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Far Infrared Radiation Property of Elbaite/Alumina Composite Materials

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Abstract. Far infrared materials have been prepared by precipitation method using natural elbaite powder as raw materials, which belongs to tourmaline group. The chemical formula of elbaite is $\text{Na}(\text{Al},\text{Li})_3\text{Al}_6\text{B}_3\text{Si}_6\text{O}_{27}(\text{O},\text{OH},\text{F})_4$. X-ray powder diffraction (XRD) shows that elbaite and alumina in composite material has good crystal form. In addition, XRD results indicate the formation of alumina crystallites show that alumina powder exists as nano-meter particles on the surface of elbaite powder. It can be calculated the particles diameter of Al_2O_3 is 47.86nm. The maximum infrared radiation rate of tourmaline/alumina composite materials is 0.89 when the ratio of alumina in elbaite powder is 20%. The infrared radiation rate has been increased by 0.03, compared with single elbaite. It shows that the infrared radiation rate of the composite materials is higher than any of a single component. Two reasons are attributed to the improve of the rate of far infrared radiation: alumina powder exists as nano-meter particles and different materials will increase the absorption peak and the vibration intensity in FTIR spectra.

1 Introduction

Elbaite is one kind of tourmaline group, which is a borosilicate mineral that belongs to the trigonal space group of R3m-C3. Tourmaline has complex composition and its crystal chemical formula is $\text{XY}_3\text{Z}_6[\text{Si}_6\text{O}_{18}][\text{BO}_3]_3(\text{O}, \text{OH}, \text{F})_4$. X position is occupied not only by Na^+ or Ca^{2+} , but also by Na^+ , K^+ , and sometimes there are vacancies (which can form alkali free tourmaline). Y position is mainly occupied by Fe^{2+} , Fe^{3+} , Mg^{2+} , Mn^{2+} and $(\text{Al}^{3+}+\text{Li}^+)$. Z position is mainly occupied by Al^{3+} , as well as Fe^{2+} , Mn^{3+} , Li^+ , Ti^{4+} , etc. Replacement of X, Y, Z is very common in tourmaline group[1]. Because of its spontaneous polarity, tourmaline can generate electrode under natural condition. It has many kinds of properties which can be applied in environmental protection and human health-care, such as generating far infrared radiation, releasing negative ions and electromagnetic shielding [2-5].

Although the composition of tourmaline is various, all kinds of mineral crystals have piezoelectric and pyroelectric properties. The difference of the composition and content of various metal ions leads to the difference of spontaneous polarization and pyroelectric properties. Among the tourmaline group, the most common mineral species are dravite, iron tourmaline, and elbaite. Yang Ruzeng through testing the infrared radiation of different kinds of tourmaline, he thinks that the main reasons for its strong infrared radiation characteristics are the crystal defects of black tourmaline[6-8]. Iron has a negative effect with the pyroelectric properties, and the more iron content, the

lower the pyroelectric properties. Because of containing few Fe element of lithium, it can be inferred that pyroelectric property of elbaite is higher than that of dravite and iron tourmaline. Therefore, the performance of far infrared radiation of elbaite should be much higher than that of Mg-Fe tourmaline group.

In order to enhance the far infrared radiation, elbaite/alumina composite materials are prepared in this paper. Alumina powder has high far infrared radiation rate at room temperature which is more than 0.90, but it is low (no more than 0.80) in the band of 5-15 μm . Therefore, the elbaite/alumina composite powders will make the absorption peak in the far infrared position, and it will enhance the rate of far infrared radiation in the low band among 5-15 μm , which is very important to human health.

2 Experimental procedure

2.1 Preparation of samples

In this research, the far infrared materials were prepared by chemical precipitation method and elbaite powder (D50=6 μm). The main raw materials of nano-meter alumina are selected as follows: $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (analytical grade), ammonia solution, deionized water, ethanol etc. the nano-meter particles of alumina powder can be made by chemical precipitation. Chemical compositions of elbaite samples from Fuping, Henan province, were analysed by X-ray fluorescence spectrometry (Philips PW2404) as showed in Table 1.

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Table 1. Chemical Component of Elbaite Samples

SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	F	Loss	Total
43.64	42.73	-	0.031	-	0.43	-	0.72	2.17	0.04	0.05	4.09	4.70	98.601

By chemical precipitation, precursor Al(OH)₃ was formed. Controlling the reaction conditions and stirring continuously, the precursor Al(OH)₃ was evenly coated on surfaces of tourmaline particles and formed elbaite/Al(OH)₃ composite particles. Then the obtained composite particles were calcined at desired temperature, and the elbaite/Al₂O₃ composite materials were prepared. The ratio of Al₂O₃ added to elbaite powder were selected at 0, 10%, 20%, 30%, noted as HN-0, HN-1, HN-2, HN-3. Ultrasonic dispersion was used to make tourmaline powder dispersed in the solution. Then, magnetic stirring was used for 30 minutes at room temperature to keep the suspension uniformly dispersed. Finally, in order to transfer to a ceramic crucible, the composite materials were sintered at 800°C for 3 hours, and then cooled to room temperature for further test.

Table 2. Compositions of the Composite Materials

Compositions	C-HN-0	C-HN-1	C-HN-2	C-HN-3	C-HN-4
Elbaite	100	90	80	70	60
Al ₂ O ₃	0	10	20	30	40

2.2 Characterization and property test

Test instruments used for this study include 5DX Fourier Transform Infrared Spectrometer and JD-1 blackbody furnace. The effective infrared rate of blackbody furnace is more than 0.998, and the integral value ratio of the radiation spectra is between 5μm and 15μm. The far infrared rate is the ratio of radiant emittance of an object to that of a blackbody.

X-ray diffraction (XRD) was used to determine the effects of tourmaline content and preparation conditions to infrared emissivity and other properties. The XRD instrument type was D/Max-IIA, and the operational parameters for the analysis were Cu target, scanning range 5°-80°, scanning speed 4°/min.

In order to analyse the form of composite materials, FTIR was used to distinguish the composite materials with different tourmaline/Al₂O₃ ratio.

The test conditions: working voltage 220-240V, resolution 4cm⁻¹, scan range 4000-400cm⁻¹. The test was completed in Beijing institute of mining and metallurgy.

3 Results and discussion

3.1 Far-infrared emission property

The samples C-HN-1, C-HN-2, and C-HN-3 have identical raw materials used for preparation but different E/A ratios in the composite materials. The results are shown in Table 3. From Table3, it can be seen that the infrared radiation rates of the samples vary greatly. The sample of C-HN-2 has the highest infrared radiation rate, which reached 0.89. Compared with the single tourmaline materials, the infrared radiation rate of composite materials has increased by 0.03, and increased by 0.04 comparing to nano-meter alumina particles. Therefore, the composite materials have a higher infrared radiation rate compared with any of single powder.

Far infrared emission rate of a composite material depends on the vibration peak of particle size, number, intensity, and interactive effect of any single component in the composite materials. For elbaite/alumina composite materials, the infrared emission rate depends on the infrared vibration of elbaite and alumina individually and their interactive effectiveness.

Tab.3 Infrared Radiation Rate of Composite Materials with Different Ratio (%)

Samples (μm)	Ratio	infrared radiation	wavelength range
C-HN-0	-	0.86	5-15
C-HN-1	10	0.86	5-15
C-HN-2	20	0.89	5-15
C-HN-3	30	0.87	5-15
Al ₂ O ₃	-	0.85	5-15

3.2 Crystal Structure (XRD)

XRD patterns of composite materials with different ratio of elbaite and alumina (C-HN-1, C-HN-2, C-HN-3) are show in Fig.1.

In addition to the diffraction peaks of elbaite (E), the diffraction peak of Al₂O₃ typical graph (A) is strong and sharp in fig.1, and it indicates that Al₂O₃ powder has good crystal integrity in the elbaite /Al₂O₃ composite materials.

Through the comparison of C-HN-1, C-HN-2, C-HN-3, it can be seen that with increasing of Al₂O₃ content, the diffraction peak of Al₂O₃ in the composite powder is more and more obvious, and the spectral peak of elbaite becomes more and more weak.

The results of XRD can be used to measure the particles size. When the grain size is less than 100nm, the X ray diffraction peak changes with the crystal size

and the average particles diameter can be calculated by Scherrer formula[9-11]:

$$D=K\lambda (\beta\cos\theta HKL) \quad (1)$$

Taking sample C-HN-1 as an example, the approximate particles size of Al₂O₃ can be calculated according to the data of XRD with the sample C-HN-1. D (HKL) in the formula (1) is the average particles size of crystal surface along the normal direction of the value, K is constant, K=0.89; X ray wavelength λ =0.15406nm, 2θ =36.10°, β =0.625-0.214=0.411°, it can be calculated that the average particles diameter of Al₂O₃ is 47.86nm, which has reached nano-meter.

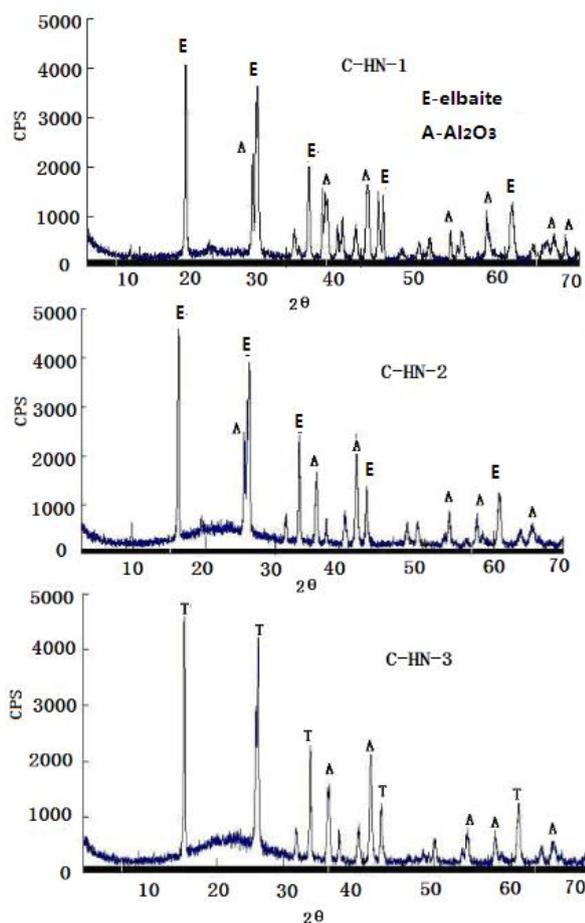


Fig.1. XRD Patterns of the Composites in Different elbaite /alumina Ratio

3.3 FTIR analysis

Three samples as mentioned above, C-HN-1, C-HN-2 and C-HN-3 were analyzed with FTIR under test conditions: working voltage 220-240V, resolution 4cm⁻¹, scan range 4000-400cm⁻¹. The FTIR patterns are shown in Fig.2.

In Fig.3, the composite materials show the typical infrared spectrums of both tourmaline and Al₂O₃ respectively. Because of the small particle size, the

infrared spectrum of tourmaline grains shifted to a certain extent, and the absorption peak become wider than the regular FTIR patterns [12-15].

Nano scale Al₂O₃ powder has two characteristic peaks on the infrared spectra. One is a broad absorption band in the range of 400-1000cm⁻¹, and another is in the vicinity of the 1380cm⁻¹ due to the phonon vibration of nanoscale Al₂O₃ particles. Both characteristic peaks of nanoscale Al₂O₃ particles appeared in Fig.3. In this study, through strict control of reaction conditions, nanoscale Al₂O₃ particles have high specific surface area, which will form a large number of dangling bonds on the surface of particles. As a result, the infrared vibration peaks of Al₂O₃ particles become strengthened.

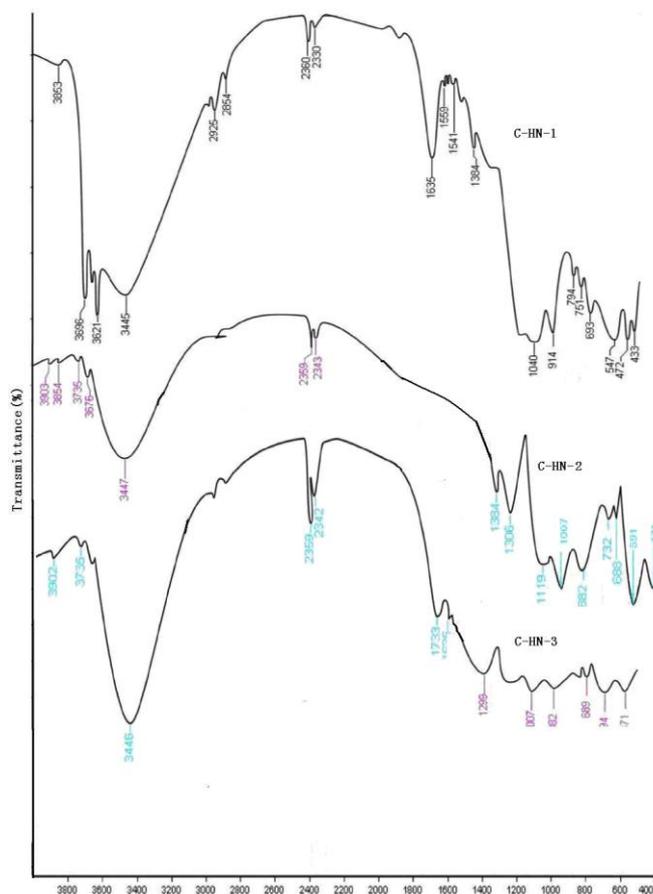


Fig. 2. FTIR Patterns of the Products with Different T/A Ratio

4. Conclusions

Select elbaite produced in Henan as the main raw material, and have obtained elbaite/Al₂O₃ composite materials by chemical precipitation method. The composite particles are analyzed by XRD and FTIR. Moreover, the far infrared radiation rates of composite materials are tested. The main conclusions are as follows: 1. Elbaite/Al₂O₃ composite materials are obtained successfully by chemical precipitation method. XRD and SEM analysis show that tourmaline and Al₂O₃ both have good crystal forms in the composite materials. The average size of Al₂O₃ particles calculated by using

Scherrer equation is 47.86nm. It is also proved by FTIR analysis. As Al₂O₃ particles have reached nanoscale size and it will enhance the performance of the tourmaline/Al₂O₃ composite materials.

2. Compared with the different ratio of tourmaline, the sample of C-HN-2 has the highest infrared radiation rate, which has reached 0.89. Compared with the single tourmaline material, the infrared radiation rate of composite materials has increased by 0.03, and increased by 0.04 compared with single nanoscale Al₂O₃ material. Therefore, the composite materials have a high infrared radiation rate. It has achieved the desired effect in the experiments. This is also consistent with the result of FTIR test.

3. The infrared radiation rate of the tourmaline/Al₂O₃ composite materials is higher than any one single material. The reasons are as follows: different materials will increase the absorption peak and the vibration intensity in FTIR spectra. Furthermore, with the number of the composite materials increasing, the different components will interact between particles, which will affect the symmetry of the crystal structure. Therefore, the infrared radiation rate of the composite materials is higher than any one single material.

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