

## FORMATION OF SOL–GEL NANOSTRUCTURED MULLITE BY ADDITIONS OF FLUORIDE ION

B. Simendić<sup>1\*</sup> and Lj. Radonjić<sup>2</sup>

<sup>1</sup>Elektroporcelan, Novi Sad 21000, Serbia and Montenegro

<sup>2</sup>Faculty of Technology, Department of Material Engineering, Bulevar Cara Lazara 1, Novi Sad, Serbia

The subject of this study was to investigate the effect of fluoride ions addition on the temperature of sol gel mullite formation based on the hypotheses that the presence of fluoride ions can decrease the temperature of mullite formation (in respect to common 980°C, in sol–gel processing). Polymeric sols were prepared by mixing TEOS and aluminum nitrate nanohydrate and by adding fluoride ions (from 2 to 5 mass%). DTA, TG, XRD and SEM were used for characterisation of mullite gel and crystalline mullite. The experimental results confirmed that the addition of fluoride ions decrease the temperature of mullite formation up to 890°C for the fluoride concentration of 3.5 mass%. Experimental results showed that the temperature of mullite formation is not a simple function of the fluoride ion content. The mechanism of fluorine effect was discussed in terms of the gelling process, gel structure and the phase separation before the mullite formation.

**Keywords:** effect of addition, mechanism of formation, phase transformation, sol–gel mullite, structure of gel

### Introduction

Mullite has received much attention during the last few decades as a matrix material for high-temperature composite development, as a substrate in multilayer packing in electronics and as an infrared-transparent window, especially for high temperature applications [1]. The mechanism of mullite formation depends upon the method of combining the alumina and silica containing reactant. The classical reactions between bulk samples of alumina and silica occur at a relatively high temperature (>1550°C) by nucleation and growth at the interface between two phases. The main difficulty in the preparation of mullite concerns getting a homogeneous mixing of alumina and silica on very fine scale [2]. Sol–gel processing of mullite, as opposed to the classical method, offers a very low temperature of the mullite formation [3–5]. Mullite can be obtained through the sol–gel process and can be considerably improved by the careful control of reaction conditions in liquid-state (particularly by homogeneous mixing of aluminium and silicon precursors), and processing parameters (gelling temperature, pH value, solubility, dilution and controlling of the impurities) [4–6]. The lowest temperature of mullite formation according to [7–12] was 980°C. However, despite these results of sol–gel mullite study, we undertook this study of sol–gel mullite formation intending further to decrease the temperature of mullite formation during sol–gel processing.

In our recent studies [7, 10, 12] we came to the conclusion that the temperature of sol–gel mullite formation could be significantly decreased by careful changing the mullite gel structure which depends on processing variables. The specific sol–gel mullite structure, which we could experimentally designed, is responsible for a low temperature formation of mullite [12]. There are many attempts in the literature with the same aims, including seeding [12–14]. The role of seeding in the heterogeneous nucleation of sol–gel mullite, proposed by Hulling and Messing [13, 14] had rather small effect in our attempts to decrease the temperature of crystalline mullite formation [12].

Using those results, which relate the mullite gel structure and the temperature of phase transformation to crystalline mullite, we try further to decrease the temperature of crystalline mullite formation by using the fluoride ions as a dopant, during gel-mullite processing.

The subject of this paper is investigation of the fluoride ions addition on the temperature of sol–gel mullite formation. The aim of this work is to obtain the sol–gel mullite at as low temperature as possible. Using fluoride ions as dopant in mullite sol–gel processing is based on hypothesis that fluoride ion could have complex effects on kinetics and mechanism of mullite formation. It is very well known that fluoride ions in silica matrix can accelerate the phase separation and phase separation usually assists a new crystal nucleation [12] (transformation of mullite gels to crystalline mullite). Besides, by adding the fluoride

\* Author for correspondence: bsim@eunet.yu

ions one can expect the change in the rate of hydrolyses of silica sols [15]. That change of hydrolyses rate gives rise to water content during silica sol gelling. In general, all those changes have influence on the final silica gel structure [15]. The final mullite gel structure is related to the temperature of mullite formation, and gel structure does have the main role in a low temperature mullite formation [12]. There are in general very little literature data on the influence of fluoride ions on the process of mullitization, but special very little in the sol–gel processing of mullite.

## Experimental

### Sample preparation

Polymeric solution with the stoichiometric composition of mullite (Al:Si=3:1) was obtained by dissolving Al-nitrate nanohydrate (MERCK, pro analysi) in absolute ethylalcohol and by mixing the solution with tetraethylorthosilicate (TEOS, Fluka, 99%) at the room temperature. Fluoride ions were added to the polymeric solution while stirring, using fluorine acid. The content of added fluoride ions in respect to the expected mullite content were 2–5 mass%. The samples with 2, 3.5 and 5 mass% fluoride ions to the expected content of mullite, were noted by letters HF and a number which means the content of fluoride ion: HF-2, HF-3 and HF-5, respectively. The sample without addition of fluoride ions was noted by HSt. The water used for the hydrolysis of the TEOS was only the bound water in the aluminium nitrate nanohydrate. This bound water in nitrate was 27 mol of water per mol of TEOS. The pH value of mullite solution before fluoride ion addition was 1.5 and after fluorine addition was 1. The solution was placed in a water bath for gelling at 60°C. The obtained gels (after different gelling times as a function of sol composition), Table 1, were dried for 2 days at 110°C and then calcined at 600°C for 1 h. After that the samples were heat-treated isothermally at 950 and 1000°C for 1 h, for crystallization of mullite.

### Characterization methods

All the gel samples and crystallized one were structurally characterized by XRD. The X-ray powder patterns

of the specimens were obtained on a Philips X-ray diffractometer. The X-ray diagrams were indexed according to orthorhombic mullite (AMST XRD card 15-776).

Thermal characterization of all samples were accomplished by differential thermal analyses (DTA and TG) on powder samples in a MOM apparatus (200 mg of the powder samples in platinum crucible at heating rate at about 10°C min<sup>-1</sup>, in air). Thermal analyses technique such as differential thermal analyses, DTA is frequently used only in a probing the crystallization kinetics. Knowledge about the temperature range in which crystallization process takes place helps one to have control over the microstructure evolution.

Microstructures evolution of the nanocrystalline mullites, after different heat treatments, were carried out by a scanning electron microscope (SEM), JEOL-35. Fresh fractured surfaces gold coated after slight etching, was standard procedure of sample preparation for SEM study.

## Results and discussion

### Gel appearance

Polymeric mullite gels with the addition of fluoride ions obtained at 60°C after rather short gelling time (Table 1), have somewhat lower transparency (transparency of the gels were checked by eye) than gel HSt. HSt gel without fluoride ions, was used as a standard for comparison with the gels containing fluoride ions.

The results presented in Table 1 show that gels change the appearance after adding fluoride ion. Gelling times for the sols with fluoride ions are somewhat shorter than for gel without fluoride ion. This difference can be explained by the effect of fluorine addition on the hydrolyses of silica sol and reduced quantity of bonded water in gel [5, 10], which change the size of silica chains or network in the mullite gels [15]. In mullite sols with fluoride ions addition, the hydrolysis of the silica sols is faster, since decrease of pH is evident (Table 1). In the same time fluoride ions addition breaks bonds in formed structural species of silica gel (more chain like). That kind of mullite gel structure is suitable for faster mullite formation after heat treatment [7, 13]. That fact was con-

**Table 1** Results after gelling and thermal analysis results of mullite gels without and with fluoride ion

| Sample notation | pH value | Fluoride content/% | Gelling time/h | Gel appearance | Mass loss/% |
|-----------------|----------|--------------------|----------------|----------------|-------------|
| HSt             | 1.5      | –                  | 24             | transparent    | 51.04       |
| HF-2            | 1.0      | 2.0                | 24             | opaque         | 50.93       |
| HF-3            | 1.0      | 3.5                | 20             | opaque         | 55.63       |
| HF-5            | 1.0      | 5.0                | 18             | opaque         | 53.50       |

firmed by XRD results study, showed in the next section of this paper.

### Thermal study

TG results (heating rate  $10^{\circ}\text{C min}^{-1}$  up to  $1000^{\circ}\text{C}$ ) of mullite gels with and without fluoride ion are given in Fig. 1. A part of the same results are given in Table 1. As it is obvious from Fig. 1, the gels drastically change the mass in the temperature interval  $150\text{--}300^{\circ}\text{C}$ . The gel with 2% fluoride ion (HF-2) has the lowest value of mass loss (50.93%), and the gel HF-3 has the highest one (55.6%). This difference in the quantity of mass loss could be related to the gelling process (the quantity of bonded water during gelling depends on added fluoride ions) and the decomposition of organic materials during the heat treatment of mullite gels after drying at  $110^{\circ}\text{C}$ . From TG results (Table 1) it could be concluded that the mass loss is not a simple function of fluorine content.

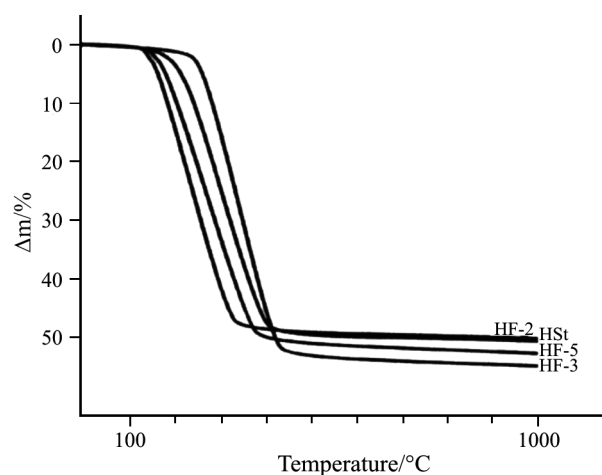


Fig. 1 Mass loss determined by TG

DTA heating curves of mullite formation, for some samples, were presented in Fig. 2. DTA curves show the presence of three peaks. The first and the second peak are endothermic (around  $220$  and  $310^{\circ}\text{C}$ ) and could be attributed to decomposition of aluminium nitrate and removal of organic constituents [5]. The third peak (between  $890$  and  $980^{\circ}\text{C}$ ) is exothermic and is related to the temperature of mullite crystallization [5]. This fact was confirmed with XRD results (Fig. 3).

In all the samples with fluoride ions, the first endothermic peak (decomposition of nitrate) is shifted to lower temperatures, which indicates that the fluoride addition accelerates the decomposition of nitrate. On the other hand, presence of the fluoride ion in the mullite gel makes the removal of organic more difficult, which leads to the shifting of the maximum of the

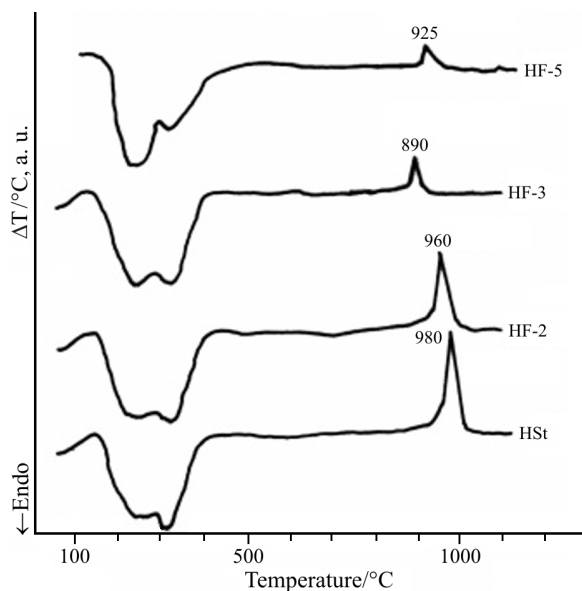


Fig. 2 DTA traces of mullite gels

endothermic peak to a higher temperature. According to Fig. 2 samples of none or low fluoride ions concentration show a rather high temperature of mullite crystallization. In the samples prepared with higher content of fluoride ions, temperatures of mullite formation are lower (Fig. 2,  $890$  and  $925^{\circ}\text{C}$  for HF-3 and HF-5, respectively). In the same case decrease of the mullite temperature formation is not proportional with the fluoride ions content.

### X-ray diffraction study

All samples were calcinated at  $600^{\circ}\text{C}$  (1 h) before heating to the temperature of mullite gel crystallization. In Fig. 3 is presented XRD result only for sample HF-3 after calcination. The XRD result revealed that at this low temperature the sample was non-crystalline (this

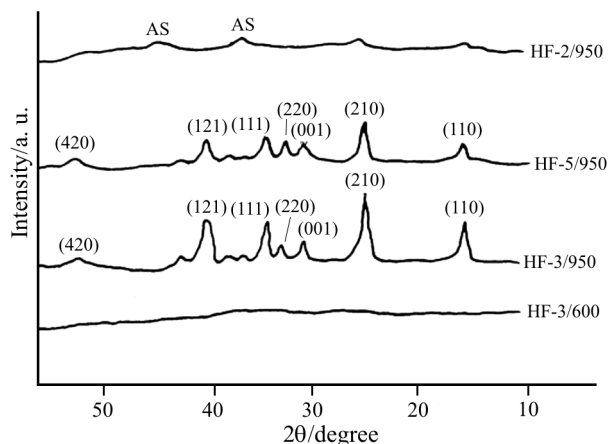


Fig. 3 XRD patterns of mullite gels transformed at  $600$  and  $950^{\circ}\text{C}$

temperature is too low for mullite crystallization or any solid-state reaction in the system). This same figure shows the XRD patterns of the samples HF-2, HF-3 and HF-5 after heat treatment at 950°C for 1 h. In this figure, the X-ray pattern of the standard sample HSt is not shown, since it crystallized at higher temperature (980°C). It is evident that mullite was formed in the samples HF-3 and HF-5, but not in the sample HF-2. X-ray pattern, for very low addition of fluoride ion (sample HF-2, Fig. 3), has a few broad and low intensity peaks which could not be used for exact phase identification. It seems that with mullite coexists some other phase, noted by AS, in Fig. 3 (AS means some aluminosilicate phase, undefined). At this temperature, with addition of 2% of fluoride ion, the crystallization rate is probably, negligible. With increasing fluorine content, in samples HF-3 and HF-5, mullite crystallized at 890 and 925°C, respectively according to the DTA results. It is interesting to note that HF-3 sample shows faster nucleation rate than sample HF-5 with a higher content of fluoride ions. This was concluded by comparing the intensities of major diffraction peaks of these samples. These results are in agreement with DTA results (Fig. 2) (the mullitization temperature of HF-3 sample is lower than HF-5 sample). It seems that addition only 2% of fluorine (sample HF-2) is not enough for remarkably decrease the temperature of mullite formation in respect to standard sample HSt without fluoride ions ( $T_{\text{mullitization}}=980^{\circ}\text{C}$ ). In the Fig. 4, are presented X-ray patterns of samples heat-treated at 1000°C for 1 h. In this figure X-ray pattern of standard HSt sample is also shown, in order to be able to compare the effect of fluoride ions addition on the mullite formation was completed. At this temperature, mullite was formed in all presented samples (HSt, HF-2, HF-3 and HF-5). From X-ray results it is obvious that the highest rate of mullite formation is in the sample HF-3 with 3.5 mass% of added fluoride ions in respect to standard sample HSt (after comparing dif-

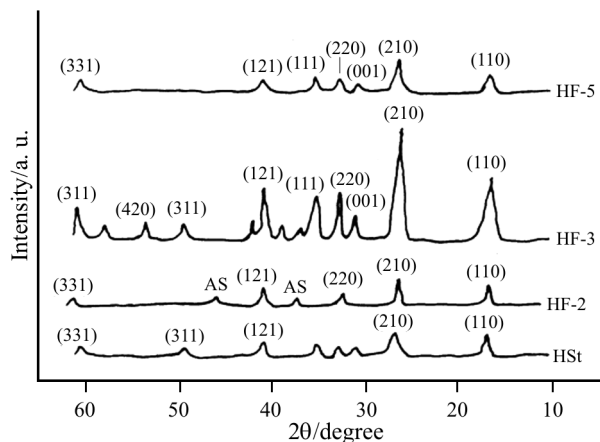


Fig. 4 XRD patterns of mullite gels transformed at 1000°C

fraction intensities of the major diffraction peaks). With increasing the fluorine content, sample HF-5, the rate of mullite nucleation and growth is decreasing, but the crystalline type of mullite [12, 16, 17] is the same as in the sample HF-3. At this temperature, in the sample HF-2, the nucleation and growth rate of mullite is somewhat lower than in the sample HF-5, but higher than in standard one, HSt. Besides, this sample contains additional phase, noted AS (from aluminosilicate family) coexisting with mullite, like in Fig. 3. This phase is formed at 950°C, Fig. 3, and by temperature increase it does not disappear or grow meaning it is not a transitional phase only. Formation of transitional phase on the beginning of mullitization is very common mechanism of mullitization in classical processing of mullite [4]. Effect of fluorine addition on the mullite formation is discussed below.

All X-ray diffraction patterns were indexed according to orthorhombic mullite (AMST card 15-776). The significant characteristic of X-ray patterns (Figs 3 and 4) is lack of reflection splitting of reflection pairs: (120)/(210), (240)/(420) and (041)/(401) [18], which is characteristic for normal mullite (orthorhombic), NM. The lack of reflection splitting means: that the lengths of the **a** and **b** lattice constants have become equal and the symmetry is tetragonal instead of orthorhombic as in normal mullite [18]. According to Schneider and Rymon-Lipinski [18] X-ray pattern of tetragonal mullite, TM, in respect to normal mullite, NM, displays slight broadening of diffraction peaks, though symmetrical X-ray reflections (which we noticed too, Figs 3 and 4 and could be rather ascribed to nano size of mullite crystals). However, the comparison of X-ray diffraction line profiles shows that crystallinity of our mullite phase is much better than that NM (since tetragonal symmetry is higher than orthorhombic one [7, 16, 18]) even they have very similar lattice constants and the volume of unit cells [16]. The formation of TM originate: from highly reactive substances used in sol-gel processing and in our experiments fluoride ion are present additionally. In polymeric processing of sol-gel mullite, TM formation is very sensitive to minor change of processing conditions [10, 12, 17] and crystallize directly from non-crystalline precursor (in our case calcinated mullite gel). In sol-gel processing of low temperature mullite, direct crystallization of TM is not straight forward procedure. But unfortunately, detailed structural data of the TM phase are not available, so far [18].

Presented experimental results show that addition of fluoride ions does increase the rate of mullite crystallization but that dependence is not simple function of fluorine content. The highest effect on the rate of mullitization has 3.5 mass% of fluorine and higher and lower content of fluoride ions do increase the rate of mullitization but in smaller extent. This could be

explained by assumption that fluoride ion addition does change the gel mullite structure by forming non-bridging fluoride in silica tetrahedral, after it replaced oxygen. Too low and too high content of fluoride ions in the mullite-gel structure do not change the gel structure so to be preferable for low temperature mullite crystallization, like it is one with 3.5 mass% of fluoride ions [10, 12]. Too low content of fluoride ions is not enough to change the mullite gel structure. Too high content of fluoride ion in mullite gel could break bonds in formed structural species too much. That kind of gel structure with very small chains is not preferable structure for mullite formation.

#### Microstructural analysis

SEM studied evolution of microstructure during heat treatment of mullite-gel samples HF-3 (Fig. 5) shows micrographs of fresh fractured surfaces of mullite samples after heat treatment at 600, 850 and 950°C. The microstructure of sample after heat treatment at 600°C is featureless, typical of non-crystalline structure (Fig. 5a). Before mullite nucleation, in Fig. 5b, phase separation is evident and after heating at 950°C, at Fig. 5c, very fine scale, nanostructured mullite is evolved.

These results which show the presence of a phase separation which precedes mullite nucleation, only prove our assumption about existence of the phase separation in presence of fluoride ions and its role in heterogeneous nucleation of mullite. However, this phase separation has only limited influence on mullite nucleation. Since influence of fluoride ions presence at temperature of mullite formation is not proportional with fluorine content, it means that fluoride ions in the structure of

mullite gel before nucleation of mullite have specific influence on the gel structure. It is possible that a high content of fluoride ions has an undesirable effect on the gel structure (explained in 'X-ray diffraction study'). Fluoride ions could break silica network structure of gel so much, that the formed gel structure is not any more preferable for crystalline-mullite formation.

#### Conclusions

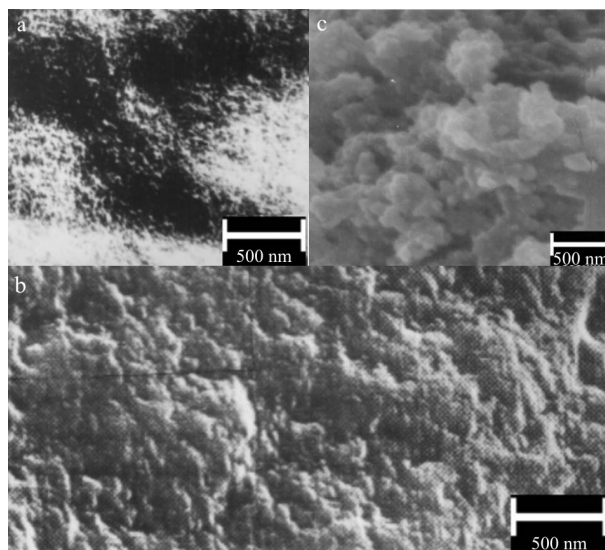
The presence of fluoride ion in mullite sol has influence on the gelling. The presence of fluoride ion has a double effect on the mullite gel structure. As first, fluorine addition contribute to breaking oxygen bonds in mullite gel structure so the scale of mixing mullite precursors existing at molecular level. On the other hand, that breaking structure should provide conditions for heterogeneous nucleation.

The lowest temperature of the mullite formation (890°C) has the mullite sample HF-3 prepared with 3.5% fluoride ion in respect to expected extent of mullite. After heat treatment at 1000°C, in samples with 3.5 and 5% fluorine addition only mullite phase was crystallized while by sample with 2% fluorine addition beside sol-gel mullite was registered crystalline phase like mullite.

Finally, comparing the temperatures of mullite formation after addition of fluorine ion it could be seen that decrease of temperature of mullite formation is not a simple function of fluorine content.

#### References

- 1 A. Aksay, D. M. Dabbs and M. Sarikaya, *J. Am. Ceram. Soc.*, 74 (1991) 2343.
- 2 A. K. K. Chakraborty, *J. Therm. Anal. Cal.*, 71 (2003) 799.
- 3 D. W. Hoffman, R. Roy and S. Komarnenei, *J. Am. Ceram. Soc.*, 67 (1984) 468.
- 4 K. Okada, N. Otsuka and S. Somiya, *Ceram. Bull.*, 70 (1991) 1633.
- 5 D. X. Li and W. J. Thompson, *J. Am. Ceram. Soc.*, 74 (1991) 574.
- 6 M. G. M. U. Ismail, H. Arai, Z. Nakai and T. Akiba, *J. Am. Ceram. Soc.*, 73 (1990) 2736.
- 7 B. Simendić and Lj. Radonjić, *Ceram. Int.*, 24 (1998) 553.
- 8 H. Schneider and K. Okada, 'Mullite and Mullite Ceramics', Edited by H. Schneider, K. Okada and J. Pask, John Wiley and Sons, New York 1994, p. 5.
- 9 D. X. Li and W. J. Thompson, *J. Am. Ceram. Soc.*, 73 (1990) 964.
- 10 B. Simendić and Lj. Radonjić, *J. Therm. Anal. Cal.*, 56 (1999) 199.
- 11 B. Simendić and Lj. Radonjić, The 14<sup>th</sup> Conference on Glass and Ceramics, Varna, Bulgaria 2002, PO-124.



**Fig. 5** SEM micrographs of samples HF-3 after heat treatment at: a – 600°C, for 1 h; b – 850°C, for 30 min; c – 950°C, for 1 h

- 12 B. Simendić, 'Low Temperature Processing of Sol-Gel Mullite', Ph.D. Thesis University of Novi Sad, Faculty of Technology, Serbia and Montenegro 2003.
- 13 J. C. Hulling and G. L. Messing, *J. Am. Ceram. Soc.*, 70 (1987) 1725.
- 14 J. C. Hulling and G. L. Messing, 'Ceramic Powder Science-IV', Edited by S. Hirano, G. L. Messing and H. Hausner, American Ceramic Society, Westerville, OH 1991.
- 15 C. T. Brinker and G. W. Scherer, *Sol-Gel Science*, Academic Press Inc., Boston 1990, pp. 342-529.
- 16 W. E. Cameron, *Am. Ceram. Soc. Bull.*, 56 (1977) 1003.
- 17 A. K. Chakravorty and D. K. Ghosh, *J. Am. Ceram. Soc.*, 71 (1988) 978.
- 18 H. Schneider and T. Rymon-Lipinski, *J. Am. Ceram. Soc.*, 71 (1988) C162.