{ mol dm}^{-3}$) was prepared by dissolution of appropriate amount of sodium silicate (exsiccated technical grade anhydrous Na_2SiO_3 ; 51 wt. % Na_2O , 48 wt. % SiO_2 ; Sigma-Aldrich) in demineralised water. Sodium aluminate solution ($[\text{Na}_2\text{O}] = 0.904 \text{ mol dm}^{-3}$, $[\text{Al}_2\text{O}_3] = 0.724 \text{ mol dm}^{-3}$) was prepared by dissolution of appropriate amount of sodium aluminate (exsiccated

technical grade NaAlO_2 ; 41 wt. % Na_2O , 54 wt. % Al_2O_3 ; Riedel-de-Haën) in demineralised water. The prepared hydrogel was additionally stirred (for 5 min) at room temperature before the phase separation. The precipitated solid phase [amorphous Na-aluminosilicate precursor; Na-gel(A)] was separated from the liquid phase (supernatant) by centrifugation. After centrifugation and removal of the supernatant, the solid phase was redispersed in demineralised water and centrifuged repeatedly. The procedure was repeated until the pH value of the liquid phase above the sediment was between 9 and 10. The washed Na-gel(A) was dried at 378 K overnight, and then was cooled down in a desiccator over dry silicagel.

Na^+ ions from the starting gel precursor were exchanged with NH_4^+ from solution as follows:

10 g of powdered gel was placed in a stainless steel reaction vessel containing 250 ml of 0.5 mol dm^{-3} solution of NH_4Cl preheated at 343 K. The suspension was stirred at 70 °C for 1 h, and thereafter the solid phase was separated from the solution by filtration. The residue on the filter paper was redispersed in a fresh 250 ml portion of 0.5 mol dm^{-3} solution of ammonium chloride and stirred again at 343 K for 1 h. The exchange and separation procedure was carried out three times in all. After final solid/liquid separation, the residue on the filter paper was rinsed with distilled water until the reaction of filtrate with AgNO_3 yielded a negative result for chloride ions, and then dried at 378 K for 3 h. The exchanged gels were kept in a desiccator with saturated NaCl solution for 24 h before analyses.

The resulting gel having composition: $(\text{NH}_4)_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.6\text{SiO}_2 \cdot 2.3\text{H}_2\text{O}$ (as determined by the chemical analysis and TG technique) was separated into two samples. One portion was exchanged with Fe^{2+} cations (10 g of NH_4 gel + 250 ml of 0.025 M FeSO_4 + 1 % of NaHSO_3 , 1h, 343 K) and the other portion with Fe^{3+} cations (10g of NH_4 gel + 250 ml of 0.025 M FeCl_3 , 343 K, 1 h). The obtained iron exchanged gel was then heated isothermally at 1263 K for 3 h, in a controlled-temperature chamber furnace (ELPH-2, Elektrosanitarij) to transform to a mixture of iron-mullite and amorphous SiO_2 . The transition temperature was determined by differential scanning calorimetry.

2.2. Procedure of dissolution of the amorphous SiO_2

Two grams of powdered material (Fe-mullite + amorphous SiO_2 obtained by thermal treatment of NH_4Fe -gel) dried at 378 K for 24 h was poured into a stainless-steel reaction vessel containing 100 ml of 2 M NaOH solution preheated at 343 K (concentration of the suspension was 20 g/dm^3). The reaction vessel was equipped with a thermostated jacket and fitted with a water-cooled reflux condenser and a thermometer.

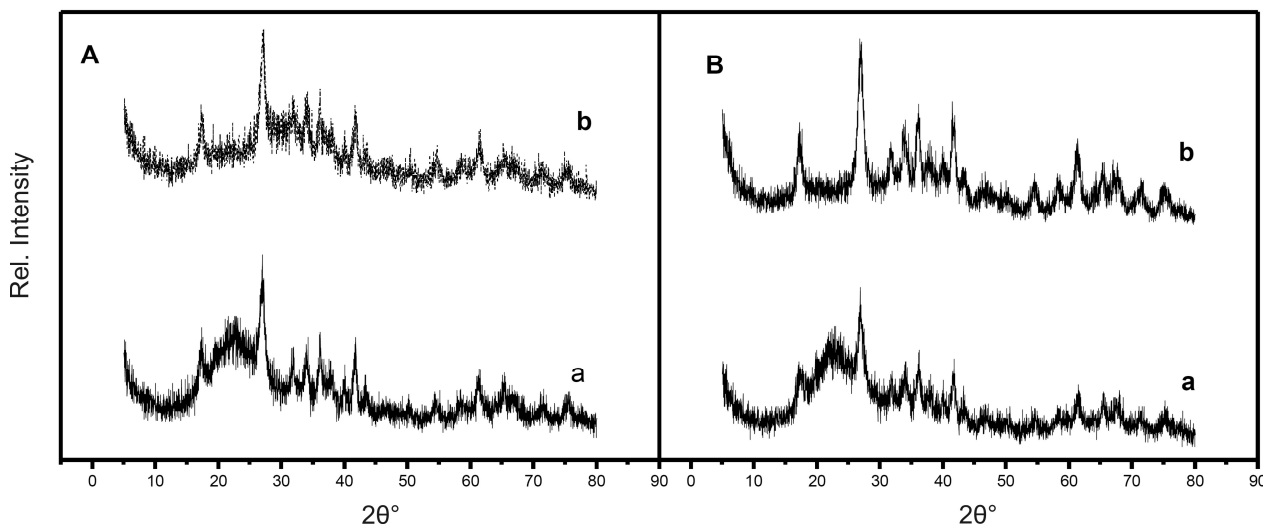


Figure 1. X-ray diffraction patterns of Fe^{3+} mullite and amorphous SiO_2 as synthesized (Aa), of Fe^{3+} mullite and amorphous SiO_2 treated in NaOH (Ab) and Fe^{2+} mullite and amorphous SiO_2 as synthesized (Ba), and of Fe^{2+} mullite and amorphous SiO_2 treated in NaOH (Bb).

The reaction mixture (suspension of the powdered material in 2 M NaOH solution) was stirred with a Teflon coated magnetic bar ($L = 5$ cm, $\Phi = 0.95$ cm) driven by a magnetic stirrer with the stirring speed of 510 r.p.m. The process was carried out for 4 h. The remained product solid phase was washed with distilled water and dried at 378 K for 3 h.

2.3. Characterization of the Starting Materials and the Obtained Product

2.3.1. X-ray powder diffraction (XRD)

The X-ray diffraction patterns of the samples were taken by an ItalStructures APD diffractometer with GD 2000 goniometer and Cu $K\alpha$ graphite radiation.

2.3.2. Fourier Transform Infrared spectroscopy (FTIR)

Infrared transmission spectra of the samples were obtained by the KBr wafer technique. The spectra were recorded on an FTIR Spectrometer System 2000 FT-IR (Perkin-Elmer).

2.3.3. Scanning-electron microscopy (SEM)

Scanning-electron micrographs of the samples were taken by JEOL JSM 7000F scanning-electron microscope.

2.3.4. Mössbauer spectroscopy

^{57}Fe Mössbauer spectra were collected at ambient temperature using an in situ Mössbauer cell suitable for treatments of the samples as well. Spectra were recorded with a KFKI spectrometer, used in constant acceleration mode applying a 1 GBq $\text{Rh}/^{57}\text{Co}$ source. Isomer shift values are related to metallic alpha iron, the accuracy of positional parameters is ca. ± 0.03 mm/s. Spectra were decomposed to Lorentzian shape

lines. Samples were measured consecutively in their as received state and after occasional 2 h evacuation at 643 K, and finally after a regular 2 h treatment in hydrogen at 633K.

3. RESULTS AND DISCUSSION

Thermal treatment of the ammonium form of the aluminosilicate gels resulted in a mixture of mullite and SiO_2 , as it was expected. Iron ions are introduced either as Fe^{3+} or Fe^{2+} from the appropriate solutions in a specific amount that does not influence the crystallization of mullite structure. The temperature induced transformations of $(\text{NH}_4^+, \text{Fe}^{3+})$ and $(\text{NH}_4^+, \text{Fe}^{2+})$ forms of the amorphous aluminosilicate gel were detected by X-ray diffraction and are presented in Figures 1Aa and 1Ba.

The obtained mixtures of iron-mullite form and SiO_2 were treated afterwards in alkaline solution of 2 M NaOH for 3 h at 343 K. A great amount of SiO_2 was dissolved in the alkaline solution, the remained solids were separated and washed with distilled water. The dried samples were characterized by X-ray diffraction (see Figure 1Ba, Bb). The patterns attest that the remained phase is mullite JCPDS, International Centre for Diffraction Data, 2004. :[15-776].

IR spectra were also recorded (Figure 2). Characteristic bands of the partially exchanged $(\text{Fe}^{2+}, \text{NH}_4^+)$ gel and $(\text{Fe}^{3+}, \text{NH}_4^+)$ gel are shown on spectra of Figures 2Aa and 2Ba, respectively. A band at 430 cm^{-1} is assigned to TO ($\text{T}=\text{Al}, \text{Si}$)^{16,17} bending mode, the weak broad band in the frequency range between 510 cm^{-1} and 650 cm^{-1} with a minimum at $558\text{--}559\text{ cm}^{-1}$ is ascribed to the symmetric stretching modes of OTO ($\text{T}=\text{Al}, \text{Si}$)^{16,18}

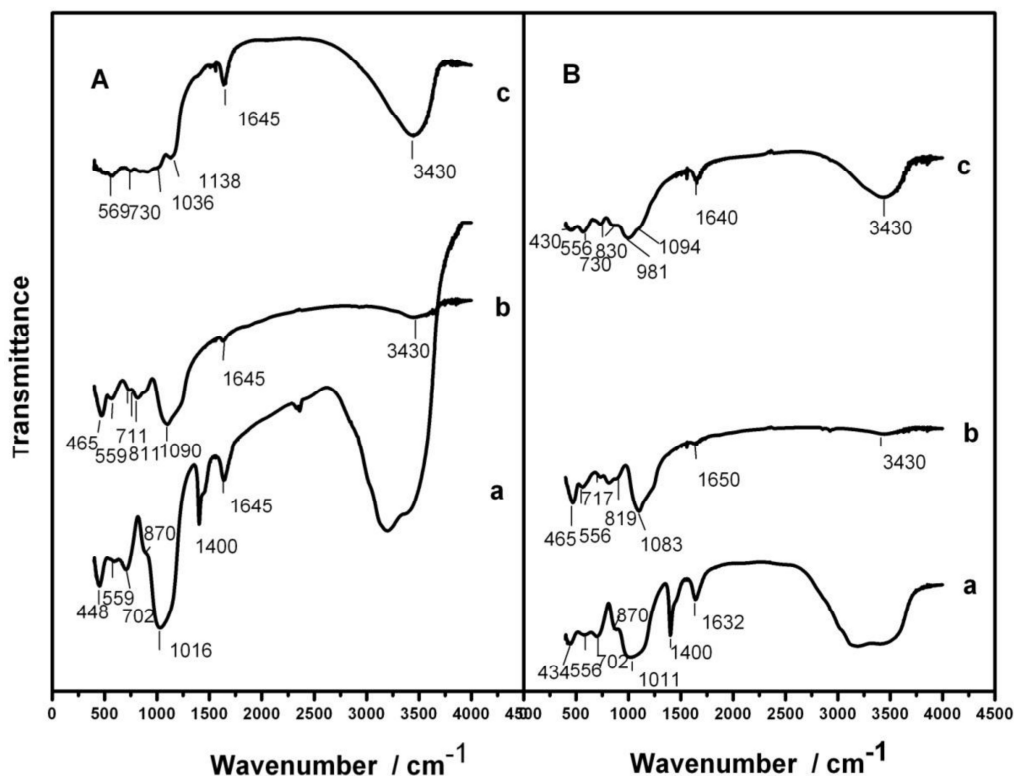


Figure 2. FT-IR spectra of the (Fe²⁺, NH₄⁺) gel (Aa) and (Fe³⁺, NH₄⁺) gel, Fe²⁺ mullite and amorphous SiO₂ as synthesized (Ab), Fe³⁺ mullite and amorphous SiO₂ as synthesized (Bb) and Fe²⁺ mullite (Ac) and Fe³⁺ mullite (Bc) after treatment with NaOH.

and the band at about 830 can be assigned to the asymmetric stretching of Al–O mode.¹⁸

The bands in the region between 1000 and 1100 cm⁻¹ are identified as Si–O–Si and Si–O–Al stretching frequencies.^{16,19}

The extra band on the spectra of the amorphous aluminosilicate gel that appears at 1400 cm⁻¹ obtained for the ion-exchanged gel with ammonium ion (Figures 2Ab, 2Bb) is assigned to the valence and deformation vibrations of the NH₄⁺ ion.²⁰ Characteristic bands for mullite form appear in the spectra²¹ as the gel is thermally treated. The recorded spectra display only the characteristic bands of mullite (Figure 2Ac, 2Bc) after dissolution. They are identified as Si–O stretching frequency in the region of 1125–1165 cm⁻¹ as well as in the region of 950–988 cm⁻¹. Al–O octahedral coordination gives Al–O stretching modes in the region 500–750 cm⁻¹ since Al–O tetrahedral coordination gives Al–O stretching modes in the region 750–850 cm⁻¹. According to ref. 17 we have indications for the presence of both tetrahedrally and octahedrally coordinated Al–O bonds. The spectra contain a band at about 550 cm⁻¹ indicated as an octahedral Al–O stretch and a band 430 cm⁻¹ assigned to Si–O stretch. Bands at 3430 cm⁻¹ are assigned to H₂O, OH stretching modes and at 1635–1645 cm⁻¹ to H₂O bending modes.²⁰ Fe²⁺ and Fe³⁺ did not effect the formation of a mullite structure. After

chemical treatment of the mixtures of both iron-mullite and amorphous SiO₂ the obtained spectra contain all the characteristic bands of mullite structure.

Size of particles either in the mixture of iron-mullite and SiO₂ or in the final sample of iron-mullite with minor content of SiO₂ is below 100 nm as scanning electron micrographs attest (Figure 3).

Mössbauer measurements were also performed on samples from Fe²⁺ and Fe³⁺ exchanged gel as well as from the obtained mixtures of iron mullite and amorphous SiO₂ and further on from the final iron mullite after alkaline treatment. At the final stage additional reduction treatment was also performed in hydrogen to probe whether there are any accessible iron ions left for Fe³⁺ ⇒ Fe²⁺ conversion in the mullite structure formed after the high temperature treatment. Figures 4 and 5 display the corresponding spectra for the Fe²⁺ and Fe³⁺ exchanged samples, data of decompositions are presented in Tables 1 and 2.

The spectrum of hydrated ferrous gel consists of two doublets; one with an isomer shift (IS) of 1.12 mm s⁻¹ and a quadrupole splitting (QS) of 2.62 mm s⁻¹ attributed to Fe²⁺ and a dominant second doublet with IS and QS values, typical for Fe³⁺ in 78 % relative intensity (RI) (Figure 4Aa). The presence of the Fe²⁺ doublet demonstrates that ion exchange has taken place with Fe²⁺ and that the ferrous state is partially stabilized in

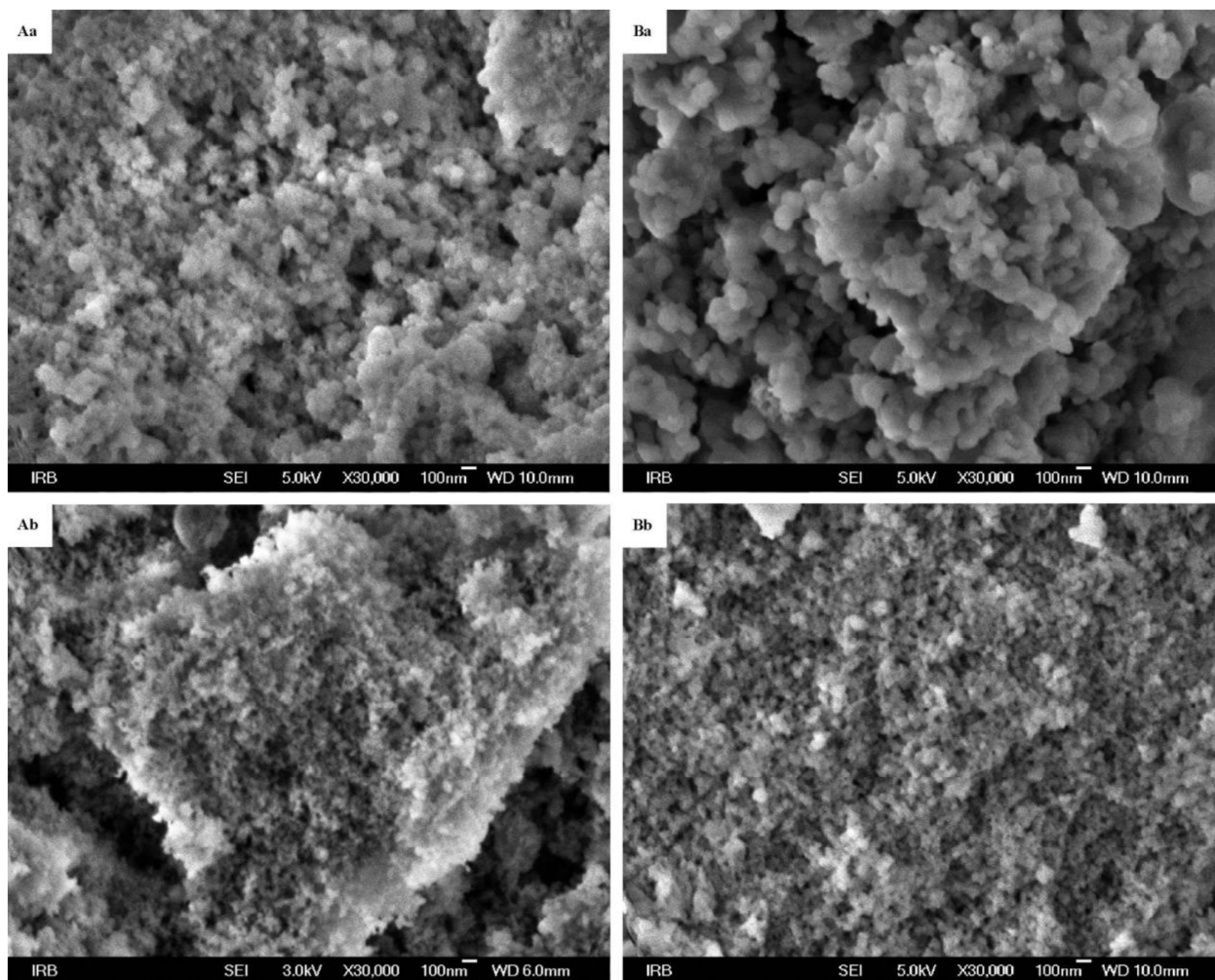


Figure 3. Scanning electron micrographs of Fe^{3+} mullite and amorphous SiO_2 as synthesized (Aa), of Fe^{3+} mullite and amorphous SiO_2 treated in NaOH (Ab) and Fe^{2+} mullite and amorphous SiO_2 as synthesized (Ba), and of Fe^{2+} mullite and amorphous SiO_2 treated in NaOH (Bb).

the gel even after having the sample stored on air for a long period. The relative intensity of the Fe^{3+} doublet decreases to 18 % on reduction with hydrogen at 633 K for 2 h, the other two doublets can be attributed to Fe^{2+} . This $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ conversion has taken place for ca. 60 % of iron, attesting that considerably large portion of iron is accessible for conversion in the gel. (However, it should be noted that the treatment in hydrogen was performed at 633 K, structural changes might have taken place already upon heating to this temperature.) Mössbauer data recorded on the mixture of Fe-mullite and SiO_2 formed upon the high temperature treatment at 1263 K showed the presence of two doublets characteristic for Fe^{3+} (Figure 4Ab, Table 1). The obtained IS, QS parameters for these doublets are in good correspondence detected earlier for Fe^{3+} sites in mullite.^{22–25} Surprisingly, reduction with hydrogen resulted still in

the presence of Fe^{2+} (in 25 % relative intensity). This significantly high portion of iron was still able to undergo an $\text{Fe}^{3+} \Rightarrow \text{Fe}^{2+}$ conversion in spite of the previous 1263 K treatment where the formation of mullite structure has already been completed. This 633 K temperature is significantly lower than the 1323 K, where the formation of carbon nano-tubes was catalyzed by mullite as mentioned previously.^{5,6} Thus, this measurement proves that c.a. 25 % of iron ions is accessible in the mullite structure and hence, it probably may take part in heterogeneous (catalytic) reactions, too. The portion of iron ions able for $\text{Fe}^{3+} \Rightarrow \text{Fe}^{2+}$ conversion was increased even to 35 % by the removal of amorphous silica by dissolution in NaOH (Table 1).

In this sample presence of hematite was not detected in the corresponding spectra, indicating that iron oxides and iron hydroxide are not present.

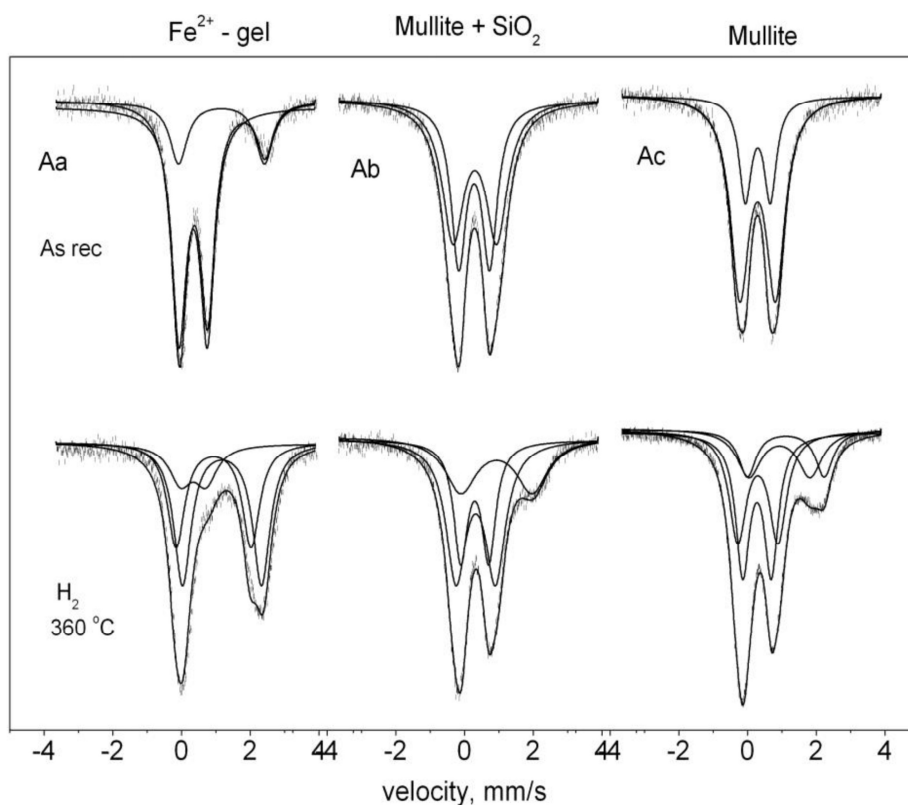


Figure 4. Mössbauer spectra of the gel partially exchanged with Fe^{2+} (Aa), of Fe-mullite+ SiO_2 as synthesized (Ab), of Fe-mullite and amorphous SiO_2 treated in NaOH (Ac) as well the spectra of the same samples recorded after treatment at 633 K in H_2 respectively.

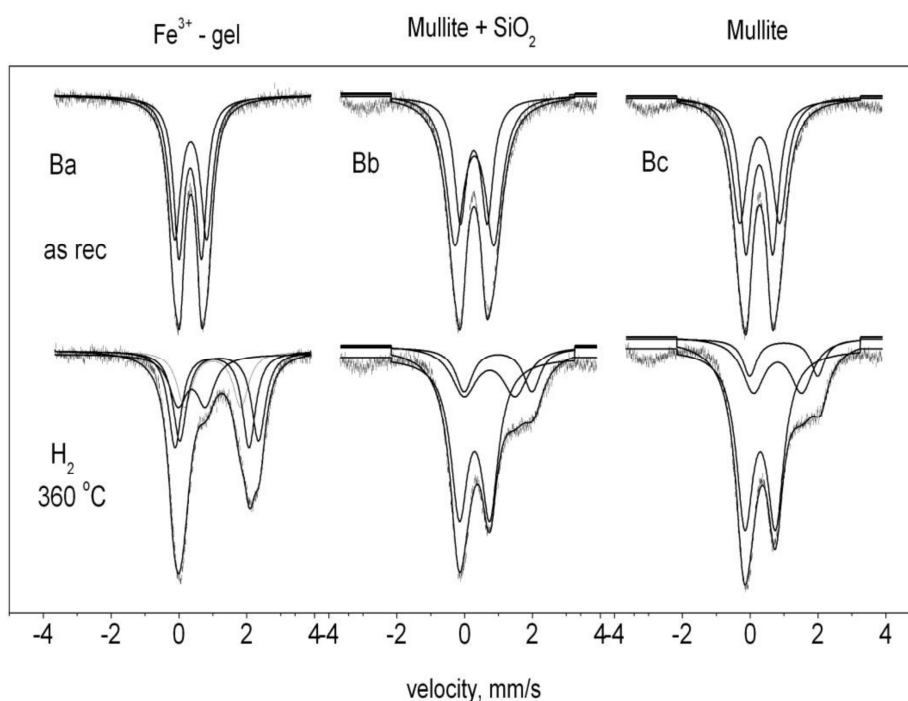


Figure 5. Mössbauer spectra of the gel partially exchanged with Fe^{3+} (Ba), of Fe-mullite+ SiO_2 as synthesized (Bb), of Fe-mullite and amorphous SiO_2 treated in NaOH (Bc) as well the spectra of the same samples recorded after treatment at 633 K in H_2 , respectively.

Table 1. Mössbauer data for gel exchanged with Fe²⁺ ions, then treated at 1263 K, and for the sample obtained after the dissolution of the SiO₂ from the thermally treated sample, afterwards

Treatment / state		As synthesised				Hydrogen 663K			
Samp	Comp	IS	QS	LW	RI	IS	QS	LW	RI
Fe ²⁺ gel	Fe ³⁺	0.36	0.80	0.49	78				
	Fe ³⁺					0.42	0.73	0.84	18
	Fe ²⁺					0.92	2.17	0.56	35
	Fe ²⁺	1.12	2.62	0.54	22				
Fe ²⁺ -	Fe ³⁺	0.28	0.84	0.47	42	0.30	0.77	0.45	29
Mullite +SiO ₂	Fe ³⁺	0.31	1.37	0.72	58	0.32	1.25	0.64	46
	Fe ²⁺					0.95	2.13	0.92	25
Fe ²⁺ -	Fe ³⁺	0.29	0.68	0.39	27	0.27	0.82	0.45	32
Mullite	Fe ³⁺	0.29	1.14	0.60	73	0.30	1.25	0.55	32
	Fe ²⁺					0.95	1.75	0.79	21
	Fe ²⁺					1.13	2.23	0.52	14

IS – isomer shift, mms⁻¹, QS – quadrupole splitting, mms⁻¹, LW – line width mms⁻¹, RI – relative intensity, spectral area %.

Table 2. Mössbauer data for gel exchanged with Fe³⁺ ions, then treated at 1263 K and for the sample obtained after the dissolution of the SiO₂ from the thermally treated sample afterwards

Treatment / state		As received				Hydrogen 663K			
Samp	Comp	IS	QS	LW	RI	IS	QS	LW	RI
Fe ³⁺ gel	Fe ³⁺	0.35	0.62	0.32	47				
	Fe ³⁺					0.43	0.76	0.63	17
	Fe ³⁺	0.35	1.00	0.41	53				
	Fe ²⁺					0.99	1.60	0.52	22
	Fe ²⁺					0.96	2.24	0.43	31
	Fe ²⁺					1.20	2.34	0.46	30
Fe ³⁺ -	Fe ³⁺	0.27	0.75	0.41	27				
Mullite +SiO ₂ (*)	Fe ³⁺	0.29	1.23	0.57	33	0.27	0.93	0.56	35
	Fe ³⁺ ("magn. oxide")	"n/d"	"n/d"	"n/d"	≈ 40	"n/d"	"n/d"	"n/d"	≈ 40
	Fe ²⁺					0.76	1.47	0.81	15
	Fe ²⁺					1.04	2.01	0.54	10
Fe ³⁺ -	Fe ³⁺	0.27	0.75	0.42	28				
Mullite (*)	Fe ³⁺	0.28	1.24	0.50	22	0.27	0.95	0.55	31
	Fe ³⁺ ("magn. oxide")	"n/d"	"n/d"	"n/d"	≈ 50	"n/d"	"n/d"	"n/d"	≈ 50
	Fe ²⁺					0.83	1.40	0.73	12
	Fe ²⁺					1.01	2.08	0.44	7

IS – isomer shift, mms⁻¹, QS – quadrupole splitting, mms⁻¹, LW – line width mms⁻¹, RI – relative intensity, %.(*) IS, QS data are evaluated from ± 4 mms⁻¹ spectra of better resolution, RI data are obtained from spectra recorded at ± 12 mms⁻¹.

Measurements on the other series of samples, on the Fe³⁺ exchanged ones resulted in slightly different spectra. The spectrum of hydrated ferric gel consists of two Fe³⁺ doublets (Figure 5Ba, Table 2). Reduction with hydrogen yields the presence of both Fe²⁺ and Fe³⁺ with very similar data as found on the previous, Fe²⁺ exchanged sample. The feature of Fe³⁺ => Fe²⁺ reduction for a large portion of iron upon hydrogen treatment of the mullite + SiO₂ sample can be detected on the Fe³⁺

exchanged sample as well (Figure 5Bb). Presence of iron oxide in a small amount is also reflected in spectra recorded after the further stages. Namely, a shoulder appears in the spectra recorded in the ± 4 mm s⁻¹ velocity range, which show only a part of the antiferromagnetically ordered structures exhibiting six line sextets.

The full sextet can be displayed at higher velocity range, e.g. at ± 12 mm s⁻¹ (shown in Figure 6). The

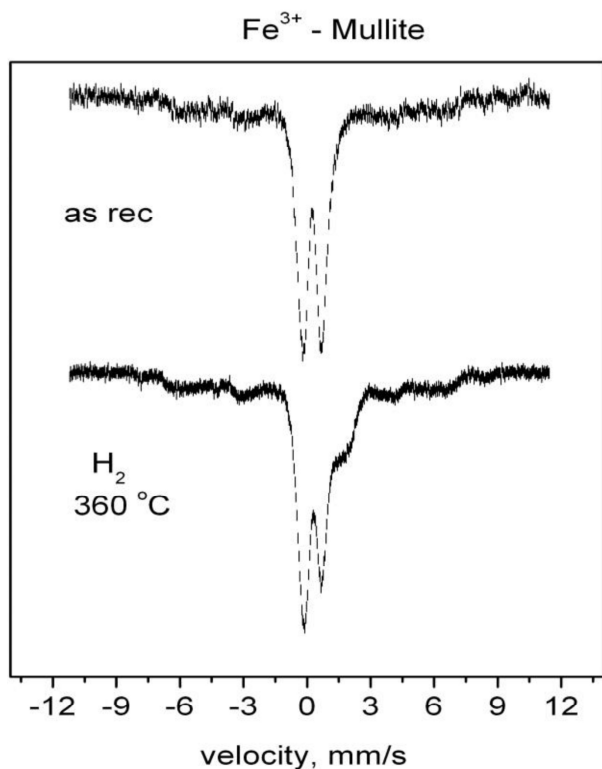


Figure 6. Mössbauer spectra of Fe^{3+} exchanged mullite + SiO_2 sample after calcination at 990°C (top), and after subsequent treatment in hydrogen at 390°C (bottom), recorded in $\pm 12 \text{ mm s}^{-1}$ velocity range.

sextet of oxide has a low intensity, appearing only in form of shoulders in the base line.

4. CONCLUSION

Procedure of the preparation of $\text{Fe}^{2+}/\text{Fe}^{3+}$ substituted mullite is described in this study using aluminosilicate gel as starting material. The main idea to use amorphous aluminosilicate gel was based on the feature of the amorphous aluminosilicate gels that they can be used as precursors for the synthesis of zeolites and that they have the ability to exchange their cations with the cations from a solution as well as the crystalline zeolites. Usage of ammonium form of such gels was preferred due to its temperature induced transformation to a mixture of mullite and SiO_2 . Sodium was exchanged for ammonium in the first stage, then ammonium was exchanged partly for iron in a second ion exchange. Mixture of mullite and silica formed upon calcination, the latter component was removed by dissolution. The stages of processes were followed by ^{57}Fe Mössbauer spectroscopy, Fourier transform infra red spectroscopy

and scanning electron microscopy for confirmation of incorporation of Fe^{2+} or /and Fe^{3+} into the mullite structure and demonstrating thereby a novel method for the preparation of iron substituted mullites.

REFERENCES

1. H. Schneider, J. Schreuer, and B. Hildmann, *J. Eur. Ceram. Soc.* **28** (2008) 329–344.
2. P. Oikonomou, Ch. Dedelouis, C. J. Stournaras, and C. Ftikos, *J. Eur. Ceram. Soc.* **27** (2007) 3475–3482.
3. C. Sadik, I. El Amrani, and A. Almizane A., *Mater. Sci. Appl.* **4** (2013) 337–346.
4. A. Ocaña, A. Caballero, T. González-Carrendo, and C. J. Serna, *Mater. Res. Bull.* **35** (2000) 775–788.
5. A. Weibel, A. Peigney, G. Chevallier, C. Estournes, and C. Laurent, *Ceram. Int.* **39** (2013) 5513–5519.
6. V. G. De Resende, X. Hui, C. Laurent, A. Weibel, E. De Grave, and A. Peigney, *J. Phys. Chem. C* **113** (2009) 11239–11245.
7. D. Roy, K. Haldar, B. K. Paul, A. Bhattacharya, S. Das, and P. Nandy, *J. S. E. M. A. T.* **3A** (2013) 11–17.
8. S. Simon, M. Tămășan, T. Radu, and V. Simon, *Eur. Phys. J. Appl. Phys.* **55** (2011) 30401–30405.
9. M. A. Subramanian, D. R. Corbin, and U. Chowdhry, *Bull. Mater. Sci.* **16** (1993) 665–668.
10. C. Kosanović and B. Subotić, *Micropor. Mesopor. Mat.* **66** (2003) 311–319.
11. C. Kosanović, B. Subotić, and I. Šmit, *Thermochim. Acta* **317** (1998) 25–37.
12. C. Kosanović, B. Subotić, and A. Ristić, *Croat. Chem. Acta* **75** (2002) 783–792.
13. S. Kameoka, T. Suzuki, K. Yuzaki, T. Takeda, S. Tanaka, S. Ito, T. Miyadera, and K. Kumimori, *Chem. Comm.* **1** (2000) 45–46.
14. K. Lázár, G. Pál-Borbély, H. K. Beyer, and H. G. Karge, *J. Chem. Soc. Faraday Trans.* **9** (1994) 1329–1334.
15. C. Kosanovic, S. Bosnar, B. Subotic, K. Lázár, N. Novak Tušar, N. Tomašić, and Z. Kajcsos, *Stud. Surf. Sci. Catal.* **174** (2008) 929–932.
16. E. M. Flanigen, H. Khatami, and H. A. Szymanski, *Infrared Structural Studies of Zeolite Frameworks*, in: R. F. Gould (editor), *Molecular Sieve Zeolites – I*, Advances in Chemistry Series, Vol. 101, Washington DC: American Chemical Society, 1971, pp. 201–227.
17. P. Padmaja, G. M. Anilkumar, P. Mukundan, G. Aruldas, and K. G. K. Warriar, *Int. J. Inorg. Mater.* **3** (2001) 693–698.
18. X. H. Jin, L. Gao, and J. K. Guo, *J. Eur. Ceram. Soc.* **22** (2002) 1307–1311.
19. K. J. D. MacKenzie, *J. Am. Ceram. Soc.* **55** (1972) 68–71.
20. O. V. Bulgakov and T. V. Antipina, *Zh. Prikl. Spekt.* **14** (1971) 412–417.
21. D. Voll, A. Beran and H. Schneider, *J. Eur. Ceram.* **18** (1998) 1101–106.
22. J. Parmentier, S. Vilminot, and J. L. Dormann, *Solid State Sci.* **1** (1999) 257–265.
23. C. M. Cardile, I. W. M. Brown, and K. J. D. Mackenzie, *J. Mater. Sci. Lett.* **6** (1987) 357–362.
24. K. J. D. MacKenzie, *Spectroscopy of Mullite and Compounds with Mullite-related Structures*, in: H. Schneider and S. Komarneri (Eds.), *Mullite*, Wiley-VCH, New York, 2005, pp. 210–215.
25. D. E. Mack, K. D. Becker, and H. Schneider, *Am. Mineral.* **90** (2005) 1078–1083.