NUKLEONIKA 2015;60(1):147–150
doi: 10.1515/nuka-2015-0027

ORIGINAL PAPER

DE GRUYTER OPEN

The role and position of iron in $0.8CaZrO_3$-$0.2CaFe_2O_4$

Jacek Szczerba, Edyta Śnieżek, Paweł Stoch, Ryszard Prorok, Ilona Jastrzębska

Abstract. The aim of the study was to characterize the $0.8CaZrO_3$-$0.2CaFe_2O_4$ composite structure with particular emphasis on the role and position of iron in the function of sintering temperature. The paper presents the results of ^{57}Fe Mössbauer effect at room temperature. It was found that the increase of sintering temperature causes an increase in the amount of incorporated iron ions in the $CaZrO_3$-crystal structure. Based on Mössbauer spectroscopy analysis, it was found that three different environments of Fe^{3+} ions were observed in the obtained materials. Two of them corresponded to $CaFe_2O_4$ phase and one was associated with the substitution of Zr^{4+} by Fe^{3+} in the $CaZrO_3$ structure.

Key words: calcium ferrite • calcium zirconate • Mössbauer spectroscopy • perovskite • spinel

J. Szczerba, E. Śnieżek✉, P. Stoch, R. Prorok, I. Jastrzębska
Department of Ceramics and Refractories, Faculty of Materials Science and Ceramics, AGH – University of Science and Technology, 30 A. Mickiewicza Ave., 30-059 Kraków, Poland,
Tel.: +48 12 617 5139, Fax: +48 12 633 4630,
E-mail: esniezek@agh.edu.pl

Received: 18 June 2014
Accepted: 2 November 2014

Introduction

$CaZrO_3$ is a member of perovskite, which has two polymorphs. At temperatures lower than 1750°C, an orthorhombic phase is stable, where Ca^{2+} ions are situated between slightly deformed ZrO_6 octahedrals. At temperatures higher than 1750°C, cubic phase is stable [1, 2]. High purity $CaZrO_3$ can be obtained by the arc melting technique. The fused $CaZrO_3$, with strong Zr-O covalent bonding and almost pure Ca-O ionic bonding, is poreless and has the density close to the theoretical one [3].

$CaZrO_3$, which is the only chemical compound in the CaO-ZrO_2 binary system, is characterized by high melting point (2345°C), thermal shock resistance, high strength and corrosion resistance against alkali oxides and cement clinker. Furthermore, $CaZrO_3$ has been wildly investigated because of its electrical properties. $CaZrO_3$ is a p-type semiconductor. Modified by some trivalent cations (e.g. In^{3+}, Ga^{3+} and Sc^{3+}) is a protonic conductor in hydrogen atmosphere. Small excess of zircona or calcia in $CaZrO_3$ structure cause oxygen ion conductivity. The analogous situation occurs in the case of Al_2O_3, MgO, Y_2O_3 substitution. Therefore, $CaZrO_3$ is a material being used as, for example, mechanical filters, resonators, capacitors, and refractory materials [4–10]. $CaZrO_3$ relatively easily incorporates actinides into its crystal structure. $CaZrO_3$ is considered as a host material for spent nuclear fuel immobilization [11].

$CaFe_2O_4$ with spinel structure is stable up to 1228°C [12]. Crystal structure of $CaFe_2O_4$ is similar to the one formed in perovskite compounds as in $CaZrO_3$ [13]. Therefore, it is interesting to study the $0.8CaZrO_3$-$0.2CaFe_2O_4$ composite, which is the combination of perovskite and spinel structure compounds. This work is focused on determining the position of the iron in the studied composite depending on the synthesis temperature.

Experiment

The $0.8CaZrO_3$-$0.2CaFe_2O_4$ composite was synthesized by solid-state reaction, starting from pure $CaCO_3$, ZrO_2, and Fe_2O_3 commercial powders. Synthesis of the material was achieved by a two-step heating process. The first step at 1200°C was calcination. The recovered material was grounded and pressed under 30 MPa before the second step heat treatment at 1400°C and 1700°C with the 10 h soaking time at each temperature.

The X-ray diffraction analysis was performed at a room temperature, using monochromatic Cu-Kα radiation (Philips Panalytical X'Pert-Pro MPD diffractometer) in order to determine the phase composition of the fired materials. The crystal structure parameters were obtained using the full-profile Rietveld method [14] implemented in the FullProf software package [15].

The ^{57}Fe Mössbauer effect measurements were performed using the standard technique at room temperature in transmission mode, using a conventional constant-acceleration spectrometer and a 25 mCi ^{57}Co source in Rh matrix. The velocity scale was calibrated using α-Fe foil. Spectra were fitted to Lorentzian lines using the non-linear least square method.

Results and discussion

Figure 1 shows X-ray diffraction (XRD) patterns and theoretical fits of the samples sintered at 1400°C and 1700°C. It was found that the main crystalline phases were $CaZrO_3$ (*Pcmn*) and $CaFe_2O_4$ (*Pnam*).

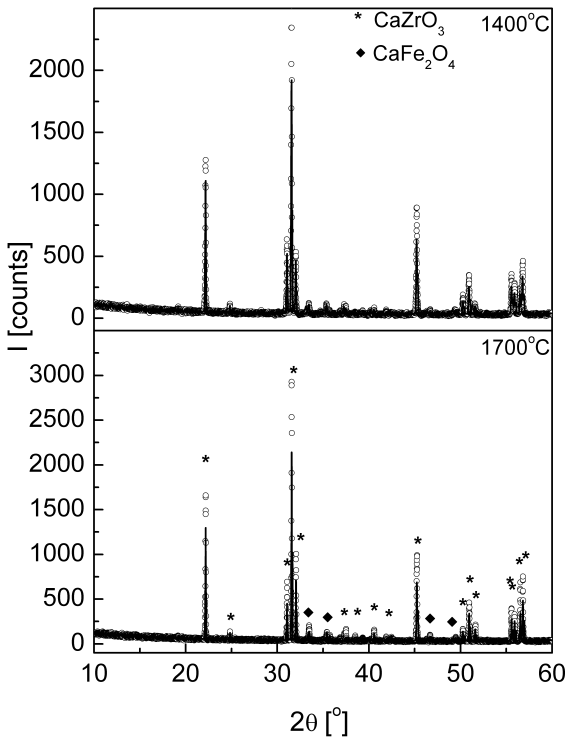

Fig. 1. X-ray diffraction patterns and the Rietveld analysis of the samples sintered at 1400°C and 1700°C.

Parameters of both the crystalline phases are summarized in Table 1. With the sintering temperature increases the amount of the $CaFe_2O_4$ phase at the cost of $CaZrO_3$, which could indicate the dissolution of $CaZrO_3$ by $CaFe_2O_4$ liquid phase. At both temperatures, a reduction of unit cell volume of $CaZrO_3$ is observed. It may be caused by diffusion and incorporation of Fe^{3+} cations, which replaced bigger Zr^{4+} cations in the perovskite structure. An effective ionic radius of Zr^{4+} (0.72 Å) is considerably bigger than Fe^{3+} (0.55 Å) [16]. Thus if part of Zr is substituted by Fe, it should decrease the crystal structure parameters. The opposite effect is observed in the case of $CaFe_2O_4$. The diffusion and incorporation process are thermally activated. Therefore, at 1700°C in comparison to 1400°C, the lowest parameters of unit cell were obtained.

Table 1. Crystal structure parameters of $CaZrO_3$ and $CaFe_2O_4$ phases (a, b, c – unit cells parameters, V – unit cell volume, A – phase share percentage)

Parameters	Sintering temperature		JCPDS
	1400°C	1700°C	
	$CaZrO_3$ (*Pcmn*)		
a [Å]	5.586(1)	5.582(1)	5.5912
b [Å]	8.011(1)	8.007(1)	8.0171
c [Å]	5.754(1)	5.754(1)	5.7616
V [Å^3]	257.54(1)	257.22(1)	258.26
A [%]	92.6(9)	88.0(9)	
	$CaFe_2O_4$ (*Pnam*)		
a [Å]	10.756(9)	10.732(9)	10.705
b [Å]	9.262(4)	9.261(4)	9.23
c [Å]	3.027(4)	3.026(4)	3.024
V [Å^3]	301.56(7)	300.86(7)	298.79
A [%]	7.4(6)	12.0(6)	

Table 2. The hyperfine interaction parameters (A – area of the subspectra, IS – isomer shift, QS – quadrupole split) of the sample prepared at 1400°C and 1700°C

Component	A [%]	IS [mm/s]	QS [mm/s]
		1400°C	
1	63.7	0.338(4)	0.647(7)
2	28.5	0.364(1)	0.322(5)
3	7.8	0.437(5)	0.643(8)
		1700°C	
1	54.4	0.313(16)	0.627(10)
2	26.1	0.353(1)	0.305(13)
3	19.5	0.429(9)	0.633(10)

The results of the Mössbauer spectroscopy measurements are shown in Fig. 2 and are summarized in Table 2. It was found that the obtained spectra are the result of three components, which correspond to the three different neighborhoods of Fe^{3+} ions. In the case of components 1 and 2, the hyperfine interaction parameters correspond to pure $CaFe_2O_4$ [17], where iron occurs in the octahedral and tetrahedral sites (approximately 2:1 contribution). In contrast, component 3 is derived from iron, which was incorporated into the $CaZrO_3$ structure and replaces zircon in octahedral sites. The substitution of Zr^{4+}/Fe^{3+} causes an imbalance of a cell charge. This is compensated by the presence of an oxygen octahedron distortion in the middle of which Fe^{3+} cations are situated, or by the removal of one oxygen unit from an octahedron corner. Its coordination number declines from 6 to 5. This effect causes the appearance of the larger electric field gradient acting on the Fe^{3+} ions, which leads to an increase of quadrupole splitting (QS) parameter. The increase of the sintering temperature causes the increase in incorporation of Fe^{3+} ions into the $CaZrO_3$ structure from approximately 8% to 20%.

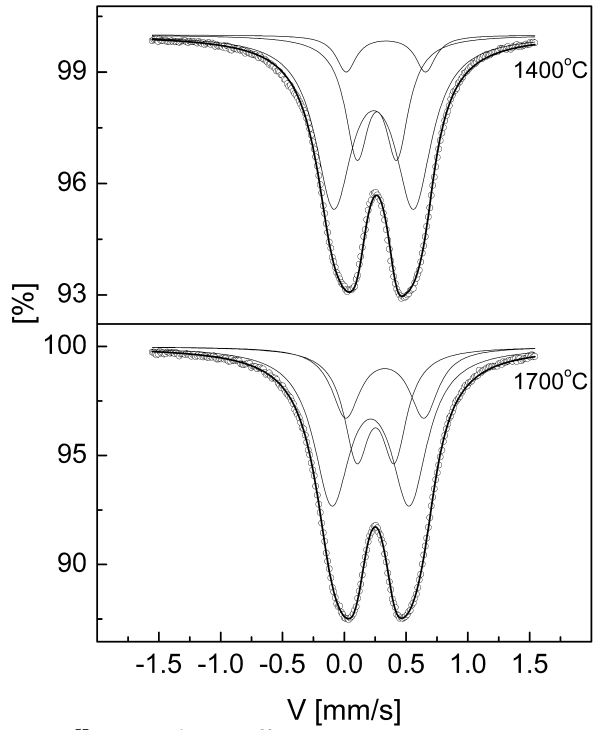

Fig. 2. ^{57}Fe Mössbauer effect measurements at room temperature of the sample sintered at 1400°C and 1700°C.

Conclusions

The aim of the study is to characterize the $0.8CaZrO_3$-$0.2CaFe_2O_4$ composite structure based on calcium zirconate with calcium ferrite in the matrix, with particular emphasis on the role and position of iron, as a function of temperature synthesis. Parameters of both the obtained crystalline phases: $CaZrO_3$ and $CaFe_2O_4$ are slightly different, compared to the reference data, which may indicate the incorporation of iron in the $CaZrO_3$ crystal structure and zirconium in $CaFe_2O_4$. With the increase of the sintering temperature, a gradual dissolution of $CaZrO_3$ in the $CaFe_2O_4$ liquid phase is observed. It was found that the sintering temperature increase causes an increase in the incorporation of iron ions into the crystal structure of calcium zirconate from approximately 8% to 20%. The study revealed that the $CaZrO_3$ structure is able to embody up to about 2 mol% of Fe^{3+}.

Acknowledgment. The work was supported by the grant no. INNOTECH-K2/IN2/16/181920/NCBR/13.

References

1. Dravid, V. P., Sung, C. M., Notis, M. R., & Lyman, C. E. (1989). Crystal symmetry and coherent twin structure of calcium zirconate. *Acta Crystallogr. Sect. B-Struct. Sci.*, *45*(3), 218–227. DOI: 10.1107/S0108768189000856.
2. Rossa, N. L., & Chaplin, T. D. (2003). Compressibility of $CaZrO_3$ perovskite: Comparison with Ca-oxide perovskites. *J. Solid State Chem.*, *172*(1), 123–126. DOI: 10.1016/S0022-4596(02)00166-4.
3. Stoch, P., Szczerba, J., Lis, J., Madej, D., & Pędzich, Z. (2012). Crystal structure and *ab initio* calculations of $CaZrO_3$. *J. Eur. Ceram. Soc.*, *32*(3), 665–670. DOI: 10.1016/j.jeurceramsoc.2011.10.011.
4. Prasanth, C. S., Padma Kumar, H., Pazhani, R., Solomon, S., & Thomas, J. K. (2008). Synthesis, characterization and microwave dielectric properties of nanocrystalline $CaZrO_3$ ceramics. *J. Alloy. Compd.*, *464*(1/2), 306–309. DOI: 10.1016/j.jallcom.2007.09.098.

5. Pollet, M., Marinel, S., & Desgardin, G. (2004). $CaZrO_3$, a Ni-co-sinterable dielectric material for base metal-multilayer ceramic capacitor applications. *J. Eur. Ceram. Soc.*, *24*(1), 119–127. DOI: 10.1016/S0955-2219(03)00122-5.
6. Levin, I., Amos, T. B., Bell, S. M., Farber, L., Vanderah, T. A., Roth, R. S., & Toby, B. H. (2003). Phase equlibra, crystal structures, and dielectric anomaly in the $BaZrO_3$-$CaZrO_3$ system. *J. Solid State Chem.*, *175*, 170–181. DOI: 10.1016/S0022-4596(03)00220-2.
7. Serena, S., Sainz, M. A., & Caballero, A. (2009). The system Clinker-MgO-$CaZrO_3$ and its application to the corrosion behavior of $CaZrO_3$/MgO refractory matrix by clinker. *J. Eur. Ceram. Soc.*, *29*(11), 2199–2209. DOI: 10.1016/j.jeurceramsoc.2009.01.015.
8. Dudek, M., & Bućko, M. M. (2003). Electrical properties of stoichiometric and non-stoichiometric calcium zirconate. *Solid State Ion.*, *157*, 183–187.
9. Dudek, M., & Drożdż-Cieśla, E. (2009). Some observations on synthesis and electrolytic properties of nonstoichiometric calcium zirconate. *J. Alloy. Compd.*, *457*, 846–854. DOI: 10.1016/j.jallcom.2008.08.020.
10. Hwang, S. C., & Choi, G. M. (2006). The effect of cation nonstoichiometry on the electrical conductivity of acceptor-doped $CaZrO_3$. *Solid State Ion.*, *177*, 3099–3103. DOI: 10.1016/j.ssi.2006.08.002.
11. Smith, K. L., Colella, M., Cooper, R., & Vance, E. R. (2003). Measured displacement energies of oxygen ions in titanates and zirconates. *J. Nucl. Mater.*, *321*(1), 19–28. DOI: 10.1016/S0022-3115(03)00197-1.
12. Muller-Buschbaum, H. K. (2003). The crystal chemistry of AM_2O_4 oxometallates. *J. Alloy. Compd.*, *349*(1/2), 49–104.
13. Muller, O., & Roy, R. (1974). *The major ternary structural families*. New York: Springer.
14. Rietveld, H. M. (1969). A profile refinement method for nuclear and magnetic structures. *J. Appl. Cryst.*, 2, 65–71. DOI: 10.1107/S0021889869006558.
15. Rodriguez-Carvajal, J. (1993). Recent advances in magnetic structure determination by neutron powder. *Diffr. Phys. B*, *192*(1/2), 55–69. DOI: 10.1016/0921-4526(93)90108-I.
16. Shannon, R. D. (1976). Revise effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr. Sect. A*, *32*, 751–767. DOI: 10.1107/S0567739476001551.
17. Tsipis, E. V., Pivak, Y. V., Waerenborgh, J. C., Kolotygin, V. A., Viskup, A. P., & Khortan, V. V. (2007). Oxygen ionic conductivity, Mössbauer spectra and thermal expansion of $CaFe_2O_{4-\delta}$. *Solid State Ion.*, *178*(25/26), 1428–1436. DOI: 10.1016/j.ssi.2007.09.003.