

PROCESSING SIMULATED HIGH-LEVEL LIQUID WASTE BY HEAT TREATMENT WITH ADDITION OF TiN AND AlN OR Al₂O₃

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Abstract

The present study aims to decrease the melting temperature of the oxide phase by the addition of the mixture of TiN and AlN or Al₂O₃ for reduction of the treatment temperature of super high temperature method. The addition of the mixture of TiN and AlN or Al₂O₃ with the atomic ratio of Al to Ti of 1:9 caused the melting of both the alloy phase and oxide phase at 1673K. The measured values of density and hardness for thus obtained oxide phase were same as those for the oxide phase obtained at 1873K without Al. Thus, above mentioned method is achieved at 1673K without degradation of the properties of the oxide phase as an waste.

1. Introduction

Although solidification of high level liquid waste (HLLW) has developed to the stage that commercial vitrification plants generate vitrified high-active waste basic studies in separation and/or transmutation with various processing schemes are prompted. We have been studied on super high temperature method by which HLLW is dry-treated in a simple process[1,2,3,4].

In this method as shown in Fig. 1, HLLW is first calcined at 973 K to vaporize water and nitric acid. And further heating with a small amount of a reducing agent, TiN at 1873 K results in, after separation of volatile species, Cs and Rb by vaporization, elements with higher standard free energy of oxide formation (platinum metals and other transition metals) than the reducing agent are reduced, melt and form the alloy phase which separates from the oxide phase of melted complex oxides of alkaline earth elements, rare earth elements, Zr, actinides and the metal element of the reducing agent.

Vaporization of all Cs from HLLW and melting and separation of both the oxide and alloy phases have been verified by the treatment of simulated calcined HLLW which contains 27 fission product(FP) elements, and corrosion products (CP;Fe, Cr and Ni). Previous studies have elucidated that the alloy phase melts up to 1673K by alloying the refractory platinum metals or Mo with corrosion products (Fe,Cr,Ni)[5], while the oxide phase melts just below 1873K by the formation of complex oxides of fission products and the metal element of the reducing agent, Ti[4].

This high treatment temperature, 1873K, however may cause difficulty in actual treatment of nuclear waste, especially in selection of crucible materials. The present study aims to decrease the melting temperature of the oxide phase by the addition of the

mixture of TiN and AlN or Al₂O₃ for reduction of the treatment temperature of this method.

2. Experimental

The composition of simulated calcined HLLW is shown in Table 1. This composition is calculated based on that of the spent fuel of 45 GWd/t after 5 years of cooling time. The simulated calcined HLLW is synthesized with elements contained beyond amount of 1g/Mg-U in spent fuel and contains Re and Ce instead of Tc and Pr, respectively, contains Fe, Cr and Ni as CP but contains no actinides.

In the previous study, the amount of the reducing agent was determined such that TiN reduce all platinum metal oxides, other transition metal oxides and CP oxides, which would come to the metallic phase. The ratio of the reducing agent to the simulated calcined HLLW was 0.28:1 in weight and the ratio of FP metal elements which may come to the oxide phase to Ti is 4:6 in atomic. In the present study, a small amount of TiN was substituted by AlN. Al₂O₃ was also used instead of AlN since previous study[6] showed that some platinum metal oxides were reduced by thermally without the reducing agent. The composition of the starting mixture is shown in table 2. TiN and the simulated calcined HLLW powder are only mixed in a agate mortar.

High temperature treatment was performed in a Nagano-Keiki carbon heater furnace. A powder sample in a ZrO₂ crucible was heated to 1273 K in 1 hour, maintained at the temperature for 1 hour and then heated to 1873 K or 1673K in 1 hour. After keeping at the temperature for 1 hour then the sample was furnace cooled. The treatment was done in flowing argon.

Phases of the reaction products were identified by X-ray diffraction. The X-ray diffraction was performed with Cu-K α radiation on a Rigaku rad r-A diffractometer equipped with a curved graphite monochromater. The distribution of elements in the reaction products was studied by Electron probe micro analysis (EPMA) using Topkon MINI-SEM 100 and Horiba EMAX-8000 units.

Density was measured by the method of Archimedes using Wardon Pycnometer supplied by Shibata scientific tec. ltd. The Vickers hardness measurement was carried out using MHT- 1 micro Vickers hardness tester supplied by Matsuzawa seiki co. ltd.

3. Results and discussion

Table 2 shows the results of melting of the products. Sample No.1, which was produced in the previous method, at 1873K without Al₂O₃ could not melt and separate up to 1873 K. Sample No.2, where 5mol% TiN was substituted by Al₂O₃ could not melt and separate at 1673K. However, by further substitution on TiN by Al₂O₃, samples Nos. 3 and 4 melted and separated to alloy and oxide phases at 1673 K.

Figure 2 shows the appearance of the products (sample No.3). The central region of the sample, presenting the metallic cluster, is the alloy phase which is surrounded by the dark oxide phase. The image shows that both phases melt at the treatment temperature. Thus, the decrease in treatment temperature by 200 K was succeeded.

Sample No.4 doping two times as much Al_2O_3 as sample No.3 melted and separated at 1673K. Since several small spheres of metal phase existed in the oxide phase the extent of melting and separation of sample No.4 was considered to be not enough. Therefore, the composition of Al_2O_3 in sample No.3(Ti:Al=9:1) was regarded as the best composition. Addition of AlN instead of Al_2O_3 made no difference in results.

The X-ray diffraction pattern for the oxide phase of sample No.3 is shown in Fig. 3. This pattern with the aid of SEM and EPMA results enable to divide the formed phases into the following several types:

- (1) the $(\text{RE})_2\text{Ti}_3\text{O}_9$ phase,
- (2) the hexagonal BaTiO_3 phase, which may contain other alkaline earth elements in the Ba site,
- (3) the tetragonal $\text{Sr}_{0.5}(\text{RE})\text{Ti}_2\text{O}_6$ phase, which may contain other alkaline earth in the Sr site and rare earth elements in the (RE) site.
- (4) the orthorhombic ZrTiO_4 phase, which may contain some rare earth elements,
- (5) the tetragonal $\text{BaTi}_8\text{O}_{16}$ phase,
- (6) the monoclinic $(\text{RE})_2\text{TiO}_7$ phase,
- (7) the cubic ZrO_2 phase.

It is found, thus that almost all alkaline earth and rare earth FPs form the complex oxides of Ti. These results agree with that of previous results without alumina[7] and no Al containing compound was observed. Thus, it is considered that each phase mentioned above melts up to 1673K by doping alumina.

According to phase diagrams[8,9], some compounds in alkaline earth elements-Ti-O systems can melt around 1673K. The doping Al_2O_3 made large influence on the melting temperatures of $\text{RE}_2\text{Ti}_3\text{O}_9$, $\text{Sr}_{0.5}\text{RETi}_2\text{O}_6$, ZrTiO_4 , $\text{RE}_2\text{Ti}_2\text{O}_7$ and ZrO_2 . The existence of ZrO_2 may result from that a compound does not condense congruently. In Nd-Ti-O system[10], mixture of Nd_2O_3 and TiO_2 , the ratio of Nd:Ti of which equals 2:9, can melt up to 1673K. However, in this case the cooled material must contain Nd_2TiO_4 and TiO_2 . The effect of alumina doping to melting temperature of $\text{RE}_2\text{Ti}_3\text{O}_9$ phase is presented elsewhere.

Table 3 shows the values of measured density and hardness. It seen that the density of sample No.3 is nearly the same as that of sample No.1. However, it was proved that the hardness for sample No.3 which nearly equals to that of ceramic waste or Synroc was quite higher than that of sample No.1 which nearly equals to that of glass waste[11]. Surface observation by SEM showed that there were many pores(up to 30 μm) in both samples but did not clarified the difference in the morphology of the both samples. Thus, it is considered that each phase mentioned above may harden by doping Al_2O_3 .

The chemical stability of a sample produced in the previous study has already reported[3]. The reachability of the sample without Al_2O_3 was smaller than that of glass waste form and compatible to that of ceramic wastes. 7 days Soxhlet leach test[12] of the present sample with Al_2O_3 made results that concentration of any elements in the leachate was below the detection limit of Inductively Coupled Plasma Spectroscopy(ICP-ES) method. A long days test and analysis by ICP-Mass Spectrometry are now in progress.

4. Conclusion

The present study aims to decrease the melting temperature of the oxide phase by the addition of the mixture of TiN and AlN or Al_2O_3 for reduction of the treatment temperature of the super high temperature method. The addition of the mixture of TiN and AlN or Al_2O_3 with the atomic ratio of Al to Ti of 1:9 caused the melting of both the alloy phase and oxide phase at 1673K. The measured values of density and hardness for thus obtained oxide phase were same as those for the oxide phase obtained at 1873K without Al. Thus, the super high temperature method was achieved at 1673K without degradation of the property of the waste by doping Al_2O_3 .

References

- [1] M. Horie, Trans. Amer. Nucl. Soc. 62, 111 (1990).
- [2] M. Horie, Proceedings of ENS/ANS-Foratom Conference(ENC'90), vol.IV, pp.2281, 1990.
- [3] M.Horie and C.Miyake, Proceedings of The forth international Conference on Nuclear Fuel Reprocessing and Waste Management(RECOD'94), vol II , Session 9A- 4, 1994.
- [4] M.UNO, Y.Kadotani, C.Miyake and M.Horie, Mat.Res.Soc.Symp.Proc., vol 353, 1339(1995).
- [5] M. UNO, Y. KADOTANI, H. KINOSHITA, C. MIYAKE and M. HORIE, J.Nucl.Sci.Technol., 33(1996)973-980.
- [6] M. UNO, H. KINOSHITA, C. Miyake and M. HORIE J.Nucl.Mater., 274(1997)191-196.
- [7] M. UNO, Y. KADOTANI, C. MIYAKE and M. HORIE J.Nucl.Sci.Technol., 33(1996)879-885.
- [8] R.S.Roth, J.R.Dennis and H.F.McMuride, Phase Diagrams for Ceramists, vol 3 (American Ceramic Society, 1975).
- [9] R.S.Roth, J.R.Dennis and H.F.McMuride, Phase Diagrams for Ceramists, vol 2 (American Ceramic Society, 1969).
- [10] M.A.Clevinger et al., Phase Diagrams for Ceramists, vol 9 (American Ceramic Society, 1991).
- [11] W. Lutze and R.C.Ewing ed, Radioactive Waste Forms for the Future(Elsevier Science Publishing, New York, 1988).
- [12] Materials Characterization Center, 9-30-81.

List of tables and figures

Table 1 Composition of simulated calcined HLLW

Table 2 Composition of the starting mixture and results of the products

Table 3 Density and hardness of the products

Figure 1 The process of the super high temperature method

Figure 2 Appearance of sample No. 3.

Figure 3 X-ray diffraction pattern for the oxide phase for sample No.3

Table 1 Composition of the simulated calcined HLLW

ELEMENT	CONTENT (at%)	OXIDE	CONTENT (mol%)
Mo	9.263	MoO ₂	12.182
Ru	5.373	RuO ₂	7.067
Pd	3.359	PdO	4.418
Re	1.999	ReO ₂	2.629
Te	0.986	TeO ₂	1.297
Rh	1.075	Rh ₂ O ₃	0.707
Cd	0.254	CdO	0.334
Se	0.191	SeO ₂	0.251
Ag	0.167	Ag ₂ O	0.110
Sn	0.189	SnO ₂	0.248
Sb	0.040	Sb ₂ O ₃	0.026
In	0.005	In ₂ O ₃	0.003
Fe	25.827	Fe ₂ O ₃	16.984
Cr	6.751	CrO	8.879
Ni	2.658	NiO	3.496
Cs	4.567	Cs ₂ O	3.003
Rb	1.122	Rb ₂ O	0.738
Ba	3.447	BaO	4.533
Sr	2.391	SrO	3.144
Ce	4.498	CeO ₂	5.916
Nd	7.471	Nd ₂ O ₃	4.913
La	2.334	La ₂ O ₃	1.535
Pr	2.108	Pr ₂ O ₃	1.386
Y	1.399	Y ₂ O ₃	0.920
Sm	1.352	Sm ₂ O ₃	0.889
Eu	0.233	Eu ₂ O ₃	0.153
Gd	0.225	Gd ₂ O ₃	0.148
Tb	0.005	Tb ₂ O ₃	0.003
Dy	0.002	Dy ₂ O ₃	0.001
Zr	10.711	ZrO ₂	14.087

Table 2 Composition of the starting mixture and results of the products

Sample No.	HLLW:Additive*	Additive (Ti:Al)	Treatment temperature(K)	Result**
1	4:6	—	1873	○
2	4:6	9.5:0.5	1673	X
3	4:6	9:1	1673	○
4	4:6	8:2	1673	○

* The ratio of FP metal elements coming to the oxide phase to metal elements of the additives.

**○:Samples melted and separated.

X:Sample did not melt and separated.

Table 3 Density and hardness of the products

Sample No	Density(g/cm ³)	Hardness(GPa)
1	5.10	6.54
3	4.91	8.75

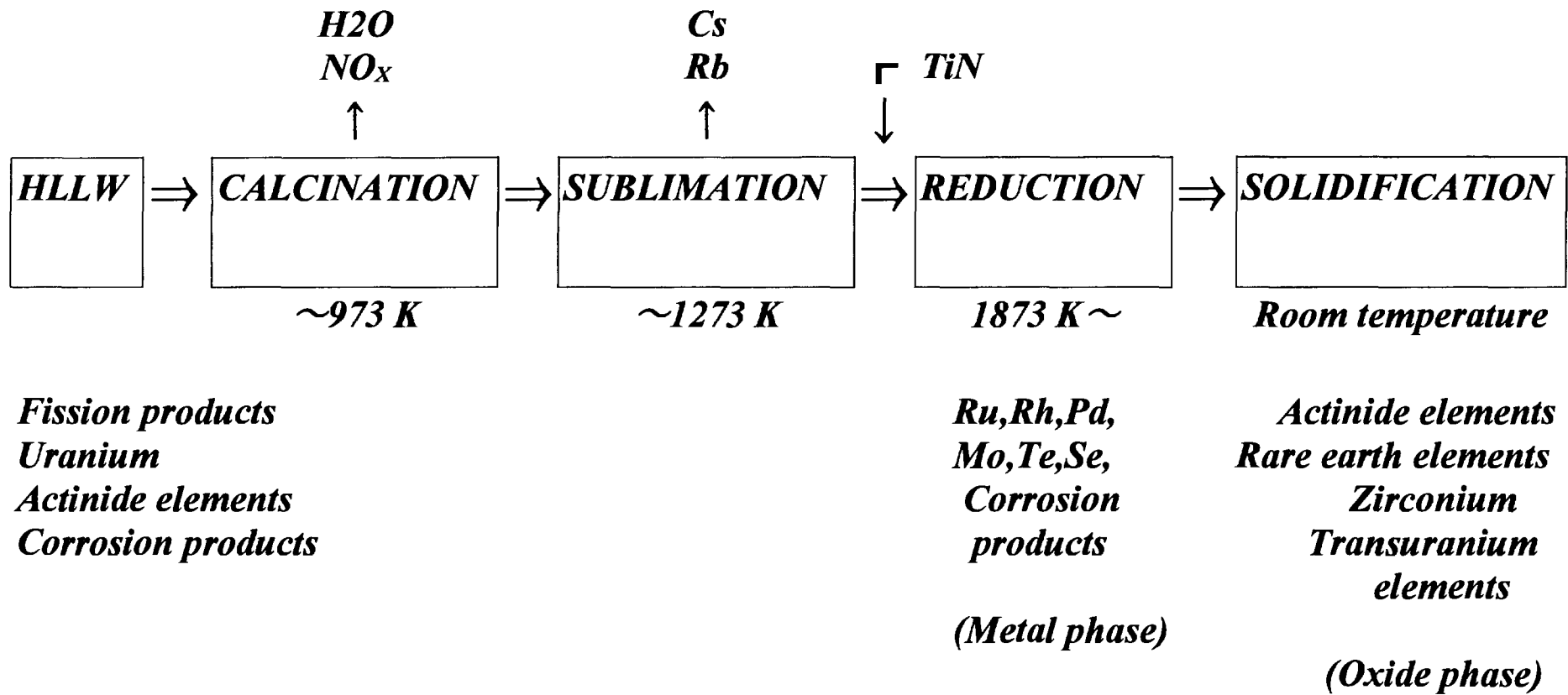


Fig.1 The process of the super high temperature method.

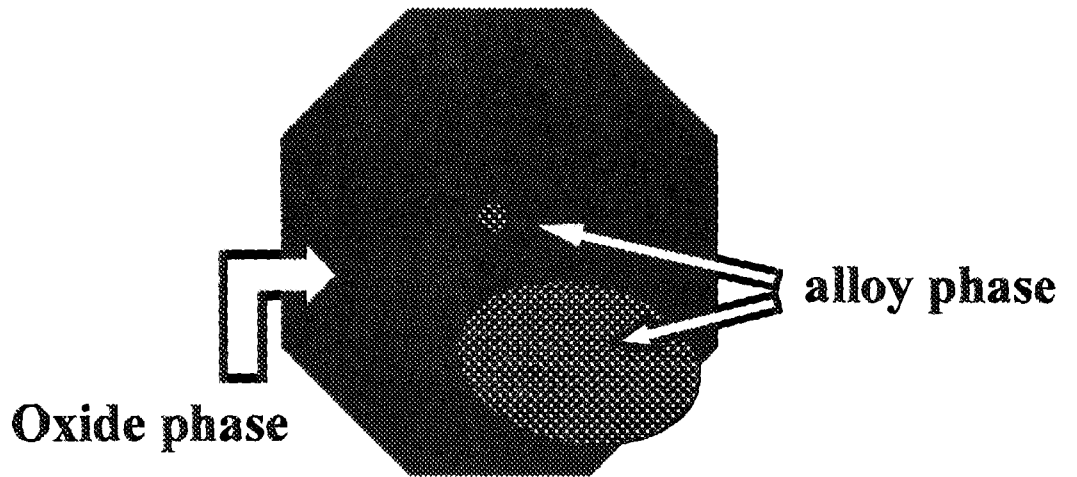
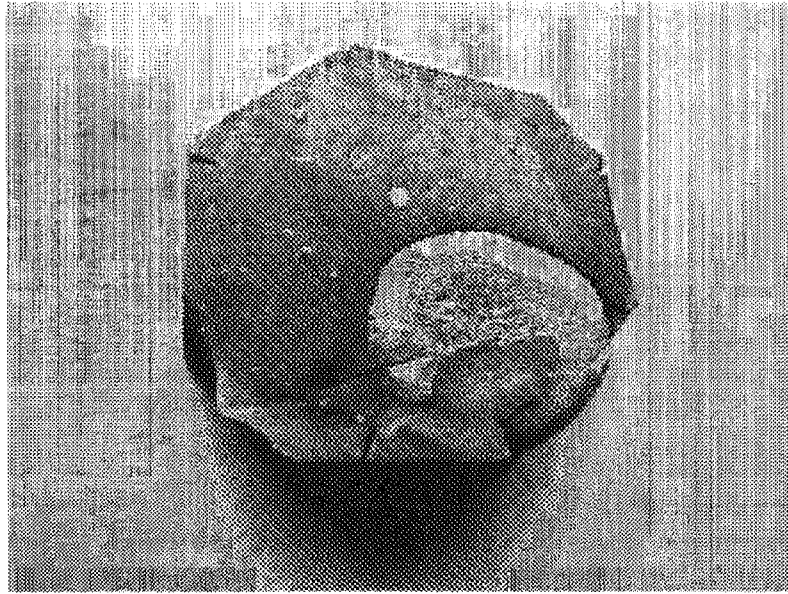


Fig.2 Appearance of sample No.3

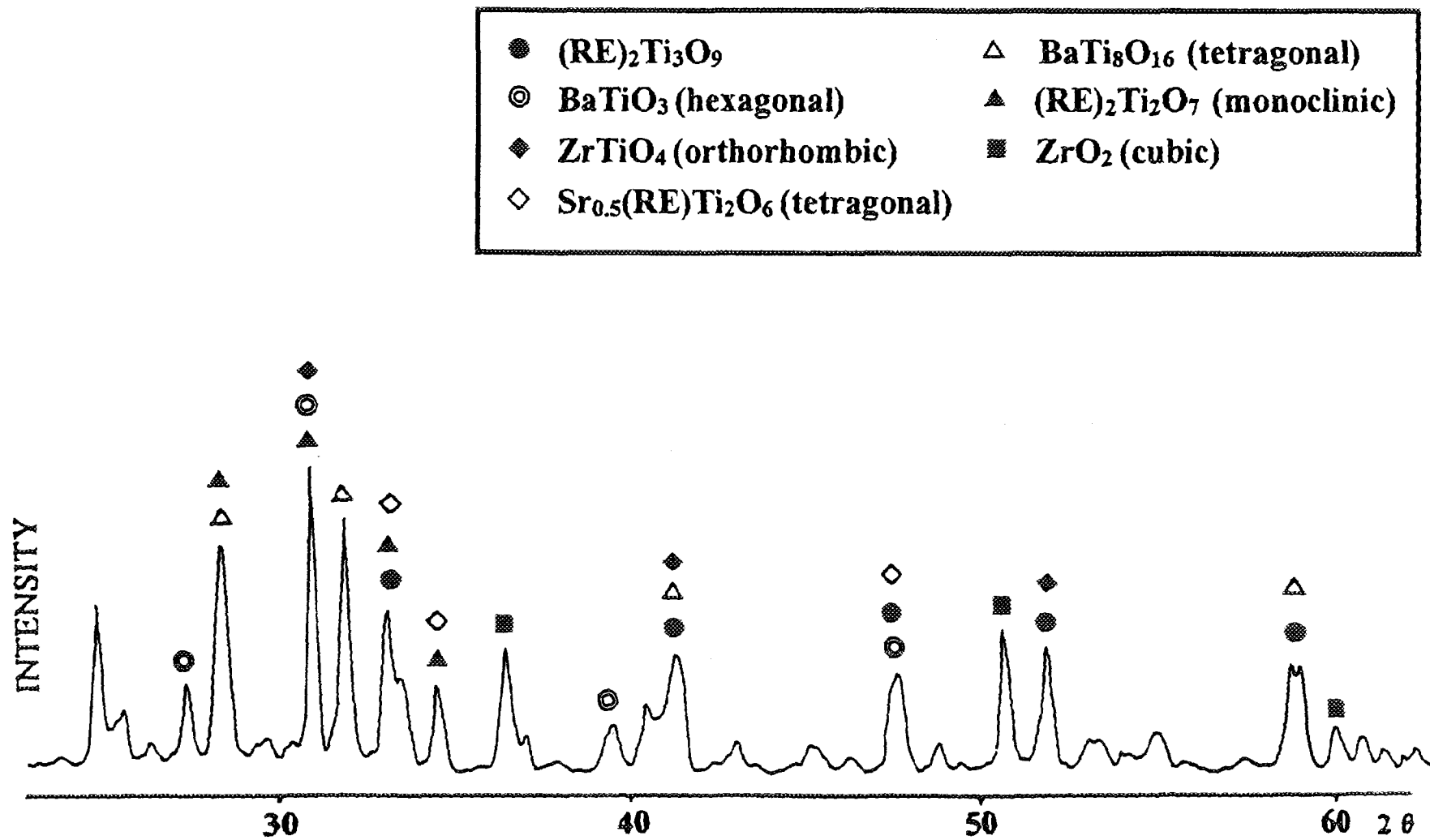


Fig.3 X-ray diffraction pattern for the oxide phase of sample No. 3