Experimental report

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Proposal: **7-03-223** **Council:** 4/2023

Title: Multiple diffusion dynamics in superionic Argyrodites Ag8GeSe6

Research area: Materials

This proposal is a continuation of 7-01-541

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Samples: Ag8GeSe6

Instrument	Requested days	Allocated days	From	To
WASP	3	3	24/11/2023	27/11/2023

Abstract:

The crystalline-amorphous hybrid structures in superionic materials yield ultralow lattice thermal conductivity along with decent electrical and ion conductivities. They attract therefore intense interest from communities working on solid-sate battery, fuel cells, and thermoelectric applications. Recently, Ag-based Argyrodites, e.g., Ag8GeSe6 (our work), have moved into the focus of interest as potential thermoelectric materials. They show a T-independent (aka glass-like thermal transport) and ultralow thermal conductivity (¿_L) of ~0.3 W/m/K at room temperature. In spite of some studies on the correlation between lattice dynamics and ultralow ¿_L of Ag-based Argyrodites, the microscopic mechanisms of diffusive dynamics on their heat and ion transport is still missing. Notably, there is disagreement on whether Ag ions feature ultrafast or ultraslow diffusion. Hence, we intend to provide a direct experimental identification of Ag diffusion dynamics and bridge the interconnection between diffusion dynamics and ion/heat transport. Our study also provides an example to study atomic diffusion at different time-scales in superionic thermoelectric materials.

Experimental report

Multiple diffusion dynamics in superionic Argyrodites Ag_8GeSe_6

Abstract:
The crystalline-amorphous hybrid structures in superionic materials yield ultralow lattice thermal conductivity along with decent electrical and ion conductivities. They attract therefore intense interest from communities working on solid-sate battery, full cells, and thermoelectric applications[1-4]. Recently, Ag-based Argyrodites, e.g., Ag_8GeSe_6[5] (our work), Ag_8SnS_6[6] (our work) and Ag_8SnSe_6[7], have moved into the focus of interest as potential thermoelectric materials. They show a *T*-independent (aka glass-like thermal transport) and ultralow thermal conductivity (κ_L) of ~0.3 W/m/K at room temperature. In spite of some studies on the correlation between lattice dynamics and ultralow κ_L of Ag-based Argyrodites, the microscopic mechanisms of diffusive dynamics on their heat and ion transport is still missing. Notably, there is disagreement on whether Ag ions feature ultrafast or ultraslow diffusion. Hence, we intend to provide a direct experimental identification of Ag diffusion dynamics and bridge the interconnection between diffusion dynamics and ion/heat transport. Our study also provides an example to study atomic diffusion at different time-scales in superionic thermoelectric materials.

In our experiments, wide-angle neutron spin-echo (NSE) were performed using the high-intensity VASP spectrometer. We collected data at temperatures between 250 K and 500 K with an incoming neutron wavelength λ = 5 Å. The temperature was controlled with an orange cryostat. The data were reduced using software developed by IL, based on the commercial software package Igor Pro 8.[8] As depicted in Figs. 1(a-d) and Figs. 2(a-b), we observed a distinct decrease in the intensity of the intermediate scattering function above 3 ns, starting from 325 K (as indicated by the dashed red line in Fig. 1(b)), which implies slow relaxation dynamics of Ag. With increasing temperatures, up to the superionic phase transition at~ 350 K, we observed a gradual decrease in the intensity of the intermediate scattering function below 3 ns, suggesting the existence of fast dynamics of Ag in this compound. These measurements confirmed the coexistence of fast and slow Ag diffusion in Ag_8GeSe_6, as also evidenced from our previous analysis of the inelastic neutron scattering and molecular dynamics simulations.

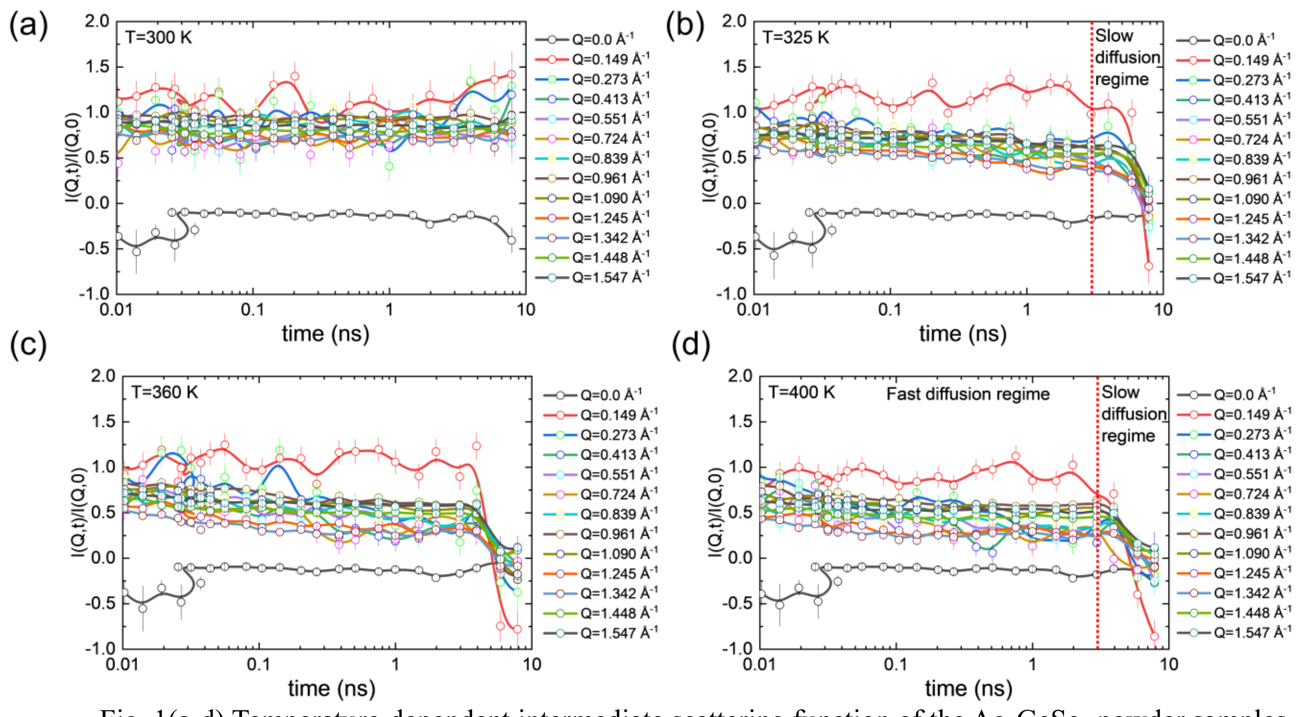

Fig. 1(a-d) Temperature-dependent intermediate scattering function of the Ag_8GeSe_6 powder samples.

We further extracted the temperature-dependent intermediate scattering function at Q ~ 0.550 Å^{-1} and 1.090 Å^{-1}, as presented in Figs. 2(c-d). The visible coexistence of two types of relaxation dynamics at both lower and higher momentum transfers were observed, indicating the emergence of fast and slow Ag diffusion.

Notably, we should point out that we may not be able to extract fast diffusive dynamics because the experimental time domain is large than the fast Ag relaxation time. A proper combined stretched function needs to be employed to obtain the relaxation parameters for the corresponding fast and slow diffusive dynamics.

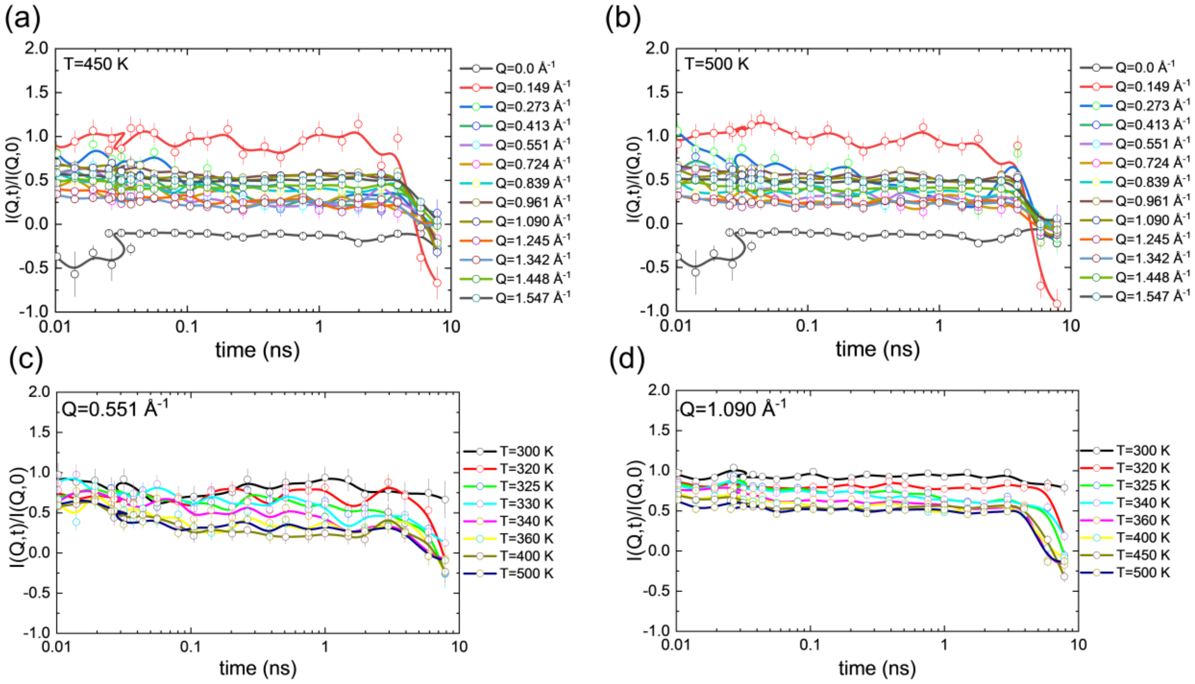

Fig. 2 Intermediate scattering function of the Ag_8GeSe_6 powder samples at (a) 400 K and (b) 500 K. Temperature-dependent intermediate scattering function at Q = (c) 0.551 Å^{-1} and (d) 1.090 Å^{-1}.

In summary, we conducted NSE on a powder Ag_8GeSe_6 sample over a wide temperature range. Our NSE experiments reveal the coexistence of fast and slow Ag diffusion, which is consistent with our previous findings from inelastic neutron scattering and simulations. To precisely extract the diffusive dynamics of Ag, further proper fitting analyses are needed.

Reference

1. Ohno S, *et al. Progress in Energy* 2, 022001 (2020).
2. Minh NQ. Ceramic Fuel Cells. *J. Am. Ceram. Soc.* 76, 563-588 (1993).
3. Zhao K, *et al. Adv. Funct. Mater.* 30, 1903867 (2020).
4. Lin S, *et al.Materials Today* 48, 198-213 (2021).
5. Shen X, *et al. ACS Appl. Mater. Inter.*11, 2168-2176 (2019).
6. Shen X, *et al. Adv. Funct. Mater.* 30, 2000526 (2020).
7. Li W, *et al. Adv. Sci.* 3, 1600196 (2016).
8. Fouquest P, *et al*. *J. Neutron Res.* 15, 39-47 (2007).