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Phase and structure of polycrystal $Sr_{0.69}La_{0.31}F_{2.31}$ + SrS solid electrolyte material ①

Tian Yanwen(田彦文), Ma Ping(马 平), Zhang Xin(张 新), Zhai Yuchun(翟玉春)
School of Materials and Metallurgy, Northeastern University, Shenyang 110006, P. R. China

Abstract: The phase and the structure of polycrystal material, which was prepared by calcining the co-precipitated fluoride powder of Sr and La with a ratio of 0.69∶0.31 mixed with SrS powder, were investigated by X-ray diffraction and electron probe scanning. In the materials, three phases were found, they are $Sr_{0.69}La_{0.31}F_{2.31}$ solid solution phase with a pure SrF_2 cubic structure whose lattice constant is 5.843 Å, SrS single phase with a NaCl cubic structure, and an unknown phase that is produced by the interaction of SrS and co-precipitated powder. It was also found that SrS has no influence on the structure of $Sr_{0.69}La_{0.31}F_{2.31}$ solid solution.

Key words: X-ray diffraction; electron probe; polycrystal $Sr_{0.69}La_{0.31}F_{2.31}$ + SrS material; phase structure

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1 INTRODUCTION

In order to make the solid electrolyte sensor used in measuring sulfur activity in metallurgical process, many investigations were carried out[1~3]. The research on measuring sulfur activity in the atmosphere at the temperature below 500 ℃ was comparatively successful[4], but the researches on measuring sulfur activity in metallurgical melts at high temperatures were developed very slowly. No suitable solid electrolyte can be used in measuring sulfur activity in the melts at present, and the researches on this solid electrolyte are still in the beginning.

The solid solution $Sr_{0.69}La_{0.31}F_{2.31}$ single crystal material, with a melting point of 1 560 ℃, has a higher ionic conductivity[5~9]. The structure of pure solid solution single crystal[10] was studied. Polycrystal $Sr_{0.69}La_{0.31}F_{2.31}$ + SrS can be used in making sulfur measurement sensor[11]. But no research on the behavior of SrS in the solid solution has been reported. In the research of this paper, the polycrystal $Sr_{0.69}La_{0.31}F_{2.31}$ + SrS solid electrolyte material was produced by mixing the co-precipitated fluoride powder of Sr and La with a ratio of 0.69∶0.31 with SrS powder. By means of X-ray diffraction and electron probe microanalysis, the phase and the structure of the polycrystal material were studied.

2 PREPARATION OF SAMPLES

First, the co-precipitated and dehydrated fluoride powder of Sr and La with a ratio of 0.69∶0.31 was mixed with SrS. And then the mixture was molded by isostatic pressure at 280 MPa. After that, the molded mixture was dehydrated for 2.5 h at 450 ℃ and calcined for 7 h at 800 ℃ in the approximately vacuum equipment with a lower oxygen activity. Finally, three kinds of samples were obtained as following: sample A without SrS, sample B and C mixed with SrS in 3 %(mass fraction) and 5 % (mass

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fraction) respectively.

Pure SrF_2, LaF_3 and SrS samples were also prepared following the same producing steps as sample A, B and C for the later comparison.

3 RESULTS OF XRD AND DISCUSSION

It was revealed by XRD analysis that in this experiment the prepared powder SrF_2, LaF_3 and SrS samples are pure SrF_2 with fluorite cubic structure, pure LaF_3 with hexagonal structure and pure SrS with NaCl cubic structure respectively, and no phase change happens. Their XRD spectra are shown in Figs.1, 2 and 3.

The XRD spectra of samples A, B and C are shown as Fig.4.

It can be found that both positions and shapes of main diffraction peaks in the spectra of the three samples were correspondence match. Comparing with the main peaks of the pure SrF_2 spectrum (seeing Fig.1), those of samples A, B, C have the same shape, but the positions of main diffraction peaks of these samples are a bit shift to the low angle, indicating an increased lattice constant. When comparing with the main peaks of the pure LaF_3 spectrum (seeing Fig.2), those of samples A, B, C have inconsistent shapes and positions, it indicates that the samples A, B and C take SrF_2 cubic structure.

The mole ratio of La to Sr in samples A, B and C is 0.31∶0.69 measured by chemical

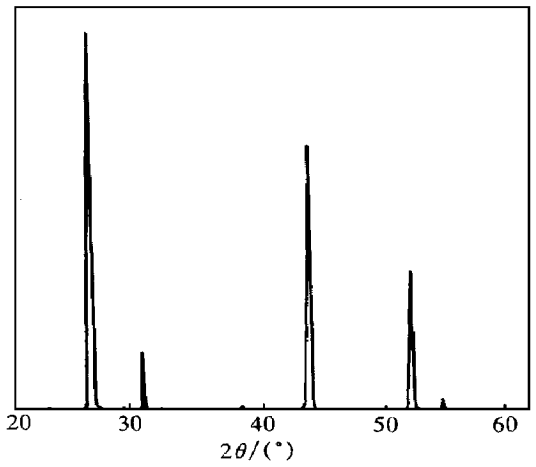

Fig.1 XRD spectrum of SrF_2

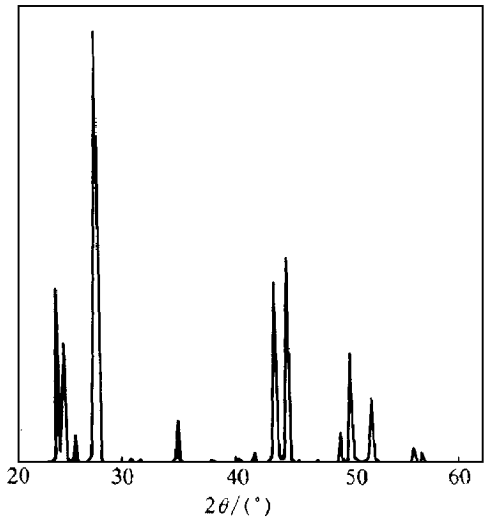

Fig.2 XRD spectrum of LaF_3

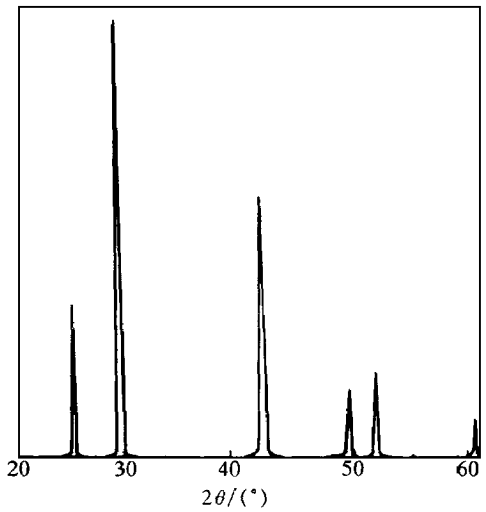

Fig.3 XRD spectrum of SrS

analysis. The atomic radius of La is proximate to that of Sr, so if not all La atoms take the same position in the lattice as Sr atoms, there will be splits on both $K_{\alpha 1}$ and $K_{\alpha 2}$ peaks of the obtained diffraction spectra. The splits will cause two peaks to become four peaks to reveal another lattice array, which is brought by La atoms. And they can be shown clearly at the high angle peaks.

The diffraction peaks between 86° and 87° of the spectra in Fig.4 are amplified and shown

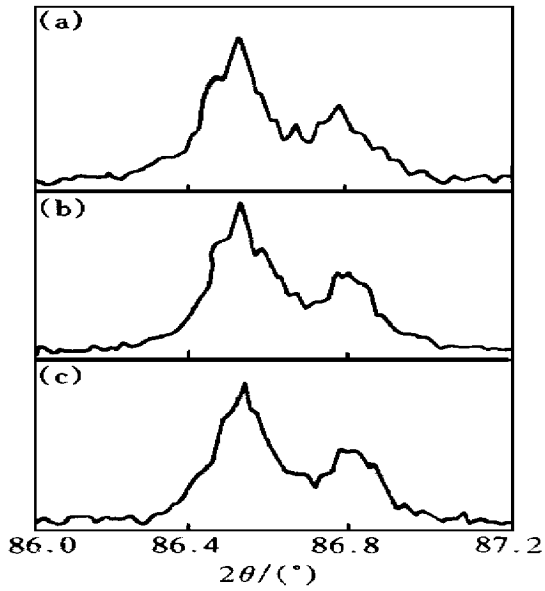

Fig.4 XRD spectra of sample A, B and C
(a) —Sample A; (b) —Sample B; (c) —Sample C

as Fig.5.

The $K_{\alpha 1}$ and $K_{\alpha 2}$ peaks of the three samples did not split and they are correspondence match. So it can be further proved that in the three samples all La and Sr atoms take the same position in the lattice and form a solid solution with SrF_2 cubic structure.

The measured lattice of the solid solution phase shows that it is a cubic phase and its lattice constant is 5.843 Å, which is a little bit larger than the lattice constant (5.800 Å) of pure SrF_2.

By comparing Fig.4 with Fig.3, it is revealed that the main diffraction peaks of SrS appeared in the spectra of samples containing SrS, and the peaks intensified with the increase of SrS content. This proves the existence of SrS phase. Moreover, the concordance of the diffraction peaks of samples A, B and C indicate that SrS had no influence on the structure of the solid solution. Because the peak position and peak shape of samples B and C containing SrS are the same as those of pure solid solution sample A containing no SrS.

Fig.5 Amplified XRD spectra of samples A, B and C
(a) —Sample A; (b) —Sample B; (c) —Sample C

In Fig.4, the diffraction peaks of solid solution phase and SrS in the samples A, B and C have been determined, but in samples B and C three peaks (seeing B and C in Fig.4 what the arrows point to) are not determined yet. The *d* value and the relative intensity of the undetermined peaks are listed as Table 1.

Table 1 *d* value and relative intensity of diffraction peaks of unknown phase

Diffraction peak	Sample B		Sample C	
	d/ Å	I/I_0	*d*/ Å	I/I_0
1	3.180	2	3.186	3
2	2.482	1	2.483	1
3	1.932	1	1.933	1

It was revealed by computer index that the undetermined peaks match the value of MnI_2 standard card. But in this research no Mn element and I element were introduced into the samples. By far, the undetermined peaks are still XRD spectra of an unknown phase.

It also can be found that the peaks of the unknown phase intensifies with increasing SrS content in the samples. This proves that the unknown phase has something to do with the addition of SrS. Because the content of the unknown phase is very small, it is difficult to separate the phase from the solid solution. Further research on the unknown phase will be carried out.

4 RESULTS OF EPS AND DISCUSSION

Morphology observation and element scanning on fresh fracture face of block samples A, B and C were carried out by EPS. Because the element whose atomic number is smaller than 10 can not be detected by the selected device, only La, Sr and S were measured by EPS.

The measurement on sample A without SrS (the results are not attached) showed that Sr and La distributed uniformly in the matrix. So it is further revealed that SrF_2 and LaF_3 have formed a uniform solid solution.

The measurement on samples B and C containing SrS are shown as Fig. 6. Sanding the sample fracture face caused the cross grain (which has nothing to do with the properties of the samples) in the image of Fig. 6. Bright points in the images stand for the detected elements.

Combined with the spectra of XRD, Fig. 6

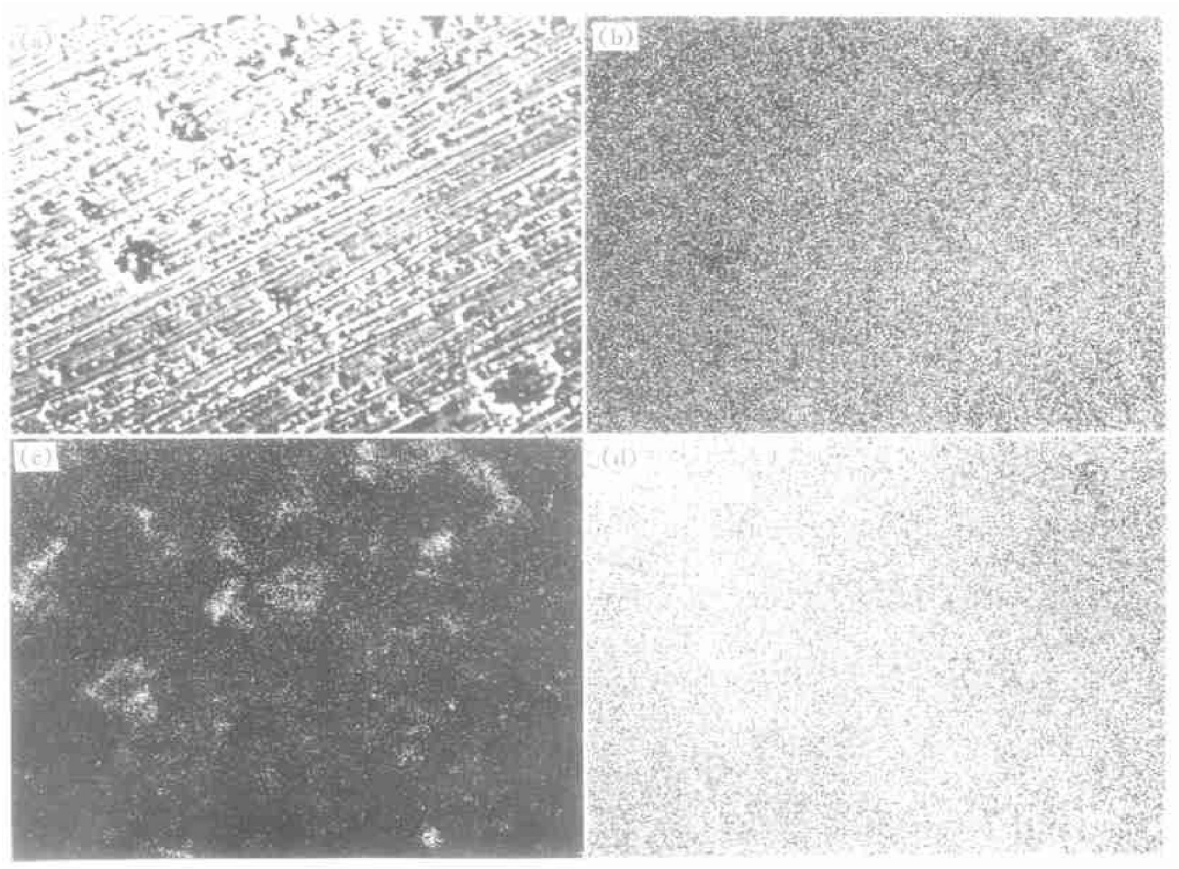

Fig. 6 EPS images of samples with SrS
(a) — Morphology; (b) —Scanning for La element; (c) —Scanning for S element; (d) —Scanning for Sr element

shows that, in the area where there is no S element, La element and Sr element coexist and distribute uniformly, forming a very uniform solid solution phase. In the area where there was much S element, Sr element but no La element existed, and this reveals that there existed the SrS phase. In the area where there was less S element, La element and Sr element coexisted, indicating an unknown phase produced by the interaction of SrS and co-precipitated powder. At present the unknown phase can not be determined.

5 CONCLUSIONS

(1) In the $Sr_{0.69}La_{0.31}F_{2.31}$ + SrS (with SrS content no more than 5 %) polycrystal material, $Sr_{0.69}La_{0.31}F_{2.31}$ solid solution matrix phase, small amount SrS phase and an unknown phase which is produced by the interaction of SrS and co-precipitated powder are found. Three diffraction peaks of the unknown phase are also obtained. Moreover, the content of SrS phase and unknown phase increases with increasing SrS content.

(2) The prepared $Sr_{0.69}La_{0.31}F_{2.31}$ solid solution takes SrF_2 cubic structure, but due to the introduction of La, the lattice constant of the solid solution is 5.843 Å which is a bit larger than that of pure SrF_2(5.800 Å). Furthermore, all La atoms take the same position as the Sr atoms and distribute uniformly in the lattice.

(3) No difference between the solid solution obtained from sample containing SrS and that obtained from sample without SrS has been found. Both of them are materials with the composition and structure of $Sr_{0.69}La_{0.31}F_{2.31}$. That indicates SrS has no influence on phase structure of the solid solution.

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