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XAFS analysis of SrF_2 at high temperature

Haruaki MATSUURA*[1], Sou WATANABE[1], Hiroshi AKATSUKA[1],
Yoshihiro OKAMOTO[2], Kazuo MINATO[2]
[1]Res. Lab. for Nucl. Reactors, Tokyo Tech., Ookayama, Meguro-ku, Tokyo, 152-8550, Japan
[2]Dept. of Material Science, JAERI, Tokai-mura, Naka-gun, Ibaraki, 319-1195, Japan

Introduction

Fluorite crystals such as CaF_2, SrF_2, β-PbF_2 and $SrCl_2$ exhibit superionic conductance behavior at high temperature below their melting points. Since electrical conductivity of fluorite superionic conductors increases with increasing temperature, number of mobile fluoride ions is also expected to increase. We have found a distinct phase shift in XAFS signal at the temperature of superionic conductance phase transition of PbF_2 (710 K) [1]. Similar phase shift in XAFS signal and structural change would be observed in XAFS analysis on SrF_2 at high temperature.

Experimental

SrF_2 was mixed with dried fine boron nitride matrix powder with the weight ratio in 1 to 9, and pressed into the pellets. A pellet was installed in an electric furnace located between ionization chambers, and heated from 300 to 1750 K regulated within ± 5 K. During 48 hours of beamtime, transmitted XAFS spectra have been collected, using Si (111) double crystal monochromator at Sr-K X-ray absorption edge (16.105keV).

Results and discussion

XAFS oscillations $\chi(k)\cdot k^3$ of SrF_2 at the temperature range of $300 < T$ (K) < 1073 are shown in Fig. 1(a). At this temperature range, both amplitude of $\chi(k)\cdot k^3$ and intensity of predominant Sr^{2+}-F^- correlation peak in $FT|\chi(k)\bullet k^3|$ decrease gradually with increasing temperature. This feature typically reflects to increasing in Debye-Waller factor and cumulants due to thermal and anharmonic vibration. Fig. 1(b) depicts XAFS of SrF_2 at $1073 < T$ (K) < 1750. At 1750 K, SrF_2 is in molten phase. Phase of XAFS oscillation clearly change between 1073 and 1273 K, which is similar to the behavior observed in PbF_2 system [1]. This temperature is reasonable to the literature values of superionic conductance, T_0 in [2] and that the phase shift observed in XAFS oscillations can be reflected to the superionic conductance phase transition of SrF_2 too.

Local structural parameters of the nearest fluoride ions around a strontium ion at each temperature obtained by the curve fitting analysis are shown in [3]. Coordination numbers decrease with increasing temperature and they are evaluated as almost the similar value ($N_{SrF} \sim 4$) at $T > T_0$, while inter-ionic distances suddenly start increasing at $T > T_0$. At $T < T_0$, defects would be produced in the crystal by heating and some fluoride ions contribute to gradual increase of intrinsic conductivity. Therefore coordination number would be evaluated to be less than 8 while inter-ionic distance remain unchanged. On the other hand, almost of all fluoride ions can be mobile in superionic state ($T_m > T > T_0$), thus average distribution of the nearest fluoride ions around a strontium ion is determined by balance of coulombic interaction between Sr^{2+} and F^- and diffusing mobility of fluoride ions. Such balance should result in increase of the inter-ionic distance at $T > T_0$, since thermal diffusion motion is activated by heat. Decrease in the inter-ionic distance by melting, which is a general feature observed in melting, should be indication of mobile strontium ions. As a consequence, 4 coordinated tetrahedron would be the most stable configuration with taking into account of symmetric structure at the state in which fluoride ions are well mobile.

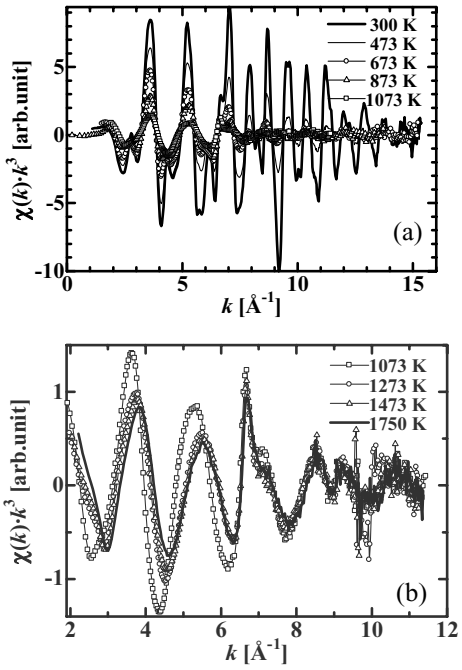

Fig. 1(a) and (b) EXAFS oscillations of SrF_2.

References

[1] S. Watanabe et al., J. Phys. Chem. Solids, 66, 402 (2005).
[2] B. M. Voronin and S. V. Volkov, J. Phys. Chem. Solids, 62, 1349 (2001).
[3] S. Watanabe et al, Electrochemistry, (2005) in press.

* hmatsuur@nr.titech.ac.jp