IMPROVEMENT IN THE STRUCTURE IDENTIFICATION OF THE PHASES IN THE INTERACTION LAYERS U-Mo/Al-Si EMPLOYING X-RAY DIFFRACTION WITH SYNCHROTRON RADIATION.

M. Mirandou[a], S. Aricó[a], S. Balart[a], L. Gribaudo[a,b] and A.M. Fortis[a]

[a]Departamento Materiales, GIDAT, GAEN, CNEA
Avda. Gral. Paz 1499, B1650KNA, San Martín, Argentina

[b]CONICET, Avda. Rivadavia 1917, C1033AAJ, Buenos Aires, Argentina.

ABSTRACT

During the last three years, out of pile interdiffusion experiments between U-Mo/Al-Si were carried out at 550ºC and 340ºC, in our laboratory. The characterization of the interdiffusion zones using optical microscopy, WDS, EDS and conventional X-ray diffraction showed benefical changes in these interaction layers compared to the one with pure Al. However a complete identification of the phases could not be attained. In this sense high intensity XRD with synchrotron radiation was considered the appropriated technique to improve the previous results.
In this work, results obtained from the experiences performed at the LNLS Synchrotron Light Source, Brasil are presented. They indicated that Si_5U_3 is the main component for UMo/Al-Si at 340 ºC. This same phase was also found, together with $U(Al,Si)_3$ and $Al_{20}Mo_2U$, in a sample treated at 550 ºC. This result, together with composition measurements, indicates that Si_5U_3 is the Si rich phase located near U-Mo which could not be identified up to now.

1. Introduction

Post-irradiation examinations of U-Mo dispersed fuel elements have shown considerable pillowing and porosity. This failure has been associated to a poor irradiation behavior of the interaction layer (IL), that is formed due to interdiffusion, between the U-Mo particles and the Al matrix, [1-4]. Important research was undertaken in several laboratories to solve this problem, pointing to change the composition of the IL.
Out of pile diffusion experiments U-Mo/Al [5, 6, 7] between 500 ºC - 600 ºC shown a three-layered morphology for the IL. Concentrations profiles indicated the presence of compounds UAl_3, $UAl_{4.4}$ and a Mo enriched layer close to the Al. In [6] XRD also identified two ternaries compounds $Al_{20}Mo_2U$ (if U-Mo remains in gamma phase) and $Al_{43}Mo_4U_6$ (if decomposition occurs). In [7] concentration measurements corresponding to the layer close to Al agree quite well with $Al_{20}Mo_2U$. They consider according to [8] that Mo is not dissolve in UAl_4. Experiments with μ-XRD [9] indicated that the other two layers may be a fine dispersion of the binary and ternary phases.
To change the composition of the IL, the addition of Si to Al was proposed [2] following previous results for U/Al [10, 11, 12]. In this sense, it has been reported that the addition of Si to Al in the U/Al system resulted in the suppression of UAl_4, the migration of Si towards the IL and the reduction of the IL growth rates. All, or part, of these features have been verified in the U-Mo/Al-Si system by different authors [13, 14, 15, 16]. All of them measured the migration of Si to the IL by EPMA. In [13] XRD allowed to identify $U(Al\text{-}Si)_3$ with ~25 at% Si, the existence of another phase richer in Si and close to the U-Mo side was proposed [13, 16]. The complete identification of the

phases that form the IL in U-Mo/Al-Si diffusion couples has not been attained yet. XRD studies [13, 9] have shown to be a fundamental tool for this purpose.
XRD experiments with synchrotron radiation performed at LNLS, Campinas, Brasil, allowed us to improve and go further in our results of the last three years of investigation. In this work a summary of our previous results is presented in section **2** and results obtained at LNLS in section **4.** Finally, both of them are discussed altogether to conclude.

2. Review of our previous results

2.1 U-7wt%Mo/Al A356 (7.1 wt%Si) at 550 ºC

In RERTR 2004 [13], first results were informed concerning the effect of Si added to Al. For a diffusion couple consisting of U-7%Mo/Al A 356 (U-7Mo/Al-7Si) heat treated (2+2) h at 550 ºC, main results were:

- The existence of a free precipitate zone (FPZ) formed, in the Al alloy in a zone contiguous to the IL, due to the dissolution of Si precipitates.
- XRD performed with laboratory equipment showed the presence of the cubic structures $(U,Mo)(Al,Si)_3$,with lattice parameter a = 4.205 Å, and $Al_{20}Mo_2U$. No UAl_4 was identified. Figure 1.
- The IL have two zones: the thinner one, close to U-Mo, was in fact a two-phased region with a very fine microstructure revealed at high magnification, Figure 2. This zone contains a high concentration of Si (~40 at% in average). The other zone, near Al alloy, is wider and contains ~22 at% of Si. Figure 3a and b
- Comparing information obtained by XRD and composition measurements, $(U,Mo)(Al,Si)_3$ was proposed to be located in the zone close to the Al alloy. Concerning the biphasic zone, close to U-Mo, composition analysis suggested $(U,Mo)(Al,Si)_{2-x}$ as one of them, but better X-ray diffraction were recomended to confirm it. Figure 3b.

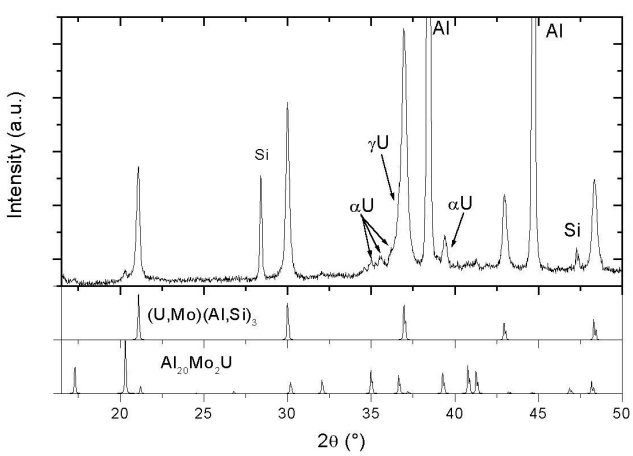

Fig. 1. U-7Mo/Al-7Si
(2 + 2) hs - 550°C – XRD. (Figure 5 in [13]).

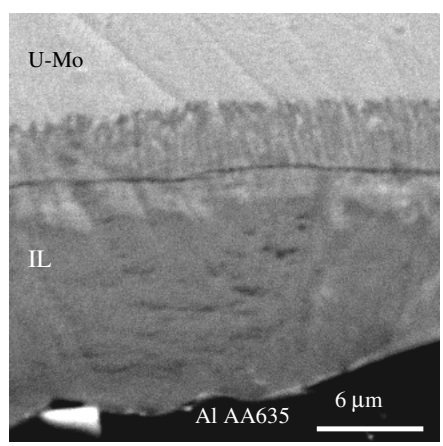

Fig. 2. U-7Mo/Al-7Si
(2 + 2) hs - 550°C – SEM. (Figure 4 in [13]).

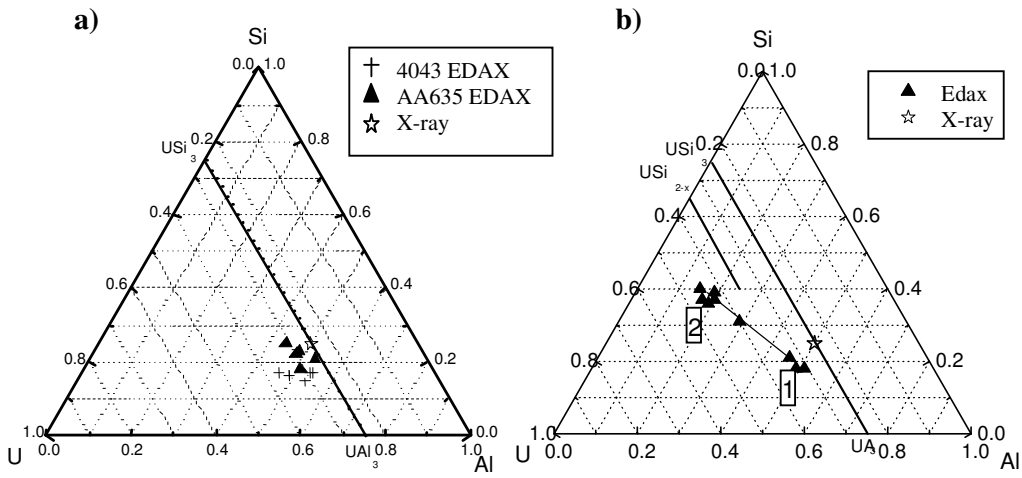

Fig. 3. U-7Mo/Al-7Si - (2 + 2) hs - 550°C – Composition measurements by EDS
a) zone close to Al A356, b) two-phased zone close to U-Mo. (Figure 7a and b in [13]).

2.2 U-7wt%Mo/Al A356 (7.1 wt%Si) at 340 ºC

In RERTR 2005 [14], results obtained from a diffusion couple U-7Mo/Al-7Si heat treated during 23 days at 340ºC were presented. They can be summarized as follows:

- An IL with its corresponding FPZ was observed by OM.
- Back scattered electron images indicated no difference in composition inside the IL. Figure 4.
- Concentration of Si of 58 at% was measured in the IL. Almost no dispersion was found in the set of measurements.
- Structure corresponding to $U(Al,Si)_3$ was suggested from XRD spectra. Figure 5.

As peaks in the XRD spectra corresponding to $U(Al, Si)_3$ were small and wide, it was considered necessary to perform longer thermal treatments to enlarge the IL.

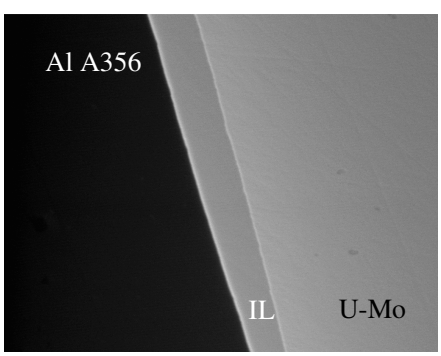

Fig. 4. U-7Mo/Al-7Si
23 days - 340°C – SEM BSE. (Figure 2 b in [14])

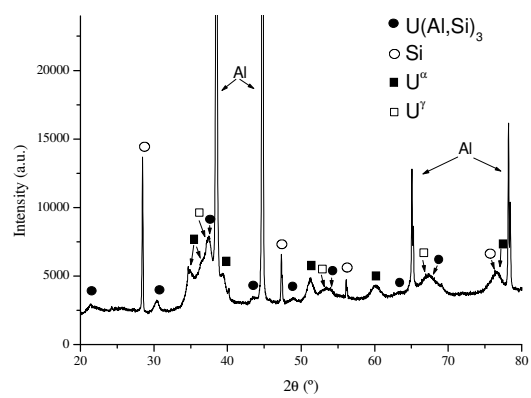

Fig. 5. U-7Mo/Al-7Si
23 days - 340°C – XRD. (Figure 3 in [14]).

2.3 U-7wt%Mo/Al 6061 (0.6 wt%Si) at 340 ºC

In RERTR 2005 [14], only preliminary results obtained for the IL in U-7Mo/Al-0.6Si heat treated during 52 days at 340 ºC were presented. They were:

- A very narrow IL (~ 1 to 2 µm) together with the FPZ was observed.
- No XRD was possible.
- A maximum of 50 at% of Si was measured in the IL. Back scattered electron image indicated no differences in composition inside the IL. Figure 6.

In RRFM 06 [17] results for another sample with a longer thermal treatment (65 + 69) days were presented.

- The IL reached 3 µm at most.
- XRD was intended but no reliable results were obtained.
- Concentration of Si reached 47 at%.

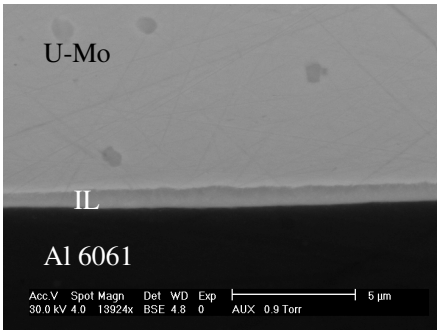

Fig. 6. U-7Mo/Al-0.6Si - 52 days - 340°C – SEM BSE. (Figure 2d in [14]).

3. Experimental

Same starting materials than in previous works [13, 14, 17] were employed in this study. They were: an U–7wt%Mo alloy, Al 6061 (0.6Si, 1Mg, 0.28Cu and 0.2Cr) and Al A356 (7.1Si, 0.37Mg, 0.12Ti, 0.10Fe, 0.02Zn, 0.01Ca and 0.001Sr). The U-Mo alloy was made with depleted U (0.2% U^{235}) in a small non-consumable tungsten electrode arc-furnace with a copper crucible under highly pure argon atmosphere. Specimens of the alloy were homogenized in composition by a heat treatment of 2 h at 1000 °C using quartz tubes under argon atmosphere. Tubes were quenched in cold water to retain, in metastable condition, γU phase.

Diffusion couples were made by the use of Friction Stir Welding (FSW) technique [18], which allows encasing the U-Mo alloy in between the Al alloy.

Characterization of the reaction layers was performed by Optical Microscopy (OM), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), Wavelength Dispersive Spectroscopy (WDS) against standards and X–ray Diffraction (XRD) with synchrotron radiation at LNLS, Campinas, Brasil. Difractometer conditions were carefully set to minimize the background, to irradiate small selected areas and to optimize spectral resolution. Phase identification and the estimation of the lattice parameters were done by the use of PowderCell program [19].

Table 1 contains the details of the diffusion anneals.

Sample	Al alloy	Thermal Treatment	
		time	Temp. (ºC)
I	A 356 (7.1Si)	(1.5 + 1.5) h	550
II	A 356 (7.1Si)	(23 + 87) days	340
III*	Al 6061 (0.6Si)	(65 + 69) days	340

Table 1. Diffusion anneals details and Al alloy of the samples.
* Sample reported in [17]

4. Results

4.1. U-7wt%Mo/Al A356 (7.1 wt%Si) at 550 ºC

The IL showed the same morphological characteristics previously described in section 2.1. An ~12 µm wide IL was observed together with its corresponding FPZ (~ 61 µm). The IL was again formed by two zones being one of them a two-phased zone situated close to the U-Mo and the other situated close to the Al A356. In the same way, composition measurements showed a distribution similar to the one plotted in the ternary representation U-Al-Si in figure 3.
XRD with synchrotron radiation allowed identifying in the IL the phases $U(Al,Si)_3$ with lattice parameter *a* ~4.19 Å, $Al_{20}Mo_2U$ and Si_5U_3, Figure 7. This last phase is hexagonal, hP3 and AlB_2 type [20]. According to Dwight [21], the crystalline structure is a defect type and a ternary element (e.g. Al) could either enter an empty lattice site or displace Si atom. Original lattice parameters are *a* = 3.896 Å and *c* = 4.017 Å. Small increase from these values were found in this work.

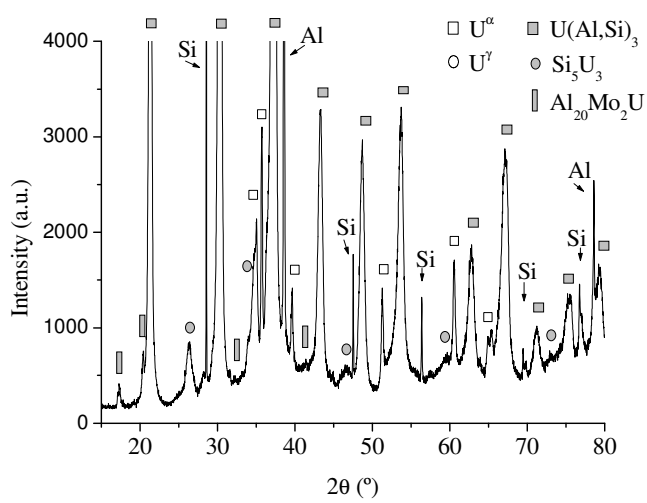

Fig. 7. U-7Mo/Al-7Si - (1.5 + 1.5) h - 550°C – XRD with synchrotron radiation.

4.2. U-7wt%Mo/Al A356 (7.1 wt%Si) at 340 ºC

Sample II, Table 1, developed a 13 µm wide IL and a 100 µm wide FPZ.
After the enlargement of the thermal treatment, (23+87) days, compositions measurements showed dispersion larger than for sample in 2.2 (23 days) suggesting the presence of more than one phase in the IL.
Crystalline structures of the phases conforming the IL were: $U(Al,Si)_3$ and Si_5U_3. Similar increase than at 550 ºC was found in the lattice parameters. An XRD spectrum is shown in Figure 8.

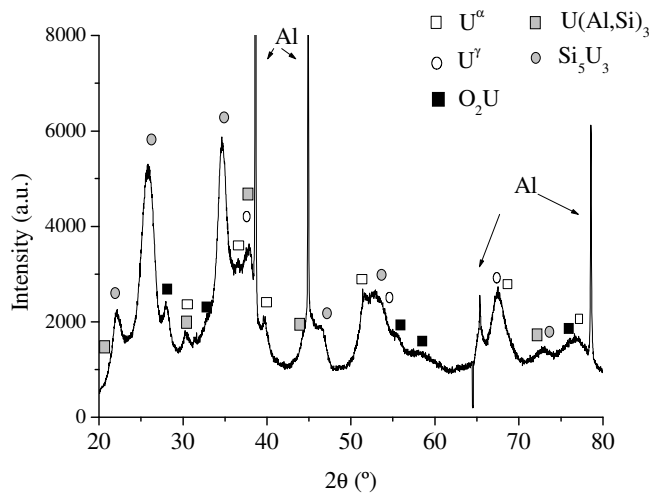

Fig. 8. U-7Mo/Al-7Si - (23 + 87) days – 340 °C – XRD with synchrotron radiation.

4.3. U-7wt%Mo/Al 6061 (0.6 wt%Si) at 340 ºC

XRD with synchrotron radiation allowed identifying crystalline structure of Si_5U_3. The presence of a large amount of αU and γU in the spectra together with the uranium dioxide made very difficult the estimation of the lattice parameters. For the same reason, the presence of $U(Al,Si)_3$ is not so evident. Concerning this, further analysis is required. An XRD spectrum is shown in Figure 9.

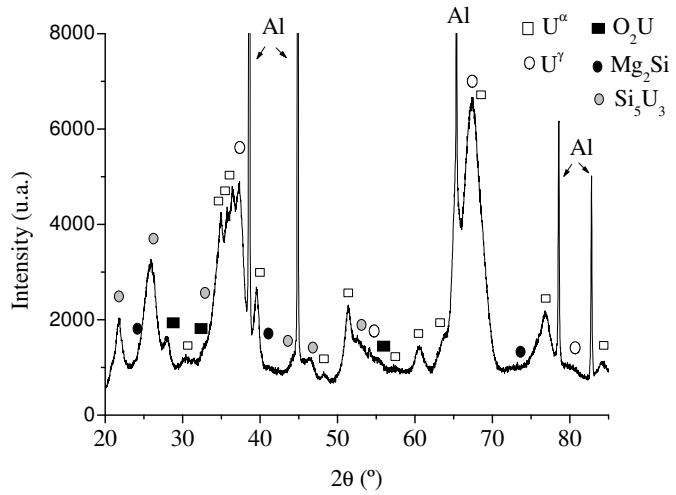

Fig. 9. U-7Mo/Al-0.6Si - (65 + 69) days - 340°C – XRD with synchrotron radiation.

5. Discussion

The study of the changes in the phases that form the IL between U-Mo/Al, introduced by the addition of Si to Al has been being studied for a couple of years and in different laboratories. However, though intended, a complete identification of the phases could not be attained. In this sense high intensity XRD with synchrotron radiation was considered an appropriated technique to improve the previous results in particular when phases in small amount are trying to be identified.

At 550 ºC, in the diffusion couple U-7Mo/Al-7Si, the hexagonal phase Si_5U_3 was identified together with the already reported cubic phases $U(Al,Si)_3$ and $Al_{20}Mo_2U$. The small increase, respect to the original lattice parameters in Si_5U_3, informed in section 4.1, could be associated to the presence of Al in solid solution. Although this phenomenon was mentioned by Dwight [21], no correlation between the Al concentration and the lattice parameters modification was studied by the author. In this sense, further investigation is needed.

According to the previous results summarized in 2.1 and the new ones presented in this work, Si_5U_3 is the Si rich phase that forms the biphasic zone close to U-Mo. In [16] the authors also agree with the presence of a Si rich zone near U-Mo. In [15], composition measurements for a diffusion couple U-7wt%Mo/Al-5wt%Si showing Si accumulation in the IL were presented, the authors considered $U(Al,Si)_3$ as the only phase in the IL.

At 340 ºC, the phase Si_5U_3 became evident for U-7Mo/Al-7Si after the second thermal treatment together with $U(Al,Si)_3$. At this point, we can not assure if this phase was present, or not, in the IL after the first thermal treatment. It could be possible that XRD with laboratory equipment was not enough to identify it or its presence is a consequence of evolution in time.

6. Conclusions

- **At 550 ºC** the interaction layer developed due to interdiffusion in a U-7wt%Mo/Al A356 (7.1%Si) couple, is formed by two zones. $U(Al,Si)_3$ phase is located in the zone near Al alloy. In the zone near U-Mo a biphasic morphology was observed and Si_5U_3 was identified as one of those phases. Deviation from the original lattice parameters, found for this phase, could be associated to the presence of Al. $Al_{20}Mo_2U$ was also identified.
- **At 340 ºC** Si_5U_3 and $U(Al,Si)_3$ were found as the phases conforming the interaction layer between U-7wt%Mo/Al A356 (7.1%Si). As for 550 ºC, small deviation in the lattice parameters were found for Si_5U_3. In the diffusion couple U-7wt%Mo/Al 6061 (0.6%Si), only Si_5U_3 was identified.

7. References

[1] A. Leenaers, S. Van den Berghe, E. Koonen, C. Jarousse, F. Huet, M. Trotabas , M. Boyard, S. Guillot, L Sannen, M. Verwerft. J.Nucl. Mater. 335 (2004) 39.

[2] G.L. Hofman, M.R. Finlay and Y.S.Kim. RERTR Int. Meeting, 7-12 November, 2004, Vienna, Austria.

[3] D. F. Sears, K. T. Conlon, J. Manson, A. Davidson, C. Buchnan. Transaction 10th International Topical Meeting ENS RRFM, 30 April-3 May 2006 , Sofia, Bulgaria.

[4] V. Popov, V. Khmelevsky, A. Lukichev, O. Golosov. Transaction 9th International Topical Meeting ENS RRFM 10-13 April 2005, Budapest, Hungary.

[5] H.J. Ryu, Y.S. Han, J.M. Park, S.D. Park, C.K. Kim. J. Nucl. Mater. 321 (2003) 10.

[6] M. Mirandou, S. Balart, M. Ortiz, M. Granovsky. J. Nucl. Mater. 323 (2003) 29.
[7] F.Mazaudier, C.Proye and F. Hodaj. Transaction 10th ENS RRFM, 30 April-3 May 2006, Sofia, Bulgaria.
[8] O. Tougait, H. Noël, Intermetallics 12 (2004) 219-223.
[9] H.Palancher, P.Martin, C.Proye, N.Wieschalla, C. Valot. Experiment Report ESRF ME-1285, 2006.
[10] R.Boucher. J. Nucl. Mater. 1 (1959) 13.
[11] D.R. Green, HW 49697, April 1957.
[12] W.C. DeLuca, H.T. Sumsion. KALP-1747, 1957.
[13] M. Mirandou, M. Granovsky, M. Ortiz, S. Balart, S. Aricó, L. Gribaudo, 2004 RERTR, November 7-12 2004, Vienna, Austria.
[14] M.Mirandou, S.Aricó, L.Gribaudo , S.Balart. 2005 RERTR, 6- 11 November 2005 Boston, Mass., USA.
[15] J.M. Park, H.J. Ryu, S. Oh, D.B. Lee, C.K. Kim, Y.S. Kim, G.L. Hofman. 2006 RERTR, 29 October-2 November, 2006, Cape Town, Republic of South Africa.
[16] M. Cornen, F. Mazaudier, X.Iltis, M.Rodier, S. Dubois, P.Lemoine. 11th International Topical Meeting ENS RRFM-IGORR, 11 -15 March 2007, Lyon, France.
[17] C. Komar Varela, M. Mirandou, S. Aricó, S.Balart and L. Gribaudo. Transaction 10th ENS RRFM, 30 April-3 May 2006, Sofia, Bulgaria.
[18] P. Cabot, A. Moglioni, M. Mirandou, S. Balart. 2004 RERTR, November 7-12, 2004, Vienna, Austria.
[19] Kraus W., Nolze G. and Müller U. (2000). PowderCell 2.3. - Pulverdiffraktogramme aus Einkristalldaten und Anpassung experimenteller Beugungsaufnahmen. http://www.bam.de/de/service/publikationen/powder_cell_a.htm
[20] A. Brown and J. J. Norreys, Nature, 183 (1959) 673.
[21] A. E. Dwight. Report ANL-14, 1982.

8. Acknowledgements

The authors thank the technical staff of Dto Materiales, GIDAT, GAEN, CNEA, for their support; Mariana Rosenbush from UAQ, CAC, for EDS measurements, Alberto Moglioni for the FSW and Roosevelt Droppa Jr from LNLS. This work was partially financed by Project PICT 12- 11186, Agencia de Promoción Cientifica y Tecnológica and Project D12A-XRD1·# 5747/06, LNLS, Campinas, Brasil.