

## Cobalt incorporation in mullite

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### ABSTRACT

Mullite samples doped with cobalt were derived from diphasic gels with constant atomic ratio (Al + Co)/Si = 3:1, where 0, 1, 2, and 3 at% of aluminum was replaced by cobalt. X-ray powder diffraction showed that the samples contained mullite phase and some amount of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (for pure and doped samples) and CoAl<sub>2</sub>O<sub>4</sub> (for doped samples). Cobalt doping caused an increase in unit-cell parameters of the mullite phase. Transmission electron microscopy and energy dispersive X-ray spectroscopy were used for sample microanalysis and determination of the chemical composition of the Co-doped mullite phase. The Rietveld method was performed for quantitative phase analysis of the samples and for structure refinement of the mullite phase in the samples. It was found that a small amount of Co<sup>2+</sup>, 0.36 wt%, substituted for Al<sup>3+</sup> in the AlO<sub>6</sub> octahedra of the mullite structure. Simultaneously, the same amount of tetrahedral Al<sup>3+</sup> ions was likely substituted by Si<sup>4+</sup> in the (Al,Si)O<sub>4</sub> tetrahedra for the purpose of charge compensation. The remaining cobalt reacted with alumina forming CoAl<sub>2</sub>O<sub>4</sub>, and dissolved in the glassy phase. The proposed formula for Co-doped mullite is Co<sub>y</sub>Al<sub>4+2x-2y</sub>Si<sub>2-2x+y</sub>O<sub>10-x</sub>.

**Keywords:** Co-doped mullite, ceramics, X-ray diffraction, Rietveld method, energy dispersive X-ray spectroscopy

### INTRODUCTION

Mullite is a material with an important role in the technology of classical and advanced ceramics due to its high thermal stability, outstanding chemical stability in severe environments, and favorable strength and creep behavior (Schneider et al. 1994). The composition of mullite refers to general formula <sup>VI</sup>Al<sub>2</sub>(<sup>IV</sup>Al<sub>2+2x</sub><sup>IV</sup>Si<sub>2-2x</sub>)O<sub>10-x</sub>, where x denotes the number of oxygen atoms missing per average unit cell, while IV and VI are the coordination numbers of the cations (Cameron 1977). Mullite structure is orthorhombic, space group *Pbam* (Sadanaga et al. 1962; Angel and Prewit 1986; Ban and Okada 1992). It consists of chains of edge-sharing AlO<sub>6</sub> octahedra running parallel to the *c*-axis that are cross-linked by (Al,Si)O<sub>4</sub> tetrahedra double chains also running parallel to *c*-axis. In comprehensive studies, Schneider (1990) and Schneider et al. (1994) reported that the mullite structure is able to incorporate considerable amounts of various transition metal cations. The incorporation of the transition metal cations strongly depends on their ionic radii and oxidation states, as well as on the synthesis procedure. Generally, transition metal cations can enter the mullite structure by substitution of aluminum in the AlO<sub>6</sub> octahedra or (Al,Si)O<sub>4</sub> tetrahedra, by incorporation in the structural channels running parallel to the *c*-axis, or by incorporation into the structural voids produced by removal of oxygen atoms from O<sub>c</sub> sites. While V<sup>3+</sup> (Schneider 1990), Cr<sup>3+</sup> (Schneider and Eberhard 1990; Rager et al. 1990; Fischer and Schneider 2000) and Fe<sup>3+</sup> (Schneider and Rager 1986; Schneider 1987) have the strongest tendency for incorporation in mullite, only low or very low amounts of Mn<sup>2+</sup> (Schneider 1990), Fe<sup>2+</sup> (Schneider and Rager 1984), and Co<sup>2+</sup> (Schneider 1990; Parmentier and Vilminot 1998) ions can enter

the mullite structure. The aim of the present work is to determine the upper limit of cobalt incorporation in mullite.

### EXPERIMENTAL METHODS

#### Sample preparation

Powder mullite samples were derived from diphasic precursors. Diphasic gel with 3Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub> nominal composition and gels in which 1, 2, and 3 at% Al<sup>3+</sup> was substituted by Co<sup>2+</sup> were prepared by dissolving nitrates, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, in water, and by mixing nitrate solutions with tetraethoxysilane (TEOS) dissolved in ethanol. TEOS solution was added dropwise under vigorous stirring. The mixture was further stirred under refluxing conditions at 60 °C for eight days. The obtained gels were dried at 120 °C for 72 h, ground and sieved. Powders with particle size <63 μm were used for further treatment. The dried gels were heated at the rate of 10 °C/min to 1600 °C and held for 2 h at this temperature. Afterwards they were slowly cooled in the furnace to room temperature. For microstructure studies and microanalysis, the powders were compacted and sintered at 1600 °C for 2 h. The prepared powdered as well as the corresponding compact samples were denoted S0, S1, S2, and S3 (Table 1).

#### Methods

Composition of the samples S1–S3 was determined by means of both Particle Induced X-ray Emission (PIXE) spectroscopy, using a nuclear microprobe facility with 3 MeV proton beam and semiconductor Si(Li) X-ray detector (Jakšić et al. 1996), and quantitative analysis using the Rietveld method (Rietveld 1969; Hill and Howard 1987). The results are shown in Table 1.

Prepared Co-doped samples were characterized by X-ray diffraction (XRD) at room temperature using a Philips MPD 1880 counter diffractometer with monochromatized CuK $\alpha$  radiation. Three data sets were collected for each prepared mullite sample: (1) XRD pattern of the sample mixed with a standard reference material, namely silicon powder (Koch-Light Lab. Ltd., 99.999% purity), scanned in steps of 0.02° (2 $\theta$ ) in the 2 $\theta$  range from 10 to 100° with fixed counting time of 5 seconds per step, for the purpose of precise determination of unit-cell parameters; (2) XRD pattern of pure sample scanned also in the 2 $\theta$  range from 10 to 100° in steps of 0.02° (2 $\theta$ ), using fixed counting time of 10 s per step, for the purpose of the Rietveld structure refinement (Rietveld 1969); (3) XRD pattern of the sample mixed with ZnO, scanned in steps of 0.02° (2 $\theta$ ) in the 2 $\theta$  range from 10 to 100° with fixed counting time of 5 s per step, for precise determination of the amorphous

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**TABLE 1.** Chemical composition of the prepared samples, S0–S3, as obtained using PIXE analysis and quantitative phase analysis by the Rietveld method

Sample	PIXE analysis			Quantitative phase analysis by the Rietveld method			
	Co content (wt%)	Al content (wt%)	Si content (wt%)	Mullite (wt%)	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> (wt%)	CoAl <sub>2</sub> O <sub>4</sub> (wt%)	Glassy phase (wt%)
S0	0	38.5 (19)	11.7(6)	89.1(1)	4.2(1)	0	6.7(1)
S1	0.82(4)	38.8(19)	10.5(6)	82.5(1)	8.7(1)	0.5(1)	8.3(1)
S2	1.46(7)	37.6(19)	11.5(6)	88.0(1)	1.5(1)	3.0(1)	7.5(1)
S3	2.40(10)	37.0(19)	11.5(6)	80.9(1)	3.6(1)	5.8(1)	9.7(1)

phase content in the samples. ZnO was used rather than the Si internal standard for this purpose because the latter exhibited preferred orientation, which was difficult to eliminate from the powder pattern.

Microstructure study and microanalysis were performed on compacted samples by a transmission electron microscope (TEM JEOL 2011, 200 kV) equipped with an energy dispersive X-ray spectrometer (EDX Oxford LINK ISIS). The specimens were prepared by typical ion-milling procedures (PIPS 691 Gatan Co., U.S.A.).

### XRD data processing

The XRD data of samples mixed with silicon powder were used for precise determination of unit-cell parameters applying the method proposed by Toraya (1986). Bragg angle positions,  $2\theta$ , of several diffraction lines of the crystalline phase in the sample and three diffraction lines of silicon were determined by individual line fitting method (program PROFIT: Toraya 1986) and taken as input data for the program UNITCELL (Toraya 1993). Initial unit-cell parameters were refined by the whole-powder-pattern fitting method (program WPPF: Toraya 1986). The fitting was performed using a split-type pseudo-Voigt profile function, the polynomial background model and peak shift correction in the form:  $\Delta T(2\theta) = t_1 + t_2 \tan \theta + t_3 \tan^2 \theta$ , where  $t_1$ ,  $t_2$ , and  $t_3$  are adjustable parameters.

Crystal structures of the phases present in the prepared samples were refined by the Rietveld method. Starting structural models were taken from the Inorganic Crystal Structure Database (2005) as follows: card no. 66452 for mullite (Ban and Okada 1992), card no. 21116 for CoAl<sub>2</sub>O<sub>4</sub> (Furuhashi et al. 1973), and card no. 25778 for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (Newnham and de Haan 1962), respectively. Rietveld structure refinement was performed with the program X'Pert HighScore Plus, version 2.1 (PANalytical 2004), using a pseudo-Voigt profile function and polynomial background model. Isotropic displacement parameters were assumed for all atoms. The preferred-orientation correction did not significantly improve the fit.

As noted above, the XRD data of samples mixed with ZnO powder were used for determination of the amorphous phase content in the samples. For this purpose Rietveld refinement with X'Pert HighScore Plus program was performed, but working in the mode for systems with an amorphous phase.

## RESULTS AND DISCUSSION

### XRD characterization of the samples

XRD studies indicated that all prepared samples, S0–S3, contained mullite phase (denoted as MU0–MU3 for clarity) and small amounts of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and glassy phase (for all samples) and additionally CoAl<sub>2</sub>O<sub>4</sub> (for doped samples). Refined unit-cell parameters of the corresponding mullite phases, MU0–MU3, present in the prepared samples S0–S3 are listed in Table 2. Unit-cell parameters ( $a$ ,  $b$ ,  $c$ ) of mullites MU1, MU2, and MU3 are equal within the standard deviations, but noticeable larger than those of MU0 ( $a$  is  $\sim 0.1\%$  larger,  $c$  is  $\sim 0.05\%$  larger, and  $b$  is  $\sim 0.01\%$  larger). The increase of all unit-cell parameters for mullites MU1–MU3 in comparison to those for MU0 indicates that some amount of Co<sup>2+</sup> (ionic radius of 0.75 Å) substituted for Al<sup>3+</sup> (ionic radius of 0.53 Å) in the mullites MU1–MU3. According to literature data (Schneider 1990) it could be expected that Co<sup>2+</sup> substituted for Al<sup>3+</sup> in the AlO<sub>6</sub> octahedra of the mullite structure. This should cause the largest increase of  $c$  parameter. However, we found the largest increase of  $a$  parameter and relatively smaller increase of  $c$  parameter. The unusual behavior of the unit-cell parameters has to be attributed to the influence of

**TABLE 2.** Results of unit-cell refinement with Si standard for mullites MU0–MU3 in the prepared samples S0–S3

Sample	Mullite phase						
	Notation	$R_p$	$R_{wp}$	$a$ (Å)	$b$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )
S0	MU0	0.073	0.109	7.5520(2)	7.6872(2)	2.8843(1)	167.44(1)
S1	MU1	0.086	0.126	7.5618(2)	7.6882(1)	2.8860(1)	167.78(1)
S2	MU2	0.087	0.124	7.5619(2)	7.6882(2)	2.8859(1)	167.78(1)
S3	MU3	0.084	0.119	7.5618(2)	7.6883(2)	2.8860(1)	167.78(1)

Notes:  $R_p$  and  $R_{wp}$  are the discrepancy factors that characterize a quality of the fit (Young et al. 1982):

$$R_p = \frac{\sum_i |y(2\theta)_i^{\text{obs}} - y(2\theta)_i^{\text{calc}}|}{\sum_i y(2\theta)_i^{\text{obs}}}$$

$$R_{wp} = \sqrt{\frac{w_i \sum_i [y(2\theta)_i^{\text{obs}} - y(2\theta)_i^{\text{calc}}]^2}{\sum_i y(2\theta)_i^{\text{obs}}}}$$

where  $y(2\theta)_{\text{obs}}$  denotes observed intensity at the  $i$ th step of recorded powder pattern,  $y(2\theta)_{\text{calc}}$  is the corresponding theoretical intensity;  $N$  is the number of observations and  $w_i$  is the weight assigned to the  $i$ th observation, which is given in the form  $1/y(2\theta)_{\text{obs}}$ .

cobalt on phase separation in gels that preceded the formed mullite. This resulted in alumina enrichment of mullite (i.e., in increase of  $a$  axis) and silica enrichment of the glassy phase. It can be expected that in the case of mullite doping by cobalt, there will be simultaneous substitutions of octahedral aluminum by cobalt and tetrahedral aluminum by silicon for the purpose of charge compensation. With this assumption, the chemical formula for Co-doped mullite may be written as Co <sub>$y$</sub> Al<sub>4+2x-2y</sub>Si<sub>2-2x+y</sub>O<sub>10-x</sub>.

The results on chemical composition of the prepared samples S1–S3 presented in Table 1 indicated that the amount of CoAl<sub>2</sub>O<sub>4</sub> increased with Co content in the samples. However, Co content in CoAl<sub>2</sub>O<sub>4</sub> is always smaller than the amount of total cobalt determined by PIXE analysis. This means that Co is also incorporated in other phases present in the system. Cobalt could be incorporated either only in the mullite phase, only in the glassy phase, or in both of them simultaneously. It is very unlikely that Co was incorporated in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as the unit-cell parameters of that phase were found to be constant in all samples, having the values as reported in Powder Diffraction File PDF-2 (2003), card no. 10-173. Assuming that all Co was incorporated only in mullite it should be smaller than 0.82 wt% Co, as even sample S1 contained CoAl<sub>2</sub>O<sub>4</sub>. This upper limit of cobalt incorporation can be estimated from the dependence of the ratio of integrated intensities on the Co content in the samples for selected diffraction lines of CoAl<sub>2</sub>O<sub>4</sub> and several lines of mullite. The values for the intensity ratios of the strongest line for CoAl<sub>2</sub>O<sub>4</sub>, namely 311, to mullite lines 130, 201, 220, and 111, are shown in Figure 1. Integrated intensities of selected diffraction lines were determined using a program PROFIT (Toraya 1986). The dependence of intensity ratios on cobalt content in the samples could be

modeled by second order polynomial functions that converged to zero in the concentration range of 0.54–0.58 wt% Co. It follows that, excluding  $\text{CoAl}_2\text{O}_4$ , the average value of cobalt remaining in the samples was  $\sim 0.56$  wt% Co. To be certain whether all this amount of Co was incorporated exclusively in mullite, we analyzed several mullite grains and the glassy interphase in sample S3 by EDX analysis.

### TEM and EDX characterization of the samples

The TEM image of the sample S3 is presented in Figure 2, showing four mullite grains and the glassy interphase. Chemical compositions of selected mullite grains and the glassy phase obtained by EDX analysis are listed in Table 3. All presented grains

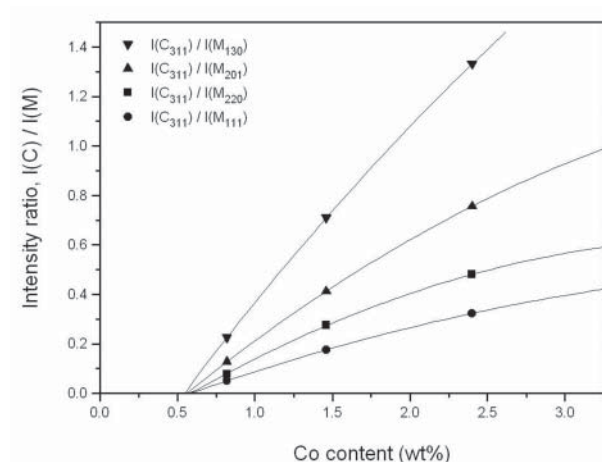


FIGURE 1. Dependence of intensity ratio of diffraction line 311 for  $\text{CoAl}_2\text{O}_4$  and selected mullite lines (130, 201, 220, or 111) on cobalt content in the samples S1–S3.

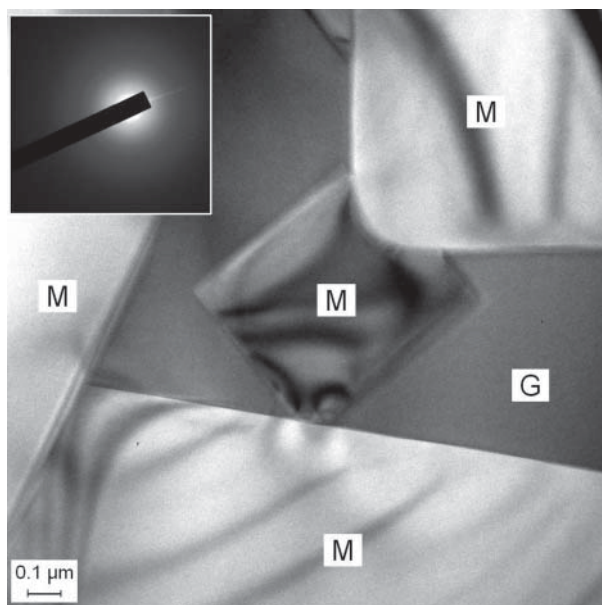


FIGURE 2. Bright-field TEM image of the sample S3. Mullite grains are denoted by M, while glassy phase is denoted by G. Electron diffraction pattern of the glassy phase is presented in the upper left corner of the picture.

have very similar chemical compositions as seen in the table. EDX analysis of mullite grains at three different areas of the compact samples gave very similar results to those listed. Therefore, the average chemical composition of mullite can be given by the formula  $\text{Co}_{0.02}\text{Al}_{4.64}\text{Si}_{1.34}\text{O}_{9.66}$ . This formula was used to determine starting values of the site occupancies for mullite phase in the Rietveld refinement of the prepared Co-doped samples.

### Rietveld structure refinement

The Rietveld refinement of the prepared samples was performed for two purposes: (1) to determine quantitative composition of the samples, (2) to elucidate the mode of Co incorporation in mullite. The refinement was started using a mullite structure model according to Ban and Okada (1992) and the formula for Co-doped mullite phase as obtained by EDX for MU3. Pure

TABLE 3. Chemical composition of selected mullite grains and the glassy phase in the sample S3 as obtained by EDX analysis

Grain no.	EDX analysis					
	Al		Si		Co	
	(at%)	(wt%)	(at%)	(wt%)	(at%)	(wt%)
1	30.00	39.82	8.32	11.34	0.14	0.41
2	29.45	39.08	8.72	12.04	0.11	0.33
3	29.02	38.48	9.08	12.53	0.13	0.39
4	29.90	39.67	8.35	11.53	0.11	0.31
Glassy phase	6.94	9.16	23.69	32.54	2.66	7.67

TABLE 4. Composition of the mullite phases MU0 and MU3 as determined by EDX and the Rietveld refinement

Mullite phase	Formula	Co content (wt%)	CoO content (wt%)	$\text{Al}_2\text{O}_3$ content (wt%)	$\text{SiO}_2$ content (wt%)
MU0	$\text{Al}_{4.56}\text{Si}_{1.44}\text{O}_{9.72}$	0	0	72.88	27.12
MU3	$\text{Co}_{0.02}\text{Al}_{4.64}\text{Si}_{1.34}\text{O}_{9.66}$	0.36	0.47	74.26	25.27

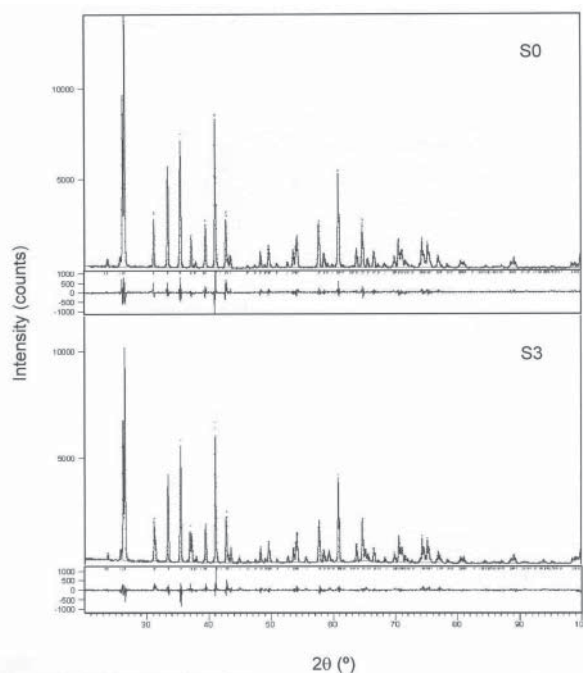


FIGURE 3. Results of the Rietveld refinement for the samples S0 and S3. The observed profile intensity is represented by black dots and the calculated intensity by the solid line. Values of  $R_p$  and  $R_{wp}$  are given in Table 5.

**TABLE 5.** Results of the Rietveld refinement for the mullite phases MU0 and MU3

Mullite phase	$x^\dagger$	$R_p$	$R_{wp}$	Atom site	Occupancy	$x$	$y$	$z$	$B_{iso}$ (Å <sup>2</sup> )			
MU0	0.28	0.079	0.104	M1	1 Al	0	0	0	0.19(4)			
				T	0.50 Al + 0.36 Si	0.1493(2)	0.3406(2)	0.5	0.36(3)			
				T*	0.14 Al	0.264(1)	0.204(1)	0.5	0.43(9)			
				O <sub>ab</sub>	1 O	0.3587(3)	0.4219(3)	0.5	0.24(6)			
				O <sub>d</sub>	1 O	0.1273(3)	0.2201(3)	0	0.45(6)			
				O <sub>c</sub>	0.58 O	0.5	0	0.5	1.12(9)			
				O <sub>c</sub> *	0.14 O	0.452(3)	0.044(3)	0.5	1.28(20)			
				MU3	0.34	0.075	0.099	M1	0.99 Al + 0.01 Co	0	0	0.31(4)
				T	0.495 Al + 0.335 Si	0.1490(2)	0.3404(2)	0.5	0.40(4)			
T*	0.17 Al	0.266(1)	0.2055(9)	0.5	0.49(7)							
O <sub>ab</sub>	1 O	0.3588(3)	0.4219(3)	0.5	0.22(6)							
O <sub>d</sub>	1 O	0.1277(3)	0.2198(3)	0	0.41(6)							
O <sub>c</sub>	0.49 O	0.5	0	0.5	0.93(9)							
O <sub>c</sub> *	0.17 O	0.458(2)	0.046(2)	0.5	1.21(8)							

Notes:  $R_p$  and  $R_{wp}$  are the discrepancy factors that characterize a quality of fitting result (Young et al. 1982).

$^\dagger x$  denotes the number of oxygen vacancies per average mullite unit cell, used in chemical formula of mullite.

**TABLE 6.** Interatomic distances (Å) and their standard deviations for the mullite phases MU0 and MU3

Distances	Mullite phase	
	MU0	MU3
<b>Octahedron (M1)O<sub>6</sub></b>		
M1-O <sub>ab</sub> (4)	1.893(1)	1.894(2)
M1-O <sub>d</sub> (2)	1.948(2)	1.948(2)
Average:	1.911(2)	1.912(2)
<b>Tetrahedron TO<sub>4</sub></b>		
T-O <sub>ab</sub> (1)	1.702(3)	1.707(3)
T-O <sub>d</sub> (2)	1.724(1)	1.724(1)
T-O <sub>c</sub> (1)	1.667(1)	1.667(1)
Average:	1.704(2)	1.705(2)
<b>Tetrahedron T*O<sub>4</sub></b>		
T*-O <sub>ab</sub> (1)	1.822(8)	1.808(8)
T*-O <sub>d</sub> (2)	1.781(5)	1.785(5)
T*-O <sub>c</sub> * (1)	1.882(23)	1.901(15)
Average:	1.817(10)	1.820(8)

mullite, MU0, had a composition with  $x = 0.28$ , where  $x$  denotes the number of oxygen vacancies per average mullite unit cell used in the chemical formula. Refinements for Co-doped samples confirmed the chemical formula  $\text{Co}_{0.02}\text{Al}_{4.64}\text{Si}_{1.34}\text{O}_{9.66}$  for mullite phase in all prepared samples. Graphical results of the Rietveld refinement for the samples S0 and S3 are presented in Figure 3. Phase compositions of the samples S0–S3 are shown in Table 1, while compositions of the mullites MU0 and MU3, are listed in Table 4. The results presented in Table 4 indicated that the upper limit of cobalt substitution for aluminum in the mullite structure, under the experimental conditions of this work, was 0.36 wt% Co.

Refined structural parameters for the Co-doped mullite phases MU0 and MU3 are given in Table 5. Table 6 lists metal-oxygen distances in (M1)O<sub>6</sub> octahedron as well in the TO<sub>4</sub> and T\*O<sub>4</sub> tetrahedra, derived from the atomic parameters listed in Table 5. Incorporation of Co<sup>2+</sup> on M1 site caused expansion of M1-O<sub>ab</sub>, T-O<sub>ab</sub>, T\*-O<sub>d</sub>, and T\*-O<sub>c</sub>\* metal-oxygen distances, that was compensated by shortening of the T\*-O<sub>ab</sub> distance. Average distances in the (M1)O<sub>6</sub> octahedra, as well in the TO<sub>4</sub> and T\*O<sub>4</sub> tetrahedra, increased slightly, which caused an increase in the unit-cell parameters for Co-doped mullite.

#### ACKNOWLEDGMENTS

We thank Ivančica Bogdanović-Radović (of IRB) for performing PIXE spectroscopy analysis. Financial support from the Ministry of Science, Education and Sports of Republic of Croatia is gratefully acknowledged.

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MANUSCRIPT RECEIVED OCTOBER 5, 2005

MANUSCRIPT ACCEPTED SEPTEMBER 21, 2006

MANUSCRIPT HANDLED BY SERGEY KRIVOVICHEV