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INVESTIGATION OF CO₂ CAPTURE PROPERTY OF CaO SORBENT IN VARIOUS MOLTEN CHLORIDE MEDIA WITH DIFFERENT OPERATION TEMPERATURE

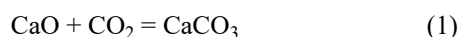
CaO sorbent dissolved in chloride molten salts was investigated to identify its CO₂ capture property. Various molten salt systems with different melting points (CaCl₂, LiCl, LiCl-CaCl₂, and LiCl-KCl) were used to control the operation temperature from 450 to 850°C in order to determine the effect of the operation temperature on the chemical reaction between CaO and CO₂. The CaO sorbent showed the best performance at 550°C in the LiCl-CaCl₂ molten salt (conversion ratio of 85.25%). This temperature is lower than typical operation temperature of the solid-state CaO sorbent (~700°C).

Keywords: radioactive carbon, ¹⁴C, CO₂ capture, CaO sorbent, molten salt

1. Introduction

Radioactive ¹⁴C is generated during the operation of nuclear power plants and the post-treatment of spent nuclear fuels [1-3]. ¹⁴C decays to stable ¹⁴N by emitting beta particles (i.e., electrons) with an average energy of 49.5 keV and a half-life of 5,730 years [3]. ¹⁴C incorporated in living organisms can easily participate in metabolism to damage living tissues [4] and, therefore, treatment of ¹⁴C in radioactive wastes is important for reducing ecological exposure. ¹⁴CO₂ is commonly formed during the treatment of ¹⁴C-containing wastes and, in this respect, the development of ¹⁴CO₂ separation techniques from the gas stream of the radioactive waste treatment process is essential for the immobilization of ¹⁴C from a safety standpoint [1]. Treatment of CO₂ is also important technique in the climate change issue [5-8].

CaO is a well-known sorbent compound of CO₂ [5-8]. The CaO sorbent is converted to CaCO₃ when reacted with CO₂ by the following Reaction 1:



CaCO₃ is regarded as a suitable waste form of ¹⁴CO₂ because of its excellent thermal and chemical stability for long-term storage or disposal [1]. Thermal energy is required to proceed the CO₂ capture reaction of the CaO sorbent properly (typically, ~700°C for solid-state CaO for fast CO₂ diffusion). However, at

higher temperature (>900°C), the CaCO₃ product is thermally decomposed back to CaO and CO₂ [5-8]. Therefore, the reaction temperature should be carefully controlled for effective CO₂ separation from the gas stream.

Recently, the CO₂ capture properties of CaO-containing molten salts (e.g., CaCl₂) have been investigated [9-10]. CaO sorbent dissolved in molten salts is believed to have enhanced reactivity compared with conventional solid-state sorbents owing to its liquid-like behavior (fast gas-liquid interaction) [9]. Here, we investigated the temperature dependency of the CO₂ capture property of CaO sorbent in molten salts because the conversion ratio of CaO to CaCO₃ by Reaction 1 is greatly influenced by the reaction temperature. It is thought that there should be a trade-off point between the thermal activation (forward direction of Reaction 1) and the thermal decomposition (reverse direction of Reaction 1). The temperature dependency of the CaO sorbent in CaF₂-CaCl₂ molten salt was investigated in literature but the trade-off point could not be identified in this system due to relatively high melting point of the molten salt (625°C under the experimental composition) [10]. In this respect, we used various molten salt systems (CaCl₂, LiCl, LiCl-CaCl₂, and LiCl-KCl) with different melting points (Table 1) to procure wide temperature range to find the trade-off point, i.e., the optimized reaction temperature of the CaO sorbent in the molten salt media.

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2. Experimental

Thermodynamic calculation was conducted using HSC Chemistry 9 software (Outotec). In this experiment, natural CO₂ was used as a surrogate of ¹⁴CO₂ for convenience. CO₂/Ar mixed gas (15 vol.% CO₂) was prepared as a CO₂ source for the experiment. CaCl₂ (Sigma-Aldrich, 99.9%), LiCl (Alfa Aesar, 99%), LiCl-KCl (Sigma-Aldrich, eutectic composition, 99.99%), and CaO (Sigma-Aldrich, 99.9%) were used after pre-heat treatment at 200°C in ambient Ar to get rid of residual water. LiCl-CaCl₂ salt was prepared by mixing them to its eutectic composition. Using the eutectic systems, the melting points of LiCl-KCl and LiCl-CaCl₂ can be decreased to the pure components [11-12].

Fig. 1 shows a schematic illustration of the CO₂ capture test system. The test system was installed inside an Ar-filled glove box to protect the hygroscopic chloride salts from moisture. 400 g of each chloride salt and 20 g of CaO were put together inside a stainless steel crucible, and the crucible was heated to an adequate temperature to melt the salt, as displayed in Table 1. Next, the CO₂/Ar mixed gas was supplied into the CaO-containing molten salt through a mass flow controller (1179A, MKS Instrument). The flow rate of the mixed gas was fixed to 200 cm³ min⁻¹ for all cases. A CO₂ sensor (M201, Beijing Shi'An Technology Instrument) (0-100% range, resolution = 1%) was installed in the gas outlet in order to monitor the CO₂ concentration of the off-gas and, thus, to quantify the progress of the CO₂ capture reaction. The CO₂ injection was stopped when the measured CO₂ concentration reached 15%. For comparison, the identical experiments were conducted without the CaO sorbent for each molten salt system.

After the reaction, the frozen salts were washed with deionized water to remove the chloride salts and the residual CaO. The washed products were then vacuum-filtered for the recovery of the reaction products. X-ray diffraction (XRD) analysis (D8 Advance, Bruker) of the recovered products was conducted to verify the phase of the reaction product.

TABLE 1

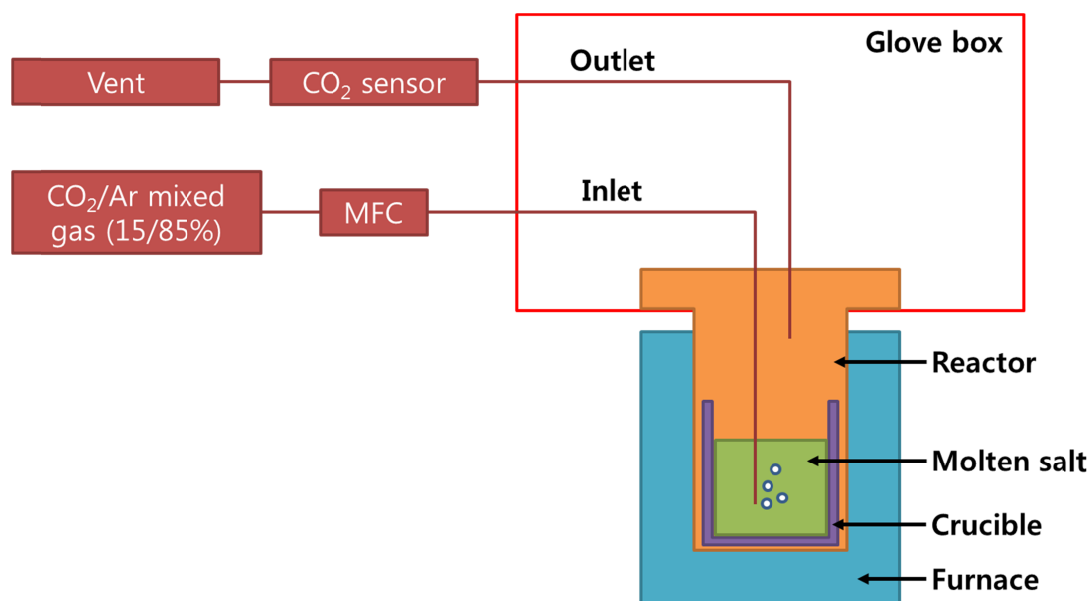
Summary of molten salt systems used in the experiment

Salt	Molar ratio	Melting point (°C)	Reaction temp. (°C)
CaCl ₂	—	772	850
LiCl	—	610	650
LiCl-CaCl ₂	LiCl :CaCl ₂ = 0.65:0.35	475	550
LiCl-KCl	LiCl:KCl = 0.41:0.59	353	450

3. Results and discussion

Fig. 2 shows the thermodynamic equilibrium composition of CaO, CO₂, and CaCO₃ as a function of CO₂ amount according to Reaction 1 at various temperatures. It is clearly seen that the conversion of CaO to CaCO₃ is favored at low temperature range (Figs. 2(a) and 2(b)). Note that, despite the high tendency of the conversion at room temperature (Fig. 2(a)), the reaction hardly occurs in reality due to the activation energy. The typical reaction temperature of the solid-state CaO sorbents is ~700°C as described previously [5-8]. As the temperature increases, the calculated conversion ratio reduces as shown in Figs. 2(c) and 2(d). The conversion reaction hardly occurs at 1000°C (Fig. 2(d)) because the reverse reaction of Reaction 1 becomes dominant. More simply, the Gibbs free energy change for Reaction 1 becomes positive above 890°C, showing the thermodynamic instability of CaCO₃ at the high temperature condition. In other words, the operation temperature window is limited to around ~700°C to suppress the reverse reaction.

Fig. 3 shows the CO₂ concentration curves of each system (with different reaction temperatures) as a function of the CO₂ injection time without and with the CaO sorbent. With the pure molten salt without the sorbent, the CO₂ concentration measured at the outlet of the test system reached maximum (15%) in a short time. The CO₂ concentration curves of the CaO-containing

Fig. 1. Schematic illustration of the CO₂ capture test system installed inside an Ar-filled glove box

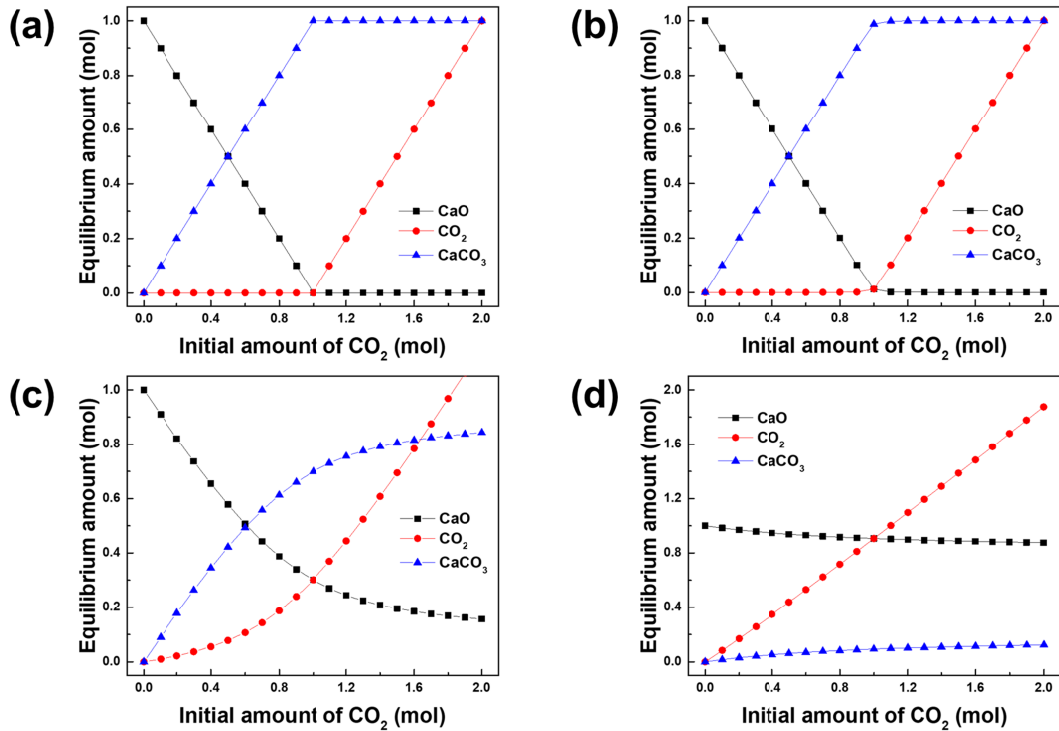


Fig. 2. Equilibrium concentration calculation of Reaction 1 as a function of CO₂ amount at various temperatures: (a) 25°C, (b) 500°C, (c) 75 °C, and (d) 1000°C (initial amount of CaO and CaCO₃ is fixed to 1 and 0 mol, respectively)

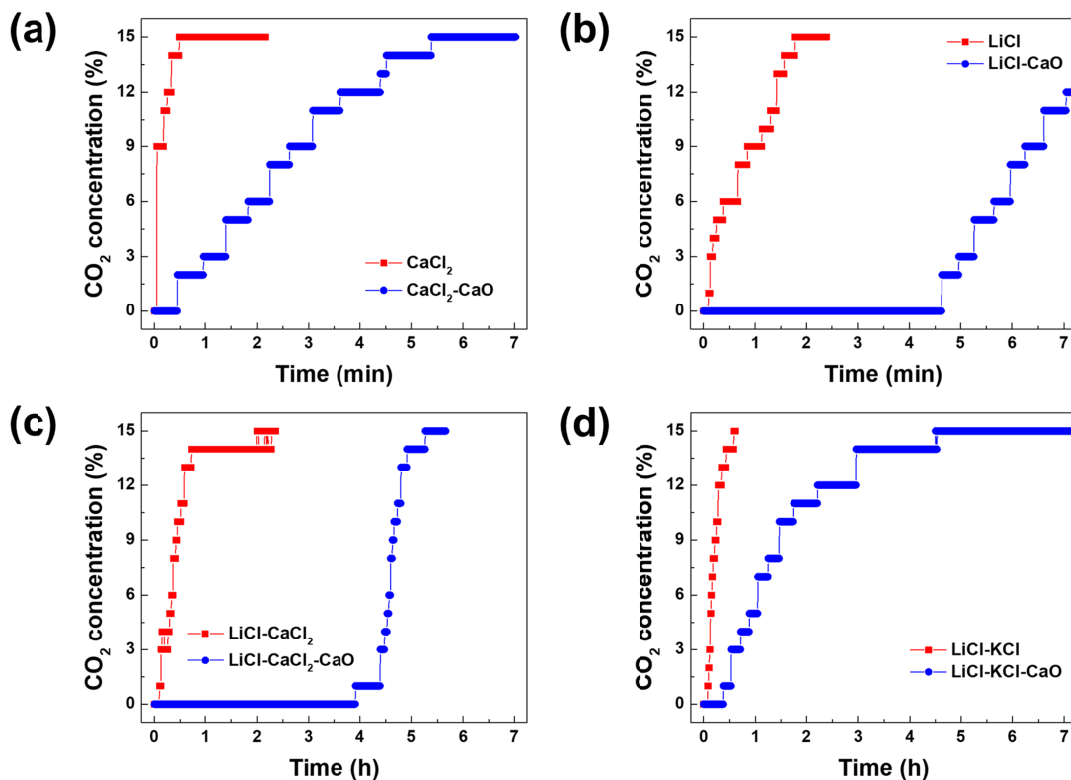


Fig. 3. CO₂ concentration measured at the outlet of the test system without and with CaO sorbent in various molten salt systems: (a) CaCl₂ at 850°C, (b) LiCl at 650°C, (c) LiCl-CaCl₂ at 550°C, and (d) LiCl-KCl at 450°C

molten salts showed two different behaviors. In cases of LiCl-CaO and LiCl-CaCl₂-CaO (Figs. 3(b) and 3(c)), at medium temperature range, the injected CO₂ was not observed at the outlet for a certain period of incubation time (~4 h). It is thought that

the CO₂ capture reaction occurred vigorously in this period. In contrast, the incubation time of the high-temperature CaCl₂-CaO (Fig. 3(a)) and low-temperature LiCl-KCl-CaO (Fig. 3(d)) systems was relatively short (tens of minutes) compared with the

previous cases. Instead, the slope of the CO₂ concentration increment decreased, implying the slow kinetics of the CO₂ capture reaction (for LiCl-KCl-CaO case) or the strengthened CaCO₃ decomposition reaction (for CaCl₂-CaO case). Combining the results, it is proposed that the LiCl-CaO and LiCl-CaCl₂-CaO systems under an operation temperature of 550-650°C provide optimal conditions for CO₂ capture.

While chloride salts are highly hygroscopic and CaO is highly reactive with water to form CaOH, CaCO₃, the expected reaction product, tends to be precipitated inside water because of its low solubility ($\sim 0.013 \text{ g L}^{-1}$). In this respect, the frozen salts after the CO₂ injection were washed with the deionized water and then vacuum-filtered to recover the reaction products. Fig. 4 shows a typical XRD pattern of the recovered products. All the patterns were well matched to the crystalline CaCO₃ phase, as expected, indicating that the CO₂ capture reaction of CaO forming CaCO₃ occurred successfully. The mass of each recovered product was measured to evaluate the conversion ratio, which was defined as a ratio of the reacted CaO amount to the initial CaO amount as expressed below equations (Table 2). The reacted CaO (56.08 g mol^{-1}) amount can be calculated from the amount of the recovered CaCO₃ ($100.09 \text{ g mol}^{-1}$).

$$\begin{aligned} \text{Mass of reacted CaO (g)} &= \\ &= \text{Mass of recovered CaCO}_3 \text{ (g)} \times 56.08 / 100.09 \end{aligned}$$

$$\begin{aligned} \text{Conversion ratio (\%)} &= \\ &= \text{Mass of reacted CaO (g)} / \text{Mass of initial CaO (g)} \times 100 \end{aligned}$$

The maximum conversion ratio was 85.25% at 550°C in the LiCl-CaCl₂ molten salt system. The captured CO₂ amount in this system (13.38 g) corresponds to the supplied CO₂ amount for 3.78 h injection ($15 \text{ vol.}\% \times 200 \text{ cm}^3 \text{ min}^{-1} \times 60 \text{ min} = 1.8 \text{ L-CO}_2 \text{ h}^{-1} = 0.08 \text{ mol-CO}_2 \text{ h}^{-1} = 3.54 \text{ g-CO}_2 \text{ h}^{-1}$), which is

comparable to the incubation time as shown in Fig. 2(b). Similar behavior was also observed in the LiCl (Fig. 2(c)) case with the relatively high CaO conversion ratio. These clearly confirm that the CO₂ capture reaction proceeded actively during the incubation time in the medium temperature range utilizing more than 78% of the incorporated CaO. On the other hand, the captured CO₂ amount was not consistent with the incubation time in the high-temperature CaCl₂ and low-temperature LiCl-KCl cases with poor conversion ratio. It seems that slow reaction kinetics (as seen in the decreased slope) and/or chemical equilibrium with the reverse reaction in the CaCl₂ case may result in such inconsistency.

TABLE 2

Summary of CaO conversion ratio calculations at various molten salt systems

Salt	CaCl ₂	LiCl	LiCl-CaCl ₂	LiCl-KCl
Reaction temperature (°C)	850	650	550	450
Recovered CaCO ₃ (g)	13.96	28.06	30.43	17.18
Reacted CaO (g)	7.82	15.72	17.05	9.63
Captured CO ₂ (g)	6.14	12.34	13.38	7.55
CaO conversion ratio (%)	39.11	78.61	85.25	48.13

The temperature dependency of the CaO sorbent dissolved in molten salts resembles that of solid-state sorbents [6]. However, compared with the solid-state CaO sorbent generally operated at around $\sim 700^\circ\text{C}$, the optimal operation temperature of the molten salt-based system is lowered (550°C). Such operation temperature reduction is thought to be originated from the liquid-like nature of the CaO sorbent dissolved in the molten salts [9]. Additionally, dissolution of CaCO₃ product into the molten salts would be helpful to improve the reactivity [13], because the growth of CaCO₃ layer onto the solid-state CaO

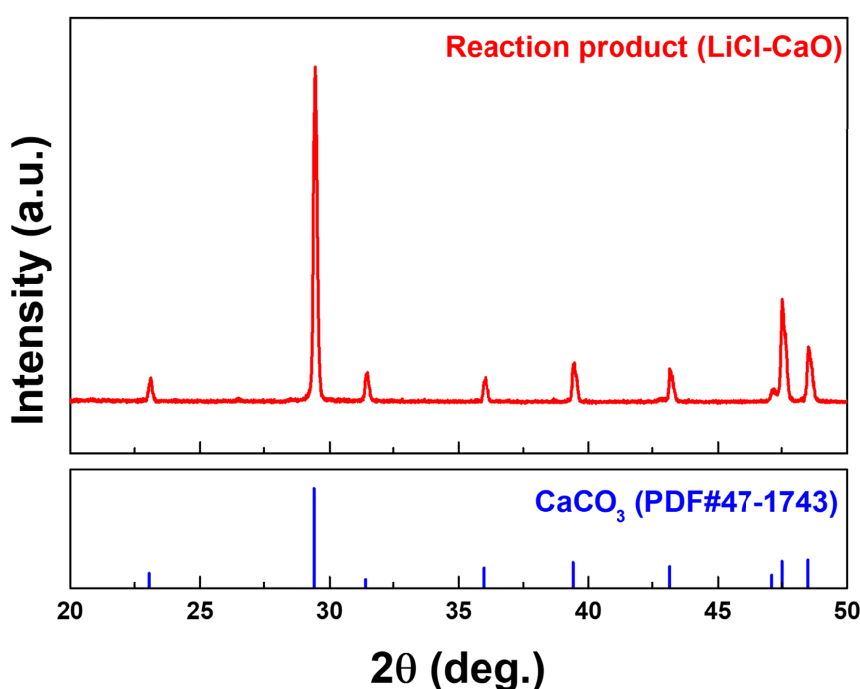


Fig. 4. A typical XRD pattern of reaction product of CaO sorbent after CO₂ injection

surface prohibits diffusion of CO₂ [6]. The high CaO conversion ratio with the reduced temperature operation achieved using the simple experimental set-up of this work suggests that the molten salt-based system is an efficient tool to enhance the reaction between CaO and CO₂. In other words, the molten salt-based CO₂ capture system has the potential to replace the solid-state CaO sorbent system with relatively simple equipment operating at a lower temperature. While we only focused on the operation temperature in this study, the different physical and chemical properties of the molten salts (e.g., viscosity, density, CaO solubility, CaCO₃ solubility, ionicity, and etc.) could affect the CO₂ capture property. In-depth investigation is needed to more clearly understand the molten salt-based CO₂ capture system.

4. Conclusions

In this study, investigation of CaO sorbent dissolved in molten salts was undertaken to determine its applicability for capturing radioactive ¹⁴CO₂. The reaction temperature was controlled by changing the molten salts (CaCl₂, LiCl, LiCl-CaCl₂, and LiCl-KCl) to identify the adequate operation temperature range. The CO₂ capture temperature of the CaO sorbent could be lowered to 450°C in LiCl-KCl molten salt with the conversion ratio of 48.13%. It showed the best performance at 550°C in LiCl-CaCl₂ molten salt with the conversion ratio of 85.25%. At a higher temperature, the conversion ratio gradually decreased as the reverse reaction became more dominant. It is believed that dissolving CaO in molten salt-based liquid media is a promising technique for immobilizing radioactive ¹⁴CO₂ to form a stable Ca¹⁴CO₃ product. This technique also can be applied to the CO₂ capture process for the reduction of the greenhouse gas emission.

Acknowledgments

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REFERENCES

- [1] M.-S. Yun, F. Caron, *Prog. Nucl. Energy* **48**, 2 (2006).
- [2] C. Kunz, *Health Phys.* **49**, 25 (1985).
- [3] W. Sohn, D.-W. Kang, W.-S. Kim, *J. Nucl. Sci. Technol.* **40**, 604 (2003).
- [4] J.R. Totter, M.R. Zelle, H. Hollister, *Science* **128**, 1490 (1958).
- [5] C.-H. Huang, H.-W. Hsu, W.-H. Liu, J.-Y. Cheng, W.-C. Chen, T.-W. Wen, W. Chen, *Energy Proc.* **4**, 1269 (2011).
- [6] H. Lu, E.P. Reddy, P.G. Smirniotis, *Ind. Eng. Chem. Res.* **45**, 3944 (2006).
- [7] J.C. Abanades, E.J. Anthony, J. Wang, J.E. Oakey, *Environ. Sci. Technol.* **39**, 2861 (2005).
- [8] Y. Hu, W. Liu, J. Sun, M. Li, X. Yang, Y. Zhang, X. Liu, M. Xu, *Fuel* **167**, 17 (2016).
- [9] V. Tomkute, A. Solheim, E. Olsen, *Energy Fuels* **27**, 5373 (2013).
- [10] V. Tomkute, A. Solheim, E. Olsen, *Energy Fuels* **28**, 5345 (2014).
- [11] K.H. Mahendran, S. Nagaraj, R. Sridharan, T. Gnanasekaran, *J. Alloys Comp.* **325**, 78 (2001).
- [12] A.S. Basin, A.B. Kaplun, A.B. Meshalkin, N.F. Uvarov, *Russ. J. Inorg. Chem.* **53**, 1509 (2008).
- [13] E.B. Freidina, D.J. Fray, *Thermochim. Acta* **351**, 107 (2000).