MECHANOCHEMISTRY AND MECHANICAL ALLOYING 2003

JOURNAL OF MATERIALS SCIENCE **39** (2004) 5283–5286

Cerium silicates formation from mechanically activated oxide mixtures

S. ZEC, S. BOSKOVIC*
Institute of Nuclear Science Vinča, Materials Science Laboratory, 11001 Belgrade, POB 522, Serbia and Montenegro
E-mail: boskovic@mf.mpg.de; boskovic@vin.bg.ac.yu

Reactions of cerium silicate formation in mechanically activated oxide powders of CeO_2 and SiO_2 (quarz) were studied. Three different mixtures were prepared, the compositions of which corresponded to $Ce_2Si_2O_7$, $Ce_{4.67}(SiO_4)_3O$ and Ce_2SiO_5. Oxide mixtures were mechanically activated in vibratory mill up to 120 min. X-ray analysis performed on activated mixtures showed that the CeO_2 crystallite size decreased with increasing activation time. However, CeO_2 lattice distortions passed through a maximum after 30 min of activation. The results obtained after heating showed that reactions proceeded via formation of intermediate compounds. Evidence of the existence of a liquid phase at 1550°C is given. © *2004 Kluwer Academic Publishers*

1. Introduction

Investigations on cerium silicates show that these compounds can have many applications in various fields of technology due to their diverse properties, which are greatly caused by the ability of cerium to form nonstoichiometric oxides and the possibility of SiO_2 to be bound in the lattice in many different ways. Some of them, especially nanocrystalline Ce silicates, emit violet/blue light and can be used as stable luminescent materials for scintillators and detectors [1]. Owing to the thermal stability of their optical transmission they can be used in optoelectronics (laser, optical fiber), then in microelectronics, catalysis and as very efficient ion exchangers for radionuclides separation [2, 3]. Besides, the importance of cerium silicate liquid phase formation during sintering of ceramics from the silicon nitride family with additives containing CeO_2 reported in many publications [4, 5], should be emphasized. In spite of this, there are not much reliable data in the literature on cerium silicates and the results on reaction pathways are ambiguous. According to the Ce_2O_3-SiO_2 phase diagram, Ce_2SiO_5, $Ce_{4.67}(SiO_4)_3O$, and two polymorphs of $Ce_2Si_2O_7$ may be formed from ceria and silica in an inert or reducing atmosphere [6, 7]. Recently, a new compound with the proposed structural formula $Ce_6[Si_4O_{13}][SiO_4]_2$ has been reported [2]. Different processing techniques are used for cerium silicates preparation. Most of them aspire to obtain reactive starting components, since the solid-state reactions between mixed oxides powders require high temperatures and/or very long heating time [6, 7]. In our previous work we applied mechanical activation as simple and time saving procedure to synthesize Ce silicates. Grinding in a high energy mill, beside providing better homogenization of the mixture, affects particle size, surface structure, introduces lattice defects and decreases the crystallite size to the nanometer range. Such changes of the starting powders can essentially alter both rate and course of chemical reactions between reactants and force new reaction products [8]. Literature data showed that mechanical activation has not been applied to cerium silicates investigations, until now. In this paper, which is a part of phase relation studies in the ZrO_2-Ce_2O_3-SiO_2 system, results on cerium silicates formation from mechanically activated mixtures of CeO_2 and SiO_2 are presented as a function of grinding time, upon heating the reaction mixture at 1550°C in argon atmosphere.

2. Experimental procedure

Three mixtures were prepared using oxide powders CeO_2 (Aldrich, particle size <5 μm) and SiO_2 quartz (Merck; particle size from 200 to 800 μm). The mixtures compositions P, R and M corresponded to $Ce_2Si_2O_7$, $Ce_{4.67}(SiO_4)_3O$ and Ce_2SiO_5 stoichiometry, respectively. Mechanical activation was performed by milling the mixtures in a vibratory mill Pulverisette 9 (Fritsch), with milling vessel and balls made of tungsten carbide (WC). Vibration speed of carrier was 1450 rpm. Ten grams of each mixture were activated for 2, 15, 30, 60 and 120 min. Activated mixtures were pressed into pellets (diameter 10 mm) under 35 MPa. Pellets were heated in an Astro furnace in an argon atmosphere at 1550°C for 1 and 24 h. Specimens were furnace cooled under argon to room temperature. X-ray powder diffraction (XRD) analysis was carried out by a Siemens D500 diffractometer using Ni-filtered Cu K_α radiation and a scanning speed of 0.02° (2θ)/s. Crystallite size and lattice distortions were determined on the base of the

---

*Author to whom all correspondence should be addressed.

0022–2461 © *2004 Kluwer Academic Publishers*

Cauchy expression: $\beta \cos\theta = K\lambda D + 4\varepsilon \sin\theta$ in which the total broadening (β) is the sum of peak broadening due to crystallite size (D) and lattice distortions (ε) [9]. The shape factor K was assumed to be 0.9. Separation of the instrumental broadening was done using an empirical formula $\beta = B - b^2 B$, where B represents the measured peak width, while b is the instrumental width obtained from a Si standard. Scanning electron microscopy (SEM) was performed using Jeol JSM-35 equipment.

3. Results and discussion

The CeO_2 starting powder had the crystallite size of 140 nm and no lattice distortions, while SiO_2 was well crystallized. XRD patterns of all three mixtures activated for the same milling time are very similar. The most intensive SiO_2 peak disappeared after 30 min of milling indicating that SiO_2 became amorphous during milling. The WC quantity introduced into the system is rising with the time of grinding, so its peaks became more intensive after 60 min of milling. Rapid decrease in CeO_2 crystallites size up to 20 nm, due to particles fragmentation and lattice defects formation, occurred during the first 30 min of milling, while its lattice distortions go through a maximum in that time (Fig. 1).

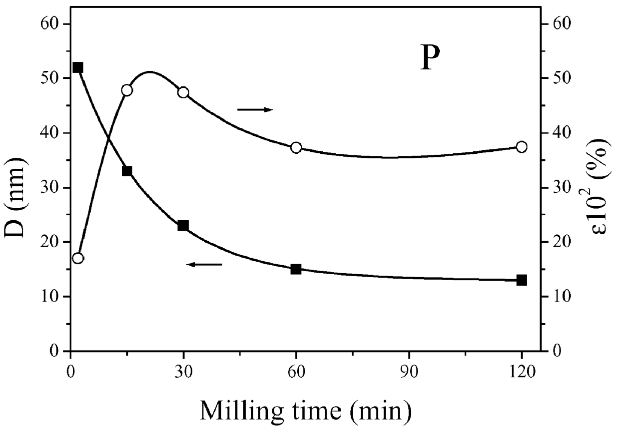

Figure 1 CeO_2 crystallite size and lattice distortions in P mixture as a function of milling time.

Reaction between the oxides was completed in all P mixtures, even in the non-activated one, at 1550°C after 1 h of thermal treatment, indicating that this compound could be formed at much lower temperatures. The high temperature polymorph of $Ce_2Si_2O_7$ was detected as well as tungsten (W) peaks, visible in XRD patterns of mixtures activated for 30 min or longer (Fig. 3a). A SEM micrograph (Fig. 2) of this composition revealed the presence of a liquid phase, which obviously assisted chemical reaction. This information contributes to phase relations in this system, which are lacking in the literature. In R mixtures, $Ce_{4.67}(SiO_4)_3O$ with the apatite structure was detected. In addition, $Ce_2Si_2O_7$ and CeO_2 diffraction lines were found (Fig. 3b), the intensity of which decreased with prolonged activation time, indicating that cerium orthosilicate formation proceeded via an intermediate $Ce_2Si_2O_7$ compound. Chemical reaction was finished after 30 min of activation (Fig. 3c), at the point at which maximum lattice distortions was observed.

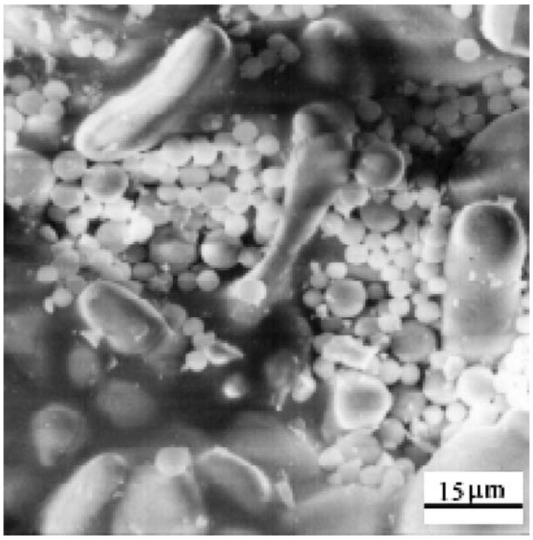

Figure 2 SEM micrograph of P mixture heated at 1550°C for 1 h.

A heat treatment at 1550°C for one hour was inadequate to produce Ce_2SiO_5 in any of the milled M mixtures. Beside $Ce_{4.67}(SiO_4)_3O$, also non-stoichiometric cerium oxides with a cubic fluorite structure, usually designated as CeO_{2-x} ($x < 0.3$), were identified. They had different oxygen content depending on milling time. It should be pointed out that in the non-activated M mixture, prepared from fused SiO_2 and CeO_2 powders, defect cerium oxide with slightly higher lattice parameter ($a = 0.543$ nm) in comparison with CeO_2 ($a = 0.541$ nm) was observed after heating (Fig. 4a). In mechanically activated M mixtures, the lattice parameter of cerium oxide is rising with prolonged milling time up to value of $a = 0.552$ nm (in the mixture activated for 30 min), see Fig. 4b, corresponding to $CeO_{1.72}$ composition [10]. $3Ce_2O_3{\cdot}2WO_3$ was produced in the mixtures milled for 60 and 120 min (Fig. 4c). However, an important fact is that at much longer heating time (24 h at 1550°C), Ce_2SiO_5 was formed in M mixture pre-activated for 120 min. On the related XRD pattern, Ce_2SiO_5 diffraction lines of rather high intensity are clearly visible, $Ce_{4.67}(SiO_4)_3O$ phase is still present while cerium oxide appears as Ce_2O_3 (Fig. 4d).

Contrary to published data [7], the results obtained suggest that formation of Ce silicates proceeds via formation of intermediate phases, namely Ce silicates richer in silica as compared to the final reaction product. It should be stressed that a liquid phase forms in the system during heating at temperatures of about 1550°C, obviously on $Ce_2Si_2O_7$ and SiO_2 side of Ce_2O_3-SiO_2 two phase system, which had not been studied up to now. Activation of CeO_2 by milling is also reflected in oxygen vacancies formation, i.e., reactive, defect cerium oxide phases appear on heating, which together with reactive amorphous SiO_2 and liquid phase make cerium silicates formation easier under the present experimental conditions in comparison with literature data [6, 7].

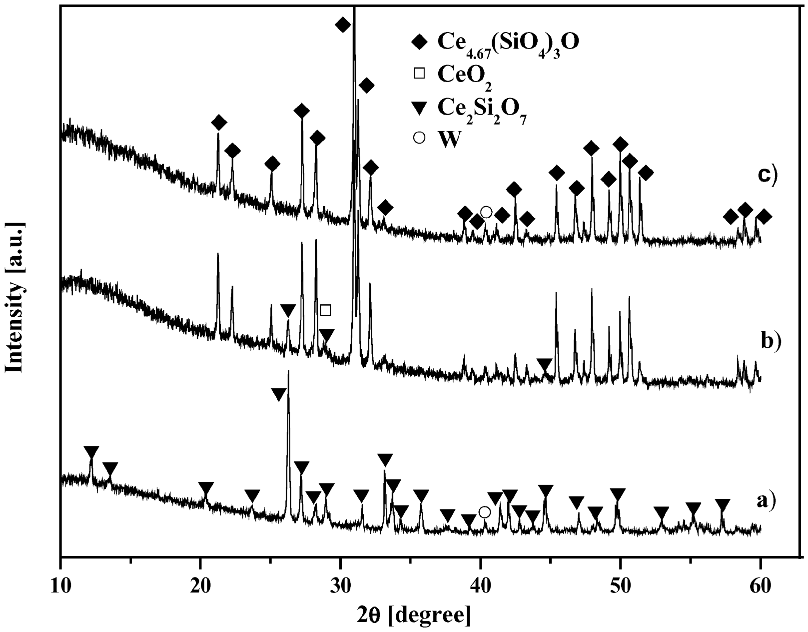

Figure 3 XRD patterns after 1 h of heating at 1550°C for (a) *P* mixture milled 30 min, (b) *R* mixture milled 15 min and (c) *R* mixture milled 30 min.

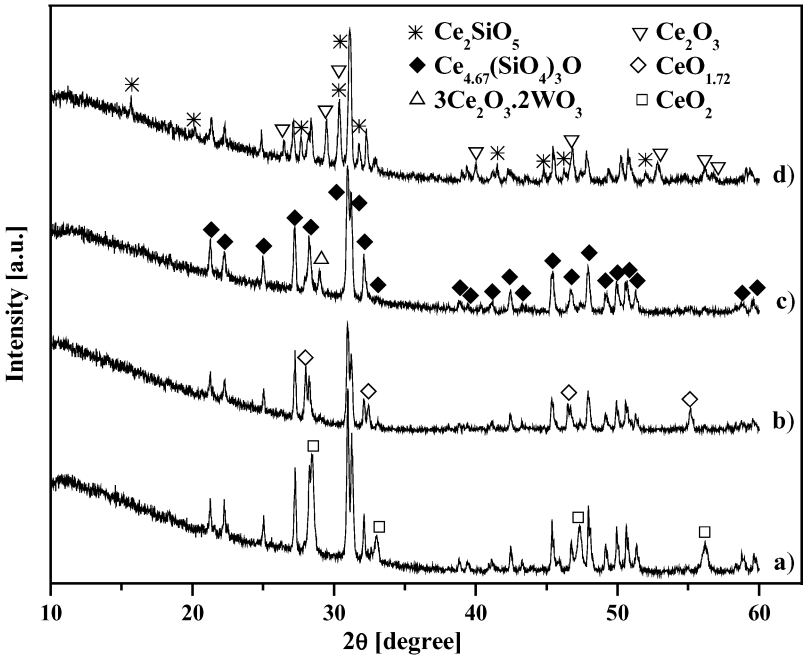

Figure 4 XRD patterns of *M* mixture heated at 1550°C for 1 h (a) non-activated mixture, (b) 30 min activated, (c) 60 min activated and (d) the pre-activated *M* mixture (120 min) heated at 1550°C for 24 h.

4. Conclusions

Mechanical activation effect on reactions between CeO_2 and SiO_2 to form $Ce_2Si_2O_7$, $Ce_{4.67}(SiO_4)_3O$ and Ce_2SiO_5 was studied. The reaction of $Ce_2Si_2O_7$ formation was completed in all mixtures studied. The reaction proceeded via liquid phase formation in the $Ce_2Si_2O_7$-SiO_2 part of the two phase diagram. $Ce_{4.67}(SiO_4)_3O$ was formed via disilicate as an intermediate compound. Instead of Ce_2SiO_5, $Ce_{4.67}(SiO_4)_3O$ and defect cerium oxides (CeO_{2-x}) were formed. The lattice parameter of $CeO_{1.72}$ was found to be $a = 0.552$ nm after 30 min of activation. Ce_2SiO_5 was obtained after heating (at 1550°C after 24 h) of the *M* mixture milled for 120 min. Formation of Ce silicates in mechanically activated mixtures proceeds via formation of intermediate phases, namely Ce silicates richer in silica as compared to the final reaction product.

Acknowledgment

This work was supported by the Ministry of Science, Technology and Development of the Government of Serbia, project No. 1947.

References

1. L. KEPINSKI, D. HRENIAK and W. STREK, *J. Alloys Compd.* **341** (2002) 203.

2. L. KEPINSKI, M. WOLCYRZ and M. MARCHEWKA, *J. Solid State Chem.* **168** (2002) 110.
3. M. G. MARAGEH, S. W. HUSAIN, A. R. KHANCHI and S. J. AHMADY, *J. Appl. Radiat. Isot.* **47** (1996) 501.
4. S. BOŠKOVIĆ, F. SIGULINSKI, G. RIXECKER and F. ALDINGER, *Z. Metallkd.* **92** (2001) 8.
5. S. BOŠKOVIĆ, F. SIGULINSKI and E. KOSTIĆ, *J. Serb. Chem. Soc.* **62** (1997) 1095.
6. C. TAS and M. AKINC, *J. Amer. Ceram. Soc.* **77** (1994) 2953.
7. H. A. M. VAN HAL and H. T. HINTZEN, *J. Alloys Compd.* **179** (1992) 77.
8. S. BOŠKOVIĆ, DJ. KOSANOVIĆ, DJ. BAHLOUL-HOURLIER, P. THOMA and S. KISS, *ibid.* **290** (1999) 230.
9. B. LÖNNBERG, *J. Mater. Sci.* **29** (1994) 3224.
10. N. A. TOROPOV, V. P. BARZAKOVSKY, I. A. BONDAR and J. P. UDALOV, "Diagrami sostyanya silikatnykh sistem" (Nauka, Leningrad, 1970) p. 54 (in Russian).

Received 11 September 2003
and accepted 27 February 2004