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Effects of BaRuO₃ addition on hydrogen desorption in MgH₂

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Keywords

Hydrogen storage; oxide bronze; MgH₂; BaRuO₃; kinetic analysis.

Abstract

Hydrogen storage in MgH₂ is strongly limited by kinetic constraints, so that several additives have been considered in order to improve the rate of hydrogen desorption. The present work is devoted to investigate the effect of BaRuO₃ addition on hydrogen absorption and desorption properties of MgH₂. BaRuO₃ was prepared by solid-state synthesis of BaO and Ru in oxidizing environment. The interaction of as-prepared BaRuO₃ with hydrogen at room temperature was examined by thermal desorption and X-ray diffraction experiments, showing that BaRuO₃ has the ability to uptake hydrogen in the bulk. The hydrogen interaction is discussed with respect to octahedral ruthenium local environment present in the oxide structure.

Addition of 1 mol% BaRuO₃ to MgH₂ was performed by ball milling. Hydrogen desorption properties were investigated by Sievert and DSC, connected with a H₂ detector. The H₂

desorbed from of the nano-structured materials is lower than the theoretical content in MgH_2 , due to the presence of a non-reactive MgO layer. A remarkable increase of the H_2 desorption kinetics in nano-structured MgH_2 was observed with respect to bare MgH_2 . The activation energy for hydrogen desorption from $\text{MgH}_2/\text{BaRuO}_3$ mixture was estimated by Arrhenius and Kissinger methods and a value around 130 kJmol^{-1} and 90 kJmol^{-1} was obtained, respectively.

Introduction

MgH_2 is an excellent material due to its high hydrogen storage capacity. However, the equilibrium dehydrogenation temperature is high, around 570 K under 1 bar of H_2 and the ab/desorption kinetics is undesirably slow [1-8]. A number of techniques has been applied to improve the ab/desorption kinetics of MgH_2 , for example, ball-milling [9-11] with different additives e.g., transition metals (TM) [12-14] and transition metal oxides (TMO) [15-20]. The addition of niobia (Nb_2O_5), in particular, has demonstrated an increase of reactivity in MgH_2 with respect to H_2 uptake/release [9,21-25]. Recently, the interaction of hydrogen with MgH_2 in presence of ternary Mg-Nb oxides has been studied [26], suggesting a prominent effect for the system $\text{Mg}_3\text{Nb}_6\text{O}_{11}$. However, the exact role of additives on reaction mechanism still remained unclear. An empirical rule suggests that TM atoms (Nb, Cr, W etc.) having multiple valence states in corresponding TMOs, show better reaction efficiency [7,21]. In addition, the interaction of H_2 with TMOs has drawn attention in order to understand their specific role on H_2 ab/desorption reactions in MgH_2 [27-32]. In particular, it has been suggested that the occurrence of a hydrogen absorption in the additive oxide phase may facilitate the overcome of the MgO layer formed at the surface of the MgH_2 particles, leading to an improved reaction kinetics [25,26].

Chabanier et al. [33] performed electrochemical studies on RuO_2 and IrO_2 and suggested that these oxides show good electrocatalytic activity towards hydrogen evolution, leading to a

$\text{RuO}_2\text{H}_{0.09}$ and $\text{IrO}_2\text{H}_{0.03}$ phases. Shelef et al. [34] reported that BaRuO_3 , after interaction with hydrogen (H_2 pressure 40 kPa) at room temperature (RT) for 6 days, absorbs 0.1 wt% hydrogen, corresponding to a $\text{H}_{0.3}\text{BaRuO}_3$ phase. These results suggest a specific investigation on the role of BaRuO_3 addition on hydrogen desorption from MgH_2 .

In this paper, BaRuO_3 has been prepared by solid-state reaction following the synthetic approach reported in the literature [35]. A preliminary study on the hydrogen interaction with the oxide phases has been performed, showing a significant hydrogen absorption at room temperature. In addition, H_2 desorption kinetics in MgH_2 promoted by ball-milling with 1 mol% BaRuO_3 has been investigated. The activation energy for hydrogen desorption has been estimated from isothermal and scanning measurements. It turns out significantly lower than that obtained for the bare MgH_2 and comparable to those reported in the literature for different TMO additives [14,23].

Experimental

The starting materials used for solid-state synthesis of BaRuO_3 were commercially barium oxide (BaO) and ruthenium (Ru) (Sigma-Aldrich, 99% pure). The compound was prepared by heating a stoichiometric mixture of reagents with a rate of 5 K/min up to 1473 K and annealing for 24 hours in oxidizing environment. Reactive milling of pure BaRuO_3 was performed in a commercial Spex model-8000 Mixer/Mill with a ball-to-powder mass ratio of 15:1 under a hydrogen pressure of 0.5 MPa for 20 h. Hydrogen absorption in as-prepared BaRuO_3 was carried out at RT for 58 h with a hydrogen pressure of 6.5 MPa inside of a Sievert-type apparatus. 1 mol% of pure BaRuO_3 was added to 5 g of commercial MgH_2 (Alfa Aesar, Johnson Matthey Company, 98% purity, balance Mg) for ball-milling, carried out in a commercial Spex model-8000 Mixer/Mill for 12 h under a high purity Ar atmosphere. The milling run was carried out at 875 rpm by employing a special hardened steel vial and two

hardened steel milling balls with a ball-to-powder mass ratio of 7:1. Pure MgH_2 was ball milled under the same conditions for comparison.

Structural features of solid-state materials have been analyzed by X-ray diffraction (XRD) at RT with an X'PERT PRO diffractometer (Panalytical) with $\text{Cu K}\alpha$ radiation. XRD patterns were collected in a step of 0.017 degree after accumulation of intensity data points in the range 10-100° for 1 h. Diffraction patterns were refined with Rietveld method using MAUD (Material Analysis Using Diffraction) program [36].

Hydrogen desorption properties were investigated by Thermal Programmed Desorption (TPD) coupled with a home-made heating apparatus to a quadruple Mass Spectrometer (MS, Pfeiffer Vacuum Prisma). Thermal desorption data were recorded during TPD measurements between 313 K and 1073 K with a heating rate of 7.5 K/min in high vacuum (10^{-6} bar) condition.

The samples were characterized by an AMC (Advanced Materials Corporation) instrument for hydrogen desorption at different programmed temperatures (573-653 K) in isothermal condition until reaching an equilibrium condition under a hydrogen pressure of 0.1 MPa. About 0.6 g sample were used for each measurement. Hydrogen desorption properties were also measured with a differential scanning calorimeter Perkin-Elmer DSC7. Measurements have been carried out with heating rate of 5, 10, 20 and 40 K/min. Two successive runs were performed and the data were subtracted from the signals of the second run defined as baseline.

Results and discussion

Pure BaRuO₃

The XRD pattern of the product after the solid state synthesis of $\text{BaO} + \text{Ru}$ is shown in Figure 1 (pattern a). The use of a logarithmic scale is adopted for the analysis because intense and weak peaks may be equally important in order to correctly reconstruct the structure properties

of materials. Indeed, the shift of the ordinate variable among the patterns is operated simply by multiplication of intensity data points by a constant factor. With this simple manipulation the signal-to-background trend is maintained, when adopting the same collection strategy in the instrument as well as the similar protocol of sample preparation in terms of density and chemistry. The Rietveld fit to the pattern ($R_{wp} = 2.1\%$) confirms the rhombohedral structure of BaRuO₃ (space group R-3m) with lattice parameters $a = 5.752 (\pm 0.001) \text{ \AA}$ and $c = 21.623 (\pm 0.003) \text{ \AA}$, that closely correspond to reference values given by the Inorganic Crystal Structure Database (ICSD) file 10253, within experimental uncertainty. Crystal size and microstrain of the ternary oxide are $>200 \text{ nm}$ and $< 3.9 \cdot 10^{-4}$, respectively, i. e., beyond the instrument resolution. The as-prepared BaRuO₃ compound was investigated by hydrogen and water desorption (TPD-MS) and results are reported in Figure 2. The curve of as-prepared sample is a flat baseline, indicating that no desorption phenomena related to water and hydrogen release occurred.

The XRD pattern registered after reactive milling of BaRuO₃ under H₂ atmosphere is shown in Figure 1 (pattern b). The ternary oxide transformed during reactive milling due to the interaction of hydrogen, so that mono/tri-hydrated barium hydroxides (25 wt% \pm 3%) and metallic Ru (28 wt% \pm 3%) were obtained, together with the parent oxide (47 wt% \pm 5%). In addition, significant broadening of the diffraction peaks is observed due to formation of nanocrystalline solids (10-90 nm) during mechano-chemical treatment. The results suggests that reactive milling under H₂ promotes chemical reactions with BaRuO₃, leading to a reduction of Ru⁴⁺ to Ru⁰ and to the formation of OH⁻ groups. The XRD pattern (not shown) remains rather similar after an annealing of the sample up to 950 K, suggesting that the observed reactions are irreversible. So, a milder hydrogenation process has been explored.

Figure 1 (pattern c) shows the XRD pattern of BaRuO₃ after interaction at RT with a H₂ pressure of 6.5 MPa for 58 h. With respect to the as-prepared pattern, the lower signal-to-

background ratio is due to peak distortion and broadening, on account for lattice parameter change of the rhombohedral structure. The XRD pattern was fit according to the Rietveld method ($R_{wp} = 4.5\%$) and allowed the evidence of a consistent fraction ($33 \text{ wt}\% \pm 3\%$) of a new rhombohedral phase, with the same structure of BaRuO_3 , but with lattice parameters elongated in the c direction ($a = 5.755 (\pm 0.001) \text{ \AA}$ and $c = 21.819 (\pm 0.003) \text{ \AA}$), together with a weak presence ($7 \text{ wt}\% \pm 1\%$) of a tetragonal phase, isostructural with BaSrTiO_3 compound (ICSD, file 54150). These effects are related to the interaction of the original phase with hydrogen. In addition, the average crystallite size ($45 \text{ nm} \pm 4$) of the distorted phase obtained after hydrogenation at 6.4 MPa is significantly reduced with respect to that of the as-prepared sample, together with an increase in the microstrain ($4.3 \cdot 10^{-3} \pm 2 \cdot 10^{-4}$). Being the rest of the mixture constituted by the parent BaRuO_3 rhombohedral phase, an incomplete hydrogenation reaction can be envisaged, in agreement with previous findings [34].

The TPD-MS spectra for hydrogen and water desorption from BaRuO_3 after hydrogen absorption at 6.4 MPa are shown in Figure 2. Desorption peaks related to hydrogen and water are observed in similar positions, at temperatures starting from 400 K and 750 K. Moreover, the hydrogen desorption peak intensity is about 30 times that related to water desorption, suggesting the occurrence of simple H_2 insertion in the crystal structure, rather than a chemical interaction with oxide anions.

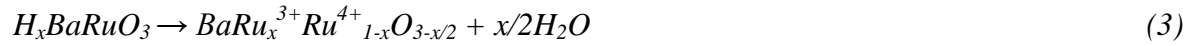
The XRD pattern after TPD-MS of BaRuO_3 hydrogenated at RT under 6.4 MPa is shown in Figure 1 (pattern d). The single rhombohedral BaRuO_3 phase is assessed by the Rietveld refinement ($R_{wp} = 3.36\%$), with lattice parameters $a = 5.750 \text{ \AA}$ and $c = 21.611 \text{ \AA}$, rather similar to those obtained for the as-prepared sample. The crystal size, above the resolution limit of 200 nm, is remarkably increased after TPD-MS measurement, due to the microstructure coarsening. These results suggest a full recovering of the original structural properties after TPD-MS measurement, indicating a reversibility of the hydrogenation process in BaRuO_3 .

Shelef et al. [34] reported that BaRuO₃ absorbed 0.1 wt% hydrogen (H_{0.3}BaRuO₃) at RT after interaction with hydrogen (H₂ pressure 40 kPa) for 6 days. From the reported results, it is worth noting that BaRuO₃ is active to hydrogen absorption at RT even using much higher pressure (H₂ pressure 6.4 MPa). This behaviour has been already observed for other oxides, like Mg₃Nb₆O₁₁ [37], Nb₂O₅ and WO₃ [32].

The crystal structure of BaRuO₃ has been derived by the bond valence method [38]. The crystal is based on a layered rhombohedral structure, which is considered to be the stable form of BaRuO₃ at ambient pressure, confirmed by Rietveld refinement of as-prepared sample (Figure 1). The unary cell of BaRuO₃ is formed by units of three face-sharing RuO₆ octahedra, which are connected to one another by corner sharing. The crystalline Ru (IV) oxide (RuO₂) has the rutile-type structure and it is also composed of RuO₆ octahedra. Recently, attention has been directed toward the use of RuO₂ electrode as an activated cathode for H₂ evolution. This oxide shows good electrocatalytic activity for H₂ evolution and excellent resistance to deactivation due to deposition of metallic impurities [33]. The fact behind H₂ interaction with RuO₂ is that H₂ can penetrate into the RuO₂ structure in the absence of polarization. Moreover, the measured H/Ru ratio suggests that surface hydroxylation occurs with no bulk modification. On the contrary, for BaRuO₃, H₂ absorption may occur also into the bulk of the material. In fact, the expansion of the unit cell has been noticed along the c-axis after H₂ interaction (Figure 1), strongly suggesting that H₂ is inserted in the a-b plane of the unary cell. The oxygen atoms of the shared faces in each unit are pulled together, thus providing a ‘shielding effect’ that reduces the Ru-Ru interactions, facilitating H₂ incorporation and diffusion inside the structure.

Hydrogen absorption and desorption in BaRuO₃ may be discussed according to reactions proposed for H₂ interaction with Nb₂O₅ [39,40]:





In reaction 1, ionization of the incoming hydrogen occurs with release of electrons which can delocalize either into the conduction band of the solid or on a ruthenium ion, which changes its oxidation state. The residual H^+ is stabilized by oxygen ions of the lattice producing OH^- groups. Upon annealing, two possible reactive channels can be followed. In the first case (reaction 2), the process leads to hydrogen desorption and tends to restore the initial oxidation state of the transition metal. In the second case (reaction 3), the process leads to water desorption and the metal ion is partially reduced. So, $BaRuO_3$ after contact with molecular hydrogen may be partially reduced by formation of hydroxyl groups and perhaps of hydride ions. Consequently, both hydrogen and water desorption can be explained on the basis of different bonding energy of OH^- groups at various crystallographic sites.

In conclusion, $BaRuO_3$ is not at all inert while interacting with hydrogen. This peculiar behavior, reminiscent of some properties of the bronze family and Nb_2O_5 [32], suggests a possible active chemical role played by $BaRuO_3$ in the mixed $MgH_2/BaRuO_3$ system.

MgH₂+BaRuO₃ mixture

The XRD pattern of physically mixed MgH_2 with $BaRuO_3$ additive is shown in Figure 3 (bottom curve). In the parent MgH_2 a small contamination (lower than 2 wt.%) of hexagonal Mg was found. The XRD pattern in Figure 3 (upper curve) refers to the mixture after ball milling for 12 h. The intensity of MgH_2 diffraction profiles is affected by a large amount of peak broadening. The phase analysis evidences that tetragonal MgH_2 is the main phase present (57 wt.%) but 23 wt.% of the sample is under the form of a γ - MgH_2 orthorhombic phase, together with a non-negligible quantity of periclase MgO (15 wt.%). The remaining 5 wt.% of the mixture is attributed to $BaRuO_3$, showing diffraction peaks with a lower degree of broadening, as expected from the brittleness of the oxide phase. The nominal amount of

BaRuO₃ present in MgH₂ is 9.9 wt% (1 mol%). The reduced amount of pure BaRuO₃ after ball milling might be related to an interaction of the additive with the MgO layer surrounding the MgH₂ particles, suggesting a possible active role of the additive in the hydrogen sorption processes.

The results of the PCI experiment of H₂ desorption from commercial MgH₂, ball milled MgH₂ and MgH₂/BaRuO₃ ball milled mixture at 593 K under 0.1 MPa of hydrogen pressure are reported in Figure 4a. Because the total amount of hydrogen released from various samples is different, the results are reported as a transformed fraction as a function of time for better comparison. Commercial MgH₂ shows very slow desorption rate, whereas ball milled MgH₂ desorbs hydrogen much faster, as already reported in the literature [10]. MgH₂/BaRuO₃ ball milled mixture shows better desorption properties, due to the effect of ball milling and to the presence of the additive. Desorption curves for MgH₂/BaRuO₃ ball milled mixture from 653 to 573 K under 0.1 MPa H₂ pressure are reported in Figure 4b, where the hydrogen release at various temperatures is reported as a function of time. The nominal hydrogen content in MgH₂/BaRuO₃ ball milled mixture is 6.9 wt.%, respectively. The total amount of hydrogen desorbed from the samples is lower than the maximum nominal capacity, likely due to the presence of a non-reactive MgO layer on the surface of the powders.

The activation energy (E_a) of H₂ desorption may be estimated from the Arrhenius equation:

$$k = A \cdot \exp(-E_a/RT) \quad (4)$$

where k is a temperature dependent reaction rate constant, A is the pre-exponential factor, R is the gas constant and T is the absolute temperature. The k values can be obtained by analyzing the isothermal H₂ desorption curves with appropriate kinetic rate expressions, which are derived from the corresponding solid-state reaction mechanism models such as nucleation, geometrical contraction, diffusion and various reaction order models. Therefore, the model parameters obtained from the fitting of desorption data with suitable models also reflects the

desorption mechanism. So, the desorption curves have been analyzed using the Johnson-Mehl-Avrami (JMA) equation [41-43]:

$$\alpha(t) = 1 - \exp[-(kt)^n] \quad (5)$$

where α is the phase fraction transformed at time t and n is the Avrami exponent. The JMA fitting of experimental data of hydrogen desorption from MgH₂/BaRuO₃ ball milled mixture are shown in Figure 4b as continuous lines. The obtained values of n and k are reported in Figure 5 as a function of the inverse temperature, together with the same results obtained for commercial MgH₂ and ball milled MgH₂. From the linear fit of $\ln(k)$ as a function of $1/T$, the E_a values were obtained according to eq. (4) and turned out equal to 170 kJmol⁻¹, 140 and 130 kJmol⁻¹ for commercial MgH₂, ball milled MgH₂ and MgH₂/BaRuO₃ ball milled mixture, respectively. Due to the progressive approaching of the equilibrium temperature at the desorption pressure (0.1 MPa) on decreasing temperatures [26], a correction of the kinetic constants obtained at various temperatures with a constant pressure has been suggested [44]. In the case of a constant sample geometry, the kinetic constant, $k(T,P)$, obtained from the JMA analysis (eq. 5) can be normalized by the driving force, $g(P/P_{eq})$, so that a purely kinetic constant, $h(T)$, can be obtained. The driving force depends on the ratio P/P_{eq} , where P is the pressure of the desorption experiment (0.1 MPa in these experiments) and P_{eq} is the equilibrium pressure at the temperature of the experiment [44, 45]. Attempts to apply the correction for the driving force led to a significant decrease of the correlation coefficient for the linear regression in the Arrhenius plot of Figure 5, with the consequence of unreasonable values for the activation energy. So, raw values of the kinetic constant have been taken for the calculation of the activation energies, in agreement with similar studies [10,46]. The application of the JMA equation to the hydrogen desorption in MgH₂ lead to different values for the Avrami coefficient [43,46], that have been associated to various reaction mechanisms. From the results shown in Figure 5, it appears clear that the n values increase for decreasing

temperature. The temperature dependence of the n value might be related to the change in the driving force for the phase transformation, as discussed above. In all cases, n values turn out in the range between 1 and 3. In addition, n values are the highest for commercial MgH_2 , become lower for the ball milled MgH_2 and are the lowest for $\text{MgH}_2/\text{BaRuO}_3$ ball milled mixtures, suggesting an active role of the ball milling process and of the additive in changing the reaction mechanism for hydrogen desorption.

The results of hydrogen desorption measured by DSC for $\text{MgH}_2/\text{BaRuO}_3$ ball milled mixture at different heating rates (5, 10, 20 and 40 K/min) are shown in Figure 6. An apparent endothermic signal is observed in correspondence of the hydrogen desorption, because of the change in thermal conductivity of the gas surrounding the sample [47]. For pure MgH_2 , a single DSC signal is usually obtained for hydrogen desorption [43]. On the contrary, for the ball milled $\text{MgH}_2/\text{BaRuO}_3$ mixture, multiple peaks signal appeared (Figure 6), suggesting the occurrence of hydrogen desorption from different crystallographic sites or phases.

The activation energy for hydrogen desorption has been estimated by Kissinger method according to [48]:

$$d(\ln(\beta/T_p^2))/d(T_p^{-1}) = -E_a/R \quad (6)$$

where β is the heating rate and T_p is the peak temperature in the DSC trace. The obtained E_a values were 140 kJmol^{-1} , 120 kJmol^{-1} and 90 kJmol^{-1} for commercial MgH_2 , ball milled MgH_2 and $\text{MgH}_2/\text{BaRuO}_3$ ball milled mixture, respectively.

The E_a values for hydrogen desorption from powdered MgH_2 with coarse microstructure reported in the literature range from 300 kJmol^{-1} [44] down to 140 kJmol^{-1} [11]. The ball milling itself accelerates the reaction of hydrogen desorption from MgH_2 simply because of a reduced diffusion path, but it generally introduces a significant amount of MgO , forming a diffusion barrier at the surface of the particles. In this case, a value of activation energy around 120 kJmol^{-1} range has been obtained, in good agreement with results previously

reported in the literature [42]. The presence of the additive promotes the hydrogen insertion inside the oxide layer, further reducing the E_a values. In fact, values around 60-70 kJmol⁻¹ have been reported when Nb₂O₅ is added during ball milling [22,23]. In particular, during the hydrogen sorption cycling of the MgH₂/ Nb₂O₅ mixture, a ternary Mg₃Nb₆O₁₁ compound is formed at the surface [25], which has been shown to be able to absorb H₂ reversibly in the bulk [37].

After BaRuO₃ addition, the E_a value for hydrogen desorption from MgH₂ becomes significantly lower with respect to that obtained for the commercial powder. In both cases, the E_a values obtained from isothermal desorption measurements turn out higher than those obtained from scanning measurements, likely because of the different experimental conditions (i.e. H₂ pressure, driving force), which might affect the reaction mechanism. On the other hand, the peculiar properties of BaRuO₃ as “oxide bronze” seems to be related to its role in promoting hydrogen desorption. In fact, the mixing of BaRuO₃ with MgO at the surface of the particles during ball milling, might produce preferential paths for hydrogen, which turn out in a decreasing of the apparent activation energy. So, it can be concluded that the BaRuO₃ addition during ball-milling of MgH₂ promotes the formation of an active system with respect to H₂ release, as already demonstrated for other oxide systems.

Conclusions

In this paper it has been demonstrated that the BaRuO₃ absorbs hydrogen at RT and 6.4 MPa H₂ pressure, leading to rhombohedral distorted phase, with a c-axis elongated with respect to the parent structure. During TPD, the hydrogenated oxide phase releases mainly hydrogen, coupled with a small amount of water, suggesting the occurrence of an oxide-bronze behaviour. The rate of the H₂ desorption in MgH₂ is accelerated by ball milling with addition of BaRuO₃. In particular, the ball milled MgH₂/BaRuO₃ mixture showed a value of the

apparent activation energy for hydrogen desorption significantly lower with respect to that obtained for commercial MgH₂, likely due to a change in the reaction mechanism. The peculiar properties of BaRuO₃ as a promoter for hydrogen desorption from MgH₂ have been correlated with its aptitude to absorb hydrogen in the bulk structure.

References

- [1] B. Sakintuna, B. Weinberger, F. Lamari-Darkrim, M. Hirscher, B. Dogan, *Int. J. Hydrogen Energy* 32 (2007) 1121.
- [2] L. Zaluski, A. Zaluska, J. O. Ström-Olsen, *J. Alloys Compd.* 253 (1997) 70.
- [3] H. Imamura, K. Masanari, M. Kusuhara, H. Katsumoto, T. Sumi, Y. Sakata, *J. Alloys Compd.* 386 (2005) 211.
- [4] M. Zhu, H. Wang, L. Z. Ouyang, M. Q. Zeng, *Int. J. Hydrogen Energy* 31 (2006) 251.
- [5] A. Zaluska, L. Zaluski, J. O. Ström-Olsen, *Appl Phys A.* 72 (2001) 157.
- [6] R. Wiswall, in: G. Alefeld and J. Völkl, Editors, *Topics in Applied Physics, Vol.29, Hydrogen in Metals 2*, Springer, Berlin/Heidelberg (1978), p. 209.
- [7] Y. Fukai, *The metal–hydrogen, system. Basic bulk properties*, Springer Series in Material Science Vol. 21, Springer-Verlag, Berlin (1993).
- [8] L. Schlapbach, A. Züttel, *Nature*, 414 (2001) 353.
- [9] K. F. Aguey-Zinsou, J. R. A. Fernandez, T. Klassen, R. Bormann, *Int. J. Hydrogen Energy* 32 (2007) 2400.
- [10] J. Huot, M. L. Tremblay, R. Schulz, *J Alloys Compd.* 356 (2003) 603.
- [11] D. Fatay, A. Revesz, T. Spassov, *J. Alloys Compd.* 399 (2005) 237.
- [12] J. L. Bobet, E. Akiba, Y. Nakamura, B. Darriet, *Int. J. Hydrogen Energy* 25 (2000) 987.
- [13] C. X. Shang, M. Bououdina, Z. X. Guo, *J. Alloys Compd.* 349 (2003) 217.

- [14] J. Huot, J. F. Pelletier, L. B. Lurio, M. Sutton, R. Schulz, *J. Alloys Compd.* 348 (2003) 319.
- [15] M. Q. Fan, L. X. Sun, Y. Zhang, F. Xu, J. Zhang, H. L. Chu. *Int. J. Hydrogen Energy* 33 (2008) 74.
- [16] A. Patah, A. Takasaki, J. S. Szmyd, *Int. J. Hydrogen Energy* 34 (2009) 3032.
- [17] F. Dolci, M. Baricco, P. P. Edwards, E. Giamello, *Int. J. Hydrogen Energ.* 33 (2008) 3085.
- [18] C. Zhi, T. Chao, P. Hui, Y. Huabin, *Int. J. Hydrogen Energy* 35 (2010) 8289.
- [19] W. Oelerich, T. Klassen, R. Bormann, *J. Alloys Compd.* 315 (2001) 237.
- [20] K. S. Jung, E. Y. Lee, K. S. Lee, *J. Alloys Compd.* 421 (2006) 179.
- [21] G. Barkhordarian, T. Klassen, R. Bormann, *Scripta Mater.* 49 (2003) 213.
- [22] G. Barkhordarian, T. Klassen, R. Bormann, *J. Alloys Compd.* 364 (2004) 242.
- [23] N. Hanada, T. Ichikawa, S. Hino, H. Fujii, *J. Alloys Compd.* 420 (2006) 46.
- [24] G. Barkhordarian, T. Klassen, R. Bormann, *J. Phys. Chem. B* 110 (2006) 11020.
- [25] O. Friedrichs, J. C. Sanchez-Lopez, C. Lopez-Cartes, T. Klassen, R. Bormann, A. Fernandez, *J. Phys. Chem.* 110 (2006) 7845.
- [26] M. W. Rahman, A. Castellero, S. Enzo, S. Livraghi, E. Giamello, M. Baricco *J. Alloys Compd.* 509S (2011) S438.
- [27] K. Schlberg, S. T. Pantelides, S. J. Pennycook, *J. Am. Chem. Soc.* 123 (2001) 6609.
- [28] S. Nieto, R. Polanco, R. Roque-Malherbe, *J. Phys. Chem. C* 111 (2007) 2809.
- [29] Q. Wan, C. L. Lin, X. B. Yu, T. H. Wang, *Appl. Phys. Lett.* 84 (2004) 124.
- [30] S. H. Lim, J. Luo, Z. Zhong, W. Ji, J. Lin, *Inorg. Chem.* 44 (2005) 4124.
- [31] F. Dolci, M. Di Chio, M. Baricco, E. Giamello, *J. Mater. Sci.* 42 (2007) 7180.
- [32] F. Dolci, M. Di Chio, M. Baricco, E. Giamello, *Mater. Res. Bull.* 44 (2009) 194.
- [33] C. Chabanier, D. Guay *J. Electroanal. Chem.* 570 (2004) 13.

- [34] M. Shelef, R. A. D. Betta, K. Otto, J. Inorg. Nucl. Chem. 38 (1976) 99.
- [35] P. C. Donohue, L. Katz, R. Ward, Inorg Chem. 4 (1965) 306.
- [36] L. Lutterotti, S. Matthies, H-R. Wenk, A. J. Schulz, J. Richardon, J. Appl. Phys. 81 (1997) 594. MAUD is available at <http://www.ing.unitn.it/~maud>.
- [37] M. W. Rahman, S. Livraghi, F. Dolci, M. Baricco, E. Giamello, Int. J. Hydrogen Energy 36 (2011) 7932.
- [38] A. Santoro, I. N. Sora, Q. Huang, J. Solid State Chem. 151 (2000) 245.
- [39] B. Reichman, A. J. Bard. J. Electrochem Soc. 127 (1980) 241.
- [40] M. A. B. Gomes, L. O. D. Bulhoes, S. C. De Castro, A. J. Damiao, J. Electrochem. Soc. 137 (1990) 3067.
- [41] M. Avrami, J. Chem. Phys. 7 (1939) 1103.
- [42] J. Huot, G. Liang, S. Boily, A. Van Neste, R. Schulz, J. Alloys Compd. 293–295 (1999) 495.
- [43] J. F. Fernandez, C. R. Sanchez, J. Alloys Compd. 356-357 (2003) 348.
- [44] J. F. Fernandez, C. R. Sanchez, J. Alloys Compd. 340 (2002) 189.
- [45] L. Pasquini, E. Callini, E. Piscopiello, A. Montone, M. Vittori Antisari, E. Bonetti, Appl. Phys. Lett. 94 (2009) 041918.
- [46] T. R. Jensen, A. Andreasen, T. Vegge, J. W. Andreasen, K. Stahl, A. S. Pedersen, M. M. Nielsen, A. M. Molenbroek, F. Besenbacher, Int. J. Hydrogen Energy 31 (2006) 2052.
- [47] M. Di Chio, S. Livraghi, M. Baricco J. Alloys Compd. 426 (2006) 180.
- [48] H. E. Kissinger, Anal. Chem. 29 (1957) 1702.

Figure captions

Figure 1. The XRD pattern of: BaRuO₃ powders as prepared from solid state synthesis of BaO+Ru (pattern a); BaRuO₃ powders after reactive milling under 0.5 MPa of hydrogen (pattern b); BaRuO₃ powders subjected to a hydrogenation at 6.5 MPa (pattern c) and BaRuO₃ powders obtained after TPD of hydrogenated sample (pattern d). Experimental data points are dots, full lines are the result of the Rietveld fit to the data. The hkl sequence of peaks for rhombohedral BaRuO₃ has been reported at the bottom of the figure.

Figure 2. TPD-MS profiles as a function of temperature for BaRuO₃ powders as-prepared (dashed lines) and after hydrogen loading at 6.5 MPa (continuous lines). H₂ and H₂O desorption are reported in top and bottom figure, respectively. Note the different scale values of the graphs.

Figure 3. XRD patterns of the mixtures of 1 mol% of BaRuO₃ and commercial MgH₂ powders as mixed (bottom curve) and subjected to a ball milling treatment of 12 h (top pattern). Experimental data points are dots, full lines are the result of the Rietveld fit to the data. The as-mixed mixture displays weak presence of hexagonal magnesium phase. In the ball milled specimen it was assessed the weak presence of periclase MgO and of a γ -MgH₂ orthorhombic phase.

Figure 4. Hydrogen desorption measured with a Sievert-type equipment as a function of time at hydrogen pressure of 0.1 MPa . Top, figure a: comparison among desorption at 593 K from as-received MgH₂ (squares), ball milled MgH₂ (circles) and MgH₂/BaRuO₃ ball milled mixture (triangles). Dashed lines are a guide for the eyes. Bottom, figure b: desorption from MgH₂/BaRuO₃ ball milled mixture at various temperatures, as indicated in the figure. Points: experimental data. Lines: fitting curves on the basis of eq. (5).

Figure 5. Rate constant, k (full points), and Avrami coefficient, n (open points), as a function of the inverse temperature for commercial MgH_2 (squares), ball milled MgH_2 (circles) and $\text{MgH}_2/\text{BaRuO}_3$ ball milled mixture (triangles).

Figure 6. DSC traces as a function of temperature for hydrogen desorption from $\text{MgH}_2/\text{BaRuO}_3$ ball milled mixture at various heating rates, as reported in the graphs.

Figure 7. Kissinger plot for commercial MgH_2 (squares), ball milled MgH_2 (circles) and $\text{MgH}_2/\text{BaRuO}_3$ ball milled mixture (triangles) based on the results of DSC measurements.

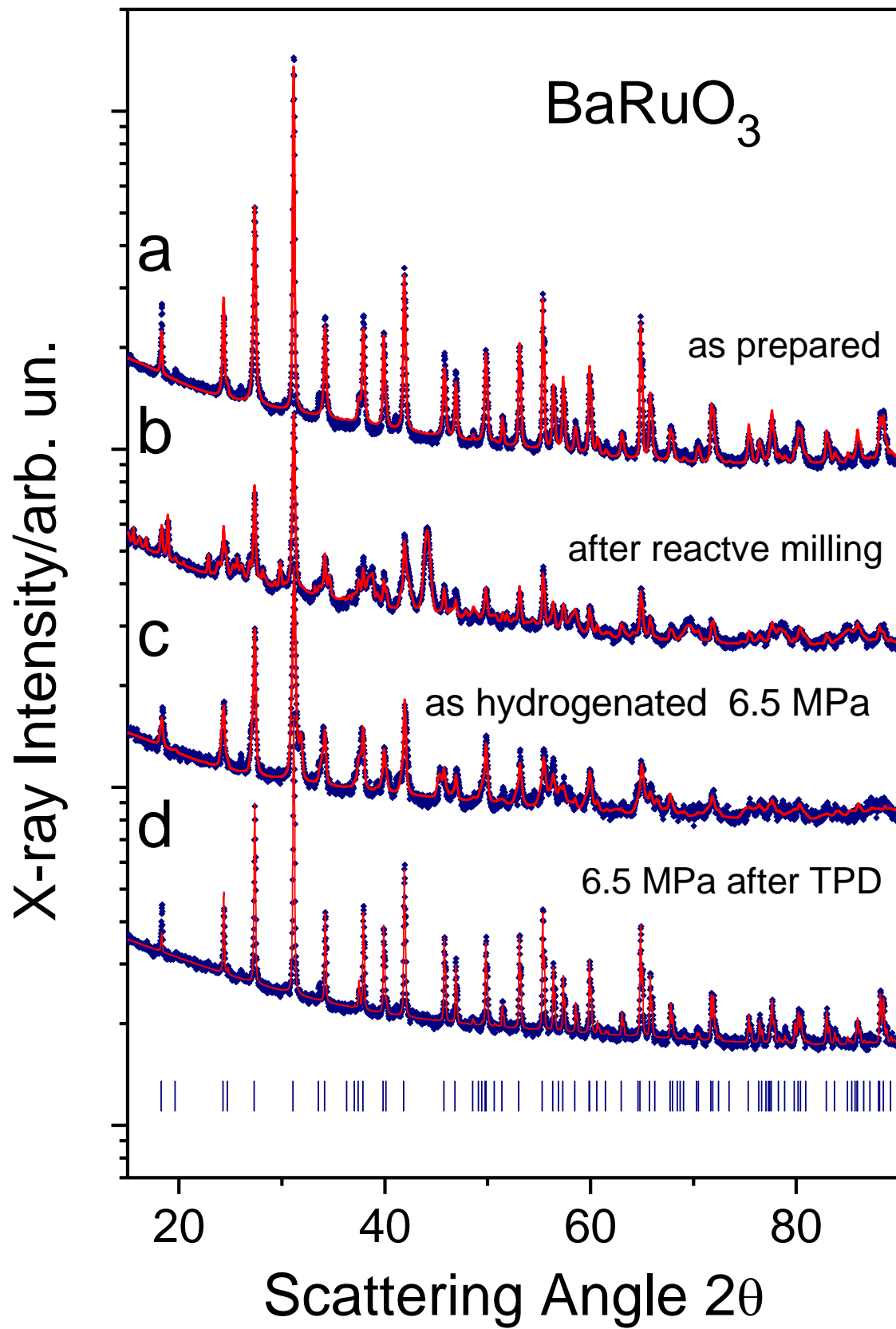
Interaction of BaRuO₃ with hydrogen studied.

BaRuO₃ is able to release hydrogen after absorption.

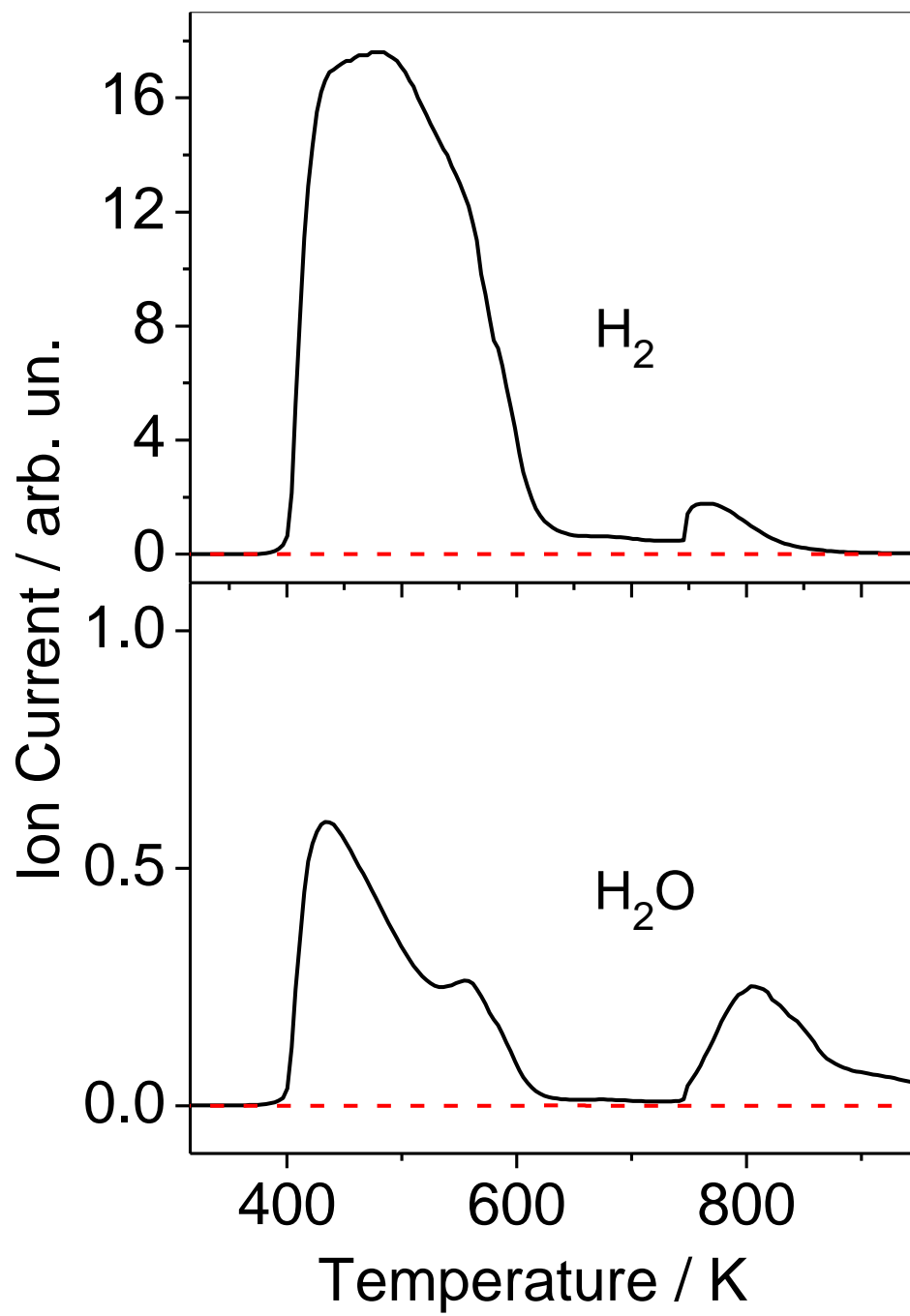
A distorted rhombohedral phase is formed in BaRuO₃ after hydrogen absorption.

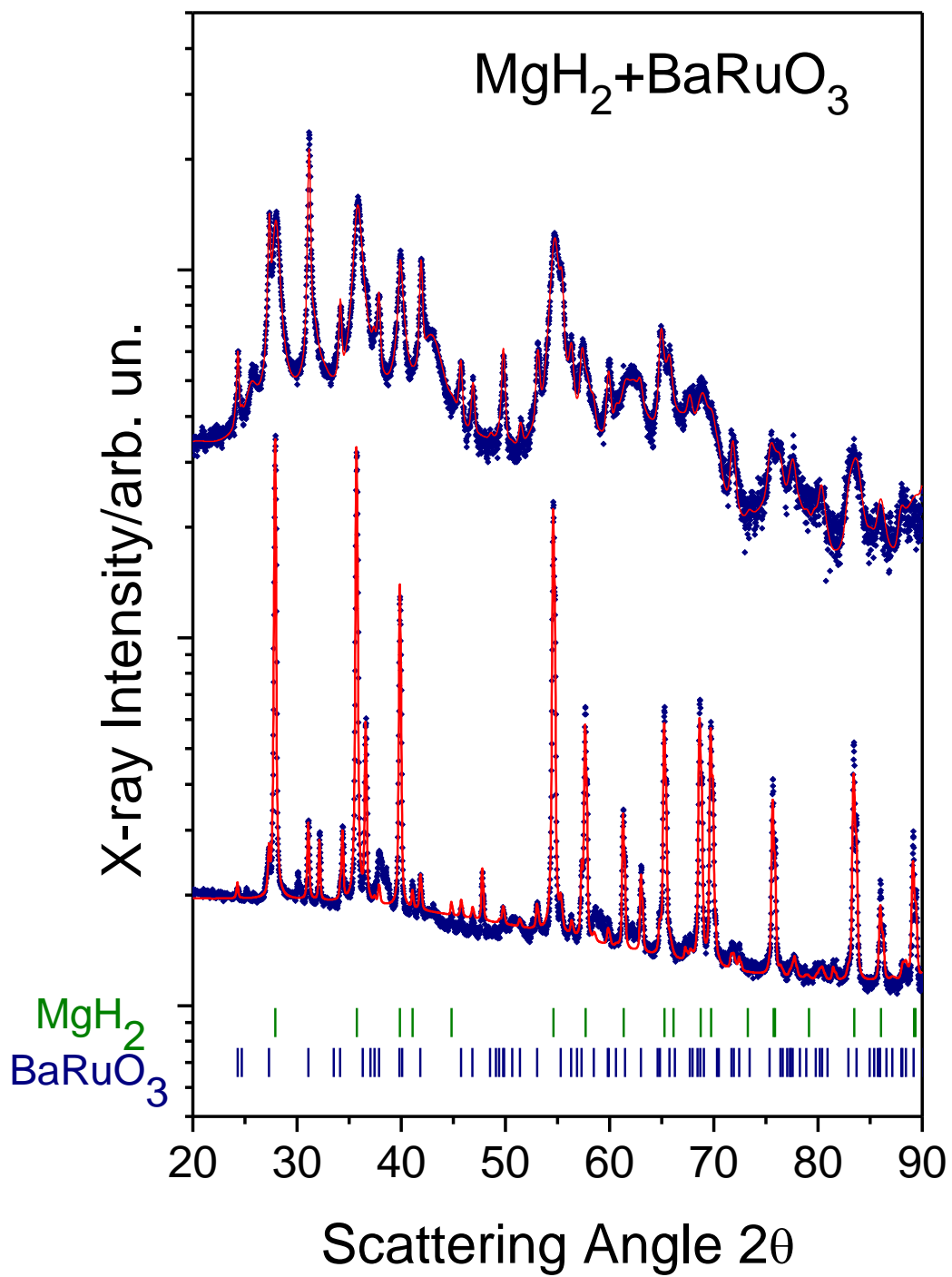
A mixture of BaRuO₃ with MgH₂ is able to desorb hydrogen much faster than the parent materials.

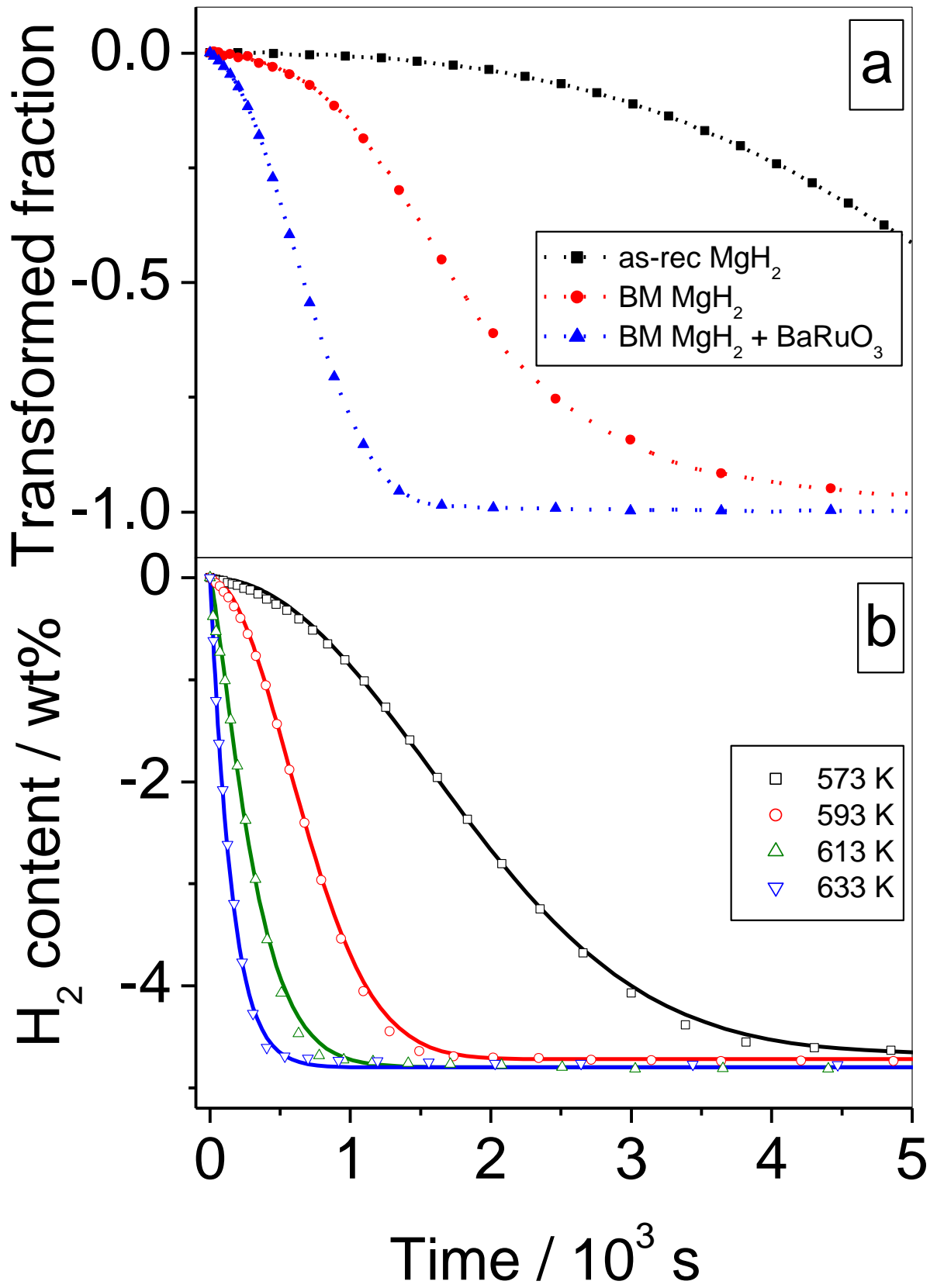
The interaction of hydrogen with the oxide additive is a crucial aspect for improving the hydrogen desorption rate.



Baricco et al. Figure 2







Baricco et al. Figure 5

