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Preparation of Cs-Immobilized Hollandite via Cold Sinter-Assisted Route

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1. Introduction

Hollandite is a tunnel-structured titanate mineral with the general formula $A_2B_8O_{16}$, where A is a large cation, particularly immobilized radioactive Cs, and B is typically a transition metal, such as Ti. This structure provides stable sites for the immobilization of large radioactive cations. To achieve a highly densified hollandite crystalline waste form, a high sintering temperature (1200°C) is required, but this can lead to a significant loss of volatile Cs[1]. To reduce Cs volatilization, demanding process conditions are required, involving high pressure (~30 MPa), a reducing atmosphere (Ar/H_2), and the addition of Ti metal as a reducing agent.

Cold sintering is an advanced densification technique for sintering ceramic powder below 300°C by adding a suitable amount of solvent and applying a pressure of several hundred MPa[2]. This sintering process is based on the interaction between a solvent or crystalline water and the surface of ceramic powder. Recently, cold sintering techniques have been used to immobilize volatile radionuclides. For instance, Cs is effectively immobilized in hydroxyapatite at only 200°C under 500 MPa[3], while I is immobilized in iodosodalite at only 300°C[4].

In this paper, we employ cold sintering during the fabrication of Cs-immobilized hollandite. Although the crystallization of hollandite requires temperatures above 1000°C, pre-sintering its precursor through cold sintering enables high densification at lower temperatures. Furthermore, the low surface-to-volume ratio of the cold-sintered pellet is expected to prevent Cs volatilization during heat treatment.

2. Methods

As shown in Fig. 1, hollandite precursors were synthesized using metal nitrates and Ti-alkoxide materials. Following the sol-ge
l reaction The precursor powder was calcined to eliminate residual water, nitrates, and organic impurities. The calcined powder was then subjected to cold sintering. Finally, hollandite was obtained through post-heat treatment of the cold-sintered pellet at 1000°C in air.

3. Results

The chemical composition of hollandite with the composition targeted as $Cs_{1.3}Al_{0.1}Fe_{0.4}Ga_{0.4}Mn_{0.4}Ti_{6.7}O_{16}$, synthesized via the cold sinter-assisted route, was analyzed using EDS, revealing that Cs leaching was as low as 3.8% (Fig. 2). Additionally, the density of the hollandite was measured at 4.27 g/cm^3, achieving 97% densification compared to the theoretical density of 4.39 g/cm^3, as estimated through XRD and Rietveld analysis (Fig. 3).

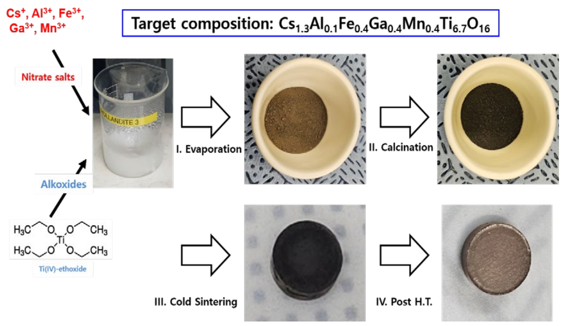

Fig. 1. Schematic diagram of hollandite fabrication process using cold-sintering route

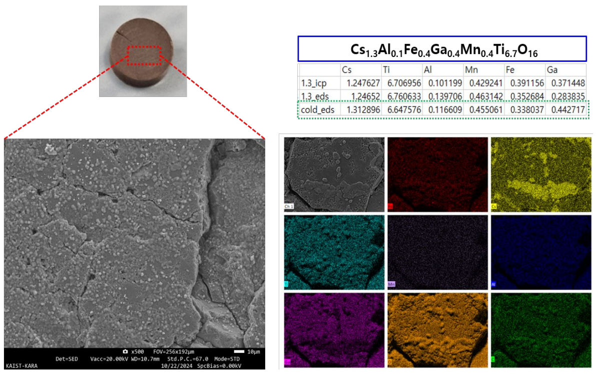

Fig. 2. Scanning electron microscopy (SEM) and images of Cs-hollandites prepared via cold sinter-assisted route

4. Conclusion

In conclusion, the cold sinter-assisted route enabled the fabrication of highly densified Cs-immobilized hollandite while significantly reducing Cs volatilization. The resulting hollandite achieved 97% densification with minimal Cs leaching (3.8%), demonstrating its potential for effective radioactive waste immobilization. In future work, the mechanical and chemical durability of the hollandite will be studied through compressive and leaching tests, respectively.

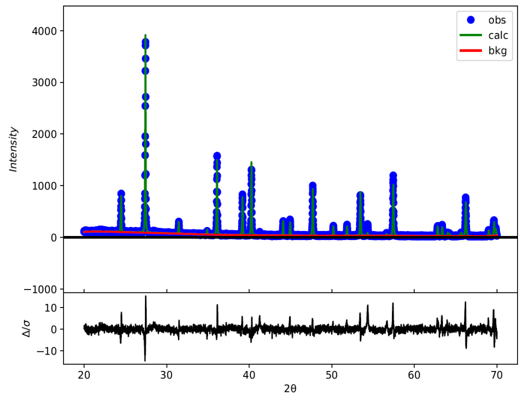

Fig. 3. X-ray diffraction patter (XRD) of Cs-hollandites prepared via cold sinter-assisted route

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